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Faculty of Mechanical Engineering
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DOCTORAL DISSERTATION

*Scale Bridging Computational and Data-Driven Design
of Microstructures in Multicomponent Alloys
for Advanced Functional Materials*

in the form of a collection of thematically related published articles in
scientific journals

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Dedicated to my mom and dad

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Abstract

Modern engineering components and systems increasingly require materials whose structural reliability, electromechanical response, and interfacial stability are specified together with their geometry and operating conditions. Grounded in material characterisation and modelling, this dissertation develops computational methodologies for predicting material response and relating it to component-, device-, and system-level requirements. The studied systems include multicomponent alloys, piezoelectric ceramics and polymers, and lithium-based battery interfaces. Their behaviour emerges from descriptors that span atomic bonding, crystal symmetry, microstructure, and interfacial morphology. No single modelling approach covers this full range of scales. The proposed scale-bridging framework therefore combines physics-based modelling with data-driven methods. It connects material descriptors to structural and functional response through an explicit intermediate material state.

In multicomponent alloys, ensemble machine learning supports structural alloy specification by mapping composition and manufacturing route jointly to the hardness-elongation balance and identifying coupled design regions rather than isolated optima. DFT-calibrated phase-field simulations indicate that matching elastic constants to the simulation temperature changes the predicted Al-Cu-Ni microstructure by 18%. This result confirms that temperature consistency is necessary for microstructure prediction relevant to process and component design. In piezoelectric materials, a crystallography-informed network predicts the complete symmetry-constrained piezoelectric tensor and evaluates it in a finite element device model. A model-identified doped-AlN composition, evaluated at an optimised orientation, raises the predicted energy-harvesting output 9.96-fold relative to the undoped baseline. A complementary physics-guided model links electrospinning conditions and filler content to the effective response of PVDF/SnO₂ nanofibres and raises the predicted d_{33} from 18 to 29 pC N⁻¹. In lithium-based battery interfaces, a coupled-field phase-field model resolves the tip-amplified mechanism of dendrite growth. A literature synthesis consolidates materials, interfacial, and operating suppression strategies into ten jointly constrained performance and stability targets for reliable electrochemical energy systems.

Across all three domains, a common design logic recurs even though the governing physics and models differ by material. Composition and processing define the attainable response. The intermediate material state carries this information to the component, device, or interface. At that level, coupled multi-physics behaviour determines the realised performance. These findings are distilled into five transferable schemes for structural alloy components, piezoelectric sensors and energy harvesters, and electrochemical energy systems.

Streszczenie

Współczesne komponenty i systemy inżynierskie coraz częściej wymagają materiałów, których niezawodność strukturalna, odpowiedź elektromechaniczna i stabilność interfejsów są projektowane łącznie z geometrią i warunkami pracy. Opierając się na charakterystyce i modelowaniu materiałów, niniejsza rozprawa opracowuje metody obliczeniowe wspierające projektowanie poprzez przewidywanie właściwości materiałowych i wiązanie ich z wymaganiami na poziomie komponentu, urządzenia i systemu. W stopach wieloskładnikowych, ceramikach i polimerach piezoelektrycznych oraz interfejsach elektroda-elektrolit w układach litowych właściwości użytkowe wyłaniają się z hierarchii deskryptorów. Deskryptory te obejmują wiązania atomowe, symetrię krystaliczną, mikrostrukturę i morfologię interfejsów. Żadna izolowana metoda modelowania nie obejmuje pełnego zakresu tych skal. Opracowane ramy wieloskalowe łączą modelowanie oparte na fizyce z metodami opartymi na danych. Wiążą także deskryptory materiałowe z właściwościami strukturalnymi i funkcjonalnymi poprzez jawny pośredni stan materiału.

W stopach wieloskładnikowych zespołowe uczenie maszynowe wspiera specyfikację stopów konstrukcyjnych, odwzorowując wspólnie skład chemiczny i metodę wytwarzania na równowagę twardości i wydłużenia. Pozwala to wskazać sprzężone obszary projektowe zamiast izolowanych punktów optymalnych. Sparаметryzowane metodą DFT symulacje pola fazowego wykazują, że dopasowanie stałych sprężystości do temperatury symulacji zmienia przewidywaną mikrostrukturę układu Al-Cu-Ni o 18%. Wynik ten potwierdza znaczenie spójności temperaturowej parametrów dla przewidywania mikrostruktury istotnego dla projektowania procesu i komponentu. W materiałach piezoelektrycznych sieć neuronowa uwarunkowana krystalograficznie przewiduje kompletny tensor piezoelektryczny ograniczony symetrią i ocenia go w modelu urządzenia metodą elementów skończonych. Wybrany przez model i optymalnie zorientowany domieszkowany AlN zwiększa przewidywaną wydajność pozyskiwania energii 9,96-krotnie względem materiału wyjściowego. Uzupełniający model wspomagany wiedzą fizyczną łączy parametry elektroprzewodzenia i zawartość wypełniacza z efektywną odpowiedzią nanowłókien PVDF/SnO₂. Zwiększa także przewidywaną wartość d_{33} z 18 do 29 pC N⁻¹. W interfejsach elektroda-elektrolit w układach litowych model pola fazowego ze sprzężonymi polami odwzorowuje mechanizm wzmacniania wzrostu dendrytów przez wierzchołek. Synteza literatury konsoliduje strategie tłumienia obejmujące aspekty materiałowe, interfejsowe i operacyjne w dziesięć wzajemnie powiązanych wskaźników wydajności i stabilności dla niezawodnych elektrochemicznych układów energetycznych.

We wszystkich trzech obszarach powtarza się wspólna logika deskryptor-właściwości, mimo że fizyka rządząca i modele różnią się w zależności od materiału. Skład chemiczny i przetwarzanie określają zakres osiągalnej odpowiedzi. Pośredni stan materiału przenosi tę

informację między skalami do komponentu, urządzenia lub interfejsu. Na tym poziomie sprzężona odpowiedź wielofizyczna określa uzyskiwane właściwości. Wyniki sprowadzono do pięciu transferowalnych schematów projektowych oraz fizycznie ugruntowanej metodologii dla strukturalnych komponentów ze stopów, piezoelektrycznych czujników i pozyskiwaczy energii oraz elektrochemicznych układów energetycznych.

List of Publications

This publication-based dissertation consists of thematically related journal articles. Its principal scientific contribution is based on the following seven peer-reviewed publications prepared during the doctoral studies. The full texts are included in Appendix A. The author contributions are described in the following chapter, and the signed co-author declarations are provided in Appendix B.

- [P-I] **S. Poudel**, U. Subedi, M. O. Hamid, K. Gyanwali*, N. Moelans, A. Timofiejczuk, and A. Kunwar*, “AlloyManufacturingNet for discovery and design of hardness-elongation synergy in multi-principal element alloys,” *Engineering Applications of Artificial Intelligence*, vol. 132, p. 107902, 2024. [1]
DOI: [10.1016/j.engappai.2024.107902](https://doi.org/10.1016/j.engappai.2024.107902)
(IF: 9.0, MNI_{SW}: 140)[#]
- [P-II] **S. Poudel***, R. Thapa, R. Basnet, A. Timofiejczuk, and A. Kunwar, “PiezoTensorNet: Crystallography informed multi-scale hierarchical machine learning model for rapid piezoelectric performance finetuning,” *Applied Energy*, vol. 361, p. 122901, 2024. [2]
DOI: [10.1016/j.apenergy.2024.122901](https://doi.org/10.1016/j.apenergy.2024.122901)
(IF: 12.2, MNI_{SW}: 200)
- [P-III] **S. Poudel***, N. Moelans, R. Thapa, A. Timofiejczuk, D. Panthi, and A. Kunwar, “Unraveling elastochemical effects in microstructural evolution of Al–Cu–Ni system through DFT-informed multi-phase field simulations,” *International Journal of Solids and Structures*, vol. 300, p. 112894, 2024. [3]
DOI: [10.1016/j.ijsolstr.2024.112894](https://doi.org/10.1016/j.ijsolstr.2024.112894)
(IF: 4.6, MNI_{SW}: 140)
- [P-IV] Y. Li, **S. Poudel***, S. Kumari, E. Azqadan, A. Kunwar*, and N. Moelans*, “Roadmaps for dendrite suppression in next generation lithium-ion batteries: Toward sustainable energy solutions,” *Energy Storage Materials*, vol. 86, p. 105000, 2026. [4]
DOI: [10.1016/j.ensm.2026.105000](https://doi.org/10.1016/j.ensm.2026.105000)
(IF: 19.3, MNI_{SW}: 200)

[P-V] **S. Poudel***, W. Smok, R. Thapa, A. Timofiejczuk, N. Moelans, and A. Kunwar, “Physics-guided machine learning for enhanced piezoelectric performance in electrospun PVDF/SnO₂ nanofibers,” *Sustainable Materials and Technologies*, p. e02008, 2026. [5]

DOI: [10.1016/j.susmat.2026.e02008](https://doi.org/10.1016/j.susmat.2026.e02008)

(IF: 9.7, MNI_{SW}: 200)

[P-VI] M. Dagnaw, **S. Poudel***, U. Subedi*, R. Thapa, Ł. Reimann, A. N. S. Appiah, P. M. Nuckowski, M. Król, Z. Brytan, N. Moelans, et al., “Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures,” *Metals and Materials International*, 2026. [6]

DOI: [10.1007/s12540-026-02369-4](https://doi.org/10.1007/s12540-026-02369-4)

(IF: 4.5, MNI_{SW}: 70)

[P-VII] M. Dagnaw, **S. Poudel***, M. Król, and Z. Brytan, “Post-process heat treatment design for tunable strength and toughness in L-PBF 2507 super duplex stainless steel,” *Materialia*, p. 102799, 2026. [7]

DOI: [10.1016/j.mtla.2026.102799](https://doi.org/10.1016/j.mtla.2026.102799)

(IF: 3.1, MNI_{SW}: 20)

* Corresponding author.

IF: Impact Factor (2025 values). MNI_{SW}: Polish Ministry of Science and Higher Education points score.

Note: All the publications are within the discipline of Mechanical Engineering.

Additional Related Publications

The publications listed below provide broader scientific and methodological context for this doctoral research. They reflect complementary work in computational solid mechanics and data-driven materials informatics. They are not part of the principal publication set, but they demonstrate the transfer of finite element and machine-learning methods to smart sensors and sustainable materials.

[AP-I] R. Thapa, **S. Poudel**, K. Krukiewicz, and A. Kunwar*, “A topical review on AI-interlinked biodomain sensors for multi-purpose applications,” *Measurement*, vol. 227, p. 114123, 2024. [8]
DOI: [10.1016/j.measurement.2024.114123](https://doi.org/10.1016/j.measurement.2024.114123)
(IF: 6.1, MNiSW: 200)[#]

[AP-II] S. Neupane*, **S. Poudel***, A. Ghimire, and S. Shakya, “Enhanced mechanical performance and biodegradability in filler-reinforced potato biopolymers for sustainable packaging,” *Materials Today Communications*, p. 114081, 2025. [9]
DOI: [10.1016/j.mtcomm.2025.114081](https://doi.org/10.1016/j.mtcomm.2025.114081)
(IF: 4.9, MNiSW: 70)

* Corresponding author.

[#] IF: Impact Factor (2025 values). MNiSW: Polish Ministry of Science and Higher Education points score.

Author's Contribution

This chapter summarises the candidate's (**Sachin Poudel**) publication position, percentage contribution, CRediT roles, and principal tasks for each of the seven publications. The signed declarations of author contribution are provided in Appendix [B](#).

Multicomponent Alloys

Publication I [P-I]

Position: First. **Contribution:** 51%.

CRediT roles: Conceptualization, methodology, software, investigation, formal analysis, validation, data curation, visualization, funding acquisition, writing: original draft.

- Framed structural alloy specification as a joint choice of composition and manufacturing route for hardness-elongation requirements.
- Enabled prediction and inverse design using curated multi-route data and the scale-invariant objective $F(x, y)$.
- Used physically grounded descriptors (ΔB , ΔG , VEC) to retain mechanical interpretation.
- Linked predicted property trends to atomistic deformation mechanisms through CoCrNiNb_x molecular-dynamics nanoindentation and led the manuscript, figures, and funding.

Publication III [P-III]

Position: First and Corresponding. **Contribution:** 65%.

CRediT roles: Conceptualization, methodology, software, investigation, formal analysis, validation, data curation, visualization, writing: original draft.

- Treated Al-Cu-Ni phase evolution as a process-design problem requiring temperature-consistent microstructure prediction.
- Enabled temperature-consistent mesoscale simulation by implementing a DFT-informed MOOSE phase-field model and transferring calibrated elastic constants.
- Quantified the 18% morphology difference relative to 0 K parameters, established the atomistic-to-mesoscale transfer procedure, and led the writing, figures, and interpretation.

Publication VI [P-VI]

Position: Second and Corresponding. **Contribution:** 14%.

CRedit roles: Conceptualization, methodology, software, data curation, visualization, writing: review & editing.

- Addressed corrosion-performance specification for LPBF-processed SDSS 2507 by extending composition-processing modelling.
- Represented heat-treatment and composition interactions through process-sensitive descriptors, including PREN-temperature and $T \times t$ features, within the Matminer/Magpie workflow.
- Contributed to SPER-based phase-stability representation, data curation, validation, figures, and interpretation.

Publication VII [P-VII]

Position: Second and Corresponding. **Contribution:** 25%.

CRedit roles: Conceptualization, software, formal analysis, data curation, visualization, writing: review & editing.

- Supported post-processing selection for L-PBF 2507 components by linking heat-treatment routes to strength-toughness response.
- Provided the analysis software and curated dataset used for process-selection interpretation, figures, and manuscript revision.

Piezoelectric Materials

Publication II [P-II]

Position: First and Corresponding. **Contribution:** 61%.

CRedit roles: Conceptualization, methodology, software, investigation, formal analysis, validation, data curation, visualization, writing: original draft.

- Addressed sensor and energy-harvester material selection by connecting complete symmetry-constrained piezoelectric tensors to oriented finite element device models.
- Ensured physically admissible tensor outputs using a hierarchical point-group classifier, symmetry-specific regressors, crystallographic descriptors, and the tensor-norm screening metric e_{mod} .
- Identified B-Er co-doped AlN as the leading MEMS energy-harvesting candidate, demonstrated a 9.96-fold predicted power gain, and led the writing and figures.

Publication V [P-V]

Position: First and Corresponding. **Contribution:** 50%.

CRedit roles: Conceptualization, methodology, software, investigation, formal analysis, validation, data curation, visualization, project administration, funding acquisition, writing: original draft.

- Addressed flexible sensor, actuator, and energy-harvester design under sparse data.
- Linked electrospinning conditions, SnO₂ content, morphology, and effective PVDF response.

- Converted dispersed literature data into a structured modelling dataset using literature mining and processing-aware descriptors.
- Evaluated predicted d_{33} improvements through FERRET device simulations and led the writing, project administration, figures, and funding.

Lithium-Based Battery Interfaces

Publication IV [P-IV]

Position: Second and Corresponding. **Contribution:** 35%.

CRedit roles: Methodology, investigation, formal analysis, validation, visualization, writing: review & editing.

- Addressed reliability of lithium-based energy systems by co-developing a dendrite-suppression roadmap.
- Linked degradation mechanisms to materials, interfacial, and operating strategies.
- Organised dispersed suppression approaches into ten coupled performance and stability metrics for design assessment.
- Co-wrote the modelling and battery-interface sections, prepared figures, and integrated phase-field insights into the roadmap narrative.

List of scientific accomplishments

This section lists selected scientific accomplishments completed during the doctoral studies. It includes research grants, participation in externally funded research projects, and conference presentations delivered at international and national scientific meetings. These activities are related to the scientific scope of this dissertation and reflect its broader research dissemination.

Research grants and awards

1. **Rector's Grant, Silesian University of Technology, Poland.**

Pro-quality competition for rector's grants awarded for highly scored publications, granted patents, acquired projects, or scientific and research work.

Project No.: 32/014/RGJ25/2037.

Participation in funded research projects

1. **Research team member, DENDRITEPHASE project.**

Research team member in the National Science Centre (NCN), Poland-funded project **DENDRITEPHASE**.

Project No.: UMO-2023/51/I/ST11/02716.

Project link: https://projekty.ncn.gov.pl/en/index.php?projekt_id=601609

2. **Graduate Researcher, Silesian University of Technology, Poland.**

Research team member in the National Science Centre (NCN), Poland-funded project **DECLARMIMA**.

Project No.: UMO-2021/42/E/ST5/00339.

Project link: https://projekty.ncn.gov.pl/en/index.php?projekt_id=526876

Conference presentations

1. **S. Poudel***, A. Timofiejczuk, N. Moelans, and A. Kunwar,

“Crystallographically gated machine learning for functional materials discovery,”

Advanced Materials and Technologies (AMT) 2026, Łódź, Poland, 15-17 June 2026.
Poster presentation.

2. **S. Poudel***, A. Timofiejczuk, D. Panthi, N. Moelans, and A. Kunwar,
“Thermal-structural modeling of additively manufactured Ni-YSZ layers for SOFC electrodes,”
Additive Manufacturing Meeting, Wrocław, Poland, 4 June 2025.
Poster presentation.

3. **S. Poudel***, A. Timofiejczuk, N. Moelans, and A. Kunwar,
“A computational model for examining the role of externally applied stress on dendrite growth pattern in solid-state lithium-ion batteries,”
The 5th International Symposium on Phase-Field Modelling in Materials Science, Zhejiang University, Hangzhou, China, 19-23 May 2024.
Presentation date: 23 May 2024.
Oral presentation.

4. **S. Poudel***, A. Timofiejczuk, D. Panthi, N. Moelans, and A. Kunwar,
“Phase field evolution in Ni-YSZ fuel cells with temperature-dependent elasticity,”
Euromat23, Frankfurt, Germany, 3-7 September 2023.
Oral presentation.

* Presenting author.

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List of Important Abbreviations

ANN	Artificial Neural Network
BCC	Body-Centred Cubic
CALPHAD	CALculation of PHase Diagrams
DFT	Density Functional Theory
FCC	Face-Centred Cubic
FEM	Finite Element Method
IMC	Intermetallic Compound
L-PBF	Laser Powder Bed Fusion
MD	Molecular Dynamics
MEMS	Micro-Electro-Mechanical System
ML	Machine Learning
MOOSE	Multiphysics Object-Oriented Simulation Environment
MPEA	Multi-Principal Element Alloy
PCA	Principal Component Analysis
PCC	Pearson's Correlation Coefficient
PG	Point Group
PREN	Pitting Resistance Equivalent Number
P-SSHI	Parallel Synchronized Switch Harvesting on Inductor
PVDF	Poly(vinylidene fluoride)
SDSS	Super Duplex Stainless Steel
SPER	Structurally Panelised Element Representation

Chapter 1

Introduction

Modern engineering materials are increasingly expected to combine structural reliability with active functions. A material or interface may need to carry load while responding to external fields. It may also need to convert energy, resist degradation, or preserve interfacial stability. These requirements arise in energy-harvesting devices, microelectromechanical systems, and flexible electronics. They also appear in sensors and electrochemical energy storage. Such behaviour is set by more than bulk composition. It depends on atomic bonding, crystal symmetry, and phase constitution. It also depends on grain or fibre morphology, interfaces, and defects. The materials considered in this dissertation are studied through their role in components and systems.

This convergence reflects a shift in component and system design practice. Material behaviour governs the performance, durability, and reliability of components. Material selection and engineering design are therefore closely linked. A component cannot be fully specified without understanding the material that constitutes it. Equally, an advanced material cannot be developed without reference to the system in which it must function. Design requirements drive the tailoring of materials and manufacturing processes for specific service conditions. Computational mechanics increasingly integrates multiscale materials modelling with data-driven methods and artificial intelligence. In this dissertation, these methods are treated as complementary tools serving common design objectives.

In this work, descriptors are measurable or computed quantities that represent composition, processing history, crystallography, thermodynamic state, and morphology. The *intermediate material state* denotes the microstructure together with the crystallographic tensor state and associated physical fields. This state connects lower-scale information to the macroscopic response. That response depends on component geometry, device architecture, loading, boundary conditions, and the operating environment. The design problem is framed as a pathway from material descriptors to engineering performance through the intermediate material state.

Designing components and systems with such materials demands scale-bridging methods. Exhaustive experimental screening is impractical across high-dimensional composition and processing spaces. Physics-based simulations provide mechanistic insight, but they are usually confined to a single length or time scale. Data-driven methods explore large spaces rapidly, but they require physically grounded descriptors to remain transferable

and thermodynamically consistent. The unresolved challenge is to transfer meaningful information between scales and modelling representations before costly physical prototyping. This dissertation addresses that challenge by integrating experiments, physics-based simulation, and materials informatics across the three material domains introduced below. The aim is to support alloy composition and manufacturing-route specification, piezoelectric sensor and energy-harvester evaluation, and reliability-target definition for electrochemical energy systems. These tasks contribute to engineering design when material behaviour limits service performance.

1.1 Advanced Functional Materials across Domains

In this dissertation, *advanced functional materials* denote materials whose structural, electromechanical, electrochemical, or coupled responses are controlled through composition and structure. Relevant controls include crystal symmetry, phase constitution, morphology, and processing history. Structural capability and functional response originate at atomic or nanometre scales but become relevant to design when expressed at component, device, or interfacial scales. Mechanical deformation can induce electrical polarisation. Electrochemical reactions can reshape interfaces. Thermal processing can alter phase balance and defect structure. Such materials cannot be designed from nominal composition alone.

Three material domains are used to exercise the pathway from descriptors to performance. In *multicomponent alloys*, composition, processing route, and microstructure govern mechanical performance. In *piezoelectric materials*, crystallographic symmetry, the complete tensor, and orientation govern electromechanical coupling. In *lithium-based battery interfaces*, evolving interfacial morphology governs electrochemical stability. The domains are complementary. Each isolates a different part of the design problem: composition-processing design, crystallography-tensor-device coupling, or dendrite-morphology evolution and suppression.

1.1.1 Multicomponent Alloy Systems

Multicomponent alloys include medium- and high-entropy multi-principal-element alloys (MPEAs). They demonstrate that service performance in structural applications depends on composition, processing route, and microstructural state. MPEAs combine several principal elements in high concentration. This produces complex phase stability, lattice distortion, and local chemical ordering. In refractory systems built from Nb, Ta, Ti, and Zr, these interactions enable property combinations unavailable in conventional single-base alloys. The composition-processing-property space is highly non-linear and high-dimensional. Small changes in composition or heat treatment can shift phase constitution and grain morphology. Relevant mechanical properties also trade off against one another.

Descriptor-based machine learning now screens large composition spaces and predicts alloy properties [10, 11]. Optimisation is also applied to trade-offs such as strength and ductility [12]. In this dissertation, these methods support structural alloy specification, with less emphasis on cataloguing alloy trends. They combine with physics-based modelling [13]. DFT supplies quantities such as elastic constants, phase energetics, and chemical

Table 1.1: Material classes studied in this dissertation, with the prospective multifunctional extension, and the engineering design challenge and thesis approach for each.

Material class	Representative system	Engineering design challenge	Thesis approach
Multicomponent alloys	MPEAs, Al-Cu-Ni	High-dimensional composition and processing spaces create strength-ductility trade-offs that complicate structural component design.	Co-specify chemistry and manufacturing routes for load-bearing alloys and use temperature-consistent microstructure modelling for process design.
Piezoelectric ceramics	Doped AlN-based systems	Scalar properties neglect anisotropic tensor behaviour and orientation, which limits the accuracy of device-level deformation models.	Predict the full electromechanical tensor to enable rotated finite element analysis of oriented device components.
Piezoelectric polymers	PVDF/SnO ₂ nanofibres	Processing-induced morphology and phase state are difficult to relate quantitatively to performance under scarce experimental data.	Apply physics-guided descriptors to link electrospinning parameters to effective electromechanical response for flexible sensor and actuator design.
Lithium-based battery interfaces	Lithium-metal electrode-electrolyte interfaces	Coupled electrochemical and mechanical fields drive dendrite growth and interfacial degradation, causing early cell failure.	Model coupled-field interfacial evolution and consolidate suppression methods into a multi-metric reliability roadmap.
Multifunctional materials (prospective)	Alloy-derived oxides and nitrides	The functional potential of refractory transition-metal alloy candidate spaces remains unexplored in oxide or nitride form.	Use symmetry-guided screening of alloy-derived cation pools to identify candidates for active functional systems.

potentials. Its principal role in the alloy study is the temperature calibration of elastic tensors for phase-field simulation of mesoscale microstructure evolution [P-III, 14]. The alloy studies use hardness-elongation prediction, DFT-informed phase stability, and processing-dependent microstructure to support material and process choices for structural applications. The same refractory and transition-metal cation spaces motivate a prospective multifunctional extension discussed later.

1.1.2 Piezoelectric Materials

Piezoelectric materials enable bidirectional conversion between mechanical and electrical energy and underpin sensors, actuators, and flexible energy-harvesting devices [AP-I]. Their response is anisotropic and depends on crystallographic symmetry, orientation, and device configuration rather than on a single scalar coefficient. In piezoelectric ceramics, one coefficient such as d_{33} is insufficient for complex geometries or off-axis loading [15]. A full description requires the third-rank piezoelectric tensor, which captures the directional electromechanical coupling. Reliable device design calls for predicting that tensor and accounting for crystallographic orientation relative to the device frame [P-II].

Piezoelectric polymers behave differently [16]. Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer whose response is governed by the fraction of the polar β -phase relative to the non-polar α -phase. This fraction is sensitive to electrospinning parameters, fibre alignment, and filler additions such as SnO_2 [17, 18]. The design challenge is to relate processing, morphology, electroactive phase fraction, and effective response for flexible energy harvesting and actuation [P-V]. Conventional metallic alloys show no intrinsic bulk piezoelectric response of practical relevance because mobile charge carriers screen sustained polarisation and static internal electric fields [19]. The common FCC and BCC structures considered here are also centrosymmetric. Odd-rank piezoelectric tensors are symmetry-forbidden in these structures [20]. Ceramics and polymers are therefore addressed through tensor-level crystallography and morphology control, respectively.

1.1.3 Lithium-Based Battery Interfaces

In lithium-based batteries, performance and safety are governed by the dynamic behaviour of internal interfaces [21]. Metallic-lithium deposition is a major challenge in lithium-metal batteries and can also arise in lithium-ion cells under adverse lithium-plating conditions. The resulting dendrites cause capacity loss, impedance rise, and short circuits [22]. The corresponding design problem is to maintain the structural and electrochemical integrity of the electrode-electrolyte interface across the battery's intended service life. The relevant conditions include temperature, current density, and mechanical loading. Phase-field modelling describes the coupled electrochemical and transport fields driving this evolution, without explicit tracking of a sharp boundary [23].

The simulations provide mechanistic insight into dendrite growth. A literature synthesis then consolidates the materials, interfacial, and operating approaches that suppress it [P-IV]. Table 1.1 collates the domain-specific descriptors, intermediate states, and performance targets for each system.

1.2 Scale-Bridging Computational and Data-Driven Framework

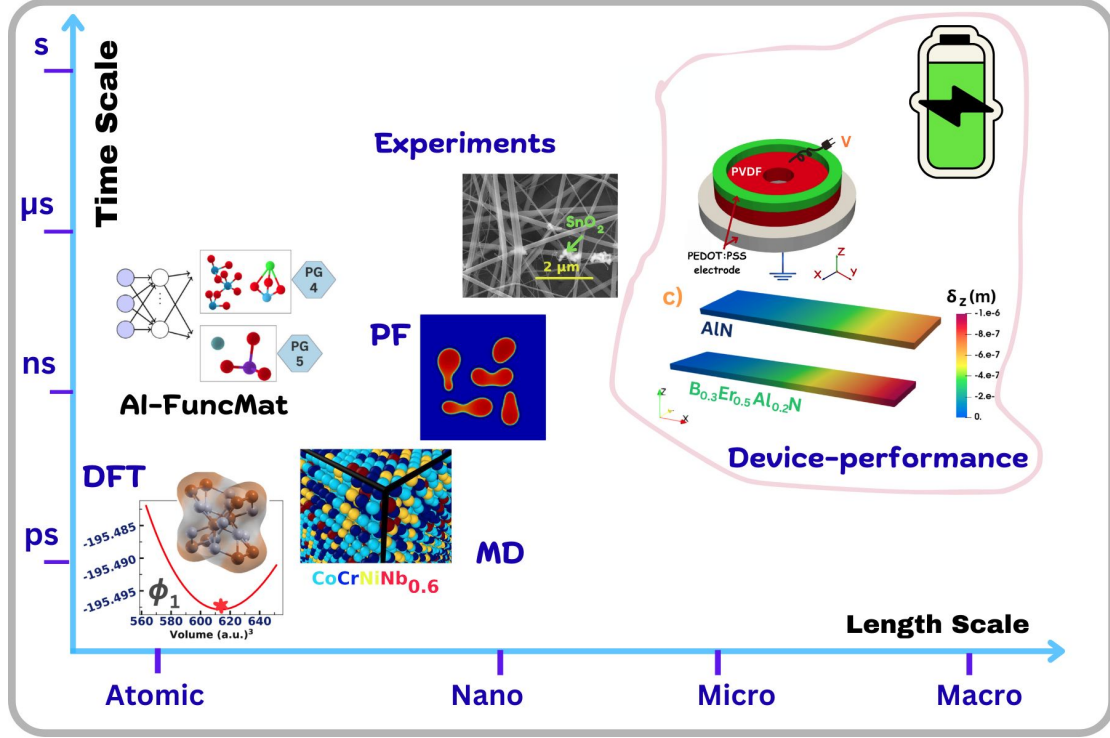


Figure 1.1: **The dissertation's scale-bridging framework converts physical descriptors into engineering performance through an explicit intermediate material state.** Composition, processing history, crystallographic information, and operating conditions form the descriptor layer. Physics-based and data-driven models transform these inputs into material parameters and the intermediate material state, comprising microstructure, crystallographic tensor state, orientation, and associated physical fields. Finite element and device-level models then connect this state to mechanical, electromechanical, and electrochemical performance at component, device, or interface scale. Experimental data supply training information, physical constraints, calibration, and selected validation at each stage. [Author's own work]

Physics-based modelling provides the mechanistic foundation. DFT, phase-field simulation, finite element modelling, and finite-strain plasticity provide the material-state and performance information needed for design decisions. In the Al-Cu-Ni system, temperature-calibrated DFT elastic constants improve the physical consistency of phase-field simulations used for process-relevant microstructure prediction. The phase-field method, implemented here in the MOOSE finite element framework [24, 25], resolves microstructure evolution and moving boundaries. Examples include elastochemical phase transformation in alloys and electrochemically driven dendrite growth at battery interfaces. Finite element modelling connects the resulting material state to device-level behaviour, for example the voltage, deformation, and actuation of piezoelectric energy harvesters. A supporting finite-strain (J_2) plasticity study extends the approach to nonlinear constitutive behaviour at

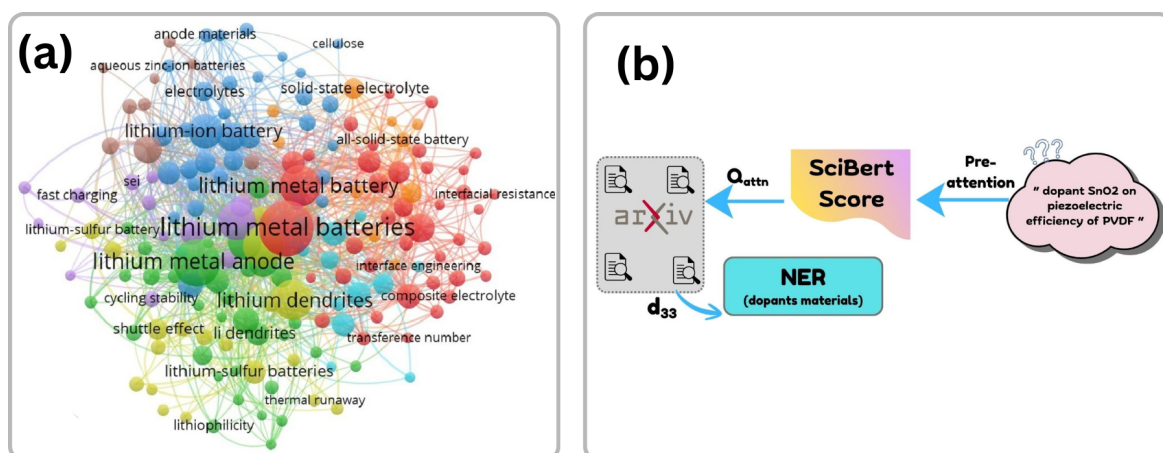


Figure 1.2: **An integrated literature-mining procedure supports trend mapping, structured extraction, and gap identification.** (a) Bibliometric co-occurrence network of the published literature, whose keyword clusters indicate dominant research directions and their boundaries [P-IV]. (b) Complementary natural-language-processing pipeline that extracts material compositions and performance metrics into structured datasets [P-V].

the continuum scale. Figure 1.1 summarises this pathway.

Data-driven methods complement this physical core by turning dispersed experimental, simulation, and literature data into design maps for property prediction, material selection, and inverse design. For studies based on literature-curated datasets, bibliometric and natural-language-processing methods structure the literature and extract compositions and performance metrics into structured datasets (Figure 1.2). These methods inform the critical literature analysis used to formulate the scientific gaps in Chapter 2.

Using these datasets, supervised models connect descriptors to engineering-relevant properties. Ensemble neural networks map compositional and manufacturing-route descriptors to mechanical properties of alloys. Crystallography-informed models couple point-group classification with symmetry-constrained tensor prediction so that predicted piezoelectric tensors remain physically consistent. In the alloy domain, model-predicted compositions are further interrogated through molecular-dynamics nanoindentation. This connects macro-scale property predictions to atomic-scale deformation mechanisms relevant to component performance. Throughout, data-driven models operate within physically meaningful descriptor spaces rather than substituting for the underlying physics.

Across the framework, descriptor formulation follows a layered logic. A structural layer captures composition, processing history, and crystal symmetry. It also records phase stability, elastic parameters, morphology, and interfacial condition. This layer provides the physical foundation for domain-specific models. Function-specific descriptors form a derived layer anchored to this foundation. They include piezoelectric tensor measures, electrochemical stability indicators, corrosion-response metrics, and device-level performance quantities. This hierarchy keeps functional predictions tied to the material state that physically enables them. The computational methods serve design objectives throughout. Material behaviour at the microstructural and device level is characterised because it governs load-bearing capacity,

energy conversion efficiency, and electrochemical reliability in engineering systems.

1.3 Scope of the Dissertation

Within this framework, the intermediate material state links lower-scale descriptors to performance and acts as the principal design variable. The work is computational and data-driven. Its objective is to provide methods for material selection, process specification, and performance prediction in structural and functional systems. It supports accelerated screening, inverse design, and future closed-loop integration. Fully automated experimentation lies outside the present scope. Experimental datasets provide training data, calibration, and selected validation. Physics-based models support mechanistic consistency, and machine learning accelerates exploration. Physical phenomena outside this focus, such as ferroelectric switching and domain-wall dynamics or shape-memory response, are considered only where alloy compositions overlap with known multifunctional families.

Principal contributions.

Each provides a computer-aided engineering capability at a specific stage of the design of structural components and functional systems:

- computer-aided specification of multicomponent-alloy composition and manufacturing route for hardness-elongation requirements.
- selection, orientation, and device-scale evaluation of piezoelectric materials for sensors, actuators, and energy harvesters.
- temperature-consistent microstructure prediction to support alloy process design.
- battery-interface reliability design through phase-field analysis of dendrite growth and synthesis of suppression approaches.

Supporting contributions.

- a finite-strain plasticity description of nonlinear mechanical response, integrable within the framework.
- a data-driven corrosion study of additively manufactured duplex stainless steel, illustrating the transferability of the composition-processing methodology to a processing-sensitive electrochemical response.
- the multifunctional oxide and nitride screening, treated as a prospective extension rather than as a completed principal contribution.

The scientific gaps arising from this scope are formalised in Chapter 2, and the corresponding research objectives are defined in Chapter 3.

Chapter 2

Scientific Problems and Hypotheses

This chapter identifies the scientific problems, research gaps, and guiding hypotheses that motivate the dissertation. It builds on materials-characterisation literature and focuses on unresolved challenges in computational support for design. These challenges include material and process selection, mechanical and functional performance prediction, and the translation of material states into component, device, or system behaviour. The chapter first defines the terms used in the gap analysis. It then formulates the gaps as scientific problem statements and concludes with hypotheses revisited in Chapter 5.

2.1 Definitions of Key Terms

The terms below are defined as they are used in this work. Together they frame the gap analysis, problem statements, and hypotheses. They cover the two methodological pillars, the principle that links them across scales, the intermediate state they act upon, and the material systems to which they are applied. They also reflect the interdisciplinary character of the work. Material behaviour is studied because it determines component performance. Design requirements shape the development of advanced materials, while computational mechanics links multiscale materials modelling with machine learning.

Computational design refers to the use of computational mechanics to simulate material behaviour, predict structural evolution, and identify configurations that meet structural and functional performance requirements. These methods include density functional theory, phase-field simulation, finite element analysis, and finite-strain plasticity. Material description therefore provides quantitative information for material selection, process specification, and component evaluation.

Data-driven design complements physics-based modelling by learning structure-property and process-property relationships from literature-derived, experimental, or simulation-generated datasets. It supports property prediction, design-space screening, dimensionality reduction, and inverse design.

Scale-bridging is the systematic linking of information, descriptors, and models across length and time scales. It encompasses two complementary modes. The first is *direct transfer* of parameters across scales, for example DFT-derived elastic constants entering phase-field simulations. The second is *indirect descriptor linking*, in which physically meaningful

composition, processing, crystallographic, or morphological descriptors represent lower-scale information and relate it to higher-scale structural or functional response. The relevant scale transition differs among the investigated systems, and each study bridges the scales required by its specific design problem [26].

Microstructure denotes the heterogeneous internal arrangement of a material at the mesoscale, between the atomic and macroscopic levels [27]. It comprises grains or domains that differ in crystal structure, crystallographic orientation, and chemical composition. It is characterised by their shape, size, spatial distribution, and interfaces. A microstructure evolves as the system reduces its interfacial, bulk, and elastic strain energy. This mesoscale morphology governs macroscopic physical and mechanical properties. Here, microstructural features are treated as design variables as well as characterisation descriptors. These features include grain morphology, phase distribution, fibre morphology, crystalline phase fractions, and dendritic interfaces. They mediate the relationship between composition, processing, and performance. Tensorial states and associated physical fields are treated as related structure-sensitive attributes.

Advanced functional materials, as used here, encompass systems designed for structural, electromechanical, electrochemical, or coupled performance in components and systems. They comprise multicomponent alloys, piezoelectric ceramics and polymers, and lithium-based battery interfaces. All are sensitive to composition, processing, and structure-dependent states.

2.2 State of the Art and Research Gaps

Advanced functional materials are increasingly studied with computational and data-driven methods. The principal challenge is to use this understanding to specify materials, processes, and system designs. Difficulties persist where performance emerges from coupling between composition, processing, the intermediate material state, and device- or interface-level behaviour. Each gap in this chain limits the reliability of computational support for component and system design. Without consistent descriptor-to-performance pathways, material selection, process specification, and component evaluation cannot form an integrated framework. The gaps are organised below by scientific theme. Table 2.1 summarises them.

Multicomponent-alloy design. Data-driven models map compositional and processing features to alloy properties and estimate mechanical properties independently [28, 29]. Processing history is often omitted or coarsely represented. The manufacturing route then serves as a proxy for the thermal and deformation histories that shape phase constitution, porosity, grain structure, texture, and defect state, without uniquely determining them. Joint prediction and inverse design of the hardness-elongation balance across realistic composition-processing spaces remains limited.

Tensorial piezoelectric design. Crystalline piezoelectrics are frequently characterised by a few scalar coefficients such as d_{33} [15], which capture neither the complete tensor nor the symmetry constraints and orientation dependence that govern device response. Few models predict the complete, symmetry-constrained tensor and carry it through to device-level evaluation.

Process-driven piezoelectric polymers. In PVDF-based systems the response depends on processing-induced morphology, filler content, and crystalline phase fraction. Purely empirical fits rarely transfer between processing conditions. Physics-directed frameworks that connect processing and morphology to the effective piezoelectric response are not well established, especially under the data-scarce conditions typical of curated polymer datasets.

Cross-scale parameter transfer. Microstructure evolution couples chemical, elastic, electrochemical, and transport phenomena. Many phase-field studies use temperature-invariant or averaged parameters [14], limiting fidelity when atomistic information must inform mesoscale evolution. Systematic transfer of temperature-dependent, phase-specific DFT parameters into phase-field models remains limited. Their effect on predicted morphology is also rarely quantified.

Lithium dendrites suppression. Phase-field simulations of lithium-dendrite evolution resolve the coupled electrochemical and transport fields that drive interfacial instability [23], but translating this mechanistic picture into actionable design guidance is difficult. The materials, interfacial, and operating approaches that suppress dendrite growth remain dispersed across the literature [30, 31] and are seldom consolidated into a coupled set of performance and stability targets.

Two further items lie outside these five principal gaps but are reported alongside them. A constitutive description of nonlinear elastic-plastic response suitable for integration within multiscale simulation addresses a methodological need and is treated as a supporting contribution. The reuse of alloy-derived cation pools to screen multifunctional oxide and nitride chemistries is treated as prospective work. It appears as the final row of Table 2.1 but is not formulated as a principal problem.

2.3 Scientific Problem Statements

Each gap is restated as a scientific problem. The dissertation addresses five interconnected problems, labelled P1-P5:

P1 Composition-processing-property linkage in multicomponent alloys is incompletely captured.

The objective is to specify alloy composition and manufacturing route for structural components that meet defined mechanical performance targets. This demands models that span the composition-processing-property chain rather than treating composition and processing as independent variables. Alloy performance depends on composition, processing history, phase constitution, and grain morphology, yet this chain is seldom modelled together. Joint prediction and inverse design of the hardness-elongation balance across realistic composition-processing spaces remain limited.

P2 Full-tensor, crystallography-informed piezoelectric prediction and device evaluation are underdeveloped.

Designing piezoelectric sensors, energy harvesters, and MEMS devices requires electromechanical output predictions under realistic loading, geometry, and orientation

Table 2.1: Gap analysis by scientific theme and engineering design response.

Theme	Current limitation for design	Computational response
Multicomponent alloys	Manufacturing route is encoded coarsely. Strength and ductility are often predicted independently rather than jointly.	Joint composition-route prediction and inverse design of the hardness-elongation balance.
Piezoelectric ceramics	Tensor anisotropy and orientation dependence are omitted when device output is approximated from scalar d_{33} alone.	Full-tensor prediction with point-group symmetry constraints and device-level finite element evaluation.
Piezoelectric polymers	Empirical processing-property fits are not physics-guided and transfer poorly across processing conditions.	Concept-enriched descriptors linking morphology and phase fraction to the effective response under data-scarce conditions.
Cross-scale transfer	Phase-field parameters are often taken at 0 K or thermally averaged, with limited verification at the simulation temperature.	Temperature-calibrated, phase-specific DFT inputs with quantified morphological sensitivity.
Battery interfaces	Coupled-field growth mechanisms are difficult to translate into suppression strategies when each metric is treated separately.	Coupled-field phase-field simulation of dendrite growth plus a consolidated multi-metric suppression roadmap.
Multifunctional materials (prospective)	Alloy-relevant cation chemistries are not yet assessed systematically in oxide or nitride forms.	Reuse of alloy cation pools with point-group classification and scalar response screening.

The final row identifies prospective work outside the five central problems (P1-P5).

conditions. A single coefficient such as d_{33} does not capture the tensor anisotropy and orientation dependence that govern complex geometries. It also cannot provide the information needed to select and orient a material within its mechanical enclosure. Models that predict the complete, symmetry-constrained tensor and carry it through rotation into finite element evaluation remain limited.

P3 Physics-guided processing-morphology-response modelling for piezoelectric polymers is not well established hitherto.

The challenge in flexible piezoelectric device manufacture is to predict the combined influence of electrospinning conditions and filler content on device output. Such prediction would allow sensing or actuation specifications to be met through informed process design rather than repeated empirical experimentation. In PVDF-based systems, the electroactive β -phase fraction, fibre alignment, and filler content govern the response. Empirical fits seldom transfer between processing conditions. Frameworks

that incorporate the processing-morphology-response chain and remain predictive with limited datasets are lacking.

P4 Temperature-calibrated atomistic parameters are rarely transferred to phase-field models consistently.

Reliable alloy process design requires microstructure predictions that are thermodynamically consistent with the processing temperature. Using 0 K atomistic parameters introduces systematic error that accumulates through predicted grain morphology to mechanical property estimates for the manufactured component. Most phase-field studies use temperature-invariant or thermally averaged parameters, reducing physical fidelity at finite temperature. Systematic transfer of phase-specific, temperature-dependent DFT quantities and assessment of their effect on predicted morphology remain limited.

P5 Dendrite-growth mechanisms are unresolved and suppression strategies lack a unified design framework.

The safety and longevity of lithium-based battery systems depend on preventing dendrite-induced short circuits. Effective suppression strategies require a mechanistic model of the coupled-field driving forces that existing approaches do not fully resolve. Solid-electrolyte interphase dynamics, field localisation, and transport phenomena interact to amplify growth at protruding tips. Coupled-field phase-field models that resolve this mechanism remain incomplete. Materials, interfacial, and operating suppression strategies are usually reported independently rather than as a jointly constrained set of performance, durability, and reliability targets.

2.4 Hypotheses

These problems are addressed through two tiers of hypotheses. The central hypothesis organises the thesis as a whole. Five specific hypotheses then operationalise it across the material domains and the cross-domain synthesis. Each is revisited against the results in Chapter 5. The criteria following each hypothesis define its evaluation. Unless stated otherwise, all predictive hypotheses are bounded by the composition, processing, and simulation domains represented in the corresponding datasets.

2.4.1 Main Hypothesis

CH A unified scale-bridging framework can establish reliable descriptor-to-performance pathways for engineering design across distinct material classes.

No single modelling approach spans the full pathway from composition and processing descriptors to component-, device-, or interface-level performance. Consistent scale transfer and physically grounded descriptor formulation through the intermediate material state are the necessary conditions for reliable, transferable design across material domains.

2.4.2 Specific Hypotheses

Table 2.2: Translating scientific problems into formulated hypotheses.

Problem	Hypothesis
P1 and P4	H2
P2 and P3	H3
P5	H4
All problems (P1-P5)	CH, H1, and SP1

H1 Coupled physics-based and data-driven modelling enables capabilities unavailable to either approach independently.

Evaluation criteria: symmetry-consistent outputs, temperature-consistent parameter transfer, or device-level evaluation unavailable from the property model alone, judged against unconstrained or scalar-only baselines.

H2 Composition-route descriptors predict alloy design regions and calibrated tensors improve mesoscale parameterisation.

H2a asserts that composition and manufacturing-route descriptors identify balanced hardness-elongation design regions, evaluated by cross-validated performance and stability under resampling. H2b asserts that temperature-calibrated DFT elastic tensors measurably alter the predicted mesoscale microstructure evolution relative to 0 K inputs.

H3 Full-tensor prediction and morphology-based descriptors outperform scalar approaches for piezoelectric design.

For crystalline piezoelectrics, predicting the complete symmetry-constrained tensor and evaluating it at device scale provides orientation-dependent performance information unavailable from scalar coefficients. For polymers, processing and morphology features carry predictive information for the effective response. Both claims are evaluated within the computational scope of the dissertation.

H4 Coupled-field simulation resolves dendrite-growth mechanisms and informs a consolidated suppression framework.

Evaluation criteria: a resolved coupled-field feedback that captures tip-localised branching, and a consolidated set of materials, interfacial, and operating suppression targets assessed as coupled rather than independent metrics.

SP1 A common descriptor-to-performance logic applies across domains, with material-specific implementation.

Evaluation criteria: the recurrence of this organisation across the investigated domains and the emergence of common, transferable design rules.

Table 2.2 maps the problems onto the hypotheses. Chapter 3 adds the corresponding objectives and evidence.

Chapter 3

Research Objectives

The scientific problems and hypotheses formulated in Chapter 2 call for a scale-spanning strategy. Isolated single-scale models and composition-only approaches have limited ability to capture the descriptor-to-performance pathway required for design. This chapter states the overarching aim, defines the specific objectives, and positions the principal contributions relative to supporting and prospective work.

3.1 Overall Objective

The dissertation develops and applies scale-bridging computational methodologies that combine physics-based modelling and data-driven methods. These methods connect material descriptors and intermediate states to structural and functional performance across multicomponent alloys, piezoelectric materials, and lithium-based battery interfaces. The aim is to support alloy and process selection, device-level electromechanical prediction, and reliability-target definition for electrochemical energy systems.

3.2 Specific Objectives

The overall objective is pursued through one specific objective per domain. Each objective is stated as a design capability and scoped to the relevant material system.

1. **To develop scale-bridging alloy models that support material and process specification for structural and functional applications.**

AlloyManufacturingNet encodes composition and manufacturing-route descriptors jointly. It enables prediction and inverse design of the hardness-elongation balance needed for mechanical performance. A complementary DFT-informed phase-field model transfers temperature-calibrated elastic constants into mesoscale simulation of Al-Cu-Ni microstructure evolution. Evaluation is based on cross-validated predictive accuracy and quantified morphological sensitivity to thermal parameterisation.

2. **To model piezoelectric performance for actuator and energy-harvester design.**

For AlN-based ceramics, PiezoTensorNet predicts the complete, symmetry-constrained piezoelectric tensor and evaluates orientation-dependent device performance through finite element simulation. This provides a physically informed basis for selecting and orienting piezoelectric materials beyond scalar d_{33} approximations. For electrospun PVDF/SnO₂ nanofibres, a physics-guided model connects processing parameters, filler content, and fibre morphology to the effective response under data-scarce conditions, supporting flexible device design.

3. To evaluate SEI-governed dendritic instability and establish a multi-metric design framework for battery’s mechanical durability and reliability.

A phase-field model resolves the coupled concentration, potential, and interfacial energy fields that drive electrochemically induced lithium deposition. It clarifies how solid-electrolyte interphase dynamics and localised field enhancement at protrusion tips amplify dendrite growth. A complementary literature synthesis consolidates materials, interfacial, and operating suppression approaches into jointly constrained performance and stability targets for electrochemical system design.

3.3 Scope and Alignment with Research Problems and Hypotheses

Table 3.1: Alignment of objectives with scientific problems, hypotheses, and engineering design evidence.

Objective	Problems	Hypotheses	Principal design evidence
O1 Multicomponent alloys	P1, P4	H1, H2	Cross-validated hardness-elongation prediction for structural alloy specification. Model-predicted design windows for load-bearing applications. Temperature-calibrated elastic tensors that modify Al-Cu-Ni phase evolution and grain area in process-relevant simulations.
O2 Piezoelectric materials	P2, P3	H1, H3	Symmetry-consistent tensor prediction for sensor, actuator and energy-harvester material selection. Finite element evaluation of orientation-dependent device output. Physics-guided polymer response prediction for flexible component design.
O3 Lithium-based battery interfaces	P5	H1, H4	Resolved coupled-field dendrite-growth mechanism for battery reliability assessment. Suppression framework for interface stability, service performance and durability. Operating targets for safer electrochemical systems.

The three specific objectives define the principal contributions and provide the evidence

for assessing the hypotheses. The remaining studies are positioned relative to this core. The data-driven corrosion analysis of additively manufactured duplex stainless steel and the finite-strain plasticity description of nonlinear mechanical response are *supporting* contributions. They demonstrate transferability without introducing new principal claims. The reuse of alloy-derived cation pools to screen multifunctional oxide and nitride chemistries is *prospective* work. It is pursued at the level of compositional screening and is not advanced to a validated outcome. The lithium-interface roadmap provides *context* for interpreting dendrite-growth mechanisms and suppression strategies, but is not itself an evaluated objective. This delineation bounds the claims assessed in Chapter 5.

Table 3.1 maps each objective to the corresponding problems, hypotheses, and evidence.

The central hypothesis (CH) and cross-domain synthesis proposition (SP1) function as assessment-level statements. Both are assessed collectively using evidence from all three objectives and the resulting transferable schemes.

Chapter 4 evaluates these objectives, distinguishes principal from supporting evidence, and derives the scale-bridging schemes that form the dissertation synthesis.

Chapter 4

Scale Bridging Design of Advanced Functional Materials

This chapter applies the scale-bridging approach developed in the preceding chapters. Process parameters and material descriptors define the attainable properties. The intermediate state controls how these properties reach the component level. Operational loads and boundary conditions then determine system performance. The studies combine data-driven models, phase-field simulations, and finite element analysis to support design decisions for structural and active components.

Structural alloys serve as the principal case study because load-bearing behaviour is strongly linked to manufacturing parameters and thermal history. Piezoelectric systems and electrochemical interfaces extend the approach to actuators, sensors, and energy storage devices. Figure 1.1 shows the overall modelling sequence. Experimental data calibrate the models, lower-scale physics constrains statistical predictions, and device-level simulations identify variables for refinement. Table 4.1 summarises how each study contributes to the synthesis.

Table 4.1: Scale-bridging synthesis of the studies discussed. Each row links a computational design method to an engineering design decision or reliability target.

Material system	Computational design method	Principal engineering finding or design rule	Source
Multi-principal-element alloys	Machine-learning models link composition and manufacturing route to hardness-ductility requirements.	Load-bearing alloy design should co-specify chemistry and manufacturing route because the strength-ductility balance depends on both.	[P-I]

Continued on the next page

Table 4.1 continued

Material system	Computational design method	Principal engineering finding or design rule	Source
Additively manufactured duplex stainless steel	Data-driven process-property models relate heat-treatment variables and phase balance to surface performance.	Post-processing heat treatment can tune phase balance and surface degradation response. This affects durability in additively manufactured components.	[P-VI]
Al-Cu-Ni alloy system	DFT-informed phase-field simulations transfer temperature-calibrated elastic tensors into microstructure models at processing temperature.	Process modelling should use temperature-consistent elastic parameters. They change predicted grain morphology and the internal state used for component performance assessment.	[P-III]
Doped AlN-based piezoelectric ceramics	Symmetry-constrained tensor prediction and finite element analysis evaluate oriented piezoelectric components.	Sensor and energy-harvester output depends on the full electromechanical tensor. Optimising tensor orientation raises simulated power output 9.96-fold.	[P-II]
PVDF/SnO ₂ piezoelectric polymers	Physics-guided descriptors connect electrospinning settings, filler content and fibre morphology to effective response.	Flexible device design should treat morphology, phase fraction and mechanical boundary conditions as coupled controls of harvested output.	[P-V]
Multifunctional oxide and nitride screening	Alloy-derived candidate spaces are screened for electromechanical and dielectric responses.	Active component design requires Pareto-optimal windows that balance electromechanical response, dielectric behaviour and structural feasibility.	[P-I, P-II]
Lithium-based battery interfaces	Coupled-field simulations resolve transport, electrical and interfacial drivers of interface failure.	Battery reliability requires suppression strategies that control local field concentration and define joint targets for lifetime, durability and service performance.	[P-IV]

4.1 Structural Alloys: Processing and Microstructure Control

The analysis begins with multicomponent alloys. Composition alone does not determine component performance. Manufacturing routes and thermal histories define the intermediate

state, which then governs mechanical properties under load. For a load-bearing component, chemistry and processing must be specified together to meet strength and ductility targets. The section first addresses strength-ductility trade-offs and temperature-consistent phase evolution. It then extends the same logic to corrosion response and prospective multifunctional screening.

4.1.1 Manufacturing Pathway-Aware Strength-Ductility Design

AlloyManufacturingNet [P-I] connects chemical composition and fabrication parameters to strength and ductility. Because these properties carry different physical units and numerical scales, a direct comparison introduces bias. A scale-invariant objective function $F(x,y)$ standardises both responses against their dataset mean and standard deviation. This produces a dimensionless synergy score. Compositions with positive standardised values define the balanced region used for inverse design. Candidates can then be ranked without arbitrary response weights.

The feature space uses elemental and stoichiometric parameters. Statistical redundancy is removed before neural network training. The retained descriptors provide physical interpretation of the prediction. They include the bulk and shear modulus mismatches (ΔB , ΔG) and the valence electron concentration (VEC). ΔB and ΔG relate to Pugh's ratio B/G and Cauchy pressure. These parameters indicate the brittle-to-ductile transition. VEC aligns with Pettifor's criteria for bonding character. In refractory alloys, VEC determines whether d-band filling stabilises BCC phases or promotes transformations that enable ductility [32]. The descriptors reflect thermodynamic and quantum-mechanical regularities of bonding.

The manufacturing route is a design variable. Casting, wrought processing, powder metallurgy, and annealing impose distinct thermal and deformation histories. Each route produces different phase distributions and defect states. This sensitivity motivates metamorphic manufacturing, where digitally controlled forming assigns different process sequences to different zones of a single component. Such control can yield site-specific mechanical properties within a compositionally uniform part, for example a wear-resistant surface combined with a ductile core. AlloyManufacturingNet quantifies the process-composition coupling needed for this type of component specification.

The synergy maps reveal differences between the two base systems. In ZrHfNb-derived systems, the high-strength and high-ductility regions are well separated. The objective function rarely yields positive values for both responses simultaneously. In VNbTa-derived systems, the co-positive window is broader. $\text{Mo}_{0.3}(\text{VNbTa})_{0.7}$ lies within this region. Cr-W additions under powder metallurgy raise hardness to 730 HV while retaining a positive elongation score. Ti-rich compositions under annealing shift the balance toward ductility. These results confirm that optimising one response can reduce the other. The objective function makes this comparison explicit.

The CoCrNiNb_x series tests the trade-off along a single composition axis. Hardness rises with Nb content. Elongation falls to a minimum near $x = 0.25$ and then recovers. The balanced region is therefore located near $x = 0.6$, yielding 600 HV with elongation above 20%. Molecular dynamics nanoindentation supplies physical validation. The penetration resistance for $\text{CoCrNiNb}_{0.6}$ is three times that of CoCrNi. The difference is rooted in Nb-driven changes

to dislocation mobility, linking macroscopic predictions to nanoscale deformation physics.

The alloy study therefore prioritises robust manufacturing regions rather than single-property extremes. A dimensionless objective function, physics-guided descriptors, and atomistic validation together support component-level specification. Figure 4.1 provides the atomistic evidence. Panel (b) links predicted hardness to nanoscale deformation mechanisms. Panel (a) presents the DFT curves used to calculate the temperature-dependent elastic tensors for the process models.

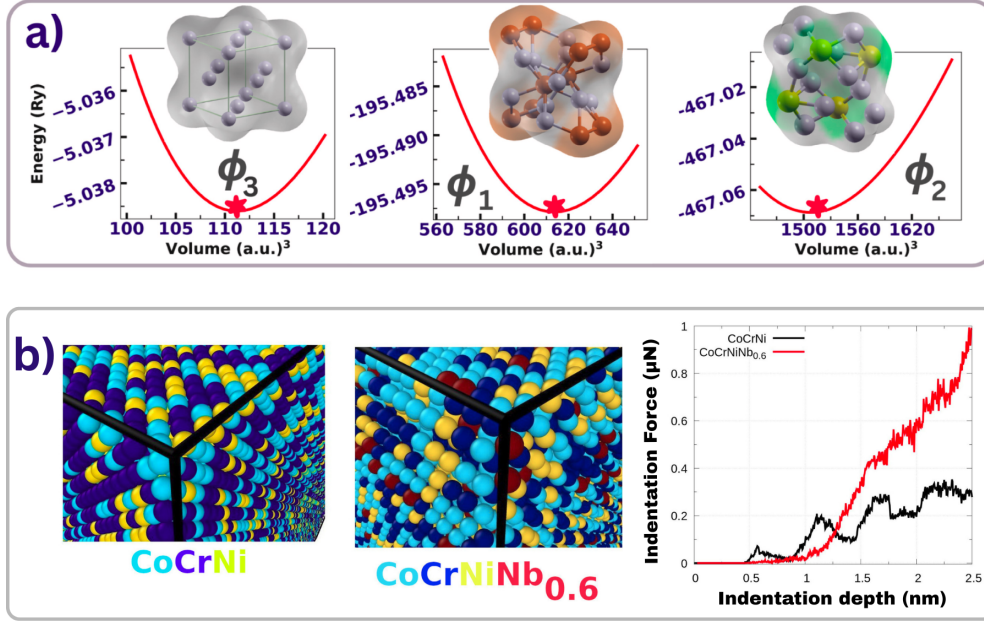


Figure 4.1: **Atomistic calculations supply the physical foundations for both the data-driven property model and the phase-field simulation.** (a) DFT energy-volume curves for representative Al-rich, Al-Cu, and Al-Ni phases. Minimum-energy structures (asterisks) provide the relaxed configurations from which phase-specific elastic tensors are derived for temperature-calibrated phase-field parameterisation. [P-III] (b) Molecular-dynamics nanoindentation of CoCrNi and CoCrNiNb_{0.6} nanoslabs. Force-depth curves and atomistic snapshots compare the local mechanical response. The substantially higher penetration resistance of the Nb-containing slab links the model-predicted hardness increase to a nanoscale deformation mechanism, connecting the macroscale composition-property trend to atomistic physics. [P-I]

4.1.2 Temperature-Calibrated Microstructure Prediction

Statistical predictions do not resolve how internal geometries develop during processing. The Al-Cu-Ni system is multi-phase, with several phases evolving during thermal processing. A DFT-informed phase-field model [P-III] predicts this evolution for three phases: Al-rich FCC, Al₂Cu, and Al₃Ni. The model is built in the MOOSE finite element framework [24, 25]. It transfers elastic tensors from atomistic calculations to a mesoscale energy description. The phase energies are coupled using a thermodynamically consistent interpolation function [33].

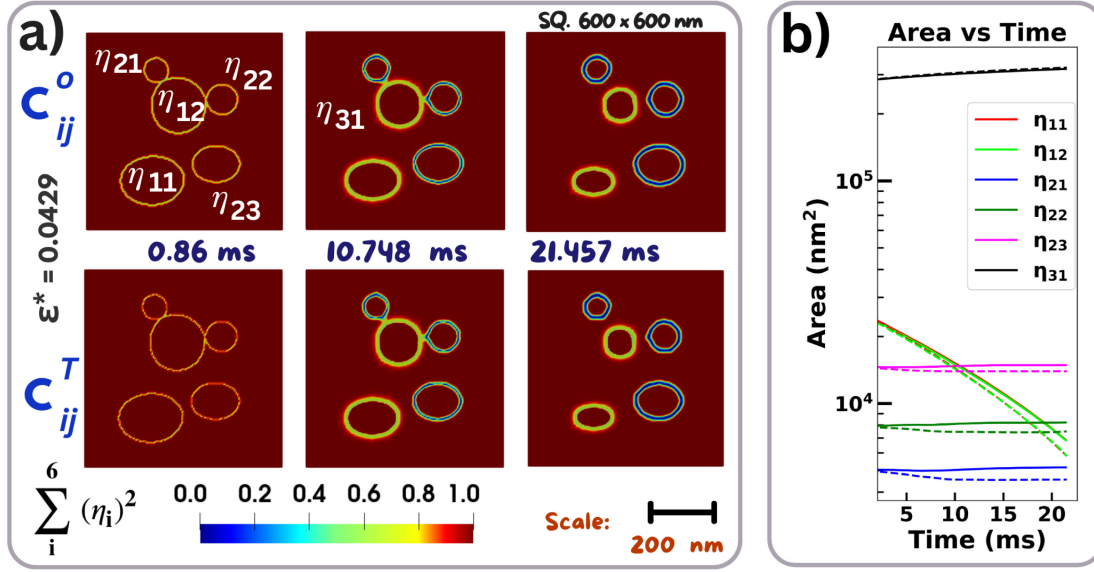


Figure 4.2: **Faithful scale bridging requires lower-scale parameters that represent the thermodynamic state of the mesoscale model.** (a) Order-parameter fields computed with elastic constants at 0 K and with temperature-calibrated values at 723 K. (b) Corresponding phase-area evolution (dotted: 0 K, solid: 723 K). The growing separation demonstrates that temperature calibration changes the phase-dependent elastic contrast and hence the kinetics of morphological selection. [P-III]

The total energy reduces to the single-phase value within each grain, keeping the interfaces well defined.

Elastic behaviour is direction dependent. Each phase is characterised crystallographically and elastically. The phases are cubic, tetragonal, and orthorhombic. All are mechanically stable. The number of independent elastic constants rises from three to nine. The full anisotropic stiffness tensor of each phase is retained instead of an isotropic approximation. Tensor anisotropy governs the response to internal coherency strains. The same symmetry-constrained tensor principle underlies PiezoTensorNet in Section 4.2. In both studies, symmetry defines the admissible tensor structure. Here the tensor is the fourth-rank elastic stiffness. In PiezoTensorNet it is the third-rank electromechanical coupling.

In the simulations, chemical energy driving forces set the baseline direction of evolution. Al_3Ni grows while Al_2Cu is consumed. Internal strain energy is not negligible. Under large elastic mismatch, it can slow evolution, halt a phase, or reverse the direction of growth. A phase that would shrink can grow instead. To separate these effects, the model decouples chemical and elastic contributions to grain evolution. This separation quantifies the elastic contribution.

Figure 4.2 demonstrates that the simulations diverge as the phases evolve. The area of a selected grain differs by 18.18% between the 0 K and 723 K parameterisations. This difference arises because stiffness changes accumulate as the boundaries move. The divergence confirms that temperature-consistent inputs alter the predicted geometry. A 0 K input is not representative when modelling fabrication at 723 K. The temperature-calibrated

tensors are therefore the consistent choice. The 0 K tensor used for Al_3Ni is a source of uncertainty.

The present model retains elastic coupling. Where internal stresses are large, a finite-strain plasticity framework provides a route to model plastic relaxation at boundaries [P-VII, AP-II].

4.1.3 Transfer to Surface Durability in Additive Manufacturing

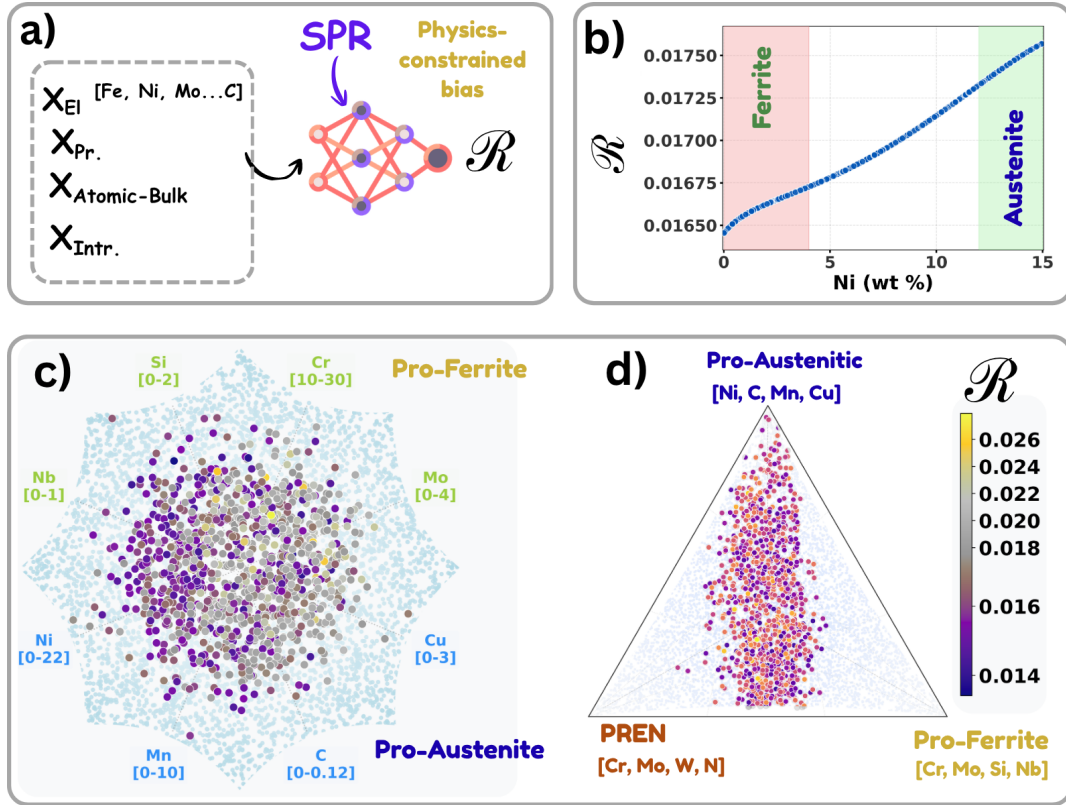


Figure 4.3: AlloyManufacturingNet's composition-processing framework extends to functional surface performance through concept-directed deep learning. (a) A Tabular ResNet with Structural Panelised Element Representation (SPER) maps composition, LPBF process parameters, and explicit interaction terms to the predicted corrosion resistance R . (b) Compositional variation of Ni with respect to the target corrosion resistance R , revealing the ferrite- and austenite-stabilising regimes. (c) Alloying elements grouped into pro-ferrite and pro-austenite families by the SPER constraint, shaded by R . (d) Candidate compositions on a PREN, pro-ferrite, and pro-austenite map, with corrosion resistance as the performance response. [P-VI]

The corrosion study tests the same composition-processing logic in additively manufactured steel components [P-VI]. It extends the model in three directions. First, categorical processing routes are replaced by granular process parameters. These include heat-treatment temperature, soaking duration, and cooling media. Second, the target is

expanded from bulk properties to surface performance, specifically polarisation resistance. Third, the architecture is adapted to the more complex process space.

The feature pipeline converts raw inputs into atomic-bulk descriptors and adds two process blocks. The first captures heat-treatment temperature and exposure duration. The second contains interaction terms that encode the non-linear coupling between potential and thermal history. Similar compositions behave differently under different thermal histories because heat treatment modifies the phase balance. Both the phase fractions and the degradation response shift with the process conditions.

The model architecture uses a Tabular ResNet with attention weighting to capture higher-order interactions. Physical constraints are formalised using a structural representation that groups elements into phase-stabilising families. The network is therefore constrained by known composition-phase trends (Figure 4.3).

The process-property logic generalises from bulk load-bearing performance to surface response. Transfer depends on target-specific feature vectors and retraining against electrochemical data. Apparent corrosion resistance serves as a supporting response. The results indicate that process-aware models can be adapted across component types and target properties.

4.1.4 Prospective Screening Techniques for Active Functional Systems

AlloyManufacturingNet [P-I] maps process parameters and compositions to the strength-ductility balance in multicomponent systems. The same transition-metal pools suggest a prospective route toward functional oxides and nitrides. In this extension, alloy-derived cation sets are recast as charge-balanced formulas and screened for electromechanical, dielectric, and polar responses. This is consistent with data-driven design of active ceramics [34]. The search space is transferred to new chemistry classes, while recognising that metallic alloys and their oxide forms require separate stability checks.

The screening combines two inputs from the preceding studies. The candidate space comes from the alloy datasets after refractory transition metals are recast as oxides and nitrides. The symmetry classification comes from PiezoTensorNet [P-II], which grouped point groups into five tensor-sparsity clusters (PG1 to PG5). These are organised as Class A and Class B. The candidate pool is therefore filtered by symmetry before property trade-offs are assessed.

Physical symmetry is a central constraint across the studies. It acts through different mechanisms in each case. It enters through the anisotropic elasticity of Al-Cu-Ni alloys (Section 4.1.2). It also enters through the electromechanical tensor of PiezoTensorNet (Section 4.2) and the prospective screening (Figure 4.4). Unlike the tensor model, this screening retains all point groups during training. The full anisotropic tensor is not predicted here. Instead, the maximum coupling response $e_{ij}^{\max}$ represents electromechanical behaviour. This value is combined with dielectric and polar properties to evaluate each candidate.

The prospective library contains about 23,000 charge-balanced formulas drawn from the transition-metal pools studied in AlloyManufacturingNet [36].

The screening identifies Nb-Ti-Zr and Nb-Ta-Ti oxides as the leading candidates (Figure 4.5). These compositions often support polar distortions. Further simulations would

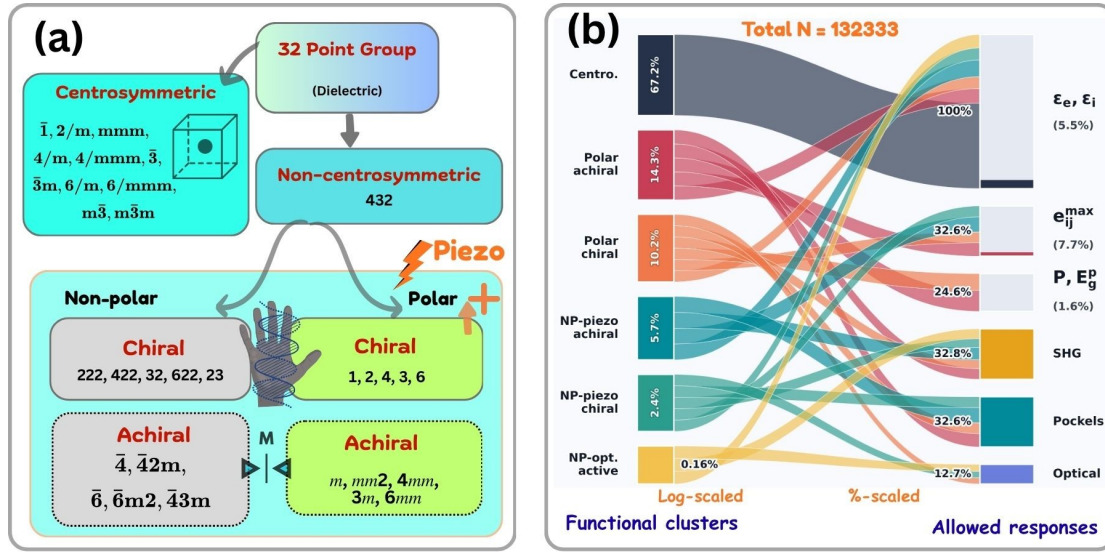


Figure 4.4: **The multifunctional extension inherits the crystallographic classification of PiezoTensorNet [P-II]. Symmetry determines which functional responses a point group can support.** (a) Selection rules across the 32 point groups. A dielectric response is generally allowed. Piezoelectricity requires a non-centrosymmetric group other than 432. A polar response requires one of the ten polar groups. (b) Functional-cluster and data-coverage summary. The panel separates symmetry-allowed responses from the availability of a measured target. N is the total number associated with functional materials entries in the materials project database. [Author’s own work. Supporting analysis: [35]]

be required to verify the mechanisms. The data reveal a trade-off in which a wider band gap accompanies a lower spontaneous polarisation. Consequently, the most promising candidates occupy a balanced design window rather than showing extreme values for a single property.

This extension provides a filtered search space by combining structural alloy data, symmetry classifications, and multi-property trade-offs. The outputs are candidates for future testing. Screening narrows the design space, but it cannot confirm phase stability or measured properties. Those steps require structure predictions and experimental verification.

4.2 Electromechanical Design from Symmetry to Device Performance

The second application concerns electromechanical energy conversion in active components. Piezoelectric devices are the principal example. The design variables differ by class. Ceramic components depend on symmetry, tensor components, and orientation. Polymer elements depend on fabrication parameters, fibre morphology, and fillers.

The objective is to identify the combined influence of process variables, orientation, and device geometry on electromechanical output. Component-level mechanical and electrical analysis is required because a large coupling coefficient alone does not ensure high performance. Output also depends on stiffness, loading, boundary constraints, and external circuits. Finite element analysis tests whether material-level improvements translate

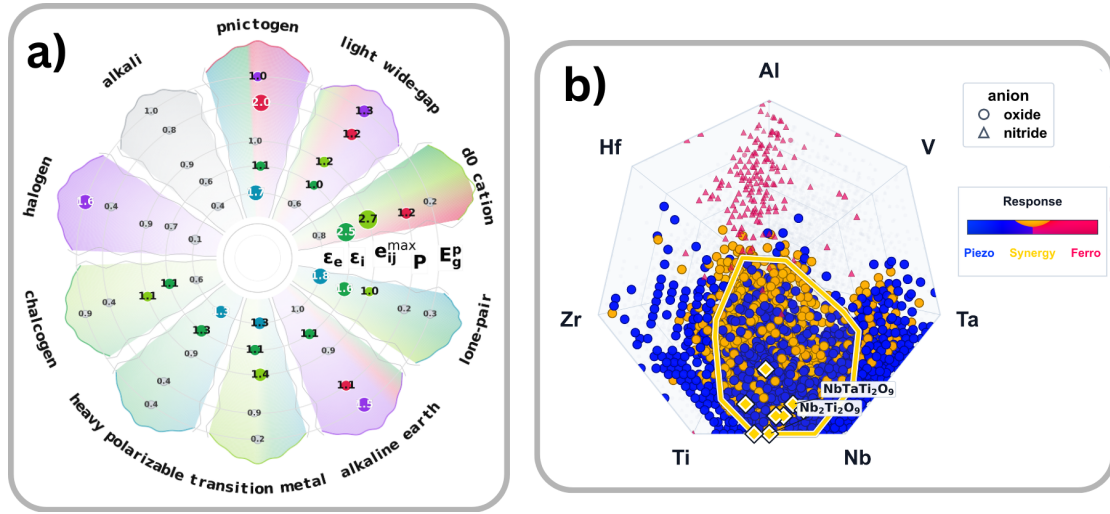


Figure 4.5: **The multicomponent-alloy cation pools of AlloyManufacturingNet datasets [P-I] map onto distinct functional regimes when reused as a screening space for oxide and nitride chemistries. (a)** Chemical-family enrichment atlas: concentric positions denote the five functional targets and printed values give top-decile enrichment ratios. **(b)** Integrated seven-axis composition map for the Al-Hf-Zr-Ti-Nb-Ta-V chemistry. Marker shape distinguishes oxides from nitrides, response colour distinguishes piezoelectric-dominant, polar-dominant, and co-functional candidates, and the closed contour marks the co-optimised region. [Author’s own work. Supporting analysis: [35]]

to device-level performance for the intended loading state.

4.2.1 Applying Tensor Methods to Piezoceramic Design

PiezoTensorNet [P-II] embeds symmetry constraints directly in the neural network architecture. A classifier first assigns each composition to a tensor-symmetry class. It then routes the candidate to one of five point-group families (PG1 to PG5) grouped by tensor sparsity. This classification directs the inputs to a dedicated regression module. The output dimension matches the number of independent coefficients for that symmetry. This ranges from a single constant for PG1 to five independent constants for PG5.

Each module populates only the symmetry-allowed tensor positions. This architecture prevents unphysical values for symmetry-forbidden components. The routing replaces a general model with specialised modules tuned to specific tensor topologies, which improves accuracy and data efficiency. The predicted 3×6 tensor is physically consistent and can be rotated into the device frame.

The feature representation is richer than for structural alloys. Composition descriptors are combined with crystallographic information. Composition alone cannot enforce symmetry or orientation behaviour. The model learns from composition together with its symmetry environment.

A single coefficient such as e_{33} captures response along only one loading axis. A tensor-based norm e_{mod} is therefore used to rank candidate chemistries. This norm combines

longitudinal, transverse, and shear components. It serves as a screening variable rather than a device figure of merit. Device performance also depends on dielectric behaviour, elastic stiffness, orientation, and loading conditions.

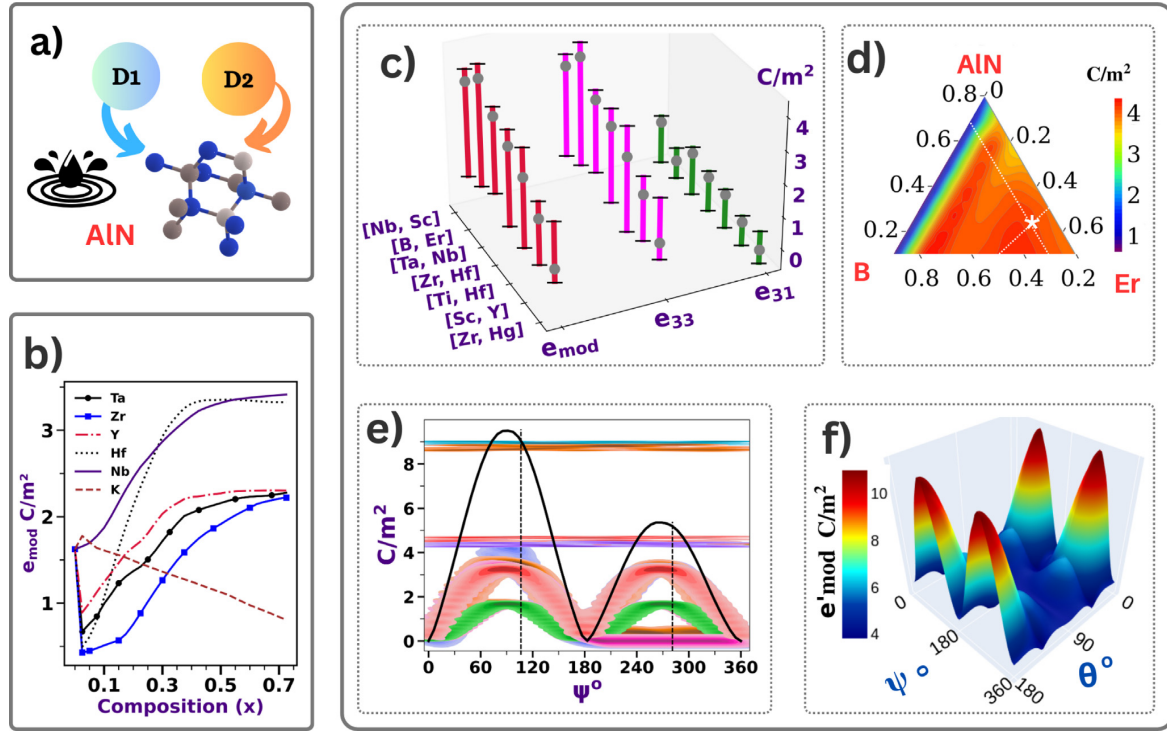


Figure 4.6: **Chemistry and orientation act as sequential design variables for the piezoelectric tensor.** (a, b) Single dopants raise e_{mod} above the pure-AlN value of 1.67 C m^{-2} . (c, d) Binary and ternary searches identify B-Er co-doping as the composition with the highest predicted response, reaching $e_{\text{mod}} = 4.37 \text{ C m}^{-2}$ near $\text{B}_{0.3}\text{Er}_{0.5}\text{Al}_{0.2}\text{N}$. (e, f) Tensor rotation produces symmetry-related maxima near $\psi = 90^\circ$ and 270° . [P-II]

The design workflow comprises three stages (Figure 4.6). First, single dopants are predicted to raise e_{mod} above pure AlN. B-Er co-doping gives the maximum value of 4.37 C m^{-2} near $\text{B}_{0.3}\text{Er}_{0.5}\text{Al}_{0.2}\text{N}$ by modifying several tensor components simultaneously.

Second, rotating the coordinate axes alters the tensor projection onto the device axes. This rotation yields response maxima near $\psi = 90^\circ$ and 270° .

Third, the rotated tensor is implemented in a finite element model of a beam component. The oriented composition is predicted to yield ten times the power of pure AlN. The simulation links chemistry, anisotropic tensor response, orientation, and power output. The optimal composition and its power gains remain computational predictions that require experimental testing.

4.2.2 Morphology-Driven Flexible Piezoelectric Design

In flexible polymers, functionality is controlled by a different state variable. The polar phase carries the electromechanical response. Its formation depends on chain alignment, stretching

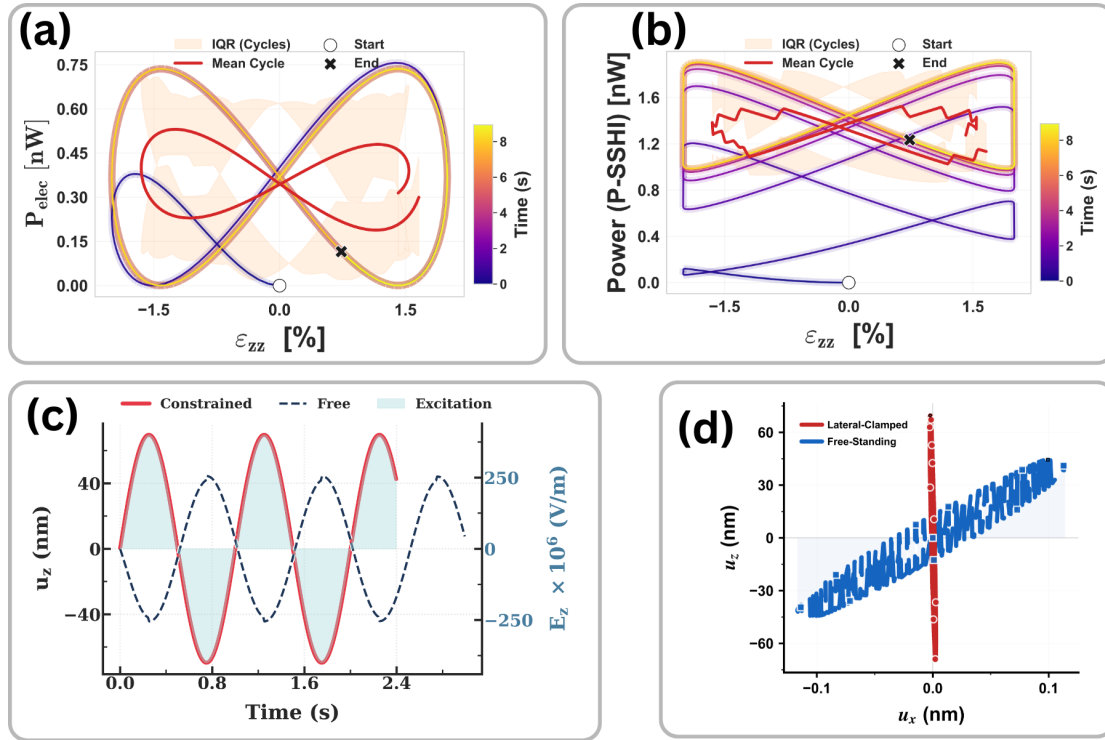


Figure 4.7: **Processing shapes the intrinsic polymer response, while circuit and boundary conditions set how much of it is realised.** (a, b) Passive and P-SSHI harvesting responses. Electrical conditioning raises the average power from 0.359 to 1.251 nW. (c, d) Free and laterally constrained actuator configurations give axial strokes of 44.41 and 69.60 nm. [P-V]

during electrospinning, and filler interactions. The relevant design link is process-induced morphology rather than point-group class alone.

The electromechanical response is crystallographic in origin. The polar phase crystallises in an orthorhombic structure with symmetry $mm2$. This structure aligns the internal dipoles and produces a large polarisation. It is the same PG5 symmetry class studied in the ceramic model [P-II]. The symmetry of the $mm2$ class determines which electromechanical coefficients are non-zero. Process parameters govern fibre morphology, alignment, and filler distribution. Physical symmetry remains a constraint in both cases, but acts through different constitutive equations.

Adding SnO_2 and optimising electrospinning reduce the mean fibre diameter from 680 to 290 nm. They also raise the polar phase fraction from 0.35 to 0.57. Finer fibres indicate stronger mechanical stretching. The filler provides active sites for the polar phase. Its effect is expressed through morphology and phase state rather than through composition alone.

The polymer dataset is limited. It contains fifty-two literature samples with filler fractions up to 20%. The data are dominated by phase formation and interface effects. Standard composition descriptors are therefore poorly suited. PGMLpiezo [P-V] combines composite mechanics baselines with interface representations in a single feature matrix. Embedding domain knowledge reduces model freedom. It does not remove statistical uncertainty from

the limited dataset. The model predicts that the coupling coefficient d_{33} rises from 18 to 29 pC N⁻¹. This prediction is then evaluated at the component level using the FERRET finite element framework [37].

The simulations identify two routes for increasing output (Figure 4.7). First, electrical conditioning circuits raise the average harvested power by a factor of 3.5 without changing d_{33} . The increase arises from improved charge extraction. Second, lateral boundary constraints increase the actuator stroke by 57%. This constraint suppresses parasitic motions and redirects the strain field into the desired direction. Component response therefore depends on both material properties and boundary conditions.

4.2.3 Shared Device-Level Piezoelectric Design Pathway

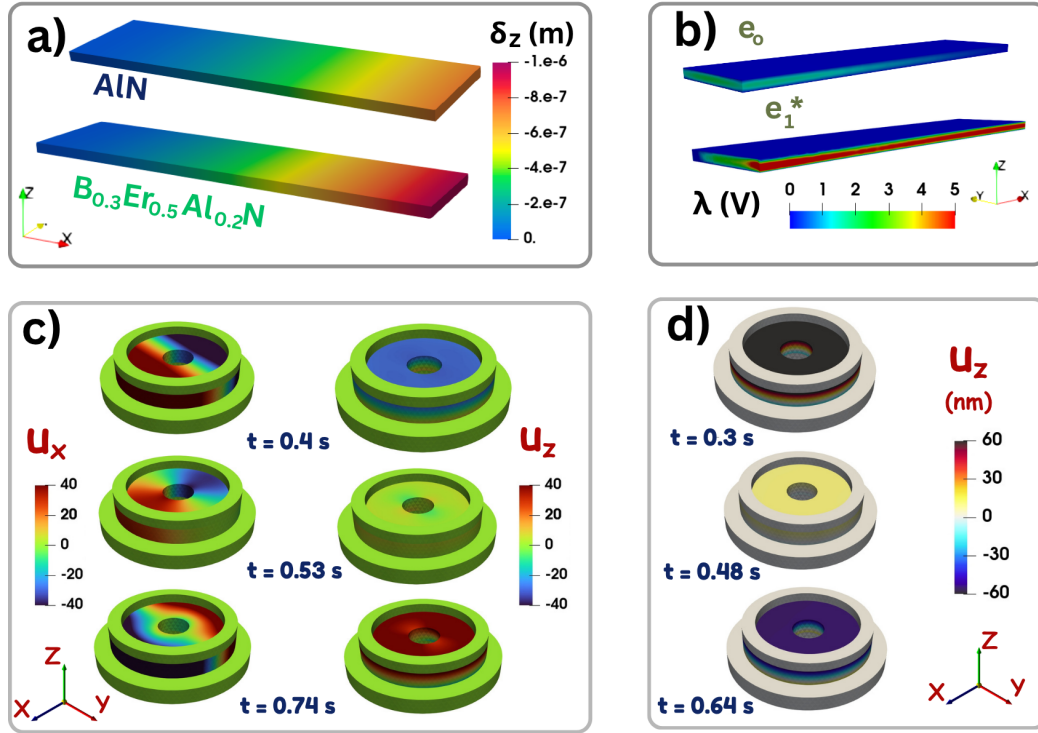


Figure 4.8: Device-level finite element evaluation is the common step that converts predicted properties into functional output for both component classes. **(a, b)** The doped wurtzite beam converts the symmetry-constrained, rotated tensor into deformation and potential. It reaches 7.8 V at a 0.97 μ m tip displacement [P-II]. **(c, d)** The polymer actuator demonstrates the redistribution of response between parasitic and desired displacements under lateral constraints [P-V].

Ceramic and polymer components use different model inputs but yield similar design rules. Material optimisation sets the intrinsic response, while component architecture determines how much of that response is realised (Figure 4.8). The pathway begins with process parameters and passes through symmetry, orientation, and morphology. It ends with the geometry, boundaries, and circuits that set the output. An oriented component with lower

intrinsic properties can outperform alternatives under suitable loads or boundary conditions.

4.3 Battery Interface Reliability and Dendrite Suppression

Electrochemical deposition can cause structural failure in battery components. Operating stability requires uniform deposition, but local perturbations can grow into branched structures. These branches consume active material, damage the interface, and may cause electrical short circuits. The durability of the energy storage component therefore depends on processing, interfacial, and operating conditions that maintain uniform deposition across the service life. Relevant parameters include operating temperature, current density, and mechanical loads.

4.3.1 Coupled-Field Mechanism of Interface Failure

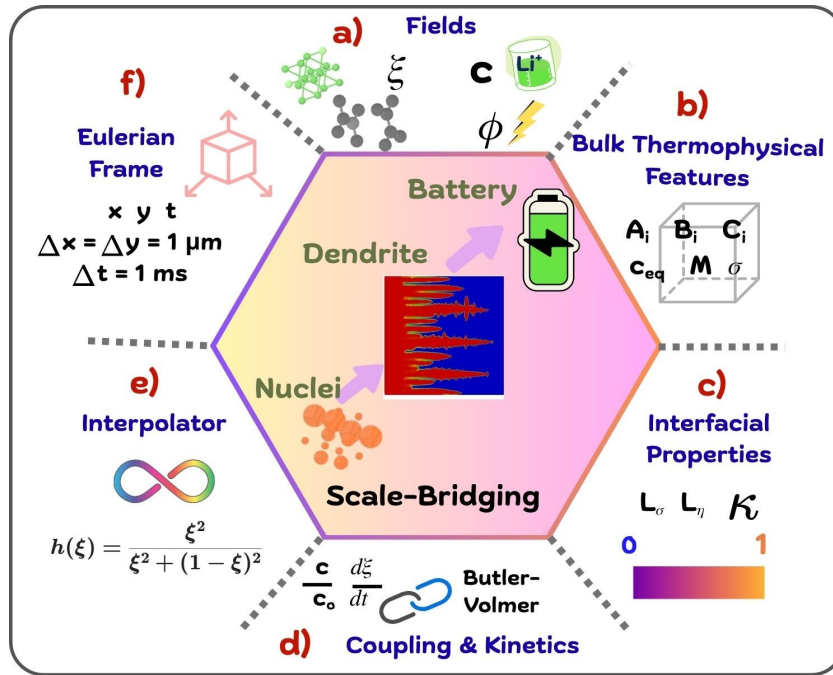


Figure 4.9: **The lithium dendrite is treated as an evolving microstructure described by coupled diffuse fields.** A continuous order parameter separates the metallic lithium and electrolyte regions. Concentration and electric-potential fields describe ionic transport and electrochemical driving. This allows branching and tip formation to emerge without explicit tracking of a sharp boundary. [Author's own work]

Phase-field modelling provides the mechanistic basis (Figure 4.9). An order parameter separates the solid and liquid regions. Ionic concentration and potential fields describe transport and charge transfer. The interface evolves under free-energy driving forces. As in the Al-Cu-Ni process model (Section 4.1.2), the diffuse interface evolves to reduce energy. The driving physics here includes electrostatic energy and reactions governed by Butler-

Volmer kinetics [38].

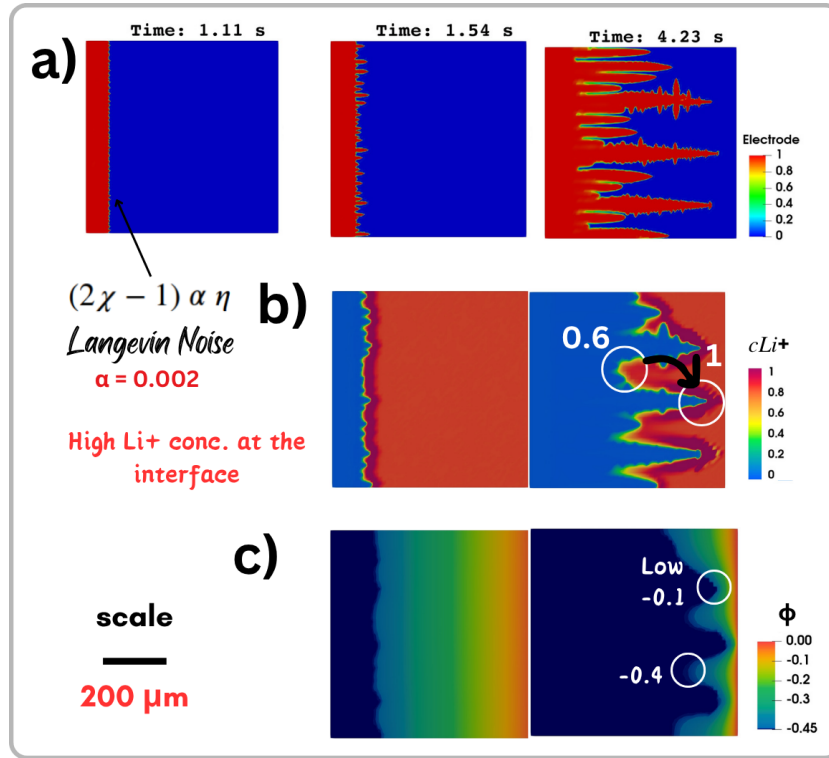


Figure 4.10: A small interfacial perturbation is amplified into a branched structure through feedback among morphology, transport, and potential. Coupled evolution of (a) electrode morphology, (b) ion concentration, and (c) electrostatic potential at $t = 1.11, 1.54$, and 4.23 s. Depleted valleys receive less deposition while protruding tips experience stronger driving. Geometry changes transport. Transport changes deposition, and deposition further sharpens the geometry. Scale bar: $200 \mu m$. [Author's own work. Supporting analysis: [39]]

The simulation (Figure 4.10) reveals a self-amplifying feedback process. When a small perturbation forms on the interface, local potential and concentration fields become non-uniform. Deposition concentrates at the tip. The sharpened geometry further localises the fields. Interfacial failure cannot be prevented using a single design variable. Stability requires compatible combinations of transport, driving forces, and kinetic rates. This mechanistic view informs the suppression strategies of the roadmap review [P-IV].

4.3.2 Suppression Targets for Reliable Operation

Suppression strategies must address multiple mechanisms simultaneously. A literature-based roadmap consolidates these strategies [P-IV]. They span interphase chemistry, collector design, loading conditions, and manufacturing quality. The roadmap organises them into ten coupled performance metrics. These range from current density and efficiency to stiffness and defect density.

The roadmap (Figure 4.11) makes the parameter coupling explicit. Stiffness, conductivity,

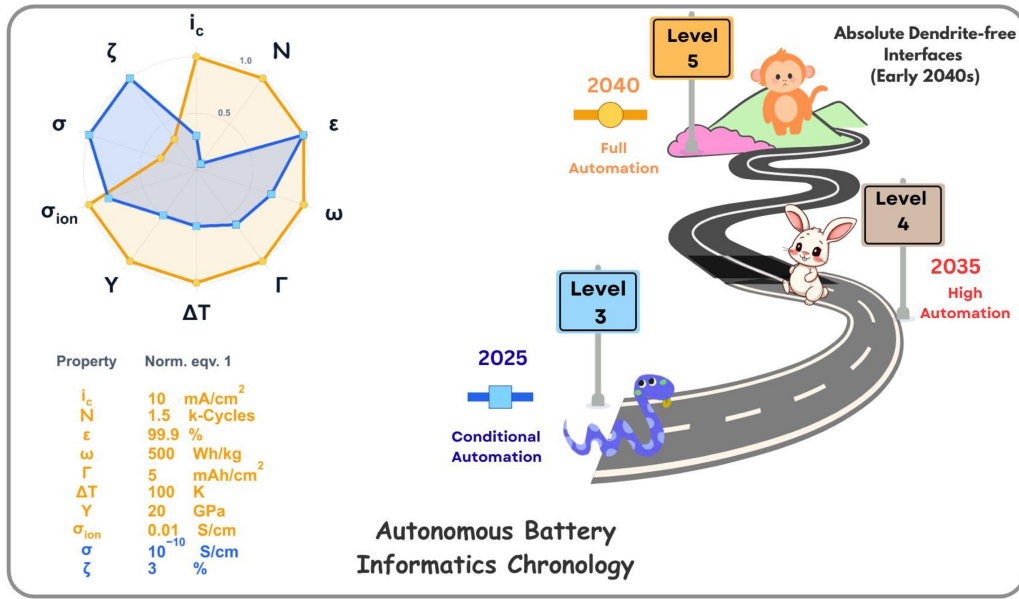


Figure 4.11: Reliable operation is a coupled, multi-metric target spanning materials, interfaces, and manufacturing. The radar comparison groups transport, mechanical, electrochemical, capacity, and defect-control metrics. It also includes temperature-related targets that should improve together. [P-IV]

and defect control should be optimised jointly. The ten metrics form a joint design envelope rather than independent targets. This mirrors the phase-field model in Section 4.3.1, where stability emerges from compatible fields. The phase-field model explains how failures occur, while the roadmap organises the prevention strategies into a coherent set of targets.

4.4 Transferable Scale-Bridging Schemes Across Three Distinct Categories: Multicomponent Alloys, Piezoelectrics, and Batteries

The studies yield five transferable schemes for active and structural components. They apply to alloys, piezoelectric devices, and battery interfaces.

1. **Chemistry and fabrication parameters should be designed together.** Composition alone does not determine performance. The manufacturing route and thermal history set the internal state. Processing must be treated as an active design variable. The same composition yields different responses under different process routes.
2. **The intermediate state bridges the scales. Parameters passed across scales must be consistent.** Grain geometries, morphologies, tensor orientations, interfacial shapes, and potential fields carry lower-scale information to the component level. Representing this state explicitly makes the design models transferable. This transfer is accurate only when the parameters match the physical state of the receiving model. The Al-Cu-Ni study demonstrates that 0 K elastic tensors yield different grain shapes at 723 K.

Thermodynamic consistency is therefore treated on the same footing as numerical convergence.

3. **Active components require balanced design windows rather than single-property maxima.** Performance depends on multiple interacting mechanisms. Strength competes with ductility. Piezoelectric output depends on both tensor orientation and device geometry. Preventing interfacial failure requires simultaneous control of transport, electric fields, and kinetics. The design target is a balanced window in which competing requirements are satisfied.
4. **Component performance and material properties are distinct design stages.** Optimisation can raise a coupling coefficient or a phase fraction. However, component geometry, loading, boundary conditions, and circuits set the realised output. Multi-physics finite element analysis is needed to evaluate these devices. This tests whether material-level improvements translate to system performance under load.
5. **Data-driven models require physical constraints and staged validation.** Process descriptors, symmetry constraints, and physical bounds prevent unphysical predictions. This keeps the optimisation within valid limits. The role of the model must remain explicit. A screening model identifies prospective candidates, while a validation model evaluates a specific component design.

A coherent methodology emerges from these studies. Composition and processing define the attainable properties. The intermediate state carries this information across scales. The coupled multi-physics response then determines performance at the component, device, or interface. Material properties therefore cannot be treated only as tabulated inputs. They are design variables that govern load-bearing capacity, energy conversion, and reliability.

In practice, the methodology leads to co-specified alloy chemistry and process parameters, jointly optimised piezoelectric orientation and device geometry, and coupled battery-interface reliability envelopes. Computational modelling can reduce experimental prototyping cycles in each domain by identifying the parameter combinations that should be evaluated first. This is the principal contribution of the scale-bridging synthesis.

Chapter 5 uses this methodology to evaluate the objectives and hypotheses. It also outlines future research directions.

Chapter 5

Conclusions and Future Work

The preceding chapters show that manufacturing routes, intermediate states, and component response cannot be optimised in isolation. No single simulation method spans the full process-to-performance chain. This dissertation therefore treats advanced functional materials as the physical basis of structural and functional systems. Material behaviour is examined because it governs component performance, durability, and operational life. The five schemes developed in Chapter 4 provide the basis for the assessment below.

This chapter evaluates the findings against the objectives of Chapter 3, assesses the hypotheses of Chapter 2, and outlines future directions for component design and simulation.

5.1 Achievement of the Research Objectives

The three objectives of Chapter 3 were achieved using computational mechanics and data-driven models. This section summarises the resulting capabilities. Section 5.2 then relates the evidence to the hypotheses.

Objective 1. A simulation-based method was developed to specify manufacturing routes for structural alloy components. The data-driven model maps process parameters to strength and ductility responses in multicomponent systems [P-I]. A coupled phase-field model transfers temperature-dependent elastic constants to simulate grain evolution during thermal processing [P-III]. A supporting study applied the same process-aware logic to corrosion resistance in additively manufactured duplex steel components [P-VI, P-VII]. Reusing structural candidate spaces for active component design remains a prospective extension.

Objective 2. Piezoelectric sensor, actuator, and energy-harvester design was addressed through tensor prediction and device-level simulation. For crystalline components, the method predicts the full electromechanical tensor under symmetry constraints and integrates the rotated tensor into a finite element model [P-II]. For active polymers, process descriptors predict the effective response of electrospun components under mechanical constraints [P-V].

Objective 3. Battery-electrode reliability was evaluated using coupled-field phase-field simulation. The model simulates interfacial degradation under electrical and transport fields

and explains how localised field concentrations at interface protrusions accelerate mechanical failure. A complementary roadmap review consolidated these findings into coupled targets for component lifetime [P-IV].

Together, these objectives cover three stages of component-oriented modelling: process specification for load-bearing alloys, device-level evaluation of piezoelectric elements, and reliability assessment of energy-storage interfaces.

5.2 Assessment of the Research Hypotheses

The central and specific hypotheses of Chapter 2 are evaluated using the evidence from Chapter 4.

CH. The integrated scale-bridging framework established process-to-performance pathways across all three domains. Individual modelling approaches could not achieve this alone. In each study, the intermediate state serves as the transfer medium between lower-scale parameters and system response. It includes grain geometries, tensor orientations, and evolving battery interfaces. Consistent parameter transfer and physics-guided descriptors are necessary for accurate predictions, although the specific descriptors and equations remain system-dependent. *Supported across all three domains.*

H1. Coupled models provided design capabilities unavailable to single-scale models. Data-driven tensor prediction combined with finite element analysis yielded device-level output estimates that neither step could provide alone [P-II]. Similarly, transferring temperature-calibrated elastic constants to the phase-field model improved process simulations and supported thermal-route optimisation [P-III]. *Supported computationally.*

H2. Process descriptors identified balanced strength and ductility regions in multicomponent alloys and supported joint optimisation of composition and manufacturing parameters [P-I]. Temperature-calibrated elastic constants altered the predicted grain morphology in phase-field simulations, showing that temperature consistency is necessary for process-relevant geometry prediction [P-III]. *Supported within the computational scope.*

H3. Full electromechanical tensor models predicted orientation-dependent performance in crystalline components. Finite element analysis showed that device response depends on the complete tensor. An optimised and oriented composition delivered a ten-fold increase in simulated output power, while e_{mod} rose from 1.67 to 4.37 C m⁻² [P-II]. For active polymers, process parameters predicted the effective response. The coefficient d_{33} increased from 18 to 29 pC N⁻¹ under optimised fabrication parameters [P-V]. *Supported computationally.*

H4. Coupled-field simulations resolved the feedback mechanisms that drive interfacial degradation and captured localised degradation at interface tips. The literature synthesis grouped prevention methods into joint target envelopes rather than isolated metrics [P-IV]. *Supported.*

SP1. The studied components follow a common logic in which process parameters influence performance through an intermediate state. This yields the five schemes of Section 4.4. Model inputs and governing equations remain application-specific, so broader transferability should be assessed in future studies. *Partially supported.*

5.3 Future Directions

Four directions follow from the present study. They extend the same process-to-performance logic while adding uncertainty analysis and domain-specific verification.

More comprehensive structural and reliability models. The phase-field model could be coupled with CALPHAD data and finite-strain plasticity to predict component geometry under process conditions. The interfacial model could be extended with temperature dependence and three-dimensional transport for reliability assessment under realistic operating conditions. In solid-state batteries, for example, interface degradation often occurs along grain boundaries. Simulating deposition within polycrystalline structures would test this failure mode. The electromechanical models could also be broadened to include multilayered and composite device geometries.

Reduced-order modelling and inverse design. Machine-learning models could be trained on phase-field simulations to compress complex interfacial shapes. The resulting surrogate would support probabilistic inverse mapping from failure morphology to electrical and transport parameters. It could also provide indicators for component stability. The same reduced-order strategy could be applied to structural and tensor models in other domains.

Prospective multifunctional component design. Alloy-derived candidate spaces could be reused to screen for combined electromechanical and dielectric responses. The cations explored for structural applications include Nb, Ta, Ti, Zr, and Hf. These same elements can form polar and high-permittivity oxides and nitrides, making the composition space suitable for active component design. The objective is to identify balanced chemistries rather than maximising a single property.

Within the screened spaces, different elements favour different responses. Transition metals such as Nb, Ta, and Ti tend toward high permittivity and large piezoelectric stress. Nitride chemistries show larger spontaneous polarisation. Light elements and alkaline earths tend toward wider band gaps. These properties do not vary independently. The analysis reveals a lower-dimensional surface of trade-offs (Figure 5.1). Spontaneous polarisation and band gap vary inversely. The electromechanical response soft-saturates at high permittivity. A viable component requires a balanced, Pareto-optimal design window. The leading Nb-Ti-Zr and Nb-Ta-Ti oxide candidates fall within this window.

These candidate chemistries remain screening outputs. Subsequent work requires structure prediction and DFT stability tests, followed by component fabrication and testing. Symmetry-based rules organise candidates by response type [40]. Applied early in the design

cycle, this filter combines with alloy data and trade-off maps to support components with multiple active functions.

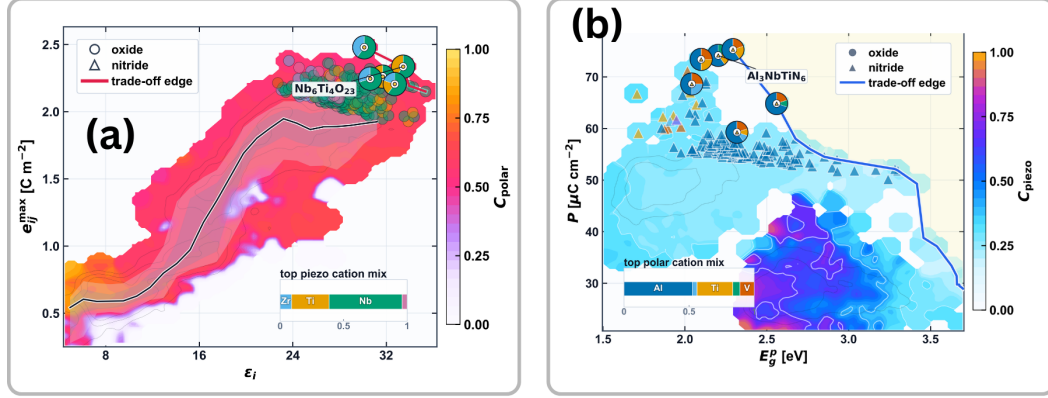


Figure 5.1: **Extending the structural alloy design of AlloyManufacturingNet screened datasets [P-I] to multifunctional components requires navigating property trade-offs.** (a) Predicted maximum piezoelectric stress response $e_{ij}^{\max}$ versus ionic permittivity ϵ_i . Background colour encodes polar compatibility C_{polar} . (b) Predicted spontaneous polarisation P versus polar-phase band gap E_g^p . Background colour encodes piezoelectric compatibility C_{piezo} and shows the trade-off in which a wider band gap accompanies a lower polarisation. [Author's own work. Supporting analysis: [35]]

Closed-loop active learning. Simulation and evaluation steps could be integrated into a self-updating design loop. In this loop, model uncertainty selects the next simulation or experiment, and each new result retraining the model. Resources are then focused where predictions are uncertain or where design gains are largest. This active-learning cycle reduces the data needed to optimise process conditions for active components. Fully autonomous operation is a prospective extension.

Related methods could be applied to other systems. Examples include the thermal design of shape-memory components and the screening of magnetic sensors. These are prospective applications rather than completed studies.

These future directions align with modern design practice. Material properties determine the performance and durability of structural components. Design requirements drive the selection of advanced functional materials and fabrication routes. Computational mechanics now integrates multiscale simulations with data-driven models to replace sequential procedures with coupled design workflows.

Scale-bridging design does not require a single universal model. It requires physics-guided descriptors, consistent cross-scale transfer, and explicit representation of the intermediate state. Integrating data-driven models, physics-based simulations, and finite element analysis provides a transferable basis for predicting component performance, durability, and reliability.

Bibliography

Publications Included in the Dissertation

- [1] **Sachin Poudel**, U. Subedi, M. O. Hamid, K. Gyanwali, Nele Moelans, Anna Timofiejczuk, and Anil Kunwar. “AlloyManufacturingNet for discovery and design of hardness-elongation synergy in multi-principal element alloys”. *Engineering Applications of Artificial Intelligence* 132 (2024), p. 107902. DOI: [10.1016/j.engappai.2024.107902](https://doi.org/10.1016/j.engappai.2024.107902).
- [2] **Sachin Poudel**, Rubi Thapa, R. Basnet, Anna Timofiejczuk, and Anil Kunwar. “PiezoTensorNet: Crystallography informed multi-scale hierarchical machine learning model for rapid piezoelectric performance finetuning”. *Applied Energy* 361 (2024), p. 122901. DOI: [10.1016/j.apenergy.2024.122901](https://doi.org/10.1016/j.apenergy.2024.122901).
- [3] **Sachin Poudel**, Nele Moelans, Rubi Thapa, Anna Timofiejczuk, Dhruva Panthi, and Anil Kunwar. “Unraveling elastochemical effects in microstructural evolution of Al–Cu–Ni system through DFT-informed multi-phase field simulations”. *International Journal of Solids and Structures* 300 (2024), p. 112894. DOI: [10.1016/j.ijsolstr.2024.112894](https://doi.org/10.1016/j.ijsolstr.2024.112894).
- [4] Yi Li, **Sachin Poudel**, Sweta Kumari, Erfan Azqadan, Anil Kunwar, and Nele Moelans. “Roadmaps for dendrite suppression in next generation lithium-ion batteries: Toward sustainable energy solutions”. *Energy Storage Materials* (2026), p. 105000. DOI: [10.1016/j.ensm.2026.105000](https://doi.org/10.1016/j.ensm.2026.105000).
- [5] **Sachin Poudel**, Weronika Smok, Rubi Thapa, Anna Timofiejczuk, Nele Moelans, and Anil Kunwar. “Physics-guided machine learning for enhanced piezoelectric performance in electrospun PVDF/SnO₂ nanofibers”. *Sustainable Materials and Technologies* (2026), e02008. DOI: [10.1016/j.susmat.2026.e02008](https://doi.org/10.1016/j.susmat.2026.e02008).
- [6] Mengistu Dagnaw, **Sachin Poudel**, Upadesh Subedi, Rubi Thapa, Łukasz Reimann, Augustine Nana Sekyi Appiah, Paweł M. Nuckowski, Mariusz Król, Zbigniew Brytan, Nele Moelans, et al. “Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures”. *Metals and Materials International* (2026). DOI: [10.1007/s12540-026-02369-4](https://doi.org/10.1007/s12540-026-02369-4).

- [7] Mengistu Dagnaw, **Sachin Poudel**, Mariusz Król, and Zbigniew Brytan. “Post-process heat treatment design for tunable strength and toughness in L-PBF 2507 super duplex stainless steel”. *Materialia* (2026), p. 102799. ISSN: 2589-1529. DOI: [10.1016/j.mtla.2026.102799](https://doi.org/10.1016/j.mtla.2026.102799). URL: <https://www.sciencedirect.com/science/article/pii/S2589152926001511>.

Additional Related Publications

- [8] Rubi Thapa, **Sachin Poudel**, K. Krukiewicz, and Anil Kunwar. “A topical review on AI-interlinked biodomain sensors for multi-purpose applications”. *Measurement* 227 (2024), p. 114123. DOI: [10.1016/j.measurement.2024.114123](https://doi.org/10.1016/j.measurement.2024.114123).
- [9] Shreekrishna Neupane, **Sachin Poudel**, Anish Ghimire, and Sangita Shakya. “Enhanced mechanical performance and biodegradability in filler-reinforced potato biopolymers for sustainable packaging”. *Materials Today Communications* (2025), p. 114081. DOI: [10.1016/j.mtcomm.2025.114081](https://doi.org/10.1016/j.mtcomm.2025.114081).

Other References

- [10] YM Zhao, JY Zhang, PK Liaw, and T Yang. “Machine learning-based computational design methods for high-entropy alloys”. *High Entropy Alloys & Materials* 3.1 (2025), pp. 41–100. DOI: [10.1007/s44210-025-00055-5](https://doi.org/10.1007/s44210-025-00055-5).
- [11] Xianglin Liu, Jiaxin Zhang, and Zongrui Pei. “Machine learning for high-entropy alloys: Progress, challenges and opportunities”. *Progress in Materials Science* 131 (2023), p. 101018. DOI: [10.1016/j.pmatsci.2022.101018](https://doi.org/10.1016/j.pmatsci.2022.101018).
- [12] Haobing Hu, Xiaoliang Shi, Chaohua Wu, Yuxuan Chen, Haowen Qin, Wenzheng Zhai, Xiyao Liu, and Ahmed Mohamed Mahmoud Ibrahim. “Accelerating inverse design of wear resistant high entropy alloys via multiscale informatics”. *Journal of Alloys and Compounds* 1070 (2026), p. 188733. DOI: [10.1016/j.jallcom.2026.188733](https://doi.org/10.1016/j.jallcom.2026.188733).
- [13] Chenchong WANG and Wei XU. “Overview: Integration and Development of Physical Models and Artificial Intelligence in Alloy Design”. *Acta Metall Sin* 61.4 (2025), pp. 541–560. DOI: [10.11900/0412.1961.2024.00355](https://doi.org/10.11900/0412.1961.2024.00355).
- [14] Yuhong Zhao, Tongzheng Xin, Song Tang, Haifeng Wang, Xudong Fang, and Hua Hou. “Applications of unified phase-field methods to designing microstructures and mechanical properties of alloys”. *Mrs Bulletin* 49.6 (2024), pp. 613–625. DOI: [10.1557/s43577-024-00720-x](https://doi.org/10.1557/s43577-024-00720-x).
- [15] Wan-Ting Cao, Ze Xu, Zhixiang Zhu, Zilong Geng, Jing-Tong Lu, Ziqing Zhong, Hao-Feng Huang, Jia-Xin Liu, Yuqi Jiang, Yi-Xuan Liu, et al. “High-power performance enhancement in PZT-based piezoceramics via hot-pressing”. *Nature Communications* 16.1 (2025), p. 9778. DOI: [10.1038/s41467-025-64752-w](https://doi.org/10.1038/s41467-025-64752-w).

- [16] Khaled S Ramadan, Dan Sameoto, and Sthephane Evoy. “A review of piezoelectric polymers as functional materials for electromechanical transducers”. *Smart Materials and Structures* 23.3 (2014), p. 033001. DOI: [10.1088/0964-1726/23/3/033001](https://doi.org/10.1088/0964-1726/23/3/033001).
- [17] Han Qiu, Yang Xiao, Mohong Xu, Yiming Zhang, Hezhi He, and Zhiwen Zhu. “Synergistic diameter control and post-treatment engineering of electrospun PVDF nanofibers toward β -phase enrichment and enhanced piezoelectric response”. *Journal of Materials Chemistry C* 14.15 (2026), pp. 6240–6250. DOI: [10.1039/D5TC03321G](https://doi.org/10.1039/D5TC03321G).
- [18] Fatemeh Mokhtari, Akbar Samadi, Ahmed O Rashed, Xue Li, Joselito M Razal, Lingxue Kong, Russell J Varley, and Shuaifei Zhao. “Recent progress in electrospun polyvinylidene fluoride (PVDF)-based nanofibers for sustainable energy and environmental applications”. *Progress in Materials Science* 148 (2025), p. 101376. DOI: [10.1016/j.pmatsci.2024.101376](https://doi.org/10.1016/j.pmatsci.2024.101376).
- [19] Raffaele Resta. “Macroscopic polarization in crystalline dielectrics: the geometric phase approach”. *Reviews of Modern Physics* 66.3 (1994), p. 899. DOI: [10.1103/RevModPhys.66.899](https://doi.org/10.1103/RevModPhys.66.899).
- [20] Susan Trolier-McKinstry. “Crystal chemistry of piezoelectric materials”. In: *Piezoelectric and Acoustic Materials for Transducer Applications*. Springer, 2008, pp. 39–56. DOI: [10.1007/978-0-387-76540-2_3](https://doi.org/10.1007/978-0-387-76540-2_3).
- [21] Fangyi Cheng, Jing Liang, Zhanliang Tao, and Jun Chen. “Functional materials for rechargeable batteries”. *Advanced Materials* 23.15 (2011), pp. 1695–1715. DOI: [10.1002/adma.201003587](https://doi.org/10.1002/adma.201003587).
- [22] Haoyu Liu, Yudan Chen, Po-Hsiu Chien, Ghoncheh Amouzandeh, Dewen Hou, Erica Truong, Ifeoluwa P Oyekunle, Jamini Bhagu, Samuel W Holder, Hui Xiong, et al. “Dendrite formation in solid-state batteries arising from lithium plating and electrolyte reduction”. *Nature Materials* 24.4 (2025), pp. 581–588. DOI: [10.1038/s41563-024-02094-6](https://doi.org/10.1038/s41563-024-02094-6).
- [23] Shuzeng Hou, Boyang Zeng, Jingwei Wu, Yongqi Lyu, and Xiayi Sun. “Effects of Key Factors on Lithium Dendrite Dissolution and Dead Lithium Formation: A Phase-Field Simulation Study”. *Batteries* 11.11 (2025), p. 413. DOI: [10.3390/batteries11110413](https://doi.org/10.3390/batteries11110413).
- [24] Derek Gaston, Chris Newman, Glen Hansen, and Damien Lebrun-Grandie. “MOOSE: A parallel computational framework for coupled systems of nonlinear equations”. *Nuclear Engineering and Design* 239.10 (2009), pp. 1768–1778. DOI: [10.1016/j.nucengdes.2009.05.021](https://doi.org/10.1016/j.nucengdes.2009.05.021).
- [25] Michael R. Tonks, Derek Gaston, Paul C. Millett, David Andrs, and Paul Talbot. “An object-oriented finite element framework for multiphysics phase field simulations”. *Computational Materials Science* 51.1 (2012), pp. 20–29. DOI: [10.1016/j.commatsci.2011.07.028](https://doi.org/10.1016/j.commatsci.2011.07.028).

- [26] Abigail Hunter, Vinamra Agrawal, Irene Beyerlein, Somnath Ghosh, Caglar Oskay, Boyang Gu, Youping Chen, Stephen Caleb Foster, Justin W Wilkerson, Xingsheng Sun, et al. “Roadmap on novel computational approaches for bridging length and time scales: addressing challenges in modeling processes, characterization, and performance of metals and alloys”. *Modelling and Simulation in Materials Science and Engineering* (2026). DOI: [10.1088/1361-651X/ae773d](https://doi.org/10.1088/1361-651X/ae773d).
- [27] Nele Moelans, Bart Blanpain, and Patrick Wollants. “An introduction to phase-field modeling of microstructure evolution”. *Calphad* 32.2 (2008), pp. 268–294. DOI: [10.1016/j.calphad.2007.11.003](https://doi.org/10.1016/j.calphad.2007.11.003).
- [28] Son Gyo Jung, Guwon Jung, and Jacqueline M Cole. “Predictive modeling of high-entropy alloys and amorphous metallic alloys using machine learning”. *Journal of Chemical Information and Modeling* 64.19 (2024), pp. 7313–7336. DOI: [10.1021/acs.jcim.4c00873](https://doi.org/10.1021/acs.jcim.4c00873).
- [29] Spyros Kamnis and Konstantinos Delibasis. “High entropy alloy property predictions using a transformer-based language model”. *Scientific Reports* 15.1 (2025), p. 11861. DOI: [10.1038/s41598-025-95170-z](https://doi.org/10.1038/s41598-025-95170-z).
- [30] Weiran Zhang, Zeyi Wang, Hongli Wan, Ai-Min Li, Yijie Liu, Sz-Chian Liou, Kai Zhang, Yuxun Ren, Chamithri Jayawardana, Brett L Lucht, et al. “Revitalizing interphase in all-solid-state Li metal batteries by electrophile reduction”. *Nature materials* 24.3 (2025), pp. 414–423. DOI: [10.1038/s41563-024-02064-y](https://doi.org/10.1038/s41563-024-02064-y).
- [31] Yang Zhou, Bingnong Jiang, Ziyang Gao, Zhao Sha, Benjamin Tynan, Andrew Rider, Vu Dao, Sonya Brown, Dewei Chu, Dawei Wang, et al. “Recent Developments in Solid-State Electrolytes for Advanced Energy Storage Devices”. *ACS nano* 19.49 (2025), pp. 41419–41458. DOI: [10.1021/acsnano.5c14335](https://doi.org/10.1021/acsnano.5c14335).
- [32] Hailong Huang, Prashant Singh, Duane D Johnson, Dishant Beniwal, Pratik K Ray, Gaoyuan Ouyang, Luke Gaydos, Trevor Riedemann, Tirthesh Ingale, Vishal Soni, et al. “Achieving high tensile strength and ductility in refractory alloys by tuning electronic structure”. *Nature Materials* (2026), pp. 1–9. DOI: [10.1038/s41563-025-02464-8](https://doi.org/10.1038/s41563-025-02464-8).
- [33] Nele Moelans. “A quantitative and thermodynamically consistent phase-field interpolation function for multi-phase systems”. *Acta Materialia* 59.3 (2011), pp. 1077–1086. DOI: [10.1016/j.actamat.2010.10.038](https://doi.org/10.1016/j.actamat.2010.10.038).
- [34] Jincheng Qin, Faqiang Zhang, Mingsheng Ma, Yongxiang Li, and Zhifu Liu. “Data-driven approaches for functional ceramics”. *Materials Science and Engineering: R: Reports* 170 (2026), p. 101213. DOI: [10.1016/j.mser.2026.101213](https://doi.org/10.1016/j.mser.2026.101213).
- [35] Sachin Poudel. *Multifunctional Screening of Multicomponent Elements Based on Crystal Symmetry*. Version v1.0. Supporting analysis dataset. Zenodo, 2026. DOI: [10.5281/zenodo.21079298](https://doi.org/10.5281/zenodo.21079298). URL: <https://doi.org/10.5281/zenodo.21079298>.

- [36] Daniel C Hayes, Shubhanshu Agarwal, Kiruba Catherine Vincent, Izoduwa M Aimiwu, Apurva A Pradhan, Madeleine C Uible, Suzanne C Bart, and Rakesh Agrawal. “A reliable, colloidal synthesis method of the orthorhombic chalcogenide perovskite, BaZrS_3 , and related ABS_3 nanomaterials ($A = \text{Sr, Ba}$; $B = \text{Ti, Zr, Hf}$): a step forward for earth-abundant, functional materials”. *Chemical Science* 16.3 (2025), pp. 1308–1320. DOI: [10.1039/D4SC06116K](https://doi.org/10.1039/D4SC06116K).
- [37] John Mangeri, Yomery Espinal, Andrea Jokisaari, S. Pamir Alpay, Serge Nakhmanson, and Olle Heinonen. “Topological phase transformations and intrinsic size effects in ferroelectric nanoparticles”. *Nanoscale* 9.4 (2017), pp. 1616–1624. DOI: [10.1039/C6NR09111C](https://doi.org/10.1039/C6NR09111C).
- [38] Zijian Hong and Venkatasubramanian Viswanathan. “Phase-field simulations of lithium dendrite growth with open-source software”. *ACS Energy Letters* 3.7 (2018), pp. 1737–1743. DOI: [10.1021/acsenergylett.8b01009](https://doi.org/10.1021/acsenergylett.8b01009).
- [39] Sachin Poudel. *Lithium Dendrite Initiation and Growth Using Phase-Field Model*. Version v1.0. Supporting analysis dataset. Zenodo, 2026. DOI: [10.5281/zenodo.21079254](https://doi.org/10.5281/zenodo.21079254). URL: <https://doi.org/10.5281/zenodo.21079254>.
- [40] Liudmila A Klimova, Ivan S Trofimov, Wenqi Jin, Qigang Song, Aleksey Arsenin, Congwei Xie, Ivan A Kruglov, and Valentyn Volkov. “Symmetry-Aware Equivariant Network for Discovering SHG-Active Materials”. *Advanced Functional Materials* 36.26 (2026), e23683. DOI: [10.1002/adfm.202523683](https://doi.org/10.1002/adfm.202523683).
- [41] Kapil Saha, Pietro Simeoni, Luca Colombo, and Matteo Rinaldi. “Piezoelectric and ferroelectric measurements on casted target-deposited $\text{Al}_{0.45}\text{Sc}_{0.45}\text{B}_{0.1}\text{N}$ thin films”. *Frontiers in Materials* 12 (2025), p. 1567614. DOI: [10.3389/fmats.2025.1567614](https://doi.org/10.3389/fmats.2025.1567614).

Appendix A

Full Texts of the Included Publications

A.1 Publication I [\[P-I\]](#): AlloyManufacturingNet for discovery and design of hardness–elongation synergy in multi-principal element alloys



Contents lists available at ScienceDirect

Engineering Applications of Artificial Intelligence

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AlloyManufacturingNet for discovery and design of hardness-elongation synergy in multi-principal element alloys

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ARTICLE INFO

Dataset link: https://github.com/Sachinscpdl/MPEA_HV-EL, <https://mpeanet.streamlit.app/>

Keywords:

Multi-principal element alloys
Feature selection
Ensemble neural network
Hardness-ductility synergy
Scale invariant optimization
Digital manufacturing

ABSTRACT

Located around the center of multicomponent phase space, multi-principal element alloys (MPEAs) are often characterized with a unique blend of contrasting physico-chemical properties, and have a good prospective of presenting hardness-ductility synergy. A datasets of MPEAs fabricated by casting, wrought, sintering, annealing procedures, was collected and the mean values for hardness and elongation was determined as 495.3 HV and 22.16 % respectively. After screening and processing the datasets with the help of feature selection by tools such as Pearson's correlation coefficient, multicollinearity analysis and principal component analysis, artificial neural networks (ANNs) were subsequently trained in this study. An ensemble of these networks known as AlloyManufacturingNet was then purposed as the prediction toolkit for the inverse alloy design in applications including metamorphic manufacturing. During the in-silico design of external elements doped ZrHfNb and VNbTa alloys for maximum hardness, the model has estimated that $\text{Cr}_{0.4}\text{W}_{0.5}(\text{ZrHfNb})_{0.1}$ and $\text{Cr}_{0.5}\text{W}_{0.3}(\text{VNbTa})_{0.2}$, both fabricated by sintering method, show hardness values of 684.49 and 733.42 HV respectively. While $\text{Ti}_{0.7}(\text{ZrHfNb})_{0.3}$ prepared via annealing procedure shows the largest elongation of 43.52 % in the category of ZrHfNb-derived alloys, $\text{Mo}_{0.1}\text{Ti}_{0.8}(\text{VNbTa})_{0.1}$ processed through the wrought process is estimated to have a maximum elongation of 34.36 % in the group of VNbTa-derived alloys. For establishment of the hardness-ductility synergy as required in structural applications, the composition spaces for given manufacturing routes have been searched with the machine learning model. In general, the MPEAs derived from base VNbTa alloy tend to perform better in context of possessing composition values having both the hardness and ductility above the aforementioned mean values. The machine learning based estimation was done in another MPEA, namely, CoCrNiNb_x alloy to quantify the change in hardness with the change in Nb content, and the mechanistic insights were obtained via molecular dynamics simulations.

1. Introduction

The high entropy alloys (HEAs) ubiquitously also known as multi-principal element alloys (MPEAs) in literature are alloys that consist of five or more principal (or base) elements having an equal or near-equal proportion ranging from 5% to 35% of base elements in them (Zhang et al., 2020; MacDonald et al., 2017; Senkov et al., 2018; Miracle and Senkov, 2017). The Medium Entropy Alloys (MEAs) are the MPEAs consisting of three or four base elements (Tan et al., 2020). The concept of HEAs was first introduced to the scientific community in 2004 by Yeh et al. (2004). Since their inception, HEAs have received attention in material design because of the possibility to obtain products with enhanced mechanical properties (Lu et al., 2020; Han et al., 2020;

Thiel et al., 2020; Průša et al., 2020), high hardness (Tian et al., 2015), greater wear resistance (Yang et al., 2020), outstanding high-temperature resistance (Soni et al., 2020; Zhao et al., 2020), fracture resistance (Gludovatz et al., 2014), lower temperature ductility (Li and Raabe, 2017) among others. Thereby making multi component alloys an excellent choice for material design. The design of MPEAs is not a straightforward task as there can be an infinitely large combination of constituent elements and their proportions that can impart given set up features and properties in the resulting alloys (Miracle, 2019). In addition to that, experiments on different element compositions by trial and error consume both time and resources without any certainty of

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better outcomes. However, various techniques have been developed for the design of MPEAs from simple empirical rules (Guo, 2015; Liang and Schmid-Fetzer, 2017) to computational complex models like calculation of phase diagram (CALPHAD) (Liu et al., 2021), Density Functional Theory (DFT) (Singh et al., 2020), ab-initio calculations (Startt et al., 2022), and Molecular Dynamics (MD) (Mishra et al., 2021; Zhang et al., 2021). Recently, machine learning (ML) techniques have gained popularity in MPEA design because of their efficient computational time and cost in contrast to the first principal methods and CALPHAD (Pei et al., 2020; Hernandez, 2015). Artificial neural networks (ANN) are quite successful in phase prediction of compositionally complex alloys (Subedi et al., 2022b; Islam et al., 2018).

Hardness is one of the crucial mechanical properties that have to be considered in material design because of its tendency to resist localized plastic deformation, indentation, and scratching. The dispersion in hardness values provides valuable physical and mechanical insights into material properties, reflecting inherent variability and aiding scientific understanding (Chausov et al., 2021). Wen et al. presented an ML-based technique to obtain new MPEAs with high hardness values in Al-Co-Cr-Fe-Ni alloys taking 91 observations (Wen et al., 2019). Although more datasets are available in the literature, this work studies the hardness of only specific MPEA systems. Chang et al. used neural network model on 155 HEA samples (Chang et al., 2019) which considered an alloy system consisting of 8 elements only. Bhandari et al. predicted the hardness of refractory HEA with 128 as-cast data observations (Bhandari et al., 2021). All of these works show decent prediction accuracy. However, they are trained with at most 155 datasets and with a limited elemental framework of 6, 8 and a maximum of 17 by Bhandari et al. This excludes considerable alloys, including refractory MPEA. Bakr et al. predicted hardness on MPEA by taking 427 datasets consisting of 18 elements and manufactured by casting and powder metallurgy (Bakr et al., 2022). Beniwal et al. presented an ensemble artificial neural network trained with 218 MPEAs consisting of 22 elements fabricated by casting, tested with separate 58 MPEAs (manufactured by casting and sintering method only) and features selected from 22 pool of alloys and elemental descriptors (Beniwal et al., 2022). The study is successful in capturing the non-linear relationship between input features and hardness. However, the model was trained only for prediction of hardness feature, and does not include the estimation of elongation. It is therefore necessary to build an inclusive model that can express on the ductility of MPEAs along with the information on the hardness. The ductility of material can be explained by yield strength, ultimate tensile strength, and elongation. Hard materials are unlikely to have large elongations. Liu et al. studied the empirical relation for the prediction of elongation on as-cast Al-Co-Cr-Fe-Ni MPEA by analyzing the volume fraction of different microstructures and the application of CALPHAD. Both root mean squared error and mean absolute error for the elongation obtained is 20.1%. Among various properties predicted using the empirical method, the prediction of elongation has very low accuracy (Liu et al., 2021). There has been no data-driven approach for the prediction of elongation in combination with hardness assessments for the MPEA.

The information on hardness is important as an alloy with high hardness usually has lower ductility which limits its design scope (Dong et al., 2013). The high-temperature plastic deformation impacts the hardening kinetics, revealing differences in intensity tied to dislocation microstructure changes (Yasnii et al., 2008). Also, the abrasion resistance of the material is dependent on the ductility in addition to the hardness. The hard and ductile alloy is found to have better wear resistance properties than the alloy with only a high hardness value (Jha et al., 2003). Therefore, it is essential to study both hardness and elongation together in order to expand the design scope of the alloy. The percentage elongation is the ductility property of a material. Singh et al. (2023) have recently introduced local-lattice distortion (LLD) metric as an estimator of the ductility for refractory multi-principal element alloys. The establishment of this quantum mechanical

dimensionless metric for ductility opens the door to benchmark percentage elongation values of different sets of alloy compositions. Pugh's ratio, positive Cauchy Pressure and Valence Electron Concentration (VEC) are among the widely accepted indicators of material ductility (Singh et al., 2023; Pugh, 1954; Hadi et al., 2016; Pettifor et al., 1991; Pettifor, 1992; Yang et al., 2018; Balasubramanian et al., 2018). A data-driven model constructed from the data encompassing these indicators can be a promising tool for the accurate foretelling of the percentage alloy of a new MPEA. The knowledge of both hardness and elongation is crucial so as to get desired applicability of the alloy. Most of the studies hitherto associated with hardness and elongation prediction uses small datasets, consisting of few elemental compositions, and fails to generalize the model for MPEAs manufactured by different techniques. Moreover, no study has been done to capture both the hardness and ductility of the MPEAs. There can be design limitations to come up with the desired combination of hardness and elongation in conventional alloys. That restriction can be avoided with the research in MPEA. Hence, a data-driven study on both hardness and elongation can provide an accelerated search for optimized MPEA.

Apart from the initial phases of digital manufacturing, computer numerical control (CNC) and additive manufacturing, a novel approach called metamorphic manufacturing, envisioned by researchers Daehn and Taub (2018), has emerged. This method employs digitally controlled incremental forming (Daehn and Taub, 2018; Liu et al., 2023), including thermal manipulation, to create engineering components with site-specific properties governed by local microstructures (Dasari et al., 2020). HEA or MPEA are ideal for metamorphic manufacturing due to their capacity to modify structural and functional properties within a single alloy composition using diverse manufacturing methods or processing strategies (Dasari et al., 2020). Yet, the challenge lies in the limited availability of property databases for MPEAs at specific compositions and processing routes. Developing design charts encompassing material properties for a given MPEA at a particular composition across various manufacturing routes is crucial for advancing the metamorphic manufacturing sector rapidly.

In this study, alloy datasets were categorized into four main manufacturing routes: casting (CAT-A), wrought and miscellaneous (CAT-B), powder metallurgy (CAT-C), and annealing (CAT-D). Casting involves repeated cycles of melting and solidification using an MPEA crucible (Fig. 1(a)) Paganotti et al. (2019). Wrought and miscellaneous processes encompass smelting, mixing, and forming billets or slabs (Fig. 1(b)). Powder metallurgy includes sintering to create a sintered MPEA with pores between grains (Fig. 1(c)), while annealing involves a series of processes like VAR, hydrogen annealing, milling, sieving, and vacuum annealing to form MPEA spheres from powder form using thermal plasma (Fig. 1(d)) (Lee et al., 2019). These categories correspond to different thermomechanical processing routes.

The machine learning toolkit **AlloyManufacturingNet** was developed to predict MPEA's contrasting mechanical properties: hardness and elongation. In our study, we emphasize the dataset's complexity's role in model accuracy. Simplifying complex datasets can enhance deep learning model accuracy, akin to "Kolmogorov complexity". Notable papers show reduced complexity boosts accuracy by curating and preprocessing data, striking a balance between advanced methods and data quality for better predictions (Bolon-Canedo and Remeseiro, 2020; Kabir and Garg, 2023). Extensive training data, including alloy and elemental descriptors, were obtained from published sources. Feature selection and hyperparameter tuning were used to optimize the model. This trained model was applied to design alloys for hardness-ductility synergy, considering various constituent element compositions and manufacturing routes. Additionally, it assessed the impact of manufacturing routes on the properties of ZrHfNb and VNbTa alloys with different dopant elements and compositions. Molecular dynamics simulations were conducted for nanoindentation tests on CoCrNiNb_x alloys produced by the casting process to elucidate predicted hardness properties.

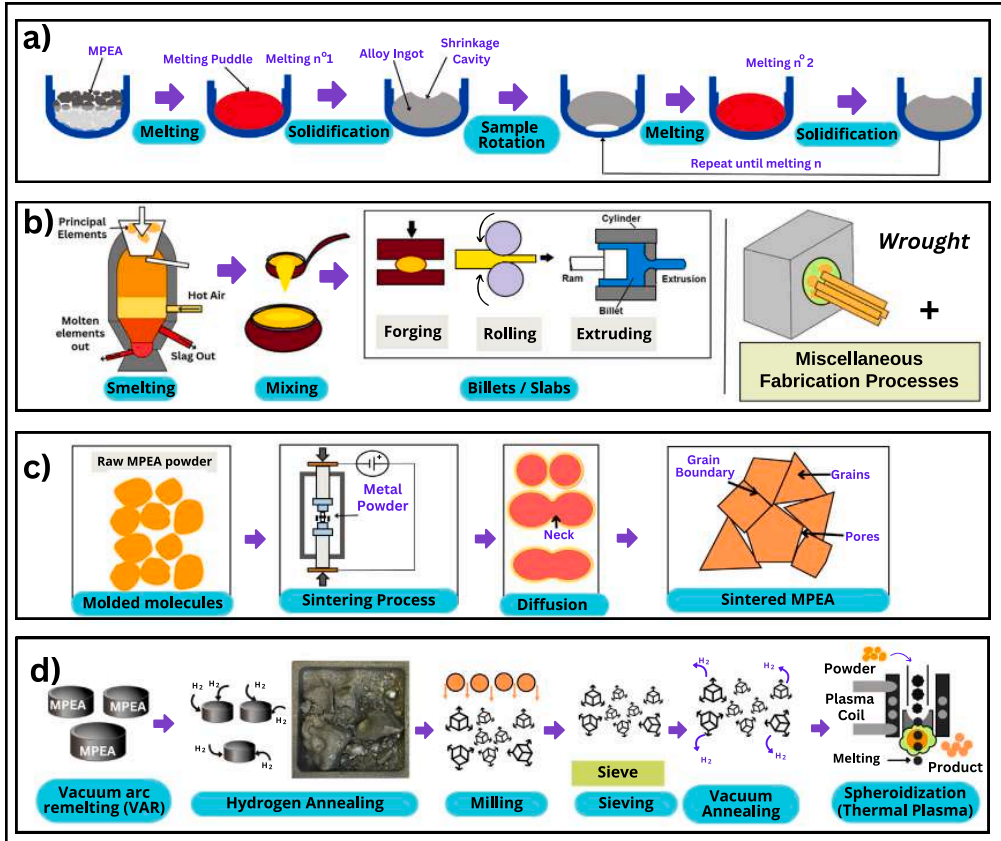


Fig. 1. Common manufacturing routes for fabricating MPEAs. (a) casting (CAT-A), (b) Wrought and remaining all (CAT-B), (c) powder metallurgy (CAT-C), and (d) annealing (CAT-D).

Source: The image in (a) is adopted from Paganotti et al. (2019) and in (d) is adopted from Lee et al. (2019).

2. Quantitative profiling and ensemble machine learning

The general workflow for data-driven design of hardness and elongation of multi-principal element alloys is presented in Fig. 2. As revealed in Fig. 2(a), it is first necessary to collect raw dataset of MPEAs from published literature. After performing numerical fingerprinting for the data, the designated features were screened for sorting out the important features as depicted in Fig. 2(b). This will help in the construction of a robust and physically intuitive machine learning model. In order to cope with the diversity in the origin of dataset sources, ensemble models (Fig. 2(c)) can be trained with the data. The prediction models will then act as the source for generic design of MPEA materials.

2.1. Featurization and numerical fingerprinting

The first task in data-driven modeling is to collect the data from sources, and in this work, the data related to hardness and elongation were obtained from published works (Yeh et al., 2004; Bhandari et al., 2021; Beniwal et al., 2022; Borg et al., 2020; Xiong et al., 2021; Gorsse et al., 2018; Salishchev et al., 2014; Thomas Chan Hien Dam, 2016; Jiang et al., 2022). Only the experimentally validated and published data are considered in this work. The collected datasets are automatically featurized so as to obtain constituents element and their corresponding compositions. The pymatgen and matminer python libraries are used for the automatic featurization (Subedi et al., 2022a). A pragmatic approach is taken by considering the nominal composition when the true composition of the material is unavailable or

not well-documented. Additionally, for model training and testing, data specifically selected from tests conducted at room temperature is employed. The collected datasets in Fig. 3 encompass various alloy compositions, mechanical properties (hardness and elongation), fabrication methods, and phases. Four manufacturing route categories (CAT-A, CAT-B, CAT-C, and CAT-D) are depicted in bar charts for hardness (Fig. 3(a)) and elongation (Fig. 3(c)) data. Regarding the hardness data for MPEAs, initially, 706 observations were gathered, excluding binary alloys. To focus on high entropy alloys with 3 to 7 components, a filtering code was applied, resulting in 683 remaining observations, categorized by manufacturing type (Fig. 3(a)) and component count (Fig. 3(e)). The final hardness dataset included 22 elements (Fig. 3(b)). For the elongation datasets, comprising 353 observations with 26 elements (Fig. 3(c)), each MPEA had $3 \leq N \leq 9$ components shown in Fig. 3(g). Box plots visually conveyed phase structure information for hardness (Fig. 3(f)) and elongation (Fig. 3(h)) datasets, showing both single- and multi-phase MPEAs. Hardness values ranged from 109 to 1084 HV (Fig. 3(f)), while elongation values in Fig. 3(h) spanned from 0 to 96.2%. The experimental specimens reported in the abovementioned sources of the elongation test datasets of MPEAs all have the length/thickness within the range of few millimeters, strain rate in the range of 1.0×10^{-4} – $10 \times 10^{-4} \text{ s}^{-1}$ and total loading time of 15–20 s. The specimens for compression based deformation were generally of cylindrical geometry whereas those for tensile ductility tests were found to be mostly of rectangular geometry. In order to accommodate the differential effects of tension and compression tests,

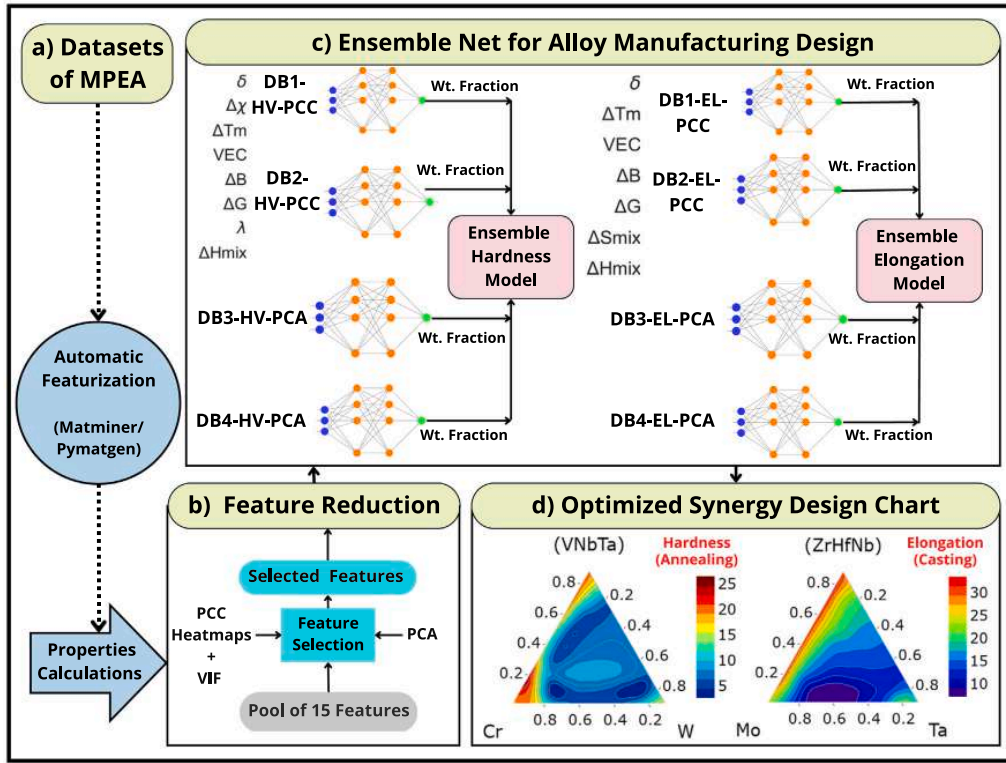


Fig. 2. Schematic workflow for distilling the high entropy alloys dataset includes the processes such as auto featurization, feature reduction, learning the characteristics of data and designing property contours. (a) The raw datasets obtained from the published literature is converted into numerical fingerprints, and the featurization is automated using Matminer and Pymatgen libraries. Property features are also obtained at this stage. (b) The pool of property features is analyzed statistically using feature selection techniques such as PCC Heatmaps and principal component analysis (PCA). The datasets with reduced features are classified into different categories in accordance with the corresponding manufacturing technique. (c) To account for the effects of categorical inputs, ensemble learning is implemented while training the neural network with hardness or elongation as an output feature. (d) The prediction models are then utilized in the hardness and elongation design of a generic refractory MPEAs.

To ensure the robustness of a data-driven approach for MPEA material design, it is essential that the selected features carry physically meaningful information. This task becomes particularly crucial given the high-dimensional materials design space, especially in the case of HEAs (Subedi et al., 2022a). The feature pool, outlined in Table 1, encompasses diverse categories. The first category includes terms derived from Hume-Rothery rules, such as atomic size difference (δ), electronegativity ($\Delta\chi$), and Valence Electron Concentration (VEC). Features like δ and $\Delta\chi$ are relevant as they capture relative atomic sizes and chemical compatibility among constituent elements in MPEAs, respectively. Another category incorporates concepts from materials and alloy thermodynamics, encompassing Enthalpy of Mixing (ΔH_{mix}), Entropy of Mixing (ΔS_{mix}), Average Molar Heat Capacity (δC_p), Geometrical Parameter (λ), and Dimensionless Parameter (Ω). Notably, Ω stands out as a feature because it amalgamates ΔH_{mix} , ΔS_{mix} , and the average melting temperature $T_m(K)$ of an MPEA, providing an alternative solution for the numerical fingerprinting of HEAs' Gibbs energy of mixing complexities. Additionally, the feature pool includes the average melting temperature $T_m(K)$ of an MPEA and its asymmetry ΔT_m as independent features, further enhancing the robustness and relevance of data-driven methods for MPEA material design.

A comprehensive pool of 15 input features was constructed, as detailed in Table 1. These features encompass a range of elemental and alloying descriptors, including Mean Atomic Radius difference (δ), Electronegativity asymmetry ($\Delta\chi$), Average Melting Temperature ($T_m(K)$), Melting Temperature asymmetry (ΔT_m), Valence Electron Concentration (VEC), Average Atomic Number (AN), Thermal Conductivity (K), Average Bulk Modulus (B), Average Shear Modulus (G), Shear

Modulus Asymmetry (ΔG), Average Molar Heat Capacity (δC_p), Entropy of Mixing asymmetry (ΔS_{mix}), Enthalpy of Mixing asymmetry (ΔH_{mix}), Geometrical Parameter (λ), and Dimensionless parameter (Ω). The mathematical expressions used for numerical fingerprinting of these features are detailed in Supplementary Materials Table S1. Notably, these features can be categorized into two groups: elemental descriptors, indicating alloy properties as an extension of the elements in the composition (S.N. 1–11), and alloying descriptors, highlighting property changes resulting from element interactions in alloy formation (S.N. 12–15). The entropy of mixing was evaluated using the *WenAlloys* class from the *matminer* library (Wen et al., 2019), while the enthalpy of mixing was derived from Miedema's model. Importantly, the feature pool intentionally excludes the feature corresponding to the manufacturing route or fabrication procedure (MR), signifying its exclusion in correlation analysis and principal component analysis, with selective utilization in the ensemble machine learning algorithm.

2.2. Data preprocessing and feature engineering

The collected datasets were divided into training and testing sets to prevent data leakage during preprocessing and model training. This split ensures that the test data can provide an accurate representation of the model's performance on new MPEAs. The random split was conducted with a 90:10 ratio for training and testing data. The distribution of hardness and elongation values in the training and testing datasets is visualized in Fig. 4(a). Fig. 4(a) (i) displays the distribution of 614 training hardness data points, with a mean of 500 HV, a median of 506 HV, and 10th and 90th percentiles at 207 HV and 782 HV,

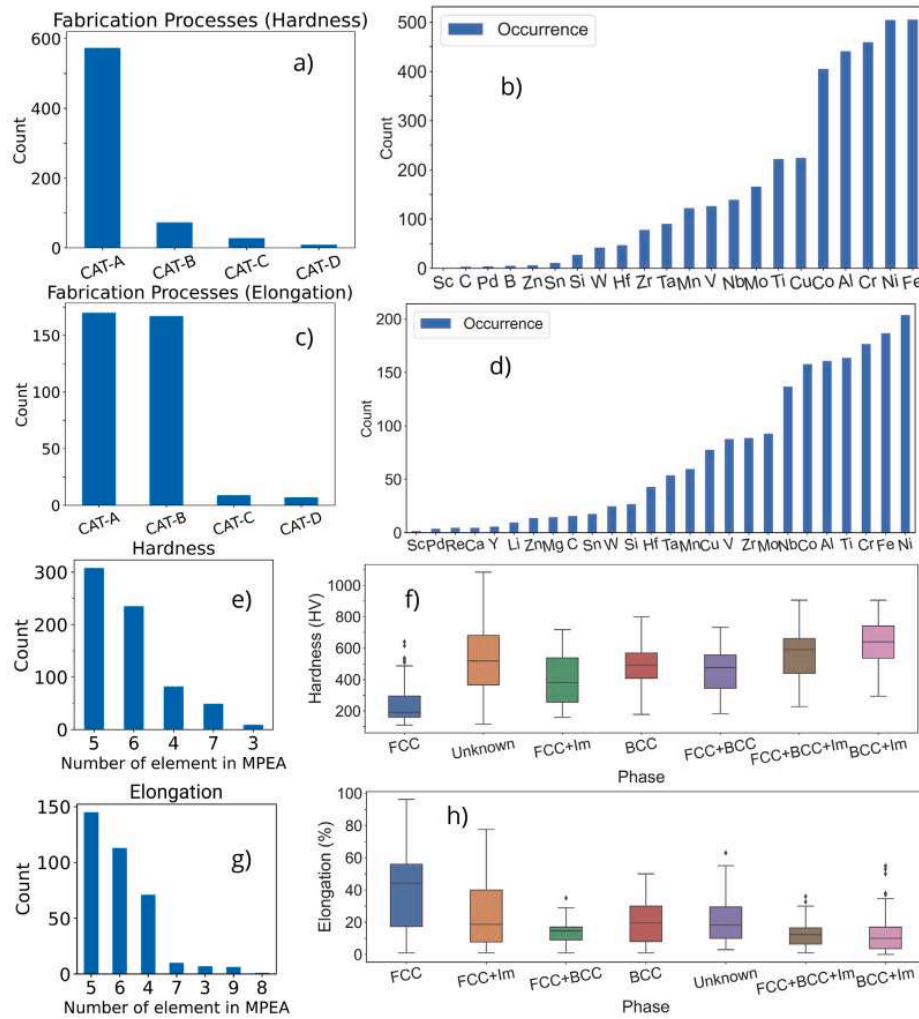


Fig. 3. Understanding the data through visualization is a prelude to featurization. Number of MPEA for different fabrication routes for (a) Hardness (c) elongation. Number of occurrence of elements in (b) hardness (d) elongation. Number of elements in an alloy system for (e) hardness (g) elongation. Statistical distribution for seven phase systems with mean, median, and quartiles (25% and 75%) for (f) hardness (h) elongation.

Table 1

The table's first column lists the initial 15 input features considered for the feature pool, applicable to both the hardness and elongation datasets. In the hardness dataset, the output feature of interest is hardness (HV), while in the elongation dataset, it is elongation (EL). To assess multicollinearity within the feature pool, variance inflation factor (VIF) analysis is conducted. It is worth noting that PCC stands for Pearson's correlation coefficient, and a comprehensive examination of PCC will be provided in Section 2.2.

Name of features	Hardness VIF		Elongation VIF	
	Before PCC	After PCC	Before PCC	After PCC
Mean Atomic Radius difference (δ)	8.3	6.43	5.02	2.2
Electronegativity asymmetry ($\Delta\chi$)	3.98	1.66	3.37	Dropped
Average Melting Temperature ($T_m(K)$)	63.1	Dropped	60.48	Dropped
Melting Temperature asymmetry (ΔT_m)	4.16	3.19	2.97	2.0
Valence Electron Concentration (VEC)	21.48	2.35	11.1	3.0
Average Atomic Number (AN)	18.55	Dropped	14.46	Dropped
Thermal Conductivity (K)	5.55	Dropped	7.40	Dropped
Average Bulk Modulus (B)	16.55	Dropped	31.21	Dropped
Bulk Modulus Asymmetry (ΔB)	7.5	2.88	6.35	3.32
Average Shear Modulus (G)	3.32	Dropped	7.47	Dropped
Shear Modulus Asymmetry (ΔG)	3.9	1.8	3.25	1.26
Entropy of Mixing asymmetry (ΔS_{mix})	1.22	Dropped	1.65	1.32
Enthalpy of Mixing asymmetry (ΔH_{mix})	4.8	3.07	2.99	1.57
Geometrical Parameter (i)	2.2	1.99	2.08	Dropped
Dimensionless parameter (Ω)	1.17	Dropped	1.17	Dropped

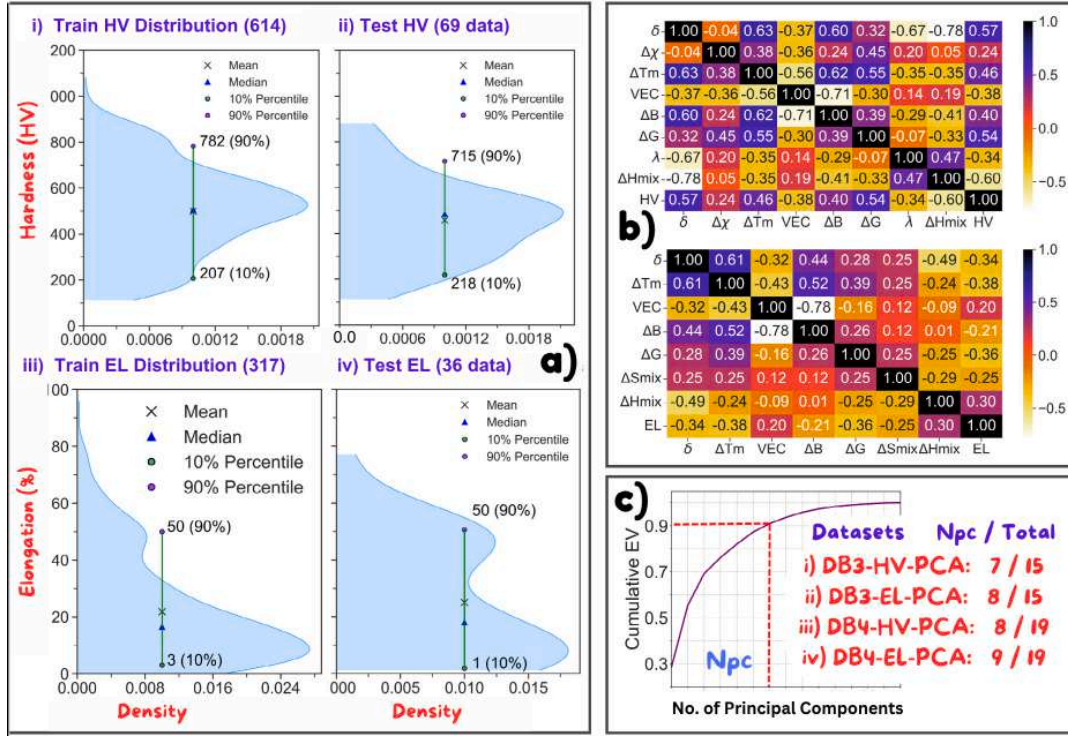


Fig. 4. Data preprocessing and analysis. (a) Distribution of Train-Test split. hardness has 614 train and 69 test data while elongation has 317 train and 36 test datasets. The plot shows test and train distribution follows similar distribution) (b) Heatmap after feature selection by PCC corresponding to the features of the refined hardness database DB1-HV-PCC and the elongation database DB1-EL-PCC. The inclusion of ΔB (denominator in Pugh's ratio), ΔG (numerator in Pugh's ratio) and VEC in the feature pool verifies that the information associated with relevant indicators of hardness and ductility is well preserved within the training datasets. (c) Cumulative Explained Variances (EVs) for PCA. This figure illustrates the feature sets' ability to capture 90% of the explained variance. DB3-HV-PCA achieves this with 7 out of 15 components, DB3-EL-PCA with 8 out of 15 components, DB4-HV-PCA with 8 out of 19 features, and DB4-EL-PCA with 9 out of the same 19 features, as determined by PCA. Additional details are available in Supplementary Material S1 and Figure S3.

respectively. In Fig. 4(a) (ii), the distribution of 69 test hardness data points closely resembles the diversity seen in the training data, with percentiles ranging from 218 HV to 715 HV and a mean of 458 HV. Similarly, Fig. 4(a) (iv) represents the distribution of 36 test elongation observations, capturing the variation observed in the training data shown in Fig. 4(a) (iii). The mean elongation values for the training and test sets are 22% and 25%, respectively.

Following the split, the training set is standardized using Sci-Kit Learn's *StandardScaler()* library to achieve a mean of zero and a standard deviation of one, a common practice in machine learning to mitigate the impact of feature magnitude variations. The test data is also standardized using the statistics from the training set. However, it is worth noting that the four features corresponding to fabrication routes (CAT-A, CAT-B, CAT-C, and CAT-D) are not standardized. These categorical inputs are one-hot encoded into columns of zeros and ones, representing the presence or absence of each route for a given MPEA. For example, if an MPEA is manufactured via the casting process (CAT-A), its corresponding column would have a value of 1, while the other columns (CAT-B, CAT-C, CAT-D) would have 0 values, resulting in a clear representation of the fabrication route (MR) for that MPEA.

In the course of machine learning model construction, feature selection is defined as a technique of identifying the subset from a given set of initial features, which can eventually help in realizing the simplification of the future model and solve problem such as the curse of dimensionality. In other words, feature selection is an important task to perform for the identification and elimination of redundant input features. The regression type model which gives a numerical target as output needs a numerical feature selection technique. Two of the

most commonly used approaches for the numerical feature selection for regression models are Correlation metrics and Principal component analysis (PCA).

2.2.1. Variable reduction with PCC heatmaps and multicollinearity analysis

Pearson's correlation coefficient (PCC) assesses linear relationships among variables, vital for classification or regression tasks (Roy et al., 2022; Khakurel et al., 2021). PCC heatmaps in Supplementary Figure S1 and S2 show correlations between 15 input variables and target hardness (HV) and elongation (EL). The coefficients range from -1 to 1 , with higher absolute PCC values indicating stronger correlations. Features with PCC above 0.9 are reduced to one, and those below 0.2 with the target variable are excluded, ensuring relevant input features for model development. Eight features (δ , $\Delta\chi$, ΔT_m , VEC, ΔB , ΔG , λ , ΔH_{mix}) were selected alongside the target HV feature for ML model development. And, in the case of elongation seven input features (δ , ΔT_m , VEC, ΔB , ΔG , ΔS_{mix} , ΔH_{mix}) emerged as finalists, following similar PCC criteria. The PCC heatmap in Fig. 4(b) reveals that each of these input features has a PCC score of absolute magnitude larger than 0.2 with target, i.e., HV or EL, and less than 0.9 with other input features. This refined dataset, named DB1-HV-PCC, comprises these eight features and HV. The corresponding refined dataset for elongation is labeled DB1-EL-PCC. To account for the influence of manufacturing routes on mechanical properties, the MR feature was manually added to the DB1-HV-PCC and DB1-EL-PCC datasets, forming DB2-HV-PCC (for hardness) and DB2-EL-PCC (for elongation). These databases are detailed in Table 2.

The assessment of input feature relevance in our analysis is complemented by the Variance Inflation Factor (VIF), a metric used to

detect multicollinearity. VIF quantifies the correlation strength between independent features by regressing one feature against all others. Mathematically, for the i th predictor feature, VIF_i is calculated as

$$VIF_i = \frac{1}{1 - R_i^2} \quad (1)$$

where R_i^2 represents the R^2 value obtained by regressing the i th predictor feature with the remaining predictors in the dataset. VIF typically ranges from 1 to infinity, with values exceeding 4.00 warranting attention and values surpassing 10.00 indicating severe multicollinearity, suggesting that a feature is redundant and can be expressed as a linear combination of others (Revi et al., 2021). In our analysis, this criterion was applied to both the hardness and elongation datasets before and after PCC analysis, as shown in Table 1. Among the 15 hardness data attributes, the average melting temperature ($T_m(K)$) exhibited the highest VIF of 63.1, signifying strong correlation with other variables. Given its PCC score of 0.00 with HV, $T_m(K)$ was excluded as a less relevant and highly redundant feature. Similarly, AN (VIF = 18.55, PCC score = -0.11 with HV) and B (VIF = 16.55, PCC score = -0.11 with the output attribute) were removed from the feature pool. Conversely, despite multicollinearity (VIF = 21.48), VEC was retained due to its strong negative correlation (PCC score = -0.38) with HV. Features δ (VIF = 8.3) and ΔH_{mix} (VIF = 4.8) exceeded the VIF threshold of 4.0, but their high correlations with HV (PCC scores of 0.57 and -0.60, respectively) justified their inclusion. λ displayed a PCC score of -0.34 with HV and a VIF of 2.2, meeting the criteria for inclusion based on minimum redundancy and maximum relevance. However, ΔS_{mix} (VIF = 1.22) and Ω (VIF = 1.17) were dropped due to weak correlations with the output attribute. After removing seven input features, multicollinearity analysis yielded VIF values well below 10.00. VEC, originally problematic with a VIF of 21.48, now had an updated VIF of 2.35, resolving the multicollinearity issue. In the final list of eight selected features, only δ (VIF = 6.43) exceeded the warning limit of 4.00, but its high correlation with the HV feature (PCC score = 0.57) underscored its relevance and utility in the model.

The combined use of Pearson's correlation coefficient (PCC) and Variance Inflation Factor (VIF) scores guided feature selection for the elongation dataset. Features like $T_m(K)$, AN, and B, which displayed poor correlations with elongation (EL) and significant multicollinearity issues with other input features (PCC scores of -0.08, -0.04, and 0.00 with EL, and VIF values of 60.48, 14.46, and 31.21, respectively), were removed from the feature pool. Features Ω (VIF = 1.17) and λ (VIF = 2.08), despite lacking multicollinearity issues, were also eliminated due to their weak correlations with EL. This led to the exclusion of 8 features ($\Delta\chi$, $T_m(K)$, AN, K, B, λ , and Ω) from the elongation dataset. The remaining 7 features, each exhibiting an absolute PCC score with EL equal to or greater than 0.2, were subjected to multicollinearity analysis, resulting in VIFs below 4.0 for all selected features (Table 1). Importantly, these analyses underscored the limited relevance of average values of physical quantities in multi-principal element alloys (MPEAs), with most averaged quantities, initially included in the feature pool, being eliminated. Instead, the asymmetry factor in the magnitudes of physical properties of constituent elements within MPEAs emerged as a significant determinant of the output features (HV or EL). Asymmetry features related to melting temperature, bulk modulus, shear modulus, and enthalpy of mixing, along with the Mean Atomic Size Difference, were included in both the hardness and elongation datasets, highlighting their role in data-driven alloy property design (Fig. 4(b)).

It is noteworthy to mention that the reduced pool of selected features from the PCC correlation method must include the attributes considered as the significant indicators of hardness and ductility metrics from the viewpoint of physics. Pugh's ratio (Pugh, 1954), defined as the ratio of shear modulus and bulk modulus, is known to be a de-facto indicator of hardness (Balasubramanian et al., 2018; Liu et al., 2014) and ductility (Singh et al., 2023; Hadi et al., 2016; Balasubramanian

Table 2

AlloyManufacturingNet as an ensemble of neural networks, will be built upon the different database types as outlined here. In context of feature selection using PCC, the input and output variables are in the same feature space of the data matrix. However, for the databases associated with PCA, the output feature (hardness or elongation) will be in a different feature space than those of the selected principal components. So, the inverse transformation of the principal component feature space to the original feature space will be performed to map input features with the output variable.

Databases/Models ID	Characteristics/Descriptions
DB1-HV-PCC	8 input features + hardness feature (HV) as exactly selected from PCC
DB2-HV-PCC	Features of DB1-HV-PCC + manufacturing route (MR) input features
DB3-HV-PCA	7 Principal Components of Hardness data w/o MR based features + HV feature
DB4-HV-PCA	8 Principal Components of Hardness data including MR based features + HV feature
DB1-EL-PCC	7 input features + elongation (EL) feature as selected via PCC
DB2-EL-PCC	Features of DB1-EL-PCC + MR features
DB3-EL-PCA	8 Principal Components of Elongation data w/o MR based features + EL feature
DB4-EL-PCA	9 Principal Components of Elongation data including MR based features + EL feature

et al., 2018) for several classes of materials. Besides, Pugh's ratio; Cauchy pressure is also regarded a significant indicator for the elongation and hardness properties. In other words, Pugh's criterion (Pugh, 1954) and Pettifor criterion (Pettifor et al., 1991; Pettifor, 1992) are the two classical criteria to estimate whether a material is ductile or brittle (Senkov and Miracle, 2021). By establishing the relationship between Pugh's ratio and Cauchy pressure, Senkov and Miracle (2021) have revealed that the two criteria are identical for cubic phase materials and alloys. It can be thus inferred that using either Pugh's criterion or Pettifor criterion would be sufficient in the study of hardness and ductility of materials. Moreover, microhardness values and percentage elongation for the FCC and BCC multi-principal element alloys are influenced by their VECs (Singh et al., 2023; Kitagawa et al., 2022; Tian et al., 2015; Kitagawa, 2022). Owing to the presence of hard elements at VEC range 5–7, BCC-phase MPEAs with VECs in the range 4–5.5 are known to exhibit the increment of hardness with increase in VEC (Hattori et al., 2023). Balasubramanian et al. (2018) have described VEC as a unified indicator for several mechanical properties including hardness and ductility. Presenting for rock-salt structure binary and ternary metal carbides, nitrides and carbonitrides; they have reported that the ductility in general increases with VEC whereas hardness first increases with increase in VEC but later on decreases at VEC = 9.5 and beyond. Since these relationship is established in materials defined with rock-salt structure using first principles calculations, it would be important to associate hardness and ductility with VEC for MPEAs. In Fig. 4(b), the features ΔB and ΔG are associated with Pugh's ratio, and the list also includes VEC. Hence, the training data for machine learning will include the features that are considered as the significant indicators of ductility and hardness.

2.2.2. PCA for feature selection in the datasets

Principal component analysis (PCA) is a valuable statistical technique used to condense extensive feature sets, facilitating data visualization and analysis (Kunwar et al., 2021). It accomplishes dimensionality reduction by breaking down a data matrix into two components: direction and magnitude, yielding multiple data directions. These directions are used to transform the original data, aligning it with possible directions. By identifying essential directions significant for regression analysis, less crucial components can be removed.

In this study, two sets of hardness and elongation data were considered, one excluding manufacturing route features, and the other including them. Each dataset, denoted as D_i (D_H for hardness and D_E for elongation), is a $k \times N$ matrix, where k is the dimension

of the dataset (15 for datasets without manufacturing route features, and 19 for those including route features), and N is the number of observations. PCA aims to project these k -dimensional datasets into a lower-dimensional p -dimensional subspace (where $p < k$) to enhance computational efficiency while preserving over 90 PCA involves eigendecomposition of the covariance matrix (A_i) to extract meaningful insights from the dataset D_i . This process yields eigenvectors $[[v_1], [v_2], \dots, [v_k]]$ and their corresponding eigenvalues $[\psi_1, \psi_2, \dots, \psi_k]$. Each eigenvector defines a direction in the new feature space, with associated eigenvalues indicating their importance. Explained variance (EV) quantifies the variance explained by each principal component, reflecting its relative significance within the feature space. EV is calculated as the ratio of eigenvalue ψ_j to the sum of all k eigenvalues for the j th principal component $[v_j]$. The orthogonal nature of the eigenvectors ensures uncorrelated principal components. Details on eigendecomposition and PCA procedures, including manufacturing route information, are provided in **Supplementary Materials Section S1.3** for the hardness dataset, with similar methods applied to other datasets.

$$EV = \frac{\psi_j}{\sum_{i=1}^k \psi_i} \quad (2)$$

From Eq. (2), it becomes evident that eigenvalues serve as indicators of the variances within the dataset along the new feature axes generated by PCA. To establish a feature subspace consisting of p principal components (PCs), a cumulative explained variance (cumulative EV) greater than 90% (0.9 in fractional value) is the chosen criterion for information retention. This criterion determines the reduced number of principal components that will exclusively represent the post-PCA dataset in the new feature space. The cumulative explained variances (EVs) for the datasets are visually presented in Fig. 4(c). For DB3-HV-PCA, it is observed that 7 out of the initial 15 components are capable of capturing 90% of the explained variance. Similarly, in the case of DB3-EL-PCA, 8 out of the original 15 components demonstrate the ability to account for 90% of the explained variance. Conversely, for DB4-HV-PCA, 8 out of the expanded set of 19 features exhibit the capability to capture this 90% explained variance, and in the context of DB4-EL-PCA, 9 out of the same 19 features achieve this 90% explained variance through Pearson's correlation coefficient analysis. The inverse transformation matrices of these selected principal components along with their corresponding output feature (in original feature space) are arranged in databases, and the names of the databases are also listed in Table 2.

2.3. AlloyManufacturingNet — trained to learn the hardness and elongation dataset

After completing data preprocessing and feature selection, the machine learning model training phase commences. Specifically, regression machine learning models are employed for predicting the hardness and elongation of MPEAs. Regression analysis, a form of supervised learning, establishes relationships between input features and target variables. In contrast to classification analysis, which yields discrete or categorical outputs, regression produces continuous functions or numerical target values (Kunwar et al., 2020). Artificial Neural Networks (ANNs) are used in this study for regression analysis, as they can capture complex and non-linear relationships between inputs and targets through the application of non-linear activation functions in each layer. These ANNs, trained with datasets containing information about the manufacturing routes of MPEAs, are denoted as AlloyManufacturingNet.

Table 2 presents four distinct sets of models for hardness data (DB1-HV-PCC, DB2-HV-PCC, DB3-HV-PCA, and DB4-HV-PCA) and four different models/databases for elongation data (DB1-EL-PCC, DB2-EL-PCC, DB3-EL-PCA, and DB4-EL-PCA). For instance, DB2-HV-PCC incorporates additional information about the manufacturing process's

Table 3

Metrics and weight factors of the individual models for hardness and elongation analyses are presented in the first four rows. The final row provides the metrics associated with the Ensemble NN. For the column of feature selection, the technique or method remarked with an asterisk (PCC* or PCA*) means that the final databases include the features corresponding to fabrication routes. Those rows with PCC and PCA not marked with asterisk imply that the databases exclude the features associated with the manufacturing route.

Model numbering	Feature selection	Hardness models	Elongation models
1	PCC	Database = DB1-HV-PCC MAE = 58.6 MAPE = 15.5% RMSE = 75.9 $R^2 = 0.822$ ideal weights = 0.3	Database = DB1-EL-PCC MAE = 7.9 MAPE = 89% RMSE = 12 $R^2 = 0.67$ ideal weights = 0.3
2	PCC*	Database = DB2-HV-PCC MAE = 51.9 MAPE = 14.6% RMSE = 71.7 $R^2 = 0.841$ ideal weights = 0.3	Database = DB2-EL-PCC MAE = 8.33 MAPE = 99.6% RMSE = 12.34 $R^2 = 0.65$ ideal weights = 0.3
3	PCA	Database = DB3-HV-PCA MAE = 57.7 MAPE = 16.3% RMSE = 75.5 $R^2 = 0.824$ ideal weights = 0.1	Database = DB3-EL-PCA MAE = 11.8 MAPE = 249% RMSE = 15.55 $R^2 = 0.45$ ideal weights = 0.2
4	PCA*	Database = DB4-HV-PCA MAE = 54.8 MAPE = 15.65% RMSE = 70 $R^2 = 0.848$ ideal weights = 0.3	Database = DB4-EL-PCA MAE = 12.26 MAPE = 212.7% RMSE = 16.27 $R^2 = 0.4$ ideal weights = 0.3
Ensemble model		MAE = 50.2 MAPE = 14.2% RMSE = 63.1 $R^2 = 0.877$	MAE = 9.7 MAPE = 139.9% RMSE = 12.1 $R^2 = 0.67$

influence on hardness, while DB1-HV-PCC lacks this information but comprises fewer input features. This reduced feature set in DB1-HV-PCC helps mitigate the curse of dimensionality compared to DB2-HV-PCC. It allows for a more pronounced measurement of the effect of changes in electronegativity difference on hardness, as it is less influenced by other input features. On the other hand, the selected input features from PCA analysis in DB3-HV-PCA and DB4-HV-PCA are uncorrelated with each other, enhancing the prediction potential of machine learning models. Similarly, the diversity among the four databases for elongation data follows a similar pattern. The key question now is how to ensure that the unique informational and functional advantages offered by each database are proportionately integrated into the machine learning model(s). The answer lies in constructing ensemble neural network models.

In machine learning, an ensemble model combines multiple sets of models to improve overall predictive accuracy Kwak et al. (2022). An ensemble neural network (NN) model is a committee of distinct models, where each model contributes to the final prediction. For mechanical property data, such as hardness, four unique databases are created after feature selection (see Table 2). The ensemble NN models built on these datasets combine the predictions of individual models through weighted averaging to maximize R^2 . The weighted-average prediction represents the ensemble model's final output. Similarly, for elongation data, the ensemble learning is based on four distinct databases listed in Table 2.

For the design of the ensemble neural network of a given mechanical property (hardness/elongation), first of all the individual models

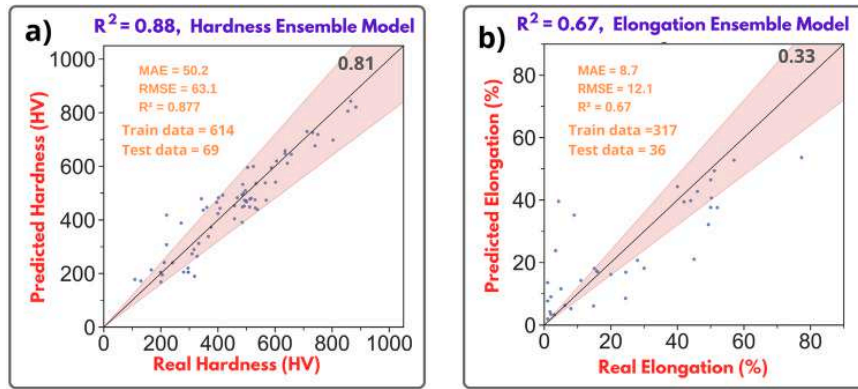


Fig. 5. Parity plot for test datasets. Parity plots along with the Mean Absolute Error (MAE), Root Mean Squared Error (RMSE), and coefficient of determinant (R^2) for (a) hardness (614 alloys from training data and 69 from test data alloys) (b) elongation (317 alloys from training data and 36 from test data). The dataset of elongation shown in the (b) corresponds to the mixture set of tensile and compression test specimens. The shaded region represents an 80% accuracy region with a number at the top right edge indicating the fraction of test predictions having >80% accuracy.

(model no. 1–4) of Table 3 are trained. For a given model number, the selected features are supplied at the input and the model is trained with the most suitable hyper-parameters. 10% of the training data is used as a validation dataset. *Tensorflow 2.7* software with *keras* frontend is used for compiling and running the neural network model. The result of the machine learning was visualized with the help of *matplotlib* library. It is desirable that the individual/ensemble neural networks can perform well beyond the training data and metrics such as *mae*, *mape*, *rmse* have been employed in this study to quantitatively ensure the cross-validation tasks.

Hyperparameters, like epochs, batch size, layer dimensions, optimization functions, activation functions, and more, exert significant control over the model's learning process. Weight initialization and constraints also influence initial weight values. Regularization and dropout rates are introduced to prevent overfitting during training. Hyperparameter tuning aims to find the optimal combination of these parameters to maximize scoring metrics, such as R^2 . *RandomSearchCV* from the *SK-learn* library was employed for hyperparameter tuning, randomly selecting 300 configurations from a grid detailed in Supplementary Materials, Table S2. These configurations were evaluated using 10-fold cross-validation, resulting in a total of 3000 model tests. The ensemble model's configuration was determined based on the highest average R^2 value from cross-validation. Additional evaluation metrics, including RMSE, MAE, and MSE (see Table 3), were considered to ensure performance consistency and generalization. These metrics bolster the model's robustness and validate the weighting methodology, aligning with the core objectives of ensemble modeling. Detailed hyperparameter values are provided in Supplementary Materials, Tables S2 and S3.

The test dataset undergoes standardization to align with the training data standardization, preventing data leakage and ensuring realistic test results. During model training, *Callbacks* are employed to track validation RMSE, helping identify the model with the best validation RMSE. This optimal model is then used as a component in the ensemble of four models, as shown in Table 2, for both hardness and elongation. Given that individual models' predictions differ, a simple average might not yield the best ensemble outcomes. To optimize model significance, the best-weighted fractions are determined. By employing the entire dataset used to build the model (combining both train and test data), weighted averages of predictions from individual models within the ensemble are computed to obtain the final model predictions. Results for each individual model and the ensemble models are detailed in Table 3. Further elaboration on cross-validation results will be provided in Section 3.1.

3. Results and discussions

3.1. Cross-validation results for ANN models and ensemble model design optimization

Moving forward, we focus on developing deterministic neural network prediction models. These ensemble neural network models, as discussed in Section 2.3, combine the strengths of four deterministic models to ensure balanced information integration. Consequently, these ensemble models will serve as our prediction models for mechanical properties.

Before adopting the ensemble neural network as the prediction model, thorough validation on an independent test dataset is essential. The results for the ensemble models on the test dataset are concisely summarized in parity plots in Fig. 5, accompanied by key performance metrics. For hardness analysis (refer Fig. 5(a)), the ensemble model boasts an MAE of 50.2 HV, RMSE of 63.1 HV, and an impressive R^2 of 0.877. Notably, 81% of the test data falls within the 80% accuracy region. In the case of elongation analysis presented in Fig. 5(b) for training datasets consisting of mixture set of both compression and tensile test specimens, the ensemble model exhibits MAE = 8.7% MAE, RMSE = 12.1% RMSE, and $R^2 = 0.67$, with 33% of the test data residing within the 80% accuracy region.

The optimization criterion for determining weighted fractions of predictions from individual member neural network models is the maximum R^2 value. In the hardness ensemble model, models 1–4 (Table 3) are assigned weighted fractions of 0.3, 0.3, 0.1, and 0.3, respectively, yielding the highest R^2 . This same order of weighted fractions is applied in designing the ensemble models. Notably, the influence of DB2-HV-PCC (weighted fraction = 0.3) and DB4-EL-PCA (weighted fraction = 0.3), which include variables related to the fabrication route, is substantial, underscoring the manufacturing route's significant role in shaping the hardness feature.

For elongation analysis, models corresponding to databases DB1-EL-PCC, DB2-EL-PCC, DB3-EL-PCA, and DB4-EL-PCA receive respective weight fractions of 0.3, 0.3, 0.2, and 0.3. Once again, the model derived from DB3-EL-PCA carries less weight compared to the other three models, highlighting the importance of including the manufacturing route in elongation prediction. This optimization procedure also confirms that PCC-based feature selection holds greater weight than PCA-based feature selection. In the hardness ensemble machine learning model, the two PCC-based models each receive a weight fraction of 0.3, while the two PCA-based models receive corresponding weight fractions of 0.1 and 0.3. Similarly, in the elongation ensemble neural network, the two PCC-based models are assigned identical weight fractions of 0.3, while the two PCA-based models receive weight fractions of 0.2 and 0.3, respectively.

Table 4

Evaluation of trained ensemble models by predicting hardness and elongation for $\text{Al}_{0.5}\text{Nb}_{0.5}\text{TiV}_2\text{Zr}_{0.5}$ alloy previously unknown to the model. The values for the experimental hardness and elongation of this MPEA are obtained from Jiang et al. (2022).

Hardness (HV)		Elongation (EL)	
Predicted HV	587.16	Predicted EL (%)	12.72
Experimental HV	577.7	Experimental EL (%)	14.1
% Error	1.63	% Error	9.8
MAE	9.46	MAE	1.38

3.2. AlloyManufacturingNet as prediction model in hardness-ductility synergy design

The successful completion of cross-validation and ensemble model optimization now paves the way for the practical application of these neural network models in predicting mechanical properties for new multi-principal element alloys. To put our models to the test, we predicted the properties of an alloy, $\text{Al}_{0.5}\text{Nb}_{0.5}\text{TiV}_2\text{Zr}_{0.5}$, which was absent from the training and test datasets of the individual models. The results are summarized in Table 4. Notably, the experimental hardness value for this alloy is 577.7 HV (Jiang et al., 2022), and our ensemble model predicts it with exceptional accuracy, yielding a prediction error of just 1.63%. This underscores the model's intelligence and its ability to provide reliable predictions for previously unencountered alloys. Moreover, the model effectively captures the broader trend that alloys with a higher proportion of Nb and Zr tend to exhibit higher hardness values, as evident in the prediction for $\text{Al}_{0.5}\text{Nb}_{0.5}\text{TiV}_2\text{Zr}$, aligning closely with its experimental hardness of 614.1 HV (Jiang et al., 2022). Table 4 also presents a comparison between the experimental and predicted elongation values for the $\text{Al}_{0.5}\text{Nb}_{0.5}\text{TiV}_2\text{Zr}_{0.5}$ alloy. The experimental elongation stands at 12.72% (Jiang et al., 2022), while the model predicts it to be 14.1% with an error of less than 10%. This indicates the model's ability to provide reasonably accurate predictions for elongation properties, further emphasizing its utility and reliability in predicting mechanical properties for a wide array of alloys, including those not covered in the training dataset.

In the era of artificial intelligence, the integration of machine learning into materials science has ushered in the era of inverse alloy design (Pei et al., 2021). Simultaneously, it has advanced the accelerated design and discovery of new materials (Yu et al., 2021), which exhibit a diverse range of mechanical properties. In practical terms, the prediction model developed through the training and validation procedures serves as a versatile virtual tool for materials design and discovery. In this study, the prediction models encompassing hardness and elongation ensemble neural networks act as crucial tools for forecasting the properties of various multi-principal element alloy (MPEA) compositions. Given that neural networks can approximate a wide range of functions, they are also capable of aiding in the reverse engineering of compositions that meet specific hardness and/or elongation criteria. Notably, these data-driven techniques can be employed to optimize MPEA compositions while adhering to the constraints defined by the hardness-ductility synergy criterion.

We employ ensemble neural networks, denoted as AlloyManufacturingNet, to facilitate the prediction-driven inverse design of two multi-principal element alloys (MPEAs). Our focus centers on two medium entropy alloys (MEAs), specifically ZrHfNb and VNbTa, as our foundational materials. Our objective revolves around gauging the impact of introducing two refractory elements simultaneously as dopants on their hardness and elongation properties. Furthermore, we delve into evaluating the significance of different manufacturing routes in the context of these doped MEAs. To provide context, it is worth noting that the reference hardness values for ZrHfNb and VNbTa stand at 365.9 HV and 403.82 HV, respectively, while their corresponding elongation values are 31.37% for ZrHfNb and 20.96% for VNbTa. In our approach, we introduce two dopant elements, D1 and D2, drawn from the list [Cr,

W, Mo, Ta, and Ti], into ZrHfNb for a given fabrication route. These dopants are incorporated in varying proportions, enabling our prediction model to estimate the hardness and elongation characteristics of $\text{D1}_x\text{D2}_y(\text{ZrHfNb})_{1-x-y}$ at diverse composition proportions represented by x and y . Similarly, for different variants of manufacturing routes, we select a pair of dopant elements (D1, D2) from the list [Zr, W, Hf, Mo, Ti, and Cr] to introduce into the base VNbTa MEA. Our ensemble neural networks then predict the properties of $\text{D1}_x\text{D2}_y(\text{VNbTa})_{1-x-y}$ MPEAs. This data-driven approach primarily focuses on the design of quinary MPEAs, offering a cost-effective and time-efficient alternative to traditional alloy design processes.

In contrast to conventional experimental methodologies that necessitate numerous trials to fabricate and test alloys with varying dopant levels, our machine learning models adeptly manage the complexity of simultaneously introducing two dopants without incurring substantial additional cost and time. Capitalizing on this advantage, our study explores the effects of different manufacturing routes when including two dopants in base MEAs simultaneously. We also ascertain the compositions of dopants that yield maximum hardness and elongation values under a given manufacturing method. Furthermore, we predict the specific compositions that achieve optimal hardness-elongation values, filtering out alloys with extreme values for one property but not the other. From this pool of candidates, including several others, we discern the best candidate through the formulation of an optimization problem. If $(HV)_{x,y}$ and $(EL)_{x,y}$ are the predicted values of the hardness feature and elongation feature resulted in a given fabrication procedure for the composition proportion x and y of dopants D1 and D2 respectively.

Hardness and elongation, vital material properties measured in different units, pose a challenge due to their disparate measurement scales rooted in distinct physics and theoretical concepts. To align these properties, a statistical approach is employed. Both hardness and elongation undergo standardization based on mean and standard deviation, a process rendering them dimensionless. This standardization facilitates composition optimization by enabling the direct comparison of these scale-invariant properties. This method results in the definition of the following objective function defined as:

$$F(x, y) = \frac{(HV)_{x,y} - \overline{HV}}{\sigma_{HV}} + \frac{(EL)_{x,y} - \overline{EL}}{\sigma_{EL}} \quad (3)$$

The objective function $F(x, y)$ in Eq. (3) is maximized after subjected to the constraints: $x \geq 0$, $y \geq 0$, $782HV \geq (HV)_{x,y} \geq 207HV$ and $60\% \geq (EL)_{x,y} \geq 5\%$. $\overline{HV} = 495.3$ HV and $\sigma_{HV} = 196.75$ HV are the respective mean and standard deviation values of the originally collected hardness feature. Similarly, $\overline{EL} = 22.16\%$ and $\sigma_{EL} = 19\%$ are respectively the mean and standard deviation of the elongation variable. While the sample hardness and elongation features are specified for a given manufacturing route, it is worth noting that the statistical mean and standard deviation values, as defined previously, remain unaffected by changes in the fabrication procedure. With the hardness feature ranging from 207 HV to 782 HV and elongation falling between 5% and 60% (as shown in Fig. 3), it becomes evident that the combined non-standardized values of HV and EL are predominantly influenced by the HV feature due to its larger range. To mitigate the bias introduced by variables with differing scales during mathematical calculations and to prevent errors, we employ a standardization procedure in this optimization task. By utilizing standardized features in the objective function, the inherent differences in scale between the hardness and elongation variables cease to impact the mathematical determination of the optimal alloy composition. This ensures scale-invariant composition optimization when dealing with two predicted unique variables of dissimilar ranges or scales.

It is important to emphasize that the standardized objective function in Eq. (3) can yield positive, negative, or zero values. If a predicted hardness variable falls below the mean value, the numerator of the first term in the right-hand side of Eq. (3) is negative, resulting in a standardized hardness feature below zero. Conversely, when the estimated

value exceeds the mean hardness, the standardized hardness takes on a positive value. Similarly, depending on the magnitude of the predicted elongation feature, the standardized elongation feature (the second term on the right-hand side of the equation) can be either greater or less than zero. From an optimization perspective, a more positive function value indicates the suitability of the multi-principal element alloy (MPEA) for structural and materials applications. Specifically, an MPEA designed with both standardized variables (hardness and elongation) represented as positive real numbers is considered favorable in materials design. Conversely, an MPEA with either one or both standardized features as negative real numbers is deemed unsuitable for structural material applications. Therefore, the necessary and sufficient condition for a multi-principal element alloy to be deemed appropriate for technological applications is that it must exhibit positive values for standardized hardness and standardized elongation while maximizing the positive real number value of the standardized objective function.

The relationship between the composition of the first generic $D1_xD2_y(\text{ZrHfNb})_{1-x-y}$, manufacturing routes, and the specified hardness features at room temperature is visually depicted in the ternary plots of Fig. 4. Corresponding information regarding elongation for these alloy systems is provided in Fig. 5. Additionally, presentations detailing hardness and elongation for the second generic $D1_xD2_y(\text{VNBtTa})_{1-x-y}$ are presented in Figs. 6 and 7, respectively. These ternary plots serve as the cornerstone of inverse alloy design. The significant coordinate points (x, y) representing dopant composition proportions in the ternary plots, along with the specific manufacturing route associated with the maximum hardness value (independently established from the hardness plots) and the maximum elongation value (solely derived from the elongation plots), are listed in Table **Supplementary Table S4** for the first generic alloy system and Table **S5** for the second generic MPEA system. The manufacturing route corresponding to the assigned property value is also presented.

3.2.1. Predictive design of maximum hardness and maximum elongations for undiscovered MPEA

In the context of alloy systems $D1_xD2_y(\text{ZrHfNb})_{1-x-y}$ and $D1_xD2_y(\text{VNBtTa})_{1-x-y}$, we present graphical representations of alloy compositions and the corresponding hardness and/or elongation properties at room temperature for different manufacturing routes in ternary plots (**Supplementary Figure S10, S11, S12, S13**). These ternary plots play a pivotal role in inverse alloy design.

For the $\text{Cr}_x\text{W}_y(\text{ZrHfNb})_{1-x-y}$ system, doping ZrHfNb with Cr and W elements leads to significantly elevated hardness values across all four manufacturing routes. Notably, the [W, Ta] dopant pair, followed by [Mo, Ta], imparts intermediate hardness to the base ZrHfNb system, while the [Ti, Ta] dopant pair results in lower hardness values. Analysis of ternary plots for dopants pair yielding maximum hardness and maximum elongation as represented in 6(a) (i) infers Powder metallurgy produces the highest hardness of 684.49 HV for $x = 0.4$ and $y = 0.5$, making it the recommended MPEA system for applications prioritizing hardness. Regarding elongation, predictions made by our machine learning model for elongation values in the $D1_xD2_y(\text{ZrHfNb})_{1-x-y}$ system are as follows: Each ternary plot corresponds to a specific dopant pair [D1,D2] and a particular manufacturing route. As detailed and demonstrated in Fig. 6(c), the alloy system $\text{Ti}_x\text{Ta}_y(\text{ZrHfNb})_{1-x-y}$, when manufactured through annealing, exhibits regions with significantly greater elongation values. The maximum elongation, reaching 43.52%, occurs at $x = 0.7$ and $y = 0$. This suggests that $\text{Ti}_{0.7}(\text{ZrHfNb})_{0.3}$, when produced via annealing, possesses the highest ductility. This observation extends to another alloy system where Ti also proves to be a favorable dopant.

In the case of the $D1_xD2_y(\text{VNBtTa})_{1-x-y}$ system, the dopant pairs [Cr, W] and the powder metallurgy-based manufacturing route favor increased hardness. The alloy $\text{Cr}_{0.5}\text{W}_{0.3}(\text{VNBtTa})_{0.2}$, manufactured via sintering, exhibits the maximum hardness of 733.42 HV. This value represents the highest hardness among all alloy systems considered. Powder

metallurgy emerges as the preferred method for preparing alloys with the highest hardness across all dopant pairs in $D1_xD2_y(\text{VNBtTa})_{1-x-y}$. Similarly, for predicted elongation distribution in the $D1_xD2_y(\text{VNBtTa})_{1-x-y}$ MPEA system. Analysis of the ternary diagrams indicates that when [Mo,Ti] dopants are added to the base VNBtTa system, they provide the highest attainable ductility in the resulting MPEA. The maximum elongation value, 34.36%, is achieved by the $\text{Mo}_{0.1}\text{Ti}_{0.8}(\text{VNBtTa})_{0.1}$ MPEA when using wrought or miscellaneous fabrication procedures as represented in triangular contour in Fig. 6(a) (ii).

Comparing the bar charts for elongation values of the $D1_xD2_y(\text{ZrHfNb})_{1-x-y}$ and $D1_xD2_y(\text{VNBtTa})_{1-x-y}$ MPEA systems in Fig. 6(c), it becomes evident that alloys compositionally designed with ZrHfNb generally exhibit superior ductility compared to those designed with VNBtTa systems. Unlike the maximum hardness property (where powder metallurgy emerges as the most favorable fabrication route), there is no single preferred fabrication procedure associated with enhanced ductility for all dopant pairs and composition variants.

3.2.2. Optimal composition and fabrication route corresponding to hardness-ductility synergy

Advanced structural materials require an optimal balance between hardness and ductility. AlloyManufacturingNet enables the prediction of suitable fabrication routes and alloy compositions that exhibit favorable hardness-elongation synergy. By combining independent hardness and elongation (Section 3.2.1) models with the mathematical model represented by Eq. (3), an ensemble of neural networks can forecast specific MPEA (Multi-Principal Element Alloy) compositions and the corresponding manufacturing routes that yield optimal hardness and elongation values.

For ZrHfNb-based alloys, as shown in Fig. 6(c), $\text{Cr}_{0.8}\text{W}_{0.1}(\text{ZrHfNb})_{0.1}$ produced through wrought processing exhibits excellent hardness at 511.81 HV and moderate elongation at 17.14%, making it suitable for applications where achieving high hardness is essential. Conversely, $\text{Ti}_{0.3}\text{Ta}_{0.4}(\text{ZrHfNb})_{0.3}$, also manufactured via wrought processing, offers an excellent elongation of 37.95% with lower hardness (374.56 HV), making it a suitable choice for applications emphasizing high ductility. **Supplementary Table S4** reveals that the base ZrHfNb alloy, when cast, possesses hardness and elongation values of 426.91 HV and 32.99%, respectively. Meanwhile, using powdered metallurgy, the same alloy exhibits hardness and elongation of 383.54 HV and 31.68%. Hence, the first of the two alloys ($\text{Cr}_{0.8}\text{W}_{0.1}(\text{ZrHfNb})_{0.1}$ and $\text{Ti}_{0.3}\text{Ta}_{0.4}(\text{ZrHfNb})_{0.3}$) prepared via the wrought process suits applications requiring elevated hardness, whereas the second is more appropriate for applications requiring higher ductility. It can be inferred that wrought processing is recommended for fabricating MPEAs from the base ZrHfNb alloy to enhance either hardness or elongation. However, it is worth noting that a trade-off between hardness and elongation often exists in ZrHfNb alloys, making it challenging to achieve hardness-elongation synergy with the given dopants and various manufacturing processes.

Similarly, alloy combinations derived from VNBtTa MEA, both $\text{Cr}_x\text{W}_y(\text{VNBtTa})_{1-x-y}$ and $\text{Mo}_x\text{Ti}_y(\text{VNBtTa})_{1-x-y}$ systems fabricated using wrought processing appear to exhibit regions with favorable hardness-elongation synergy, as depicted in Fig. 6(c). For instance, $\text{Cr}_{0.7}(\text{VNBtTa})_{0.3}$ manufactured via the wrought process is predicted to possess excellent hardness (575.87 HV) and moderately good elongation (23.73%). Consequently, the alloy $\text{Cr}_x\text{W}_y(\text{VNBtTa})_{1-x-y}$ with $x = 0.7$ and $y = 0$, manufactured by wrought method (**Supplementary Table S5**), is suitable for structural applications that require high hardness. Similarly, when wrought processed, $\text{Mo}_x\text{Ti}_y(\text{VNBtTa})_{1-x-y}$ alloys show hardness and elongation values of 566.43 HV and 27.79% at $x = 0.3$ and $y = 0$, respectively. Thus, $\text{Mo}_{0.3}(\text{VNBtTa})_{0.7}$ MPEA offers nearly equal hardness to $\text{Cr}_{0.7}(\text{VNBtTa})_{0.3}$ but with improved ductility. $\text{Mo}_{0.3}(\text{VNBtTa})_{0.7}$ alloy manufactured through wrought processing is estimated to possess excellent hardness-ductility synergy, especially

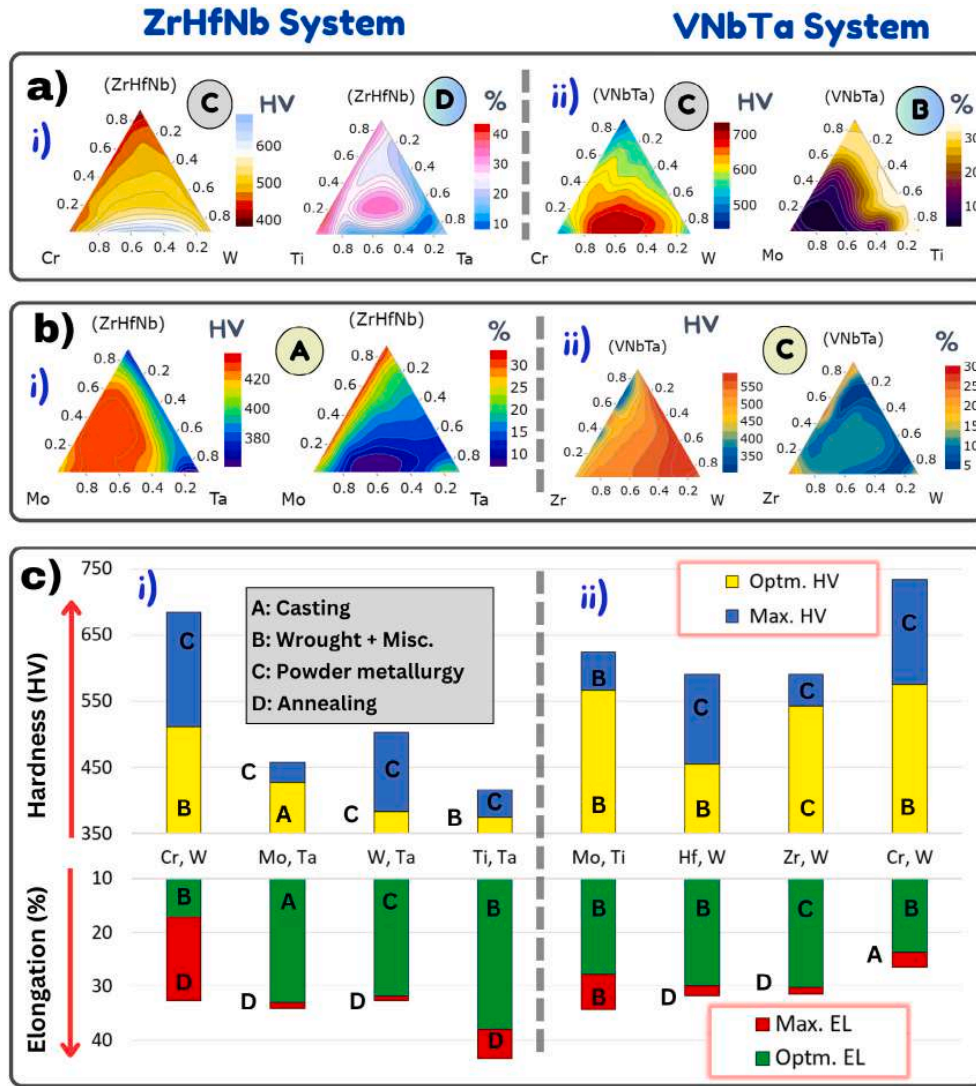


Fig. 6. (a) Maximum hardness and maximum elongation Powder metallurgy results in the highest hardness (684.49 HV) when Cr = 0.4 and W = 0.5 in ZrHfNb. In the case of elongation, [Ti = 0.7, Ta = 0] with annealing yields 43.52%. For VNbTa, powder metallurgy with Cr = 0.5 and W = 0.3 achieves a hardness of 733.42 HV, while an elongation of 34.36% is obtained with Mo = 0.1 and Ti = 0.8 in the Wrought + Misc route. (b) Optimized hardness-elongation pairs For, $\text{Mo}_{0.6}(\text{ZrHfNb})_{0.4}$ with obtained from prediction model of AlloyManufacturingNet. (c) The manufacturing route associated with the predictions is also provided as labels in the bar diagrams. It is to be noted that the single alloy composition and a single manufacturing route are associated with a specific optimal hardness-elongation pair. It is to be noted that the letters A, B, C and D drawn inside the colorful circles of (a) and (b) denote the manufacturing methods labeled in (c) The detailed version of the specially highlighted results presented in this figure is provided in Supplementary section S4.

favoring hardness. On the other hand, $\text{Zr}_{0.4}(\text{VNbTa})_{0.6}$ MPEA produced via powder metallurgy is predicted to exhibit a hardness of 542.60 HV and elongation of 30.22%. This alloy also demonstrates a perfect combination of hardness-ductility synergy, albeit favoring ductility. Notably, these MPEAs with improved hardness-elongation synergy typically comprise four elements, with a relatively higher proportion of the base alloy VNbTa. In terms of elements doped into the VNbTa system, wrought manufacturing and powder metallurgy are considered preferable methods for achieving a balance between elongation and hardness properties.

In contrast to alloys derived from the ZrHfNb system, MPEAs obtained from the base VNbTa system exhibit robust hardness-ductility synergy, quantitatively expressed through standardized and summed values of optimal hardness and optimal elongation features (refer to

Eq. (3)). For instance, in the case of $\text{Cr}_{0.8}\text{W}_{0.1}(\text{ZrHfNb})_{0.1}$ (fabrication route = wrought + misc), the standardized hardness is +0.084, while the corresponding elongation is -0.264, resulting in an objective function value of -0.1802. This alloy falls into the category of less preferable candidates due to its negative standardized objective function value, despite having an overall positive objective function value. In contrast, $\text{Ti}_{0.3}\text{Ta}_{0.4}(\text{ZrHfNb})_{0.3}$ MPEA (manufacturing route = wrought + misc) exhibits a highly favorable standardized elongation value (+0.83) but an undesirable standardized hardness value (-0.61), yielding an objective function value of +0.217. Although the objective function is positive, the negative hardness value renders this MPEA unsuitable for technological applications. The maximum attainable positive value of the overall objective function for ZrHfNb-derived MPEAs is +0.2229, found in the case of $\text{Mo}_{0.6}(\text{ZrHfNb})_{0.4}$ alloy fabricated using the casting process. The standardized values of hardness and elongation

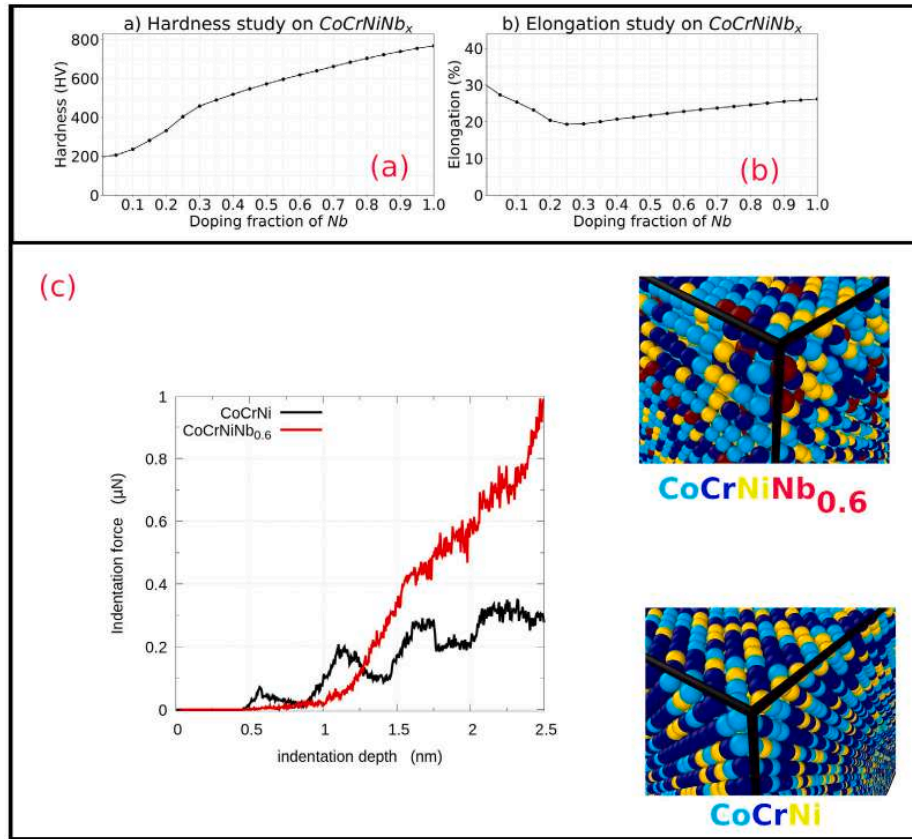


Fig. 7. Predicting the variation of (a) hardness and (b) elongation with the change of Nb dopant proportion (x) in the CoCrNiNb_x MPEA at macroscale (specimen samples in the dimension of mm) using the ensemble neural networks. The manufacturing route for the predicted alloys is casting process. The two alloy variants CoCrNi (absence of Nb element) and $\text{CoCrNiNb}_{0.6}$ are chosen as the candidates for the virtual nanoindentation test using molecular dynamics (MD). The results for the plots of indentation force against indentation depth during the MD simulations are presented in (c). The color of atoms of a given element in the slabs of these two alloys are expressed by the font color of the element in the alloy name (below the image of the nano slab). In the CoCrNi and $\text{CoCrNiNb}_{0.6}$ nano slab, Co, Cr, and Ni atoms are represented by spheres of sky blue, dark blue and yellow colors respectively. Nb atoms, present in $\text{CoCrNiNb}_{0.6}$ nanoslab but absent in CoCrNi nano slab, are represented by red color. The atomic arrangement in the slabs cores. The nanoscale simulation being in line with the macroscale prediction of hardness, reveals that the macroscale response of a MPEA regarding hardness is contributed by mechanisms occurring at nanoscale or atomic scale.

for this alloy are -0.34 and $+0.57$, respectively. The lower value of the overall objective function in ZrHfNb -derived MPEAs can also be observed in ternary plots (**Supplementary Figs. S10 and S11**). For example, triangular diagrams corresponding to $\text{Cr}_x\text{W}_y(\text{ZrHfNb})_{1-x-y}$ alloys prepared by the wrought procedure are positioned second from the top left corner in both figures. The region near the top corner of the triangle, highlighted by a rectangular box, consists of a large proportion of ZrHfNb (i.e., $1-x-y \geq 0.8$) and is characterized by high elongation and low hardness. Observing the 32 ternary plots in these figures, it can be inferred that, most of the time, a given composition of a $\text{D1}_x\text{D2}_y(\text{ZrHfNb})_{1-x-y}$ alloy prepared by a specific manufacturing route corresponds to above-average hardness when elongation is below average, and vice versa. This observation implies that doping the ZrHfNb alloy system with these dopant pairs is unsuitable when aiming to achieve hardness-ductility synergy. However, MPEAs derived from the VNbTa base alloy system offer solutions to mitigate the trade-off between hardness and ductility. $\text{Mo}_{0.3}(\text{VNbTa})_{0.7}$ (MR = wrought + misc) and $\text{Zr}_{0.4}(\text{VNbTa})_{0.6}$ (MR = sintering) represent composition values and manufacturing routes that result in positive values for all three standardized quantities: the objective function, hardness, and elongation. These alloys are recommended for applications requiring a combination of enhanced hardness and greater ductility. $\text{Mo}_{0.3}(\text{VNbTa})_{0.7}$ alloy exhibits standardized hardness and

elongation values of $+0.36$ and $+0.296$, respectively, with a combined sum of $+0.656$ according to Eq. (3). Similarly, $\text{Zr}_{0.4}(\text{VNbTa})_{0.6}$ alloy has standardized hardness and elongation values of $+0.24$ and $+0.42$, respectively, resulting in a sum of $+0.6648$ (the maximum value predicted thus far). Interestingly, it has been discovered that $\text{Zr}_x\text{W}_y(\text{VNbTa})_{1-x-y}$ alloys offer composition values for each of the four manufacturing routes that exhibit positive standardized values for all three quantities (hardness, elongation, and the objective function). In **Supplementary Figs. S12 and S13**, triangular diagrams for $\text{Zr}_x\text{W}_y(\text{VNbTa})_{1-x-y}$ for the four manufacturing routes are positioned on the top row. The region near the mid-length of the left side of these triangles, highlighted by a rectangular box, exhibits both excellent hardness and excellent ductility. Notably, this region is present in the alloy for all four manufacturing routes, making $\text{Zr}_x\text{W}_y(\text{VNbTa})_{1-x-y}$ an optimal candidate for applications requiring excellent hardness-ductility synergy. The hardness-ductility favoring regions also exist in $\text{Mo}_x\text{Ti}_y(\text{VNbTa})_{1-x-y}$ alloys for three manufacturing routes, except for the casting process. In the context of $\text{Cr}_x\text{W}_y(\text{VNbTa})_{1-x-y}$ MPEA, casting, wrought, and annealing processes offer composition proportions favoring hardness-ductility synergy, characterized by regions with high hardness and elongation. However, powder metallurgy does not favor this synergy. When using the dopant pairs Hf and W, the behavior of the VNbTa system is similar to that of the ZrHfNb alloy

doped with [Cr,W], [Mo,Ta], [W,Ta], and [Ti,Ta] in most cases. This means that a given composition coordinate in the triangular diagrams of $\text{Hf}_x\text{W}_y(\text{VNBa})_{1-x-y}$ MPEA for wrought, sintering, and annealing procedures represents low hardness when elongation is high, and vice versa. In the case of casting, the situation is even worse, with overall hardness and elongation values for $\text{Hf}_x\text{W}_y(\text{VNBa})_{1-x-y}$ consistently below average throughout the composition points, indicating an absence of hardness-ductility synergy.

It is noteworthy to mention that the Figs. 6(a) and (b) have a big prospect for being utilized in the design of digital manufacturing (metamorphic manufacturing) methods. The given composition of an MPEA can be checked in the ternary diagrams for hardness or elongation at different manufacturing methods. Importantly, the triangular diagrams have values of hardness and elongation for all sets of composition, so each and every composition value can be inspected. The information about any two different manufacturing routes imparting different hardness for a single alloy composition, then this information can be utilized to design a digitally controlled incremental forming system.

An online software tool can enable the performance of test, design, and discovery tasks for MPEAs, expediting the pursuit of hardness-ductility synergy in these class of materials. The prediction model of AlloyManufacturingNet has been launched online as a software app (Poudel and Kunwar, 2023). In the web interface, the user can perform two distinct tasks — (i) alloy design, and (ii) hardness and ductility optimization. The task of alloy design refers to the task of obtaining the hardness and elongation values independently for a given new alloy composition. When the input for multi-principal element alloy composition and fabrication type is provided by the user, the estimated hardness (in HV) and percentage elongation values are presented on the screen. Besides the target values, the input features (including VEC) and Pugh's ratio are also automatically shown by the software. The user can select between default category (which includes the mixture set of tension and compression datasets), compression tests only, and tensile tests only to find the corresponding values of estimated elongation percentage. It is important to note that the software predicts well for ductile and highly ductile MPEAs and it is not recommended for use in materials with ductility less than 5%. The software performs well for all range of hardness values. In context of the hardness-ductility synergy optimization task, besides the information of the composition of the base MPEA, manufacturing route, and test type; the user has to additionally supply the names of two dopant elements. The software then outputs two ternary diagrams one for hardness distribution and another for ductility distribution in the doped MPEAs. In addition to this, AlloyManufacturingNet also maps the composition data in the Hardness-Elongation chart. Such scatter data can inform the user in knowing the compositions (for a given manufacturing process) that possess good hardness+good ductility; excellent hardness only and excellent ductility only.

3.3. Coupling nanoscale simulation with prediction result at macroscale for Nb-doped CoCrNi MPEA to analyze the hardness

Many materials scientists and engineers are conducting research on the medium entropy alloy CoCrNi as it has piqued their interest for various reasons. It has been demonstrated that this ternary equiatomic MEA possesses greater toughness and strength than the quinary equiatomic CrCoFeMnNi high entropy alloy (Courty et al., 2018). This notable strength-ductility synergy in CoCrNi MEA has been attributed to its low stacking fault energy (Ge et al., 2022). Numerous efforts have been made to improve the mechanical properties of CoCrNi MEA by introducing dopants in varying proportions (Chang et al., 2021). In our pursuit of enhancing hardness, we present our study on doping CoCrNi with Nb atoms. Fig. 7(a) displays the hardness values estimated by the AlloyManufacturingNet for Nb-doped CoCrNi alloys fabricated via the casting procedure. It can be observed that hardness increases with an increasing amount of Nb in the CoCrNiNb_x MPEA. To optimize

the material properties, we employ the ensemble model to predict the elongation feature of CoCrNiNb_x alloy (manufactured using the casting route), and the results are presented in Fig. 7(b). The data reveals that the elongation of the CoCrNi alloy initially decreases with the addition of Nb, reaching its lowest point at $x = 0.25$. In other words, Nb has a negative impact on ductility in CoCrNiNb_x for values of $x \leq 0.25$. While the CoCrNi alloy exhibits the highest ductility, with an elongation of nearly 30%, the $\text{CoCrNiNb}_{0.25}$ alloy has the lowest ductility, with an elongation slightly below 20%. However, for $x > 0.25$, ductility is observed to increase again with the rise in Nb content.

From the perspective of hardness-ductility synergy, it is recommended to design materials and devices with CoCrNiNb_x compositions where the Nb proportion (x) exceeds 0.25, particularly when employing the casting manufacturing procedure. At $x = 0.6$, the CoCrNiNb_x MPEA exhibits a hardness of approximately 600 HV and an elongation well above 20%. Although the exact property values (hardness and elongation) may vary, and the specific value of x associated with minimum elongation may change with different manufacturing routes, it has been confirmed that the trends in hardness and elongation curves are consistent across all four manufacturing categories. Therefore, we will focus on the MPEA produced via the casting procedure in this section to understand the mechanism of hardness enhancement with Nb content. It is to be noted that the training datasets for hardness in the ensemble learning models correspond to millimeters (continuum scale) sized samples. For accurate understanding of the materials science of the MPEAs, it is always important to relate the macroscale behavior with structure-property relationship studied at atomic scale or nanoscale. In the context of predicting the hardness of CoCrNiNb_x MPEA, understanding the structure-property relationship is crucial. While CoCrNi typically has a face-centered cubic (FCC) crystal structure, CoCrNiNb_x with a higher Nb proportion can exhibit a different crystal structure. Our previous work (Subedi et al., 2022b) highlighted that $\text{CoCrNiNb}_{0.5}$ MPEA exists as an IMC phase, while Lu et al. (2019) reported that the Nb-rich phase in CoCrNiNb_x MPEA corresponds to a hexagonal close-packed (HCP) Laves phase. These different crystal structures can influence the mechanical behavior of Nb-rich and Nb-deficient CoCrNiNb_x MPEA/CoCrNi MEA. A nanoscale computational analysis can provide insights into the behavior of these alloys.

In this study, we selected MEA CoCrNi (with atoms arranged in an FCC structure) and $\text{CoCrNiNb}_{0.6}$ MPEA (with a unit cell of HCP structure) for nanoscale indentation tests. We conducted atomistic simulations for nanoindentation using Molecular Dynamics (MD) methods with LAMMPS software (Plimpton, 1995). The supercells of CoCrNi and $\text{CoCrNiNb}_{0.6}$ MPEAs were constructed using Atoms software (Hirel, 2015). The CoCrNi nanoslab consisted of 600,000 atoms, while the $\text{CoCrNiNb}_{0.6}$ nanostructure consisted of 602,688 atoms. We visualized the nanoslabs and analyzed the MD simulation results using OVITO software (Stukowski, 2010). We used a non-atomic spherical indenter (radius = 5 nm, specific force constant = $1000 \text{ eV}/\text{\AA}^3$). The indenter initially touched the top of the nano slabs and then moved vertically downward at a rate of $0.5 \text{ \AA}/\text{ps}$. The results of the MD simulation, showing the variation of indentation force (in μN) with the indentation depth (in nm), are presented in Fig. 7(c).

The black curves in the figure represent the indentation force exerted on the spherical indenter by the constituent atoms (Co, Cr, and Ni) of the FCC CoCrNi alloy. The force shows a peak-valley profile, starting from near-zero and reaching a peak value of $0.2 \mu\text{N}$, then decreasing before rising again with larger peaks. In contrast, the red curve represents the indentation force for HCP $\text{CoCrNiNb}_{0.6}$. It remains negligible until the indenter reaches a depth of 1 nm. Beyond this depth, the force increases continuously as the indenter penetrates the material, without a peak-valley profile. When the indenter reaches a depth of 2.5 nm, the indentation force for CoCrNi MPEA is around $0.3 \mu\text{N}$, while that for $\text{CoCrNiNb}_{0.6}$ is approaching $1.0 \mu\text{N}$. These different indentation profiles provide mechanistic insight into the role of Nb-doping in promoting the hardness of the alloy. The presence of Nb in

larger amounts alters the interaction mechanism among the constituent atoms, strengthening their cohesion and resistance to the indenter. The initial arrangement of Co, Cr, Ni, and Nb in an HCP unit cell allows for enhanced flexibility in atom rearrangement through dislocation motions and twinning, leading to a robust nanostructure that provides greater resistance force. The MD simulation results (performed at nanoscale) confirm the predictions from the ensemble model (built on the data obtained from continuum scale experiments), validating the latter as a physically explainable machine learning model.

4. Conclusion

In this study, we developed a data-driven machine learning ensemble neural network model to predict the hardness and elongation of multi-principal element alloys (MPEAs). We trained the model using selected features and fabrication routes, optimizing hyper-parameters through hyper-parameter tuning. The trained model allowed us to make predictions for both hardness and elongation of the MPEA system. Additionally, we visualized how hardness and elongation vary with changes in the composition of certain elemental components using ternary plots. An online software application has been developed to estimate hardness-elongation values. The software currently provides accurate predictions across a wide range of hardness levels but is particularly effective for ductile and highly ductile MPEAs.

Here are the key conclusions from our work:

- We constructed a weighted ensemble of four neural networks based on feature sets derived from feature selection engineering techniques, including PCC heatmap, VIF, and PCA for predicting hardness and elongation.
- Alloy design was performed for both ZrHfNb- and VNbTa-derived MPEAs based on maximum hardness criteria. The optimal combinations were [Cr, W] dopant pairs and sintering (powder metallurgy) manufacturing routes, resulting in hardness values of 684.49 HV for $\text{Cr}_{0.4}\text{W}_{0.5}(\text{ZrHfNb})_{0.1}$ and 733.42 HV for $\text{Cr}_{0.5}\text{W}_{0.3}(\text{VNbTa})_{0.2}$.
- Elongation-based alloy design revealed $\text{Ti}_{0.7}(\text{ZrHfNb})_{0.3}$ prepared via annealing as the alloy with the highest elongation of 43.52% among all candidates. For VNbTa-derived MPEAs, $\text{Mo}_{0.1}\text{Ti}_{0.8}(\text{VNbTa})_{0.1}$ processed through the wrought manufacturing route exhibited an elongation of 34.36%. Ti was identified as a favorable dopant for improving elongation properties in both alloy categories.
- To achieve a hardness-ductility synergy-based composition design of MPEAs, we introduced a scale-invariant optimization technique for maximizing the objective function of both mechanical properties. The results indicated that VNbTa-derived MPEAs were more suitable for achieving an optimal combination of hardness and elongation.
- We also investigated the hardness enhancement in Nb-doped CoCrNi alloys manufactured by casting. The study revealed that as the Nb content (x) increased in CoCrNiNb_x MPEAs, hardness increased proportionally. Elongation decreased for $x \leq 0.25$ and increased for $x > 0.25$, indicating that a higher proportion of Nb is preferable for hardness-elongation synergy.
- Finally, we used a numerical approach, specifically the MD method, to perform nanoindentation tests on FCC CoCrNi and HCP CoCrNiNb_{0.6} alloys. This allowed us to gain mechanistic insights into how the dopant influences the mechanical behavior of MPEAs.

CRedit authorship contribution statement

Sachin Poudel: Conceptualization, Methodology, Investigation, Validation, Formal analysis, Software, Data curation, Visualization, Funding acquisition, Writing – original draft. **Upadesh Subedi:** Methodology, Validation, Visualization, Formal analysis, Writing – review &

editing. **Mohammed O.A. Hamid:** Validation, Formal analysis, Writing – review & editing. **Khem Gyanwali:** Supervision, Validation, Resources, Writing – review & editing. **Nele Moelans:** Methodology, Validation, Supervision, Funding acquisition, Writing – review & editing. **Anna Timofiejczuk:** Validation, Supervision, Data curation, Visualization, Resources, Writing – review & editing. **Anil Kunwar:** Conceptualization, Investigation, Methodology, Software, Validation, Visualization, Data curation, Formal analysis, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The codes and data of AlloyManufacturingNet for the construction of the machine learning models in this study are made available at https://github.com/Sachinscnpdl/MPEA_HV-EL. The visualization and interactive web application of the code is available at <https://mpeanet.streamlit.app/>.

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Appendix A. Supplementary data

The data constituting the supplementary information to this article is provided together in a single PDF file with 5 different sections (S1. Feature Engineering, S2. Scatterplot of the variables of databases DB1-HV-PCC and DB1-EL-PCC, S3. Hyper-parameter Tuning and Learning Curves of the Neural Networks, S4. Results for MPEA: Optimized Hardness-Elongation synergy, and S5. Simulation setup for nanoindentation test of Multi-principal element Alloys). In total, the supplementary information file contains 5 tables and 15 figures.

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.engappai.2024.107902>.

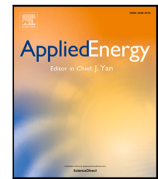
References

- Bakr, M., Syarif, J., Hashem, I.A.T., 2022. Prediction of phase and hardness of HEAs based on constituent elements using machine learning models. *Mater. Today Commun.* 31, 103407.
- Balasubramanian, K., Khare, S.V., Gall, D., 2018. Valence electron concentration as an indicator for mechanical properties in rocksalt structure nitrides, carbides and carbonitrides. *Acta Mater.* 152, 175–185.
- Beniwal, D., Singh, P., Gupta, S., Kramer, M., Johnson, D., Ray, P., 2022. Distilling physical origins of hardness in multi-principal element alloys directly from ensemble neural network models. *npj Comput. Mater.* 8 (1), 1–11.
- Bhandari, U., Zhang, C., Zeng, C., Guo, S., Adhikari, A., Yang, S., 2021. Deep learning-based hardness prediction of novel refractory high-entropy alloys with experimental validation. *Crystals* 11 (1), 46.
- Bolon-Canedo, V., Remeseiro, B., 2020. Feature selection in image analysis: a survey. *Artif. Intell. Rev.* 53 (4), 2905–2931.
- Borg, C.K., Frey, C., Moh, J., Pollock, T.M., Gorse, S., Miracle, D.B., Senkov, O.N., Meredig, B., Saal, J.E., 2020. Expanded dataset of mechanical properties and observed phases of multi-principal element alloys. *Sci. Data* 7 (1), 1–6.
- Chang, Y.-J., Jui, C.-Y., Lee, W.-J., Yeh, A.-C., 2019. Prediction of the composition and hardness of high-entropy alloys by machine learning. *Jom* 71 (10), 3433–3442.
- Chang, H., Zhang, T., Ma, S., Zhao, D., Xiong, R., Wang, T., Li, Z., Wang, Z., 2021. Novel Si-added CrCoNi medium entropy alloys achieving the breakthrough of strength-ductility trade-off. *Mater. Des.* 197, 109202.

- Chausov, M., Pylypenko, A., Maruschak, P., Menou, A., 2021. Phenomenological models and peculiarities of evaluating fatigue life of aluminum alloys subjected to dynamic non-equilibrium processes. *Metals* 11 (10), 1625.
- Courty, F.G., Clarke, K.D., Kiminami, C.S., Kaufman, M.J., Clarke, A.J., 2018. High throughput discovery and design of strong multicomponent metallic solid solutions. *Sci. Rep.* 8 (1), 8600.
- Daehn, G.S., Taub, A., 2018. Metamorphic manufacturing: The third wave in digital manufacturing. *Manuf. Lett.* 15, 86–88, Industry 4.0 and Smart Manufacturing.
- Dasari, S., Chaudhary, V., Gwalani, B., Jagetia, A., Soni, V., Gorsse, S., Ramanujan, R.V., Banerjee, R., 2020. Highly tunable magnetic and mechanical properties in an Al_{0.3}CoFeNi complex concentrated alloy. *Materialia* 12, 100755.
- Dong, Y., Lu, Y., Kong, J., Zhang, J., Li, T., 2013. Microstructure and mechanical properties of multi-component AlCrFeNiMox high-entropy alloys. *J. Alloys Compd.* 573, 96–101.
- Ge, J., Chen, C., Zhao, R., Liu, Q., Long, Y., Wang, J., Ren, Z., Yin, S., 2022. Strength-ductility synergy of CoCrNi medium-entropy alloy processed with laser powder bed fusion. *Mater. Des.* 219, 110774.
- Gludovatz, B., Hohenwarter, A., Catoor, D., Chang, E.H., George, E.P., Ritchie, R.O., 2014. A fracture-resistant high-entropy alloy for cryogenic applications. *Science* 345 (6201), 1153–1158.
- Gorsse, S., Nguyen, M., Senkov, O.N., Miracle, D.B., 2018. Database on the mechanical properties of high entropy alloys and complex concentrated alloys. *Data brief* 21, 2664–2678.
- Guo, S., 2015. Phase selection rules for cast high entropy alloys: an overview. *Mater. Sci. Technol.* 31 (10), 1223–1230.
- Hadi, M.A., Nasir, M.T., Roknuzzaman, M., Rayhan, M.A., Naqib, S.H., Islam, A.K.M.A., 2016. First-principles prediction of mechanical and bonding characteristics of new T2 superconductor Ta₅GeB₂. *Phys. Status Solidi (b)* 253 (10), 2020–2026.
- Han, Y., Li, H., Feng, H., Li, K., Tian, Y., Jiang, Z., 2020. Enhancing the strength and ductility of CoCrFeMnNi high-entropy alloy by nitrogen addition. *Mater. Sci. Eng. A* 789, 139587.
- Hattori, T., Watanabe, Y., Nishizaki, T., Hiraoka, K., Kakiyama, M., Hoshi, K., Mizuguchi, Y., Kitagawa, J., 2023. Metallurgy, superconductivity, and hardness of a new high-entropy alloy superconductor Ti-Hf-Nb-Ta-Re. *J. Alloys Metall. Syst.* 3, 100020.
- Hernandez, S., 2015. Development of Methods for Reducing the Cost of Density Functional Theory and Time-Dependent Density Functional Theory (Ph.D. thesis). UCLA.
- Hirel, P., 2015. AtomsK: A tool for manipulating and converting atomic data files. *Comput. Phys. Comm.* 197, 212–219.
- Islam, N., Huang, W., Zhuang, H.L., 2018. Machine learning for phase selection in multi-principal element alloys. *Comput. Mater. Sci.* 150, 230–235.
- Jha, A., Prasad, B., Modi, O., Das, S., Yegneswaran, A., 2003. Correlating microstructural features and mechanical properties with abrasion resistance of a high strength low alloy steel. *Wear* 254 (1–2), 120–128.
- Jiang, W., Wang, X., Kang, H., Jiang, B., Dong, D., Wang, Y., Zhu, D., 2022. Microstructure and mechanical properties of AlNbTiVZr system refractory high entropy alloys. *J. Alloys Compd.* 925, 166767.
- Kabir, H., Garg, N., 2023. Machine learning enabled orthogonal camera goniometry for accurate and robust contact angle measurements. *Sci. Rep.* 13 (1), 1497.
- Khakurel, H., Taoufik, M., Roy, A., Balasubramanian, G., Ouyang, G., Cui, J., Johnson, D.D., Devanathan, R., 2021. Machine learning assisted prediction of the Young's modulus of compositionally complex alloys. *Sci. Rep.* 11 (1), 1–10.
- Kitagawa, J., 2022. Magnetic properties, electrical resistivity, and hardness of high-entropy alloys FeCoNiPd and FeCoNiPt. *J. Magn. Magn. Mater.* 563, 170024.
- Kitagawa, J., Hoshi, K., Kawasaki, Y., Koga, R., Mizuguchi, Y., Nishizaki, T., 2022. Superconductivity and hardness of the equiatomic high-entropy alloy HfMoNbTiZr. *J. Alloys Compd.* 924, 166473.
- Kunwar, A., Coutinho, Y.A., Hektor, J., Ma, H., Moelans, N., 2020. Integration of machine learning with phase field method to model the electromigration induced Cu₆Sn₅ IMC growth at anode side Cu/Sn interface. *J. Mater. Sci. Technol.* 59, 203–219.
- Kunwar, A., Malla, P.B., Sun, J., Qu, L., Ma, H., 2021. Convolutional neural network model for synchrotron radiation imaging datasets to automatically detect interfacial microstructure: An in situ process monitoring tool during solar PV ribbon fabrication. *Sol. Energy* 224, 230–244.
- Kwak, S., Kim, J., Ding, H., Xu, X., Chen, R., Guo, J., Fu, H., 2022. Machine learning prediction of the mechanical properties of γ -TiAl alloys produced using random forest regression model. *J. Mater. Res. Technol.* 18, 520–530.
- Lee, W.-H., Park, K.B., Yi, K.-W., Lee, S.Y., Park, K., Lee, T.W., Na, T.-W., Park, H.-K., 2019. Synthesis of spherical V-Nb-mo-ta-w high-entropy alloy powder using hydrogen embrittlement and spheroidization by thermal plasma. *Metals* 9 (12), 1296.
- Li, Z., Raabe, D., 2017. Strong and ductile non-equiatom high-entropy alloys: design, processing, microstructure, and mechanical properties. *Jom* 69 (11), 2099–2106.
- Liang, S.-M., Schmid-Fetzer, R., 2017. Evaluation of calphad approach and empirical rules on the phase stability of multi-principal element alloys. *J. Phase Equilib. Diffus.* 38 (4), 369–381.
- Liu, Z.T.Y., Gall, D., Khare, S.V., 2014. Electronic and bonding analysis of hardness in pyrite-type transition-metal pernitrides. *Phys. Rev. B* 90, 134102.
- Liu, Z., Kumar, D., Jirathearanat, S., Wong, W.H., 2023. A multiple-tool method for fast FEM simulation of incremental sheet forming process. *Int. J. Adv. Manuf. Technol.*
- Liu, Y.-c., Yen, S.-y., Chu, S.-h., Lin, S.-k., Tsai, M.-H., 2021. Mechanical and thermodynamic data-driven design of Al-Co-Cr-Fe-Ni multi-principal element alloys. *Mater. Today Commun.* 26, 102096.
- Lu, W., Luo, X., Yang, Y., Huang, B., 2019. Effects of Nb additions on structure and mechanical properties evolution of CoCrNi medium-entropy alloy. *Mater. Express* 9 (4), 291–298.
- Lu, W., Luo, X., Yang, Y., Le, W., Huang, B., Li, P., 2020. Co-free non-equilibrium medium-entropy alloy with outstanding tensile properties. *J. Alloys Compd.* 833, 155074.
- MacDonald, B., Fu, Z., Zheng, B., Chen, W., Lin, Y., Chen, F., Zhang, L., Ivanisenko, J., Zhou, Y., Hahn, H., et al., 2017. Recent progress in high entropy alloy research. *Jom* 69 (10), 2024–2031.
- Miracle, D., 2019. High entropy alloys as a bold step forward in alloy development. *Nat. Commun.* 10 (1), 1–3.
- Miracle, D.B., Senkov, O.N., 2017. A critical review of high entropy alloys and related concepts. *Acta Mater.* 122, 448–511.
- Mishra, S., Maiti, S., Rai, B., 2021. Computational property predictions of Ta-Nb-Hf-Zr high-entropy alloys. *Sci. Rep.* 11 (1), 1–12.
- Paganotti, A., Bessa, C., Silva, L., Silva, R., 2019. Metallic sample preparation for phase transformation analysis. *MethodsX* 6, 2348–2366.
- Pei, Z., Rozman, K.A., Dogan, O.N., Wen, Y., Gao, N., Holm, E.A., Hawk, J.A., Alman, D.E., Gao, M.C., 2021. Machine-learning microstructure for inverse material design. *Adv. Sci.* 8 (23), 2101207.
- Pei, Z., Yin, J., Hawk, J.A., Alman, D.E., Gao, M.C., 2020. Machine-learning informed prediction of high-entropy solid solution formation: Beyond the Hume-Rothery rules. *npj Computat. Mater.* 6 (1), 1–8.
- Pettifor, D.G., 1992. Theoretical predictions of structure and related properties of intermetallics. *Mater. Sci. Technol.* 8 (4), 345–349.
- Pettifor, D.G., Aoki, M., Murrell, J.N., Cottrell, A., Stoneham, A.M., Haydock, R., Inglesfield, J.E., Pendry, J.B., 1991. Bonding and structure of intermetallics: a new bond order potential. *Phil. Trans. R. Soc.* 334 (1635), 439–449.
- Plimpton, S., 1995. Fast parallel algorithms for short-range molecular dynamics. *J. Comput. Phys.* 117 (1), 1–19.
- Poudel, S., Kunwar, A., 2023. AlloyManufacturingNet: Hardness-ductility synergy design tool. <https://mpeanet.streamlit.app/>, Accessed: 21.09.2023.
- Průša, F., Cabibbo, M., Šenková, A., Kučera, V., Veselka, Z., Školáková, A., Vojtěch, D., Cibulková, J., Čapek, J., 2020. High-strength ultrafine-grained CoCrFeNiNb high-entropy alloy prepared by mechanical alloying: Properties and strengthening mechanism. *J. Alloys Compd.* 835, 155308.
- Pugh, S., 1954. XcII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. *Lond. Edinb. Dublin Philos. Mag. J. Sci.* 45 (367), 823–843.
- Revi, V., Kasodariya, S., Talapatra, A., Paliana, G., Alankar, A., 2021. Machine learning elastic constants of multi-component alloys. *Comput. Mater. Sci.* 198, 110671.
- Roy, A., Roy, I., Santodonato, L.J., Balasubramanian, G., 2022. Data-guided feature identification for predicting specific heat of multicomponent alloys. *JOM* 74 (4), 1406–1413.
- Salishchev, G., Tikhonovsky, M., Shaysultanov, D., Stepanov, N., Kuznetsov, A., Kolodiy, I., Tortika, A., Senkov, O., 2014. Effect of Mn and V on structure and mechanical properties of high-entropy alloys based on CoCrFeNi system. *J. Alloys Compd.* 591, 11–21.
- Senkov, O.N., Miracle, D.B., 2021. Generalization of intrinsic ductile-to-brittle criteria by Pugh and Pettifor for materials with a cubic crystal structure. *Sci. Rep.* 11 (1), 4531.
- Senkov, O.N., Miracle, D.B., Chaput, K.J., Couzinie, J.-P., 2018. Development and exploration of refractory high entropy alloys—A review. *J. Mater. Res.* 33 (19), 3092–3128.
- Singh, P., Smirnov, A.V., Alam, A., Johnson, D.D., 2020. First-principles prediction of incipient order in arbitrary high-entropy alloys: exemplified in Ti_{0.25}Cr_{0.75}Al_{0.25}. *Acta Mater.* 189, 248–254.
- Singh, P., Vela, B., Ouyang, G., Argibay, N., Cui, J., Arroyave, R., Johnson, D.D., 2023. A ductility metric for refractory-based multi-principal-element alloys. *Acta Mater.* 257, 119104.
- Soni, V., Gwalani, B., Alam, T., Dasari, S., Zheng, Y., Senkov, O.N., Miracle, D., Banerjee, R., 2020. Phase inversion in a two-phase, BCC+ B2, refractory high entropy alloy. *Acta Mater.* 185, 89–97.
- Startt, J., Kustas, A., Pegues, J., Yang, P., Dingreville, R., 2022. Compositional effects on the mechanical and thermal properties of MoNbTaTi refractory complex concentrated alloys. *Mater. Des.* 213, 110311.
- Stukowski, A., 2010. Visualization and analysis of atomistic simulation data with OVITO—the open visualization tool. *Modelling Simul. Mater. Sci. Eng.* 18 (1).
- Subedi, U., Coutinho, Y.A., Malla, P.B., Gyanwali, K., Kunwar, A., 2022a. Automatic featurization aided data-driven method for estimating the presence of intermetallic phase in multi-principal element alloys. *Metals* 12 (6), 964.
- Subedi, U., Kunwar, A., Coutinho, Y.A., Gyanwali, K., 2022b. pyMPEALab toolkit for accelerating phase design in multi-principal element alloys. *Met. Mater. Int.* 28 (1), 269–281.

- Tan, X., Tang, Y., Tan, Y., Deng, Q., Jiao, H., Yang, Y., Xu, H., 2020. Correlation between microstructure and soft magnetic parameters of Fe-Co-Ni-Al medium-entropy alloys with FCC phase and BCC phase. *Intermetallics* 126, 106898.
- Thiel, F., Geissler, D., Nielsch, K., Kauffmann, A., Seils, S., Heilmaier, M., Utt, D., Albe, K., Motylenko, M., Rafaja, D., et al., 2020. Origins of strength and plasticity in the precious metal based high-entropy alloy AuCuNiPdPt. *Acta Mater.* 185, 400–411.
- Thomas Chan Hien Dam, S.S., 2016. Ductilizing refractory high entropy alloys.
- Tian, F., Varga, L.K., Chen, N., Shen, J., Vitos, L., 2015. Empirical design of single phase high-entropy alloys with high hardness. *Intermetallics* 58, 1–6.
- Wen, C., Zhang, Y., Wang, C., Xue, D., Bai, Y., Antonov, S., Dai, L., Lookman, T., Su, Y., 2019. Machine learning assisted design of high entropy alloys with desired property. *Acta Mater.* 170, 109–117.
- Xiong, J., Shi, S.-Q., Zhang, T.-Y., 2021. Machine learning of phases and mechanical properties in complex concentrated alloys. *J. Mater. Sci. Technol.* 87, 133–142.
- Yang, S., Liu, Z., Pi, J., 2020. Microstructure and wear behavior of the AlCrFeCoNi high-entropy alloy fabricated by additive manufacturing. *Mater. Lett.* 261, 127004.
- Yang, T., Zhao, Y.L., Liu, W.H., Zhu, J.H., Kai, J.J., Liu, C.T., 2018. Ductilizing brittle high-entropy alloys via tailoring valence electron concentrations of precipitates by controlled elemental partitioning. *Mater. Res. Lett.* 6 (10), 600–606.
- Yasnii, P., Marushchak, P., Hlad'o, V., Baran, D.Y., 2008. Correlation of the microdislocation parameters with the hardness of plastically deformed heat-resistant steels. *Mater. Sci.* 44 (2), 194–200.
- Yeh, J.-W., Chen, S.-K., Lin, S.-J., Gan, J.-Y., Chin, T.-S., Shun, T.-T., Tsau, C.-H., Chang, S.-Y., 2004. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. *Adv. Eng. Mater.* 6 (5), 299–303.
- Yu, J., Xi, S., Pan, S., Wang, Y., Peng, Q., Shi, R., Wang, C., Liu, X., 2021. Machine learning-guided design and development of metallic structural materials. *J. Mater. Inform.* 1 (2), 9.
- Zhang, L., Qian, K., Schuller, B.W., Shibuta, Y., 2021. Prediction on mechanical properties of non-equiatom high-entropy alloy by atomistic simulation and machine learning. *Metals* 11 (6), 922.
- Zhang, C., Zhu, J., Zheng, H., Li, H., Liu, S., Cheng, G.J., 2020. A review on microstructures and properties of high entropy alloys manufactured by selective laser melting. *Int. J. Extrem. Manuf.* 2 (3), 032003.
- Zhao, Y., Yang, T., Li, Y., Fan, L., Han, B., Jiao, Z., Chen, D., Liu, C., Kai, J., 2020. Superior high-temperature properties and deformation-induced planar faults in a novel L12-strengthened high-entropy alloy. *Acta Mater.* 188, 517–527.

A.2 Publication II [\[P-II\]](#): PiezoTensorNet: Crystallography informed multi-scale hierarchical machine learning model for rapid piezoelectric performance finetuning



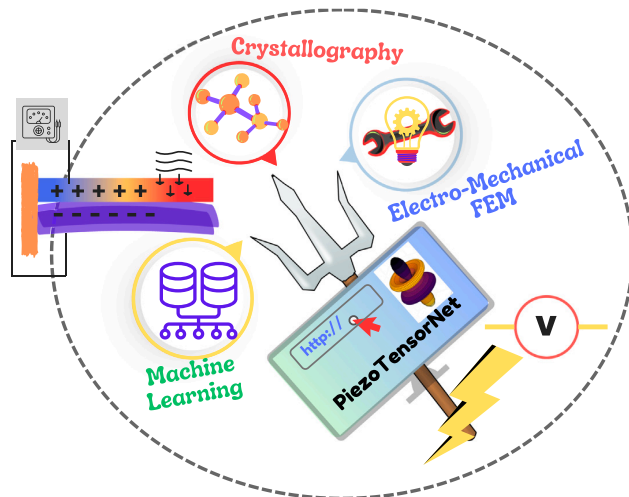
PiezoTensorNet: Crystallography informed multi-scale hierarchical machine learning model for rapid piezoelectric performance finetuning

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GRAPHICAL ABSTRACT



ARTICLE INFO

Dataset link: <https://github.com/Sachinscpdl/PiezoTensorNet-Data>, <https://piezotensornet.streamlit.app/>

Keywords:

Piezoelectric tensors
Crystal rotation
Energy conversion
Quasi-effective coefficients
Electromechanical finetuning

ABSTRACT

Piezoelectric devices offer numerous opportunities for sustainable harvesting of wasted mechanical energy, leading to a significant interest in data-driven research on these materials. This study presents the design of PiezoTensorNet, a comprehensive framework that encompasses a hierarchical classification neural network for crystal point group determination and modular ensembles of regression-based multi-dimensional models for predicting piezoelectric tensors. The machine learning models capable of forecasting tensors for dopant element alloying and various crystallographic transformations is integrated along with finite element analysis for electromechanical performance evaluation. The efficacy of integrated toolkit is demonstrated through the computational design and discovery of a lead-free microelectromechanical system based on AlN. The introduction of Boron and Erbium dopants in AlN enhances its piezoelectric performance, particularly when

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the crystal undergoes rotations along a preferred axis. Specifically, under a vertical loading of $5 \times 10^{-5} \text{ N/m}^2$ applied to a cantilever beam, the preferentially oriented $\text{B}_{0.3}\text{Er}_{0.5}\text{Al}_{0.2}\text{N}$ material generates a power 9.96 times larger than that of AlN ceramics.

1. Introduction

Energy harvesting has gained significant attention as a crucial technology for applications including but not limited to sensors and actuators [1], Internet of Things (IoT) [2], and e-health [3,4]. Main types of micro and nano energy harvesters include piezoelectric, triboelectric, electromagnetic, electrostatic, and acoustic [5,6]. Piezoelectric materials, including single crystals, ceramics, composites, and films, are indispensable components in electromechanical devices [7]. These functional materials possess the capability for efficient interconversion of mechanical and electrical energy due to the linear coupling between mechanical stress and electric polarization [8]. They manifest the direct piezoelectric effect, where mechanical stress induces alterations in surface charge density, as well as the inverse piezoelectric effect, where electric fields elicit material deformation [8]. As polarization represents a vector and stress corresponds to a second-rank tensor, the coupling phenomenon encompasses three distinct directions, thereby giving rise to a third-rank piezoelectric tensor [9]. In a Euclidean crystal reference frame because of the symmetry, the piezoelectric tensor is typically represented as a 3×6 matrix [10]. The concise overview of the piezoelectric coefficients, their relations with electric and mechanical terms, and corresponding expressions are provided in Supplementary Information S1.

The functional characteristics of these materials are directly linked with their non-centrosymmetric structures [11]. Perovskite-structured piezoelectric materials, including barium titanate, lead titanate, and lead zirconate titanate, show significant promise for a wide range of practical and industrial applications [12]. The European Union has imposed stringent restrictions on the utilization of lead-based materials, thereby instigating scientific communities to seek lead-free piezoelectric alternatives [13] that not only demonstrate environmental compatibility but also exhibit exceptional characteristics for the advancement of novel devices [14]. Unfortunately, the identification of suitable Pb-free substitutes, capable of fulfilling the requisite criteria, continues to elude the current state of research [15].

Several studies have made endeavors to apply machine learning techniques in the pursuit of high piezoelectric coefficient lead-free materials, showcasing their potential in this field [16–18]. These works have successfully improved piezoelectric performance through the identification of novel materials. However, a limitation of these studies is that they solely rely only on specific components of the piezoelectric tensor. Piezoelectric ceramics, characterized by ∞mm symmetry [19], typically possess limited independent piezoelectric coefficients, namely longitudinal mode d_{33} , transversal mode d_{31} , and thickness-shear mode d_{15} [20]. It is important to note that only these three coefficients may not fully capture the polarization distribution, which can be accurately represented by the entire tensor. The tensor encompasses contributions from both ionic and electronic sources, providing a more comprehensive understanding of the material's behavior [21,22]. Moreover, studying crystal rotation in such functional materials is challenging without prior knowledge of the complete tensor elements [23].

The presence of a non-zero piezoelectric tensor in materials leads to a high electro-mechanical coupling polarization, which results in an increased figure of merit [24]. By introducing quasi-symmetry breaking in metamaterial design, it becomes possible to induce unconventional piezoelectric coefficients in perovskite ceramics. These unconventional coefficients, referred to as “quasi-effective piezoelectric coefficients”, when combined with conventional coefficients, form a 3×6 matrix with technically all elements being non-zero. This expanded coefficient matrix opens up a broader range of possibilities for developing

devices based on piezoelectric ceramics [25,26]. Hence, there is a need to develop methods that can predict piezoelectric tensors, enabling a more thorough investigation of polarization and facilitating the study of crystal rotation effects and their advancement in piezoelectric performance.

This study integrates alloying of base piezoelectric materials with crystallographic-supported data-driven computational modeling, incorporating the physics of crystal rotations based on tensor mathematics. This comprehensive approach offers a rapid screening tool for evaluating the piezoelectric performance of materials by establishing a link between the microscopic crystal structure and resulting piezoelectric polarization. The effectiveness of this approach is demonstrated using AlN-based materials in various scenarios, including pure AlN, single and paired dopant alloying, and crystal rotations along three Cartesian coordinate axes. Energy generation in these scenarios is investigated, and the machine learning-supported finite element method is employed for energy harvesting modeling, aiming to design materials that exhibit high voltage generation under similar loading conditions. The findings showcase the extensive capabilities of this integrated approach in piezoelectric material design and engineering applications.

2. Methodology

2.1. Data acquisition, processing and analytics

The piezoelectric properties of training materials consisting of 3301 were extracted from the Materials Project (MP) [27,28]. A dataset of 1354 piezoelectric materials was used for machine learning model formulation. That harvested dataset consists of piezoelectric properties for various crystal structures. Selected materials comprising 367 cubic (23, $\bar{4}2m$), 152 tetragonal $\bar{4}2m$, 305 orthorhombic 222, and 195 hexagonal 6 mm + tetragonal 4 mm, and 335 orthorhombic $mm2$ piezoelectric materials were undertaken for further data analysis and machine learning model training purpose. Numerical featurization of physical properties played a pivotal role in the data-driven study. Therefore, the assessment of numerical descriptors for structural, physical, and thermo-mechanical characterization carries crucial in data processing and analytics.

Featurization involved transforming materials-related quantities into physically relevant numerical descriptors, capturing complex relationships between inputs and targeted piezoelectric tensors. Initial features were derived from chemical composition formulas using Materials Agnostic Platform for Informatics and Exploration (Magpie) [29]. While the Magpie featurization package includes 132 features encompassing elemental properties and stoichiometric attributes, it does not include thermodynamics, elastic, and the structural properties [30]. Thus, Magpie featurization is complemented by 13 additional descriptors to account for missing descriptors.

Principal Component Analysis (PCA) was employed for dimensionality reduction. By decomposing the data matrix into the direction and magnitude components, PCA identifies multiple data directions and eliminates less relevant features. The retained information's importance was quantified using explained variance (EV). Incorporating PCA-based feature selection enhanced analysis efficiency and interpretability, focusing on impactful data aspects [31]. Detailed information regarding each component of the harvested data, including its visualization, numerical feature calculations, and feature engineering, can be found in Supplementary Information S3.

Table 1

Crystallographic impact on piezoelectric tensors: This table explores the relationship between crystallography and piezoelectric tensors through symmetry constraints and graphical representations. The category class serves as a pseudo-grouping mechanism in the hierarchical classification machine learning model, enhancing the efficiency of the parent classification process. Similar tensor structures cluster point groups into PG1, PG2, PG3, PG4, and PG5. The symbol $\#e_{ij}$ denotes the number of independent piezoelectric coefficients. Notably, the cubic (23, $\bar{4}2m$) and hexagonal 6 mm + tetragonal 4 mm point groups share the same tensor structure, resulting in seven point groups represented by five sibling labels.

Category Class	Crystal and Point groups	Crystal Structure representation	Piezoelectric tensor	$\#e_{ij}$	Tensor visualization ^a
Class A	PG1 Cubic 23 Cubic $\bar{4}3m$		$\begin{pmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{14} \end{pmatrix}$	1	
	PG2 Tetragonal $\bar{4}2m$		$\begin{pmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{36} \end{pmatrix}$	3	
	PG3 Orthorhombic 222		$\begin{pmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{36} \end{pmatrix}$	2	
Class B	PG4 Hexagonal 6mm Tetragonal 4mm		$\begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix}$	3	
	PG5 Orthorhombic mm2		$\begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{24} & 0 & 0 \\ e_{31} & e_{32} & e_{33} & 0 & 0 & 0 \end{pmatrix}$	5	

^a The tensor visualization was performed using the following tensor component values: For Class A: $e_{14} = 0.5$. For Class B Hexagonal 6 mm and Tetragonal 4 mm: $e_{15} = 0.0743$, $e_{31} = 0.0588$, $e_{33} = -0.0983$. For Class B Orthorhombic mm2: $e_{15} = 0.015$, $e_{15} = 0.0081$, $e_{31} = 0.014$, $e_{31} = 0.011$, $e_{33} = -0.02$. The unit of these coefficients is C/m².

2.2. Crystal point group clustering based on piezoelectric tensor symmetry

The lack of inversion symmetry in a crystal structure can give birth to a variety of unique characteristics including piezoelectricity [32]. Neumann's symmetry principle elucidates the profound interplay between the intrinsic symmetry of a material's structure and the resulting constraints imposed on tensors (a reference to the number of independent components) characterizing its physical properties. This fundamental principle asserts that the properties of a material cannot possess a symmetry lower than that exhibited by its crystal structure. The choice of crystallographic unit cell axes aligns with the principal symmetry elements, and basis coordinate systems for tensors are established accordingly. This alignment simplifies tensor descriptions by reducing the number of independent components. Neumann's principle highlights the interplay between crystal symmetry and material properties [33].

Crystal symmetry classes categorize the symmetry elements and operations of crystals, enabling analysis of their properties including impact on piezoelectric behavior [34]. Among 32 unique crystal classes, 20 point groups exhibit piezoelectricity [19]. The higher symmetry crystals such as cubic structures display simplified piezoelectric tensors due to their symmetry. This higher symmetry results in a reduction in the number of independent non-zero piezoelectric coefficients [35]. Conversely, crystals with lower symmetry, as found in trigonal, tetragonal, or orthorhombic crystal systems, exhibit more intricate piezoelectric tensor forms. The number of independent piezoelectric coefficients

is determined by the crystal's symmetry [36]. Supplementary Information S2 provides further elaboration on the relationship between crystallography and piezoelectricity.

While symmetry considerations can identify the potential for piezoelectricity, their ability to fully capture the magnitude and nature of the piezoelectric response is limited [37]. Incorporating all 20 point groups into a machine learning model is not feasible first because of the classification of higher nodal targets and higher dimensions of piezoelectric component prediction. To address this constraint, the application of crystal symmetry-guided clustering becomes imperative. Initially, this involves excluding monoclinic and triclinic crystals because of a higher number of independent coefficients from the scope of the regression-based ML model. Subsequently, the positions and structure of non-zero elements are systematically grouped to form distinct category classes. The organization of these classes is informed by the collected piezoelectric data, resulting in two main categories. These criteria capture the piezoelectric behavior of 7 crystal point groups.

The crystal symmetry-based grouping is included in Table 1. In the first category, four crystal point groups together form three distinct sub-categories. Conversely, the second category comprises three point groups organized into two sub-categories. This classification of crystal points operates on multiple layers, forming sub-classes within an overarching category class. Consequently, a data-driven approach necessitates a multi-level hierarchical classification in a specific sequence that is explained in a subsequent section.

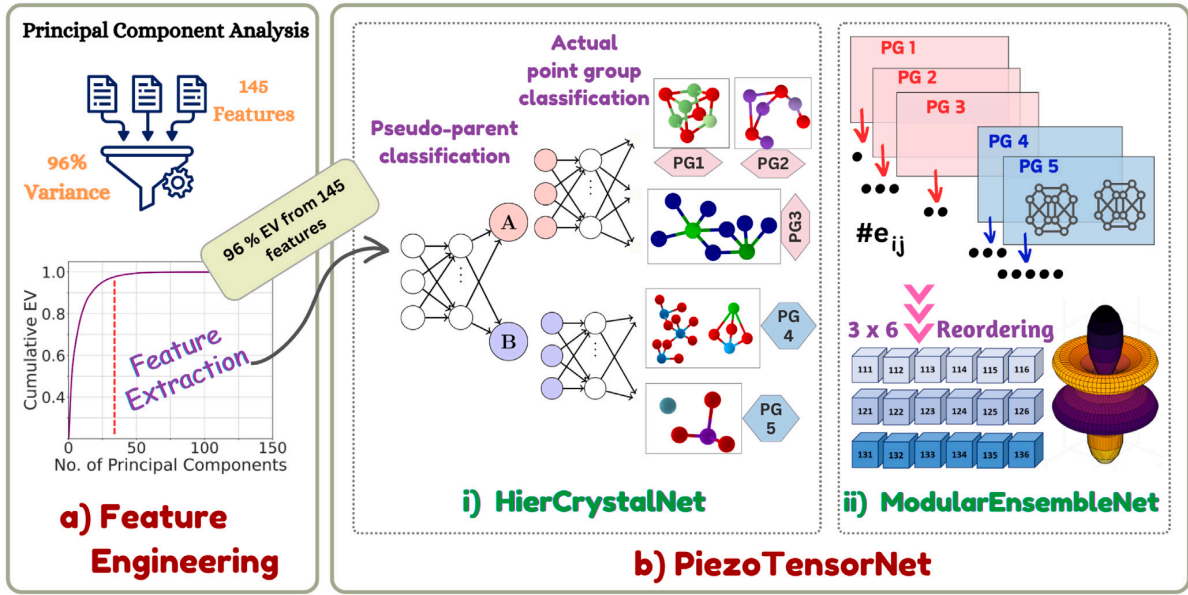


Fig. 1. A hierarchical multi-scale ML framework for piezoelectric material design: (a) The featured piezoelectric database undergoes preprocessing, which involves PCA for feature compression. This step achieves a 96% explained variance by selecting 28–32 features. (b) The PiezoTensorNet operates at two scales: (i) The hierarchical multi-level classifier, HierCrystalNet, categorizes materials in the initial layer into pseudo-parent classifications: class A or class B. Subsequent children's classifications assign crystal point groups, resulting in PG1, PG2, or PG3 for class A, and PG4 or PG5 for class B. (ii) The regression-based ModularEnsembleNet ultimately provides the independent non-zero piezoelectric coefficient ($\#e_{ij}$) which is reordered into 3×6 tensor. The outputs from HierCrystalNet activate distinct modules within an ensemble artificial neural network, ensuring accurate prediction of the tensor.

2.3. Prognosticating piezoelectric tensors: Introducing PiezoTensorNet.

The integration of neural networks and crystallography discloses substantial potential for accelerated exploration of optimum materials design [38,39]. In this study, this interdisciplinary fusion of pattern understanding ability of ML with crystallographic insights is considered which latter will be assisted by crystal rotation and Finite Element Analysis (FEM) in the design of functional material. The schematic depiction of this process is elucidated sequentially in Fig. 1. The phenomenon of crystal point group classification unfolds within a two-tiered structure, activating a module-based ensemble neural network exclusively tailored for independent piezoelectric coefficient predictions. The final output of the ML model is further restructured to form a piezoelectric tensor in the 3×6 order. A detailed explanation of the crystal point group classification and $\#e_{ij}$ prediction process is explained in a subsequent sub-section within this section.

2.3.1. Hierarchical multi-level classification of crystal groups in piezoelectric materials

Multi-label classification poses significant benefits as it involves the assignment of parent categories to closely related labels [40]. In this investigation, a two-layer classification was employed, focusing on the consistent patterns exhibited by mathematically homogeneous piezoelectric tensors. It is noteworthy that the child group is a true representation of the actual classification label which is the primary objective of this classification model. On the other hand, the parent groups are pseudo-clustering of the closely related point groups in assisting multi-level classification. The five sibling classes of seven crystal point groups are characterized by their proximity to one another because of the same mathematical piezoelectric tensor as represented by piezoelectric tensor in Table 1. The initial step of the process involves the preliminary classification of piezoelectric materials, assigning them to either class A or class B. This pseudo-parent assignment serves as the first layer of classification, and the model achieves an accuracy of 68%. Subsequently, the predictions from the first layer are

utilized in the second layer for specific point group classification. In the second stage, when the first layer results in class A, the focus of the classification process is on PG1, PG2, and PG3. Sub-classification within class A is carried out with an accuracy of 71.43%. Conversely, if the first layer results in class B, the attention of the second stage shifts to the classification of PG4 and PG5, achieving an accuracy of 82.22%, as illustrated in Fig. 1 b(i). This entails a finer level of categorization based on the pseudo-parent classification and then sibling point group recognition. The core of this hierarchical methodology lies in the precise identification of the material's crystal point group. Upon completion of the entire classification model, the ultimate outcomes are the crystal point groups denoted as PG1, PG2, PG3, PG4, and PG5. After the identification of the material's crystal point group, it serves as a trigger for activating the prediction process of independent piezoelectric coefficients. This prediction is accomplished through a multi-target regression-based ModularEnsembleNet.

2.3.2. Modular ensemble models to foretell the piezoelectric coefficients

After the two successive classifications, this work introduces a well-engineered and intricate ensemble neural network model, comprising five meticulously designed modules. Each of them comprises an ensemble of two distinct ANN architectures. The collaborative synergy between these two ANN models involves arithmetic averaging their predicted values. This ensemble approach contributes to the generalization of the multi-dimensional regression model, resulting in a compact modular block. The multi-dimensional regression-based modular ensemble ANN seamlessly integrates with hierarchical classification, significantly improving the speed and efficiency of piezoelectric performance design.

The fusion of multi-layered classification HierCrystalNet (Fig. 1bi) and multi-dimensional regression ModularEnsembleNet (Fig. 1bii) is achieved from the unique activation mechanism of the ModularEnsembleNet to activate the specific modules among five different module set. This activation mechanism is designed to selectively choose a specific module from a set of five different modules. The crystal point groups are identified through the HierCrystalNet framework (Fig. 1b(i)). The

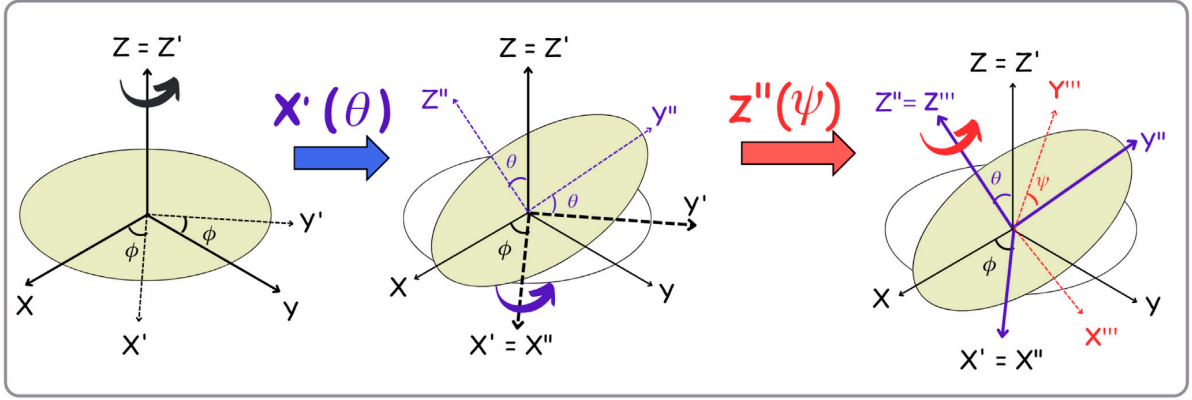


Fig. 2. Crystallographic rotations for a crystal with three sets of Euler angles are described as follows: (a) Counterclockwise rotation (ϕ) about the Z -axis, with a range of 0° to 360° . (b) Counterclockwise rotation (θ) about the X' -axis, with a range of 0° to 180° . (c) Counterclockwise rotation (ψ) about the Z'' -axis, with a range of 0° to 360° . The transformation of the tensor by these rotations is given by a_1 , a_2 , and a_3 , respectively, where each of them represents a 3×3 matrix of direction cosines. It is noteworthy that some of the zero value position of the piezoelectric coefficient transforms into non-zero coefficients.

activation of one among the five different modules is contingent on the outcome of the classification model, determining whether the result corresponds to PG1, PG2, PG3, PG4, or PG5. Given that a piezoelectric material possesses a unique point group, only one module is activated. This unified framework plays a crucial role in the model's architecture, where hierarchical classification guides the activation of ANN modules, as illustrated by ModularEnsembleNet in Fig. 1b(ii). The root mean squared error (RMSE) of each modular ensemble network is: 0.65, 0.85, 0.53, 1.05, 1.02 for PG1, PG2, PG3, PG4, and PG5 respectively. The outcome from the ML model is the prediction of piezoelectric coefficients in a 1D array having the same order as the $\#e_{ij}$ of the classified point group. Subsequently, the predicted results are reorganized into the format of a piezoelectric tensor with a 3×6 order.

By integrating the crystallography dominant HierCrystalNet into piezo-tensor focused ModularEnsembleNet framework, a powerful and versatile tool called PiezoTensorNet [41] is forged. This integrative approach enhances the model's capacity to first classify crystal point groups and then predict the piezoelectric coefficients, enhancing the field of piezoelectric material design and facilitating advancements in diverse scientific applications. For more detailed information on the architecture of the machine learning models, please refer to Supplementary Information S4, Tables A3, A4 and A5.

2.4. Crystal transformation of piezoelectric tensor

Piezoelectric tensors, as 3rd rank tensors follow specific transformation laws. The orientation of a molecule or crystallographic lattice in relation to the laboratory coordinate system is determined by three Euler angles: ϕ , θ , and ψ as visualized in Fig. 2. Two angles, θ and ϕ , specify a direction in space, while ψ fixes the orientation of the other two sets in orthogonal axes. This can be visualized as three consecutive rotations. The direction cosine matrix is commonly used to derive the orientation of a general rotation.

$$\begin{aligned} a_1 &= \begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ a_2 &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{bmatrix} \\ a_3 &= \begin{bmatrix} \cos \psi & \sin \psi & 0 \\ -\sin \psi & \cos \psi & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{aligned} \quad (1)$$

The relationship between the e_{ijk} tensor in the laboratory coordinate system obtained after Eulerian rotation (ϕ , θ , ψ) of the e_{lmn}^o tensor in the crystal coordinate system is given by the transformation for 3rd rank tensor as follow: [42]

$$e'_{ijk} = (a_1)_{il} (a_2)_{jm} (a_3)_{kn} e_{lmn}^o \quad (2)$$

where, $[i, j, k, l, m, n] = 3$

$(a_1)_{il} (a_2)_{jm} (a_3)_{kn}$ are the direction cosines representing both the coordinate systems. In the representation of 3rd rank $3 \times 3 \times 3$ in 3×6 piezoelectric tensors, the new tensor after transformation is given by [43]:

$$e'_{ij}(\phi, \theta, \psi) = A_{il} e_{lm}^o N_{mj} \quad (3)$$

$[i, l] = 3$; $[j, m] = 6$.

The Cartesian tensor notation and Einstein summation convention were used in the analytical solution of tensor mathematics and performing crystal rotations. In these engineering notations, repeated indices imply summation over those indices. The convention also allows for partial differentiation with respect to the coordinate associated with an index [44,45]. These notations provide a concise and precise way to express and manipulate the piezoelectric tensors obtained from the multi-scale machine learning models. A_{il} and N_{mj} are 3×3 and 6×6 rotation matrix of direction cosines. The analytical calculation of crystal rotation guided by tensor mathematics can be found in Supplementary Information S5.

3. Discovering materials with enhanced piezoelectric performance

This section showcases the potential of PiezoTensorNet in the rapid fine-tuning and discovery of piezoelectric materials. Aluminum Nitride (AlN) is a commonly used material in microelectromechanical systems (MEMS) due to its advantages of high-temperature stability, better thermal conductivity, and enhanced mechanical strength. However, its low piezoelectric coefficient has prompted studies on performance enhancement through alloying with transition metals (TM) [46,47]. Previous investigations in this area have focused on a limited number of TM. For instance, Uehara et al. [46] and Hirata et al. [47] explored the preparation and enhancement of AlN with specific TMs of a small subset in their analysis. Zha et al. [48] expanded the scope by investigating 28 sets of TM in AlN, alloying a single TM at a time. Despite the comprehensive approach, these studies lacked a data-driven methodology, resulting in limitations such as a focus on fewer alloying metals and primarily examining single alloying scenarios.

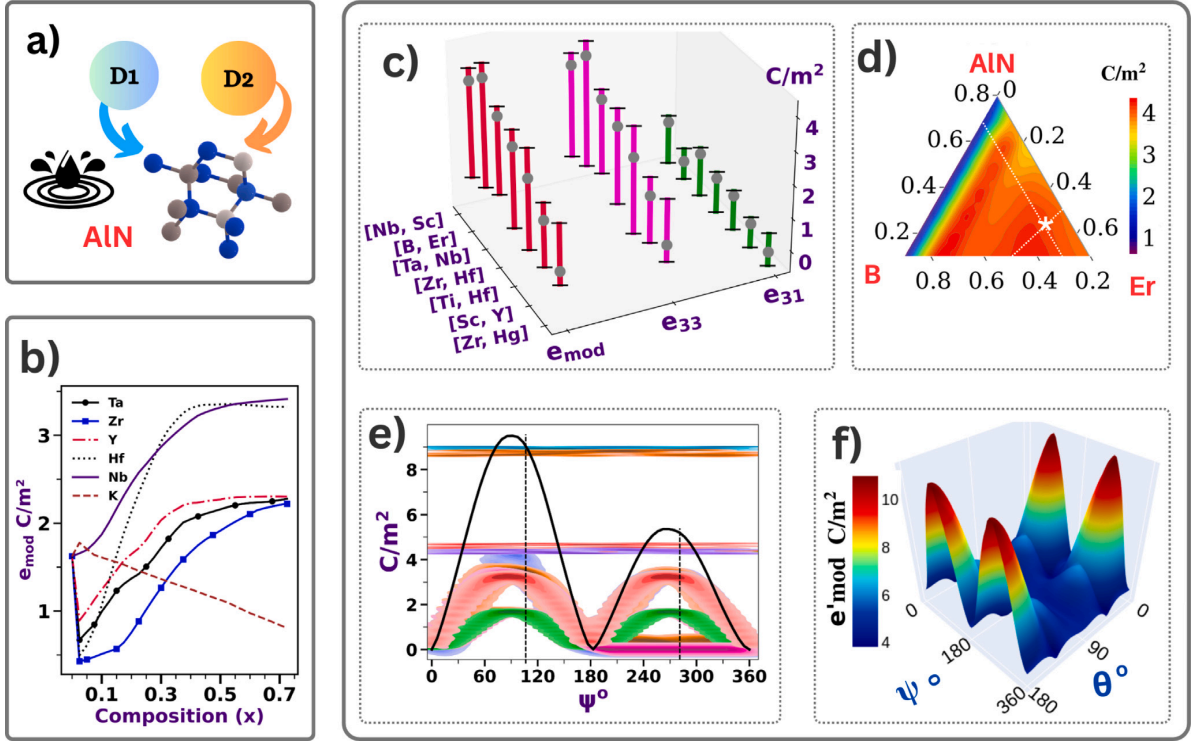


Fig. 3. Rapid materials design and discovery for achieving optimum piezoelectric performance by strategic incorporation of alloy doping and crystal rotation. (a) The introduction of foreign elements, D1, D2, or a combination thereof, into the AlN base material initiates the alloying process. (b) The influence of single dopants (Ta, Zr, Y, Hf, Nb, K) on the reference modulus of elasticity, e_{mod} , is visually elucidated. Remarkably, all dopants yield higher e_{mod} values compared to the base AlN, which itself exhibits a value of 1.67 C/m². (c) Comparative plots of e_{mod} , e_{33} , and e_{31} for various binary dopant combinations unveil the superiority of the [B, Er] dopant pair, followed by [Nb, Sc], in terms of achieving elevated e_{mod} values. (d) The distribution of e_{mod} values across diverse compositions of B, Er, and the AlN ceramic material is visualized through a ternary surface heatmap. Notably, a maximum value of 4.37 C/m² is attained at a composition of 0.3 B and 0.5 Er. Crystal rotation analysis. (e) is conducted to investigate the impact of angular variations, specifically the ψ and θ angles, on the 18 components of the rotated piezoelectric coefficient tensor. The individual linear heatmap depicts the density distribution of each component as a function of varying ψ angles, with dark curves representing the density distribution of maximum values observed. Intriguingly, the density peaks at angles of 91.52° and 268.47°. (f) Moreover, the interplay between e'_{mod} and the angular variations of ψ and θ is explored, yielding valuable insights into the piezoelectric properties under rotational transformations.

PiezoTensorNet is utilized in this study to investigate the different scenarios starting from pure AlN which is hexagonal 6 mm crystal. The doping effect of foreign elements, both single alloying and binary configurations as visualized in Fig. 3(a) is done. Singular dopants [Ta, Zr, Y, Hf, Nb, K] result in higher e_{mod} values compared to pure AlN, with Hf and Nb showing significantly larger 3.35 and 3.41 C/m² values at a doping composition of 0.525 and 0.725 respectively as represented in Fig. 3(b). This study focuses on observing the collective impact of the longitudinal, transverse, and shear modes within the piezoelectric coefficient. A statistical approach was implemented to deduce the overall influence of these coefficients by employing a reference coefficient modulus, denoted as e_{mod} and explained by Eq. (4). The e_{mod} solely serve as a criterion for selecting materials with superior longitudinal, transverse, and shear modes of piezoelectric components.

$$e_{\text{mod}_i} = \sqrt{\sum_{j=1}^6 e_{ij}^2} \quad (4)$$

$$e_{\text{mod}} = \max(e_{\text{mod}_i}) \quad [i = 1 \text{ to } 3]$$

Binary dopants exhibit superior piezoelectric modulus values, and among the seven binary dopant pairs studied [Zr, Hg], [Sc, Y], [Ti, Hf], [Zr, Hf], [Ta, Nb], [B, Er], and [Nb, Sc] which is illustrated in Fig. 3(c). The [B, Er] pair achieves the optimal e_{mod} values of 4.36 C/m² (e_{33} 4.36 C/m² and e_{31} 0.09 C/m²) which is followed by 3.74 C/m² (e_{33} 3.54 C/m² and e_{31} 0.86 C/m²) for [Nb, Sc]. The ternary surface representation in Fig. 3(d) demonstrates the distribution of modulus

values across different compositions of B, Er, and AlN, with a maximum value of 4.36 C/m² attained at B_{0.3}Er_{0.5}Al_{0.2}N. The doped piezoelectric material is also analyzed for crystal transformation using Euler angular transformations (ϕ, θ, ψ) as discussed in Section 2.4.

The impact of angular variation is clearly encapsulated by the plots of Fig. 3(e) and (f). It is noteworthy that the variation of angle ϕ shows no variation in tensor structure whereas there was a significant variation of tensor component diversification because of θ and ψ . The angular variations of ψ and θ depict that distribution of maximum values of all 18 components of the piezoelectric tensor falls in 91.52° and 268.47° value of ψ in Fig. 3(e) which is again validated from e'_{mod} value lying for same values of ψ of Fig. 3(f). Also, the maximum modulus is achieved for θ values of 180° and 0°. This analysis yields valuable insights into the comprehensive piezoelectric enhancement of amalgamated materials under rotational transformations.

The piezoelectric tensors obtained from the sequence of the above analysis will be used for the electro-mechanical characterization in the microelectromechanical self-energy sufficient system design.

$$e_o = \begin{bmatrix} 0 & 0 & 0 & 0 & -0.2893 & 0 \\ 0 & 0 & 0 & -0.2893 & 0 & 0 \\ -0.5801 & -0.5801 & 1.461 & 0 & 0 & 0 \end{bmatrix}$$

$$e^* = \begin{bmatrix} 0 & 0 & 0 & 0 & 0.2283 & 0 \\ 0 & 0 & 0 & 0.2283 & 0 & 0 \\ 0.0943 & 0.0943 & 4.363 & 0 & 0 & 0 \end{bmatrix}$$

$$e_1^{*'} = \begin{bmatrix} 0 & 0.08 & 0 & -0.0808 & 0.459 & -0.4554 \\ -0.1882 & -4.563 & -4.3232 & 8.7947 & -0.0807 & 0.146 \\ 0.1899 & 4.3775 & 4.3636 & -8.6464 & 0 & -0.0667 \end{bmatrix}$$

$$e_2^{*'} = \begin{bmatrix} 1.1354 & 0.947 & 0.9856 & -1.825 & -2.005 & 1.9339 \\ 0.9564 & 1.098 & 0.9799 & -1.9783 & -1.8336 & 1.93 \\ -0.9946 & -0.9778 & -1.0156 & 1.9799 & 2.0 & -1.838 \end{bmatrix}$$

where,

e_o = Piezoelectric tensor for pure AlN

e^* = Piezoelectric tensor for alloyed AlN,

$$B_{0.3}Er_{0.5}Al_{0.2}N$$

$e_1^{*'}$ = Rotated piezoelectric tensor for alloyed AlN,

$$\theta = 0^\circ, \psi = 268.47^\circ, 91.52^\circ; 0^\circ \leq \phi \leq 360^\circ$$

$e_2^{*'}$ = Rotated piezoelectric tensor for alloyed AlN,

$$\theta = 180^\circ, \psi = 268.47^\circ, 91.52^\circ; 0^\circ \leq \phi \leq 360^\circ$$

The tensor structure of pure AlN and doped material has a similar structure with five non-zero elements and has elevated piezoelectric effects because of a higher coefficient of 4.363 C/m² in e^* in comparison to 1.461 C/m² of e_o . However, there is significant variation in tensor structure because of crystal rotation. The surface plot in Fig. 4(b) illustrates the tensor components e_o , e^* , $e_1^{*'}$, and $e_2^{*'}$ that are utilized in the FEM analysis.

3.1. Finite element analysis for micro-sized beams of ML-assigned piezoelectric tensors

With the in-silico toolkit to predict the piezoelectric tensors from new composition information, it can be very useful for beneficial applications if the properties can be tested for energy generation using finite element models [49,50]. A microelectromechanical model of a cantilever beam can be a substantially understandable and comprehensible formulation for assessing the property-performance characteristics of ML-designed novel piezoelectric materials. The governing equations for polar materials can be expressed with linear constitutive equations, which are close to those presented in Ref. [51]. For steady-state conditions the stress tensor (T_{ij}) of a piezoelectric beam of Fig. 4(a) undergoing elastic deformation is expressed by Eq. (5),

$$-\nabla \cdot T_{ij} = \bar{f}_b \quad (5)$$

The deformation of the piezoelectric solid material is quantified in terms of displacement vector (δ_i), and it will be known that the stress tensor is a composite function of δ_i . The term $\bar{f}_b$ in the right-hand side of the equation is the volumetric body force vector.

Variation of electric field potential (λ) in the micro-sized piezoelectric beam is mathematically defined by the Poisson Eq. (6):

$$-\nabla \cdot \epsilon \nabla \lambda = \rho \quad (6)$$

In Eq. (6), ϵ is the permittivity of the piezoelectric material constituting the loaded cantilever beam, whereas ρ is the volumetric charge density in the medium. Electric field intensity vector E_k for the computational domain is computed as the gradient of the scalar field λ .

The electro-mechanical characterization within the simulation domain involves the interaction between mechanical stimuli (Eq. (5)) and electrical response (Eq. (6)). The piezoelectric tensor plays the crucial role of representing the tightly coupled physics of the electromechanical system such as the piezoelectric beams. As shown in Eq. (7), the linear piezoelectric constitutive equations are in the Stress-Electric Displacement form with strain components and electric field components as independent variables.

$$T_{ij} = c_{ijkl} S_{kl} - e_{kij} E_k \quad (7)$$

$$D_i = e_{ijk} S_{kl} + \epsilon_{ik} E_k \quad (8)$$

In the equation, the strain tensor annotated as S_{kl} , is a function of displacement variables. c_{ijkl} is of fourth-order stiffness tensor, e_{kij} and e_{ijk} are third order piezoelectric tensors, and the dielectric tensor ϵ_{ik} is of second order. Applying materials symmetry conditions, the piezoelectric tensors can be reduced into the form of e_{ki} and e_{ij} , and PiezoTensorNet is currently suited to work with the tensors of this format. The 3D surface representation of e_{ij} tensors for four types of considered piezoelectric materials are graphically shown in Fig. 4(b). The tensor for undoped AlN i.e. e_o as visualized in (b)(i) has its maximum peak value of 1.461 C/m² and maximum depth value of -0.5801 C/m². The corresponding tensors for the different doped variants are presented graphically in (b)(ii)–(iv). Without incorporating the rotation effect, the doping of AlN with B and Er in the composition $B_{0.3}Er_{0.5}Al_{0.2}N$ produces the 3D profile of e^* tensor of (b)(ii). The maximum peak (maximum positive valued coefficient = 4.363 C/m²) for this material is much higher than that of undoped AlN. However, each of the coefficients of the e^* tensor is zero or larger, and so it loses the merit associated with the depth of the surface. For doped alloy ($B_{0.3}Er_{0.5}Al_{0.2}N$), and rotated with $\psi = 91.52^\circ$ or 268.47° and $\theta = 0^\circ$, both the peak and depths are of larger magnitudes. Referring to (b)(iii), the maximum peak of $e_1^{*'}$ tensor is of 8.7947 C/m² whereas the maximum depth is of -8.6464 C/m². When the rotational angle ψ is maintained at 91.52° or 268.47° and θ is changed to 180° , the profile of $e_2^{*'}$ for $B_{0.3}Er_{0.5}Al_{0.2}N$ as shown in (b) (iv) has relatively smaller peak values (largest positive value of 2.0 C/m²) and shallower depth (most negative valued coefficient -2.005 C/m²). For the AlN ceramic materials and doped-materials, the relative permittivity of 9.1 is utilized. As illustrated earlier, the piezoelectric tensor for the 3D cantilever beam of AlN ceramics or doped alloys is represented by 18 coefficients in a 3×6 matrix. Applying symmetry conditions, the stiffness matrix for isotropic and orthotropic 3D beam materials can be represented with a 6×6 matrix with a total of 36 elements.

For isotropic assumption, the following stiffness tensor is used to represent the case of AlN piezoelectric material:

$$C_{ijkl}^{AlN} = 10^{11} \times \begin{bmatrix} 3.54 & 1.12 & 1.12 & 0 & 0 & 0 \\ 1.12 & 3.54 & 1.12 & 0 & 0 & 0 \\ 1.12 & 1.12 & 3.54 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1.21 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1.21 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1.21 \end{bmatrix} \text{ N/m}^2$$

Composition-based feature vector (CBFV) methodology, illustrated in Poudel et al. [31] has been utilized to compute the effective stiffness tensor for doped alloy. The stiffness tensor for $B_{0.3}Er_{0.5}Al_{0.2}N$ alloy (annotated as d-AlN) for elastic isotropy condition is:

$$C_{ijkl}^{d-AlN} = 10^{11} \times \begin{bmatrix} 2.65 & 0.84 & 0.84 & 0 & 0 & 0 \\ 0.84 & 2.65 & 0.84 & 0 & 0 & 0 \\ 0.84 & 0.84 & 2.65 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.91 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.91 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.91 \end{bmatrix} \text{ N/m}^2$$

The conditions for materials isotropy are utilized in this section to highlight the sole effect of alteration in piezoelectric coefficients in doped alloys. The values of Young's modulus (Y_E) and Poisson's ratio ν for AlN are 300 GPa and 0.24 respectively. Whereas, for $B_{0.3}Er_{0.5}Al_{0.2}N$ the corresponding stiffness tensor indicates Y_E and ν as 225 GPa and 0.24 respectively. The FEM simulations corresponding to orthotropic elasticity are presented in Supplementary Information S6. The cantilever beam in Fig. 4(a) has a dimension of $l = 200 \mu\text{m}$, $b = 50 \mu\text{m}$ and $h = 5 \mu\text{m}$. At the end face of the beam (AlN ceramics or its doped versions) attached to the fixed wall, fixed boundary condition (zero displacement with $\delta_x = \delta_y = \delta_z = 0$) is applied. At the face at the opposite end of this piezoelectric beam, a surface load (F_z) is applied in the downward direction. This stress load is applied with constant values ranging from 1×10^{-5} to $(F_z)_{\max} = 5 \times 10^{-5} \text{ N/m}^2$. The top and bottom faces of

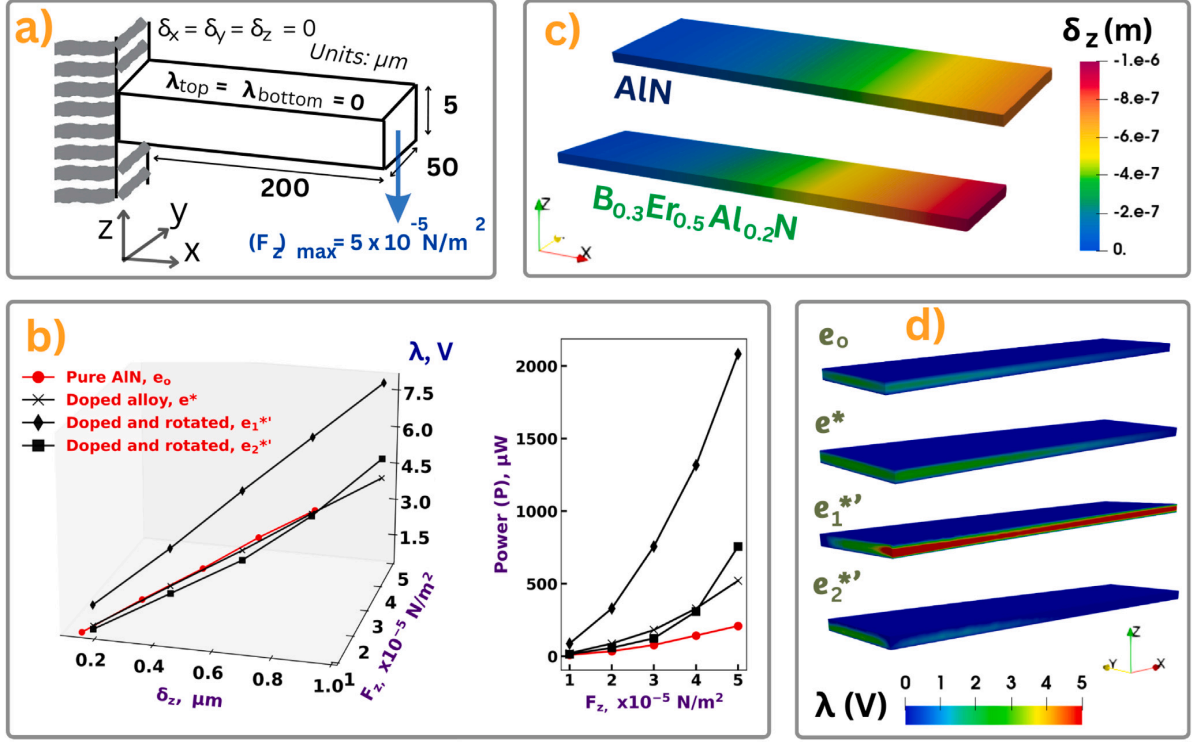


Fig. 4. Finite element analysis for micro-sized beams. (a) The cantilever beam ($200 \times 50 \times 5$) μm is subjected to varying loading conditions ranging from 1×10^{-5} N/m^2 to a maximum $(F_z)_{\text{max}} = 5 \times 10^{-5}$ N/m^2 . The dimensions are not according to the scale. The top and bottom surfaces are electrically grounded for boundary conditions. (b) Deformation, voltage generation, and power results obtained from the electro-mechanical coupled FEA for five different loading conditions of four different tensor properties. (c) Results of deformation distribution along the z-axis (δ_z) for a load $(F_z)_{\text{max}}$ in the pure AlN and alloyed beam. (d) Electric potential (λ) for $(F_z)_{\text{max}}$ showing the maximum value of 7.8 V for the corresponding maximum deformation of 0.97 μm .

the beam are grounded electrically. With the materials properties and boundary conditions, the set of Eqs. (5) and (6) is solved using finite element method in Elmer Multiphysics software [52,53].

As illustrated in Fig. 4(b), the potential distribution and deformation variation for $\text{B}_{0.3}\text{Er}_{0.5}\text{Al}_{0.2}\text{N}$ alloy (with the orientation described as $\psi = 91.52^\circ$ or 268.47° and $\theta = 0^\circ$) are presented. With the matrix for e_1^* tensor being asymmetric, the voltage distribution pattern is characterized by spatial anisotropy. For a stress load of $(F_z)_{\text{max}}$, maximum displacement with a magnitude of 0.97 μm is attained and potential field with a maximum value of 7.8 V is generated in this material type. It is further revealed from the curves of Fig. 4(d) that the value of maximum λ for this piezoelectric material (represented by the curve for Doped and rotated, e_1^*) is around 3.39 times that of the maximum value obtained in the AlN beam (material denoted by the curve named Pure AlN, e_o) at the stress loading of $(F_z)_{\text{max}}$. The maximum value of potential in pure AlN for the above loading is 2.3 V. The maximum voltage for the other two variants of doped alloys with piezoelectric tensors of e^* and e_2^* are 3.9 and 4.7 V respectively for the same loading. Thus, the doped material in general offers better electromechanical merits compared to the AlN beam. Moreover, the doped candidate with rotation orientation resulting in e_1^* is far superior to any of the other three candidates. The results of voltage and deformation distribution for a range of constant loads, varying from 1×10^{-5} N/m^2 to 5×10^{-5} N/m^2 , as presented in Fig. 4(b) offer more insights than just the finetuning of electric potential for a given mechanical loading. The deformation curve for pure AlN material is of visibly shorter length than that of the other three variants all composed of the same doped material ($\text{B}_{0.3}\text{Er}_{0.5}\text{Al}_{0.2}\text{N}$). Due to the compositional differences between AlN and $\text{B}_{0.3}\text{Er}_{0.5}\text{Al}_{0.2}\text{N}$, their stiffness tensors are distinct. This variation in elastic response between the two materials

leads to different deformations in pure AlN and its doped variants. For the vibrating beam of mass density (ρ) of 7500 kg/m^3 and moment of inertia ($I = bh^3/12$), the natural frequency at first mode is given as $f = \frac{1.875^2}{2\pi} \sqrt{\frac{YET}{\rho b h^4}}$ [54]. From Fig. 4(c), Under $(F_z)_{\text{max}}$, the curves demonstrate that a cantilever beam composed of AlN ceramic exhibits a maximum vertical displacement of only 0.73 μm at a first mode frequency of 629.11 kHz. In contrast, the $\text{B}_{0.3}\text{Er}_{0.5}\text{Al}_{0.2}\text{N}$ beams already deform by 0.97 μm at 544.82 kHz.

The average power (P) for the MEMS computed in accordance to the relation $P = (2\pi f)CV^2$ [55]. Where, f , C , and V are the vibrational frequency of the beam, capacitance of the connected capacitor, and generated voltage respectively. For this system, considering the capacitance of 0.0492 pF and for $(F_z)_{\text{max}}$, the power is obtained as 2082.71 μW for the rotated $\text{B}_{0.3}\text{Er}_{0.5}\text{Al}_{0.2}\text{N}$ (e_1^*) beam, whereas it is 209.1 μW for pure AlN (e_o). This represents a 9.96-fold increase compared to pure AlN. In the case of the other system, the maximum power is 520.82 μW for e^* and 756.19 μW for e_2^* . In energy harvesting applications, the devices are designed based on loading conditions so the inclusion of finite element analysis will add to the flexibility of choosing the materials that provide the optimum range of deflections for a given applied force.

4. Conclusion

The integration of computational engineering, crystallography, and electro-mechanical characterization in the design of piezoelectric materials is the focus of this study. The introduced framework, PiezoTensorNet, is scientifically robust and combines the interdisciplinary science of crystal structure, tensor mathematics, and machine learning techniques. It combines a hierarchical neural network-based crystal point

group classification with a modular ensemble neural network for piezoelectric coefficient prediction. The fusion of these interdisciplinary approaches results in an efficient model that combines a multi-layer classification model and a multi-dimensional regression-based modular network. The crystal point group classification influences the activation of specific blocks within the modular network. This framework also incorporates the study of piezoelectric behavior variations in the presence of single or binary foreign elements as dopants. Furthermore, it includes crystal transformation and the enhancement of the piezoelectric coefficient using Euler angular rotation by the combinations of (ϕ, θ, ψ) . The application of tensor mathematics supports the physics of crystal rotation. This framework effectively utilizes and enhances the piezoelectric response of the material through electro-mechanical coupling. The integration of computational engineering, crystallography, and electro-mechanical characterization enables rapid design improvements in piezoelectric materials.

In this research, the multidisciplinary integrated PiezoTensorNet was applied to a MEMS based on Aluminum Nitride (AlN). The study focused on the impact of singular and binary foreign element dopants on the piezoelectric performance of the system. It was determined that the composition [B, Er] with a ratio of $B_{0.3}Er_{0.5}Al_{0.2}N$ exhibited optimal piezoelectric properties. Using crystallography-guided ML and FEM, the performance of a cantilever beam was analyzed. The five different loading conditions which cause varying deformation were studied. The results showed that the power increased from 209.1 μW 520.67 μW in the doped system when subjected to a case of maximum deformation of 0.97 μm . Furthermore, crystallography rotation was performed on the doped alloy, and it was found that rotating the crystal through 91.52° along the vertical axis (Z-axis) from either direction resulted in the highest power generation, reaching a value of 2082.71 μW . This study demonstrates the scientific application of PiezoTensorNet in the field of piezoelectric materials, specifically in the context of MEMS based on AlN. By exploring the effects of dopants and crystallography rotation, significant improvements in the piezoelectric performance of the system were achieved.

CRedit authorship contribution statement

Sachin Poudel: Writing –original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Rubi Thapa:** Writing – review & editing, Visualization, Validation, Investigation, Formal analysis. **Rabin Basnet:** Writing – review & editing, Validation, Methodology. **Anna Timofiejczuk:** Writing – review & editing, Validation, Supervision, Methodology. **Anil Kunwar:** Writing – review & editing, Validation, Supervision, Software, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data used in this work is available in <https://github.com/Sachinscnpdl/PiezoTensorNet-Data>. The graphical user interface of PiezoTensorNet can be accessed via: <https://piezotensornet.streamlit.app/>.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.apenergy.2024.122901>. A document of Supplementary Information to this article is provided together in a single PDF file with 6 different sections.

S1. Piezoelectric Coefficients: Mathematical Expressions: contains **Table A1**, expressing piezoelectric coefficients in terms of electric field, electric displacement, mechanical stress, and strain.

S2. Crystal Point Group and Piezoelectricity: includes **Table A2**, with noncentrosymmetric point groups and piezoelectric tensor in 20 crystal classes.

S3. Data Visualization and Feature Engineering: comprises **Table A3**, Magpie Descriptors for Materials Analysis with added complementing features, alongside **Fig. A1**, Visualization and feature engineering of collected Piezoelectric datasets.

S4. Machine Learning Descriptions: consists of **Tables A4, A5, and A6** detailing hyperparameter selection and machine learning descriptions, along with **Fig. A2** presenting learning curves for training and validation accuracy.

S5. Crystal Rotation Supported by Tensor Mathematics:

S6. FEM for Orthotropic Stiffness: features **Fig. A3**, illustrating FEM results of generated voltage and corresponding deformation for the orthotropic stiffness matrix.

References

- [1] Liu Y, Yang J, Deng S, Zhang Y, Zhang Y, Sun S, Wang L, Jiang X, Huo C, Liu H, et al. Flexible polarization configuration in high-entropy piezoelectrics with high performance. *Acta Mater* 2022;236:118115.
- [2] Sui G, Shan X, Hou C, Tian H, Hu J, Xie T. An underwater piezoelectric energy harvester based on magnetic coupling adaptable to low-speed water flow. *Mech Syst Signal Process* 2023;184:109729.
- [3] Chen S, Zhu P, Mao L, Wu W, Lin H, Xu D, Lu X, Shi J. Piezocatalytic medicine: An emerging frontier using piezoelectric materials for biomedical applications. *Adv Mater* 2023;2208256.
- [4] Wang C, Hu Y, Liu Y, Shan Y, Qu X, Xue J, He T, Cheng S, Zhou H, Liu W, et al. Tissue-adhesive piezoelectric soft sensor for in vivo blood pressure monitoring during surgical operation. *Adv Funct Mater* 2023;2303696.
- [5] Tian H, Shan X, Li X, Wang J. Enhanced airfoil-based flutter piezoelectric energy harvester via coupling magnetic force. *Appl Energy* 2023;340:120979.
- [6] Sun W, Ji G, Chen J, Sui D, Zhou J, Huber J. Enhancing the acoustic-to-electrical conversion efficiency of nanofibrous membrane-based triboelectric nanogenerators by nanocomposite composition. *Nano Energy* 2023;108:108248.
- [7] Deng J, Chen W, Wang Y, Zhang S, Liu Y. Modeling and experimental evaluations of a four-legged stepper rotary precision piezoelectric stage. *Mech Syst Signal Process* 2019;132:153–67.
- [8] Muganda JM, Jansen B, Homburg E, van de Burgt Y, den Toonder J. Influence function measurement technique using the direct and indirect piezoelectric effect for surface shape control in adaptive systems. *IEEE Trans Autom Sci Eng* 2021;19(2):994–1002.
- [9] Erhart J, Pülpán P, Pustka M. Piezoelectric ceramic resonators. Springer; 2017.
- [10] Benveniste Y, Dvorak G. Uniform fields and universal relations in piezoelectric composites. *J Mech Phys Solids* 1992;40(6):1295–312.
- [11] Khan H, Mahmood N, Zavabeti A, Elbourne A, Rahman MA, Zhang BY, Krishnamurthi V, Atkin P, Ghasemian MB, Yang J, et al. Liquid metal-based synthesis of high performance monolayer SnS piezoelectric nanogenerators. *Nat Commun* 2020;11(1):3449.
- [12] Sekhar MC, Veena E, Kumar NS, Naidu KCB, Mallikarjuna A, Basha DB. A review on piezoelectric materials and their applications. *Cryst Res Technol* 2023;58(2):2200130.
- [13] Baraskar BG, Kolekar YD, Thombare BR, James AR, Kambale RC, Ramana C. Enhanced piezoelectric, ferroelectric, and electrostrictive properties of lead-free (1-x) BCZT-(x) BCST electroceramics with energy harvesting capability. *Small* 2023;2300549.
- [14] Li J, Shen Z, Chen X, Yang S, Zhou W, Wang M, Wang L, Kou Q, Liu Y, Li Q, et al. Grain-orientation-engineered multilayer ceramic capacitors for energy storage applications. *Nat Mater* 2020;19(9):999–1005.
- [15] Pomeroy M. Encyclopedia of materials: technical ceramics and glasses. Elsevier; 2021.
- [16] He J, Yu C, Hou Y, Su X, Li J, Liu C, Xue D, Cao J, Su Y, Qiao L, et al. Accelerated discovery of high-performance piezocatalyst in BaTiO₃-based ceramics via machine learning. *Nano Energy* 2022;97:107218.

- [17] Yuan R, Xue D, Xu Y, Xue D, Li J. Machine learning combined with feature engineering to search for BaTiO₃ based ceramics with large piezoelectric constant. *J Alloys Compd* 2022;908:164468.
- [18] Oh S-HV, Hwang W, Kim K, Lee J-H, Soon A. Using feature-assisted machine learning algorithms to boost polarity in lead-free multicomponent niobate alloys for high-performance ferroelectrics. *Adv Sci* 2022;9(13):2104569.
- [19] Kholkin AL, Pertsev NA, Goltsev AV. Piezoelectricity and crystal symmetry. In: *Piezoelectric and acoustic materials for transducer applications*. Springer; 2008, p. 17–38.
- [20] Abbasipour M, Khajavi R, Akbarzadeh AH. A comprehensive review on piezoelectric polymeric and ceramic nanogenerators. *Adv Energy Mater* 2022;24(6):2101312.
- [21] Choudhary K, Garrity KF, Sharma V, Biacchi AJ, Hight Walker AR, Tavazza F. High-throughput density functional perturbation theory and machine learning predictions of infrared, piezoelectric, and dielectric responses. *NPJ Comput Mater* 2020;6(1):64.
- [22] Rao G, Fang H, Zhou T, Zhao C, Shang N, Huang J, Liu Y, Du X, Li P, Jian X, et al. Robust piezoelectricity with spontaneous polarization in monolayer tellurene and multilayer tellurium film at room temperature for reliable memory. *Adv Mater* 2022;34(35):2204697.
- [23] Bartasyte A, Clementi G, Micard Q, Labbaveettil I, Moreira ASL, Boujnah S, Ouhabaz M, Verma A, Ichangi A, Malandrino G, et al. Material strategies to enhance the performance of piezoelectric energy harvesters based on lead-free materials. *J Micromech Microeng* 2023;33(5):053001.
- [24] Wegert ZJ, Roberts AP, Challis VJ. Novel properties of multi-poled piezoelectric network structures. *Smart Mater Struct* 2021;30(10):105016.
- [25] Yang J, Li Z, Xin X, Gao X, Yuan X, Wang Z, Yu Z, Wang X, Zhou J, Dong S. Designing electromechanical metamaterial with full nonzero piezoelectric coefficients. *Sci Adv* 2019;5(11):eaax1782.
- [26] Wu J, Hu Z, Gao X, Cheng M, Zhao X, Su W, Wang L, Guan M, Du Y, Mao R, et al. Unconventional piezoelectric coefficients in perovskite piezoelectric ceramics. *J Mater* 2021;7(2):254–63.
- [27] Jain A, Ong SP, Hautier G, Chen W, Richards WD, Dacek S, Cholia S, Gunter D, Skinner D, Ceder G, Persson KA. Commentary: The materials project: A materials genome approach to accelerating materials innovation. *APL Mater* 2013;1(1):011002.
- [28] De Jong M, Chen W, Geerlings H, Asta M, Persson KA. A database to enable discovery and design of piezoelectric materials. *Sci Data* 2015;2(1):1–13.
- [29] Ward L, Agrawal A, Choudhary A, Wolverton C. A general-purpose machine learning framework for predicting properties of inorganic materials. *NPJ Comput Mater* 2016;2(1):1–7.
- [30] Deffrennes G, Terayama K, Abe T, Tamura R. A machine learning-based classification approach for phase diagram prediction. *Mater Des* 2022;215:110497.
- [31] Poudel S, Subedi U, Hamid MO, Gyanwali K, Moelans N, Timofiejczuk A, Kunwar A. AlloyManufacturingNet for discovery and design of hardness-elongationsynergy in multi-principal element alloys. *Eng Appl Artif Intell* 2024;107902.
- [32] Chang Y-R, Nanae R, Kitamura S, Nishimura T, Wang H, Xiang Y, Shinokita K, Matsuda K, Taniguchi T, Watanabe K, et al. Shift current photovoltaics based on a noncentrosymmetric phase in in-plane ferroelectric SnS. *Adv Mater* 2023;2301172.
- [33] Newnham RE. *Properties of materials: anisotropy, symmetry, structure*. Oxford University Press on Demand; 2005.
- [34] Kelly A, Knowles KM. *Crystallography and crystal defects*. John Wiley & Sons; 2020.
- [35] Smith M, Kar-Narayan S. Piezoelectric polymers: Theory, challenges and opportunities. *Int Mater Rev* 2022;67(1):65–88.
- [36] Yang M-M, Luo Z-D, Mi Z, Zhao J, E SP, Alexe M. Piezoelectric and pyroelectric effects induced by interface polar symmetry. *Nature* 2020;584(7821):377–81.
- [37] Trolter-McKinstry S. *Crystal chemistry of piezoelectric materials*. In: *Piezoelectric and acoustic materials for transducer applications*. Springer; 2008, p. 39–56.
- [38] Veasna K, Feng Z, Zhang Q, Knezevic M. Machine learning-based multi-objective optimization for efficient identification of crystal plasticity model parameters. *Comput Methods Appl Mech Engrg* 2023;403:115740.
- [39] Trezza G, Bergamasco L, Fasano M, Chiavazzo E. Minimal crystallographic descriptors of sorption properties in hypothetical MOFs and role in sequential learning optimization. *NPJ Comput Mater* 2022;8(1):123.
- [40] Huang H, Liu H. Feature selection for hierarchical classification via joint semantic and structural information of labels. *Knowl-Based Syst* 2020;195:105655.
- [41] Poudel S, Thapa R, Kunwar A. *PiezoTensorNet: A machine learning based toolkit for exploratory design and discovery of PiezoElectric materials*. 2023, <https://piezotensornet.streamlit.app/>. Accessed: 03.07.2023.
- [42] Kalinin SV, Rodriguez BJ, Jesse S, Shin J, Baddorf AP, Gupta P, Jain H, Williams DB, Gruverman A. Vector piezoresponse force microscopy. *Microsc Microanal* 2006;12(3):206–20.
- [43] Jin Y, Lu X, Zhang J, Kan Y, Bo H, Huang F, Xu T, Du Y, Xiao S, Zhu J. Studying the polarization switching in polycrystalline BiFeO₃ films by 2D piezoresponse force microscopy. *Sci Rep* 2015;5(1):12237.
- [44] Coope J, Snider R, McCourt F. Irreducible cartesian tensors. *J Chem Phys* 1965;43(7):2269–75.
- [45] Harrison AP, Joseph D. Numeric tensor framework: Exploiting and extending Einstein notation. *J Comput Sci* 2016;16:128–39.
- [46] Uehara M, Amano Y, Anggraini SA, Hirata K, Yamada H, Akiyama M. Preparation of YbAlN piezoelectric thin film by sputtering and influence of Yb concentration on properties and crystal structure. *Ceram Int* 2021;47(11):16029–36.
- [47] Hirata K, Yamada H, Uehara M, Anggraini SA, Akiyama M. Enhancement of piezoelectric property in MgTMAIN (TM=Cr, Mo, W): First-principles study. *J Phys Chem Solids* 2021;152:109913.
- [48] Zha X-H, Ma X, Luo J-T, Fu C. Enhanced piezoelectric response of AlN via alloying of transitional metals, and influence of type and distribution of transition metals. *Nano Energy* 2023;111:108390.
- [49] Herth E, Algre E, Rauch J-Y, Gerbedoen J-C, Defrance N, Delobelle P. Modeling and characterization of piezoelectric beams based on an aluminum nitride thin-film layer. *Phys Status Solidi (a)* 2016;213(1):114–21.
- [50] Hara M, Minh L, Oguchi H, Kuwano H. Power estimation for piezoelectric energy harvesters in flexure mode with large displacement amplitude. In: *Journal of physics: conference series*. Vol. 476, IOP Publishing; 2013, 012024.
- [51] Zhang C, Wang X, Chen W, Yang J. An analysis of the extension of a ZnO piezoelectric semiconductor nanofiber under an axial force. *Smart Mater Struct* 2017;26(2):025030.
- [52] Sikanen T, Zwinger T, Tuomikoski S, Franssila S, Lehtiniemi R, Fager C-M, Koti-aho T, Pursula A. Temperature modeling and measurement of an electrokinetic separation chip. *Microfluid Nanofluid* 2008;5(4):479–91.
- [53] Gustafsson T, Råback P, Videman J. Mortaring for linear elasticity using mixed and stabilized finite elements. *Comput Methods Appl Mech Engrg* 2023;404:115796.
- [54] Barboni L, Gillich G, Chioncel C, Hamat C, Mituletu I. A method to precise determine the Young's modulus from dynamic measurements. In: *IOP conference series: materials science and engineering*. Vol. 416, IOP Publishing; 2018, 012063.
- [55] Kim G-W, Kim J, Kim J-H. Flexible piezoelectric vibration energy harvester using a trunk-shaped beam structure inspired by an electric fish fin. *Int J Precis Eng Manuf* 2014;15:1967–71.

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Unraveling elastochemical effects in microstructural evolution of Al–Cu–Ni system through DFT-informed multi-phase field simulations

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ABSTRACT

Through the multi-phase field method, this research explores microstructure evolution within the Al–Cu–Ni system comprising Al-rich FCC, Al₂Cu, and Al₃Ni intermetallic compounds (IMCs). Notably, the Al₃Ni exhibits substantial growth due to its higher free energy magnitude, while the Al₂Cu phase diminishes within the FCC matrix. Additionally, this study investigates the impact of heterogeneous elastic effects on these microstructural changes. Density functional theory calculations were employed to determine temperature-dependent elastic tensor at a simulation temperature of 723 K. Initially both cases, simulations with elastic constants at 0 K and 723 K, start with identical grain areas. But by 21.45 ms, deviations notably intensify to 18.18% for single grains, underlining the importance of temperature-calibrated elastic tensor in the phase evolution driven by elastochemical effects.

1. Introduction

Aluminum (Al) alloys are renowned for their excellent strength-to-weight ratio, making them the best fit for lightweight structural materials in automotive and aerospace (Tan and Zhang, 2024). However, their application is hindered by their low strength at high temperatures (Cui et al., 2023). Recent advancements aim to address this challenge with microalloying as a promising technique. Among Al-based alloys, the Al–Cu series is a crucial candidate for high-temperature applications (Zhang et al., 2022). Adding Ni to Al–Cu alloys further enhances mechanical performance across different temperatures (Luo et al., 2022), forming diverse Ni-based intermetallic compounds (IMC) that improve wear resistance and high-temperature strength (Wen et al., 2017). Consequently, Ni–Al alloys find applications in high-temperature structural components and as coatings for corrosion and friction resistance (Osório et al., 2010). Additionally, spraying Ni in Al–Cu alloys has been shown to mitigate the formation of brittle phases at interfaces (Hou et al., 2021). When aluminum is alloyed with copper (Cu) and nickel (Ni), it opens up the possibility of forming various intermetallic compounds, with Al₂Cu and Al₃Ni being predominant at temperatures below 723 K (Aravind et al., 2004; Shao et al., 2023). Understanding the microstructural evolution within these Al–Cu–Ni alloys is crucial for predicting their behavior (Bai et al., 2022). Studies

by Kundin et al. (2015, 2014) have delved into the phase evolution and nucleation processes in solidifying Al–Cu–Ni ternary compounds, shedding light on their intricate microstructural dynamics.

The phase-field method is a robust interface tracking technique that utilizes distinct phase fields to represent grains with the same crystallographic phase but varying attributes (Feyen and Moelans, 2023; Liu et al., 2023). This approach is powerful for studying the interface evolution between grains (Moelans et al., 2008a). This methodology employs a vector order parameter to characterize a spectrum of properties, including crystal structures, composition, and orientation (Steinbach and Salama, 2023; Zhao et al., 2023). As a versatile computational tool, it has significantly advanced alloy development by enabling the prediction of microstructure evolution. The non-linear wave equation for the phase field could potentially be coupled with a linear Schrödinger-type equation for quantum-mechanical excitations, where atomistic-level properties are directly imposed in phase field equations (Steinbach, 2024; Kundin and Steinbach, 2020). This concept is considered futuristic, and its numerical implementation is regarded as a challenge for future research.

Quantum-mechanical method such as density functional Theory (DFT) is very useful for computing material properties required by continuum scale calculations such as phase-field methods. The influence

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of elastic energy on phase morphology in dual and multi-phase alloys has garnered increased attention (Zhao et al., 2020). Researchers have extensively explored the equilibrium shapes of precipitates, investigating the relationship between elastic and interfacial energies (Li et al., 2004). A particularly studied aspect is the impact of elastic deformation energy on microstructural evolution, especially in precipitates exhibiting misfit strain Gao et al. (2012), Ji et al. (2014). Particularly, several studies have delved into the examination of elastic effects in phase evolutions (Durga et al., 2020; Hektor et al., 2016; Wu et al., 2022; Simon et al., 2020; Zuo and Moelans, 2023). However, it is essential to highlight that these studies do not incorporate temperature-calibrated elastic constants when considering the elastochemical effect in phase evolution. This omission results in the inappropriate accounting of phase evolution at high temperatures, as the elastic constants are based on absolute zero temperature conditions instead of the simulation temperature. The temperature-dependent elastic effects were studied in the phase field crystal model (Ainsworth and Mao, 2019; Pisutha-Arnond et al., 2013).

The connection of phase-field evolution and elastochemical effects within multi-phase alloys has become a pivotal area for understanding microstructural behaviors. This study strives to advance phase-field models by integrating the elastic energy in the bulk free energy of individual phases. This integration forms a robust framework that accounts for the coupling between phase evolution and elastic distortion. The approach involves incorporating suitable interpolation functions or boundary conditions to effectively address the elastic contributions in microstructure evolution. To seamlessly integrate the elastic effects into microstructural evolution, this study utilizes *ab initio* simulations to compute stiffness tensor values. The primary focus here is to underscore the importance of using temperature-calibrated elastic constants over 0 K values, recognizing that calculating elastic energy with elastic constants at simulated temperatures reflects more realistic microstructural features. With this attempt, this analysis stands as an initiative effort in simulating phase evolution, considering temperature-dependent elastochemical effects in multi-phase systems.

2. Temperature calibrated stiffness tensor using DFT

Elastic constants (ECs) are essential for characterizing a material's mechanical and thermodynamic properties, influencing sound velocity, stability, and thermal response (Gillan et al., 2006). Typically, Density Functional Theory (DFT) calculations focus on zero-temperature ECs due to computational constraints. However, the temperature dependence of ECs can be addressed through two approaches. First, quasi-static approximation (QSA) examines temperature-dependent ECs considering thermal expansion and identifying geometries that minimize free energy. Second, the quasi-harmonic approximation (QHA) utilizes second derivatives of free energy concerning strain to evaluate ECs in temperature-dependent configurations (Malica and Dal Corso, 2020). The theoretical explanation of DFT is explained based on Malica et al. (2021) in Appendix A.1.

The equilibrium lattice constants for the compounds were determined by interpolating the total energy (E_{tot}) as a function of the unit cell volume (V). Murnaghan's equation of state, represented by Eq. (1), played a key role in this process (Wafula et al., 2022):

$$E(V) = E(V_0) + \frac{B_0}{B'_0 + (B'_0 - 1)} \left[V \left(\frac{V}{V_0} \right)^{B'_0} B'_0 - V_0 \right] + \frac{B_0}{B'_0} (V - V_0) \quad (1)$$

In this equation, $E(V)$ represents the ground state energy with a volume of the cell (V), V_0 is the volume of the unit cell at zero pressure, and B_0 and B'_0 are the modulus of compressibility and its derivative, respectively.

Elastic constants, including bulk moduli, shear moduli, Young's moduli, and Poisson's ratios, were calculated using the Voigt–Reuss–average method. Hill's averages of bulk and shear moduli were instrumental in determining sound velocities. An accurate Debye temperature

was derived, considering sound velocities in various propagation directions and solving the Christoffel wave equation. This appropriate Debye temperature played a pivotal role in computing vibrational energy, free energy, entropy, and constant strain heat capacity (Wafula et al., 2022; Palumbo and Dal Corso, 2017).

In crystal deformation, a symmetric strain tensor ϵ^{ij} is applied, where i and j denote Cartesian coordinate indices. To counterbalance the effects of deformation and maintain the solid in its strained configuration, stress tensors σ^{ij} are exerted. The relationship between stress and strain is established through the equation: (Parrinello and Rahman, 1982)

$$\sigma^{ij} = \sum_{kl} C^{ijkl} \epsilon^{kl} \quad (2)$$

Here, C^{ijkl} signifies the components of the elastic tensor, characterizing the stress–strain relationship for small strains. These ECs can also be derived as derivatives of stress with respect to strain:

$$C^{ijkl} = \left. \frac{\partial \sigma^{ij}}{\partial \epsilon^{kl}} \right|_{\epsilon=0} \quad (3)$$

At absolute zero temperature ($T = 0$ K), the ECs can also be expressed as the second derivatives of total energy (U) obtained from DFT with respect to strain:

$$\tilde{C}^{ijkl} = \frac{1}{\Omega} \left. \frac{\partial^2 U}{\partial \epsilon^{ij} \partial \epsilon^{kl}} \right|_{\epsilon=0} \quad (4)$$

Where Ω signifies the volume of the reference system. The reference geometry minimizes the energy in equilibrium and the energy-based ECs ($\tilde{C}^{ijkl}$) match the components of the elastic tensor (C^{ijkl}). However, if isotropic pressure p is exerted on the solid in the reference geometry, the elastic constants differ:

$$C^{ijkl} = \tilde{C}^{ijkl} + \frac{1}{2} p (2\delta^{ij}\delta^{kl} - \delta^{il}\delta^{jk} - \delta^{ik}\delta^{jl}) \quad (5)$$

To incorporate the influences of zero-point quantum effects and temperature, the same formulation can be utilized by replacing U in Eq. (4) with the Helmholtz free energy F_{Hz} :

$$\tilde{C}_T^{ijkl} = \frac{1}{\Omega^T} \left(\frac{\partial^2 F_{\text{Hz}}}{\partial \epsilon^{ij} \partial \epsilon^{kl}} \right)_{\epsilon=0} \quad (6)$$

Where Ω^T represents the volume of the structure at temperature T , and F_{Hz} signifies the Helmholtz energy approximated within the QHA at temperature T and is computed as Balasubramanian et al. (2023):

$$F_{\text{Hz}}(V, T) = U(V, 0) + F_{\text{hr}} + F_{\text{anhr}} \quad (7)$$

Here, $U(V, 0)$ corresponds to the DFT enthalpy at 0K, F_{hr} denotes the vibrational contributions from the harmonic approximation of phonons, and F_{anhr} represents the anharmonic phonon contribution to the free energy. Within QHA, the term F_{anhr} (electronic contribution) is neglected. The F_{hr} portion is evaluated as:

$$F_{\text{hr}}(V, T) = \frac{1}{2N} \sum_{q\eta} \hbar \omega_{\eta}(q, \epsilon) + \frac{k_B T}{N} \sum_{q\eta} \ln \left[1 - \exp \left(-\frac{\hbar \omega_{\eta}(q, \epsilon)}{k_B T} \right) \right] \quad (8)$$

In this equation, $\hbar$ is reduced Planck constant, N is number of q -points, $\omega_{\eta}(q, \epsilon)$ stands for the phonon angular frequencies at wave vector q and strain ϵ , k_B denotes the Boltzmann constant, and T is the temperature.

2.1. *Ab initio* simulation setup

The study utilized DFT with projector augmented-wave (PAW) pseudopotentials (Dal Corso, 2014) to explore the structural, mechanical, electronic, and thermodynamic properties of crystals. Computation of Al and Al₃Cu employ the Perdew–Burke–Ernzerhof (PBE) functional alongside generalized gradient approximations (GGA) while local density approximation (LDA) for Al₃Ni (Perdew et al., 1996; Perdew and

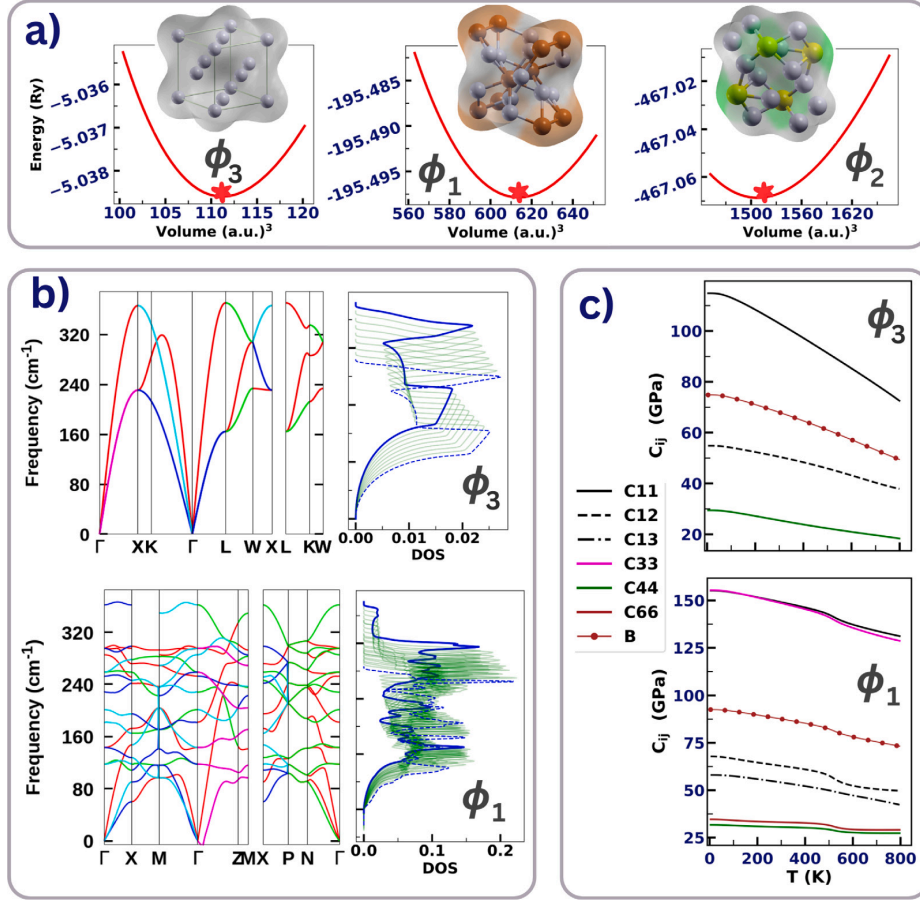


Fig. 1. DFT-computed temperature-calibration of elasticity. (a) Energy versus volume plots for single-element cubic Al-rich FCC (ϕ_3), double-element tetragonal Al₂Cu IMC (ϕ_1), and octagonal Al₃Ni IMC (ϕ_2), identifying the minimum energy structure with (*). (b) Phonon dispersion curves across high-symmetry directions and DOS featuring 9 distinct geometries for ϕ_3 and 25 for ϕ_2 . Solid lines depict the initial marked structure (*) from panel a), while faint lines correspond to intermediary geometries, and dotted lines represent the DOS of the final geometry. Notably, non-negative phonon frequencies signify the dynamic stability of the bulk material. (c) The temperature-dependent calibration of elastic constants emphasizes the higher impact of temperature on FCC (ϕ_3) in comparison to Al₂Cu IMC (ϕ_1).

Wang, 1992). The computation of exchange–correlation energies was conducted using varying plane wave cutoff energies: 30 Ry for Al and 38 Ry for Al₂Cu and Al₃Ni. Investigation of Al's elastic properties was done with $24 \times 24 \times 24$ k-point grid and Al₂Cu and Al₃Ni utilized a $9 \times 9 \times 9$ k-point grid in the Brillouin zone. The introduction of smearing as explained in Appendix A.2 alters electron orbital occupation.

Furthermore, this study extended to the phonon dispersions of Al and Al₂Cu, which were calculated using density functional perturbation theory (DFPT) within the Quantum Espresso (QE) post-processing package Thermo_pw code (Dal Corso, 2017). A $2 \times 2 \times 2$ q-point grid was utilized for phonon frequency calculations, with Fourier interpolation applied for other points within the Brillouin zone, ensuring a broad analysis of vibrational properties. Computation of temperature-dependent ECs employed QHA for Al and QSA for Al₂Cu. The Helmholtz energies at various strains were fitted to a polynomial function, allowing for the determination of elastic constants at temperatures from 0 K to 800 K with the step of 3 K.

2.2. Stiffness tensors for crystalline phases

In Fig. 1a, the atomic structure of three distinct materials is depicted: cubic Al-rich FCC (ϕ_3), double-element tetragonal Al₂Cu IMC

(ϕ_1), and octagonal Al₃Ni IMC (ϕ_2). These structures represent the configurations with minimized energy. Fig. 1b showcases the density of states (DOS) against frequency for nine different ϕ_3 geometries and twenty-five for ϕ_2 . The plot provides a comparative analysis of the crystal structure during different stages of geometry optimization. The solid line represents the initial relaxed crystal structure, which serves as the reference state. The green-colored dim lines illustrate the intermediate geometries encountered during the optimization process. Finally, the dotted lines denote the final optimized structure. For each geometry, the local minima of energy were computed, with the initial geometry's local minimum depicted in Fig. 1a. Notably, the temperature-dependent elastic constants in Fig. 1c reveal a more noticeable influence of temperature on ϕ_3 in comparison to ϕ_1 . Given the relatively lower impact of temperature on the IMC phase, the elastic constants for ϕ_2 are computed exclusively at 0 K.

The elastic constants obtained from Fig. 1(c) have been compiled into Table 1 to showcase values at both absolute zero (0 K) and the simulation temperature used in the DFT-informed phase field simulations. This table emphasizes stiffness values (measured in GPa), encompassing experimental 0 K data for Al and Al₂Cu, while providing computationally derived values for Al₃Ni as a reference of previously published literature. Notably, significant attention is given to the elastic constant

Table 1

Elasticity constants (GPa) for investigated materials, including experimental values at 0 K for Al and Al₂Cu, and computational values for Al₃Ni. Additionally, the elastic constant at 723 K relevant to this study is provided. The structures of Al, Al₂Cu, and Al₃Ni are characterized by cubic, tetragonal I, and orthorhombic arrangements, respectively which are identified by their international space group (SG) numbers. For detailed insights into the elastic tensor structures and stability criteria, please refer to [Appendix B, Table B.1](#).

Crystalline structures	T (K)	C ₁₁	C ₁₂	C ₁₃	C ₂₂	C ₂₃	C ₃₃	C ₄₄	C ₅₅	C ₆₆	Ref.
Al	0	116.3	64.8	64.8	116.3	64.8	116.3	30.9	30.9	30.9	Vallin et al. (1964) Exp.
SG: 225	0	114.83	54.84	54.84	114.83	54.84	114.83	29.42	29.42	29.42	This Work
FCC	723	77.52	39.66	39.66	77.52	39.66	77.52	19.34	19.34	19.34	This Work
Al ₂ Cu	0	159.0	63.0	50.0	159.0	50.0	163.0	29.0	29.0	46.0	Fribourg-Blanc et al. (1979) Exp.
SG: 140	0	155.14	67.84	58.01	155.14	58.01	155.35	31.72	31.72	34.63	This Work
Tetragonal	723	133.18	50.3	44.24	133.18	44.24	130.09	27.33	27.33	29.04	This Work
Al ₃ Ni	0	169	87	94	167	81	164	89	74	51	Shi et al. (2009) DFT
SG: 62	0	225.85	90.68	68.97	241.57	76.89	223.41	95.69	86.86	70.09	This Work
Orthorhombic											

at a simulation temperature of 723 K from temperature dependence elastic values ranging from 0 K to 800 K. A cautious observation reveals that the FCC matrix exhibits lower values across all nine symmetry positions for elastic constants, while Al₃Ni demonstrates higher values. The Born stability criteria (Born, 1940), as detailed in [Appendix B](#) and in [Table B.1](#), serves as a valuable reference in computing the stiffness tensor values with elastic tensor's structural configurations and stability criteria.

3. DFT-informed interface tracking mesoscale model

In the current study, the KKS approach (Kim et al., 1999, 2004) is employed which is a widely used method of PF models. The benefit of the KKS method is its ability to independently control the interface energy and diffuse interface width. This flexibility allows the use of larger widths at the interface without affecting the thermodynamic and kinetic properties. As a result, computational efficiency is improved in the interface tracking model. In KKS model, the chemical potential of a component between any two adjacent phases are equal. For a multi-phase multi-component system chemical potential (μ) is expressed as:

$$\mu_i = \frac{\partial f_1(c_i)}{\partial c_i^1} = \frac{\partial f_2(c_i)}{\partial c_i^2} = \dots = \frac{\partial f_N(c_i)}{\partial c_i^N} \quad (9)$$

The global concentration (c_i) of i th component is related to its phase compositions via the following expression:

$$c_i = \sum_{\tau}^N h_{\tau}(\eta_{11}, \dots, \eta_N) c_i^{\tau} \quad (10)$$

Where h is a thermodynamically consistent interpolation function (Moelans, 2011) representing the material properties at the interface which is dependent on a non-conserved quantity order parameter (η).

$$h_{\tau}(\eta_{11}, \dots, \eta_N) = \frac{\sum_{j=1}^{N_{\phi}} \eta_{\tau j}^2}{\sum_{k=1}^{N_{\phi}} \sum_{j=1}^{N_{\phi}} \eta_{kj}^2} \quad (11)$$

$N_{\phi} = 3$ represents the total number of phases in the system encompassing: Al₂Cu IMC (ϕ_1), Al₃Ni IMC (ϕ_2), and FCC (ϕ_3). The grains (χ) for a phase have the same bulk free energy but are distinct interfacially. In this work N_{χ} are 2, 3, 1 for ϕ_1 , ϕ_2 , and ϕ_3 respectively. In the case of ϕ_3 consisting of a single grain, $\chi_3 = \phi_3$. The mathematical representation of the phase state employs order parameter (η) fields, as outlined by Moelans et al. (2008b), which can take the form of ϕ for multi-phase, χ for multi-grains, or a combination of both $\phi(\chi)$ for multiphase-multigrain microstructures. Consequently, the total number of order parameters required in the model, as represented by Eq. (11), is $N = 6$. N_{χ} and N_{ϕ} in a multiphase multigrain system are related to N as: $N = \sum_{i=1}^{N_{\phi}} N_{\chi_i}$. Therefore, the computational model is specifically designed to accommodate a 3-phase system with 6 order parameters.

3.1. Free energy functional

The PF model derives the driving force for microstructural evolution from the free energy of the system. The total free energy of the thermodynamic system represented as F_{total} , is a combination of the bulk free energy (F_{bulk}), interfacial free energy (F_{int}), and elastic free energy (F_{el}). This relationship is expressed as follows:

$$F_{\text{total}} = F_{\text{bulk}} + F_{\text{int}} + F_{\text{el}} \\ = \int_V (f_{\text{bulk}} + f_{\text{int}} + f_{\text{el}}) dV \quad (12)$$

3.1.1. Chemical free energy density

The bulk free energy density for the system is given as:

$$f_{\text{bulk}}(c, \eta) = \sum_{\tau=1}^N h^{\tau}(\eta_{11}, \dots, \eta_N) \cdot f_{\text{bulk}}^{\tau}(c_1, \dots, c_{C-1}) \quad (13)$$

$f_{\text{bulk}}^{\tau} = \frac{G_{\text{m}}^{\tau}}{V_{\text{m}}}$ represents the bulk chemical free energy density for τ^{th} phase. The Gibbs free energy G_{m}^{τ} is quantified in J/mol and is associated with three distinct phases. At $T = 723$ K, it follows a paraboloid composition dependence (Kunwar et al., 2020), and the detailed quantification for its mathematical expression is provided in [Appendix C](#). The assumption is made that the molar volumes of the FCC, Al₂Cu, and Al₃Ni phases are equivalent, and a value of 10^{-5} m³/mol is assigned to each phase. This value is referenced from Figure 1 of Kaptay's study (Kaptay, 2015).

3.1.2. Interface free energy density

The interfacial free energy density is composed of a barrier term, f_o , and gradient energy density, f_{grad} . f_o is determined by the order parameter expressed as a 4th order Landau polynomial. This energy density is influenced by two model parameters, m and $\gamma_{i,j}$. On the other hand, the gradient free energy density f_{grad} depends on the model parameters $\kappa_{i,j}$, as indicated below:

$$f_{\text{int}} = f_o + f_{\text{grad}} \\ = m \sum_{i=1}^{N_{\phi}} \sum_{j=1}^{N_{\phi}} \left(\frac{\eta_{ij}^4}{4} - \frac{\eta_{ij}^2}{2} \right) + m \gamma \sum_i \sum_{j=1}^{N_{\phi}} \left(\sum_k \sum_{l=1, l \neq k}^{N_{\phi}} \eta_{ij}^2 \eta_{kl}^2 + \frac{1}{4} \right) \\ + \sum_{i=1}^{N_{\phi}} \sum_{j=1}^{N_{\phi}} \frac{\kappa_i}{2} |\nabla \eta_{ij}|^2 \quad (14)$$

Where, $N_{\chi A}$ and $N_{\chi B}$ represents number of grains in phase ϕ_A and ϕ_B . m , κ , and γ are barrier height, gradient free energy coefficient, and respectively. The minima of the Landau polynomial occur within the interior of each phase field domain, specifically at points where the order parameter values ($\eta_{11}, \eta_{12}, \dots, \eta_n$) are (1, 0, ..., 0), (0, 1, 0, ..., 0), ..., (0, ..., 0, 1). At these points, the interfacial free energy density $f_o = 0$, indicates that the contribution of the bulk materials to the interface energy is negligible. Additionally, due to the strictly positive

nature of the parameter κ_τ , interfaces will always possess energetically unfavorable characteristics.

The phase field parameters are determined as described by the following expressions.

$$\begin{aligned}\kappa &= \frac{3}{4} \sigma \delta \\ m &= 6 \frac{\sigma}{\delta} \\ L &= \frac{16}{3} m M / \kappa\end{aligned}\quad (15)$$

3.1.3. Elastic free energy density

The information about elastic free energy density is derived from the constitutive equation of linear elasticity. The expression of elastic deformation of solids is given by the following partial differential equation:

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} - \nabla \cdot \boldsymbol{\sigma}_c = \bar{\mathbf{f}} \quad (16)$$

Where ρ , $\mathbf{u}$, $\bar{\mathbf{f}}$ represents density, displacement fields, and body force respectively. The body force is ignored in this work, and $\boldsymbol{\sigma}_c$ the Cauchy stress tensor. At steady state mechanical equilibrium, $\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = 0$ and thus, $\nabla \cdot \boldsymbol{\sigma}_c = 0$. The concept of elastic energy density can be expressed as demonstrated in [Jokisaari et al. \(2017\)](#):

$$f_{el} = \frac{1}{2} \sigma_{el}^{ij} \epsilon^{ij} \quad (17)$$

In the equation above, the Einstein summation convention is applied over cartesian indices i, j, k , and l . In this context, σ^{ij} denotes the Piola–Kirchhoff stress. It is important to highlight that the elastic stiffness tensor exhibits smooth interpolation between distinct phases along the diffuse boundary.

$$\sigma_{el}^{ij} = \sum_{\tau=1}^N h^\tau (\sigma^{ij})^\tau \quad (18)$$

In a bulk phase, the elasticity (C^{ijkl}) is defined separately for each phase without considering the interface. Following Hooke's law, elastic stress can be expressed in terms of the stiffness tensor and strain as:

$$\sigma^{ij} = C^{ijkl} \epsilon^{kl} \quad (19)$$

The eigenstrain ϵ^{*ij} and the elasticity tensor C^{ijkl} are both influenced by concentration and temperature, resulting in intriguing elastochemical coupling effects ([Park et al., 2019](#)). Elastic strain is characterized by the difference between total strain and eigenstrain, represented as the stress-free strain ϵ^{kl*} . Additionally, the eigenstrain, representing the lattice strain misfit of each phase, is affected by composition ([Kamara et al., 1996](#)). However, this study focused on understanding the impact of elasticity on interfacial energy, so composition dependence was disregarded. Here, the misfit strain was solely dependent on the order parameter which is commonly used in elastic phase field simulations. The elastic strain ϵ_{el}^{ij} thus can be expressed as:

$$\epsilon_{el}^{ij} = \bar{\epsilon}^{ij} + \delta \epsilon_{el}^{ij} - \epsilon^{ij*} - \epsilon_{pl}^{ij} \quad (20)$$

Applied strain $\bar{\epsilon}^{ij}$ and local heterogeneous strain $\delta \epsilon_{el}^{ij}$ are together represented as ϵ_{tot}^{ij} . Also, plastic strain ϵ_{pl}^{ij} is not considered in this formulation.

$$\epsilon_{el}^{ij} = \epsilon_{tot}^{ij} - \epsilon^{ij*} \quad (21)$$

In this context, $\bar{\epsilon}^{ij}$ represents the applied strain, $\delta \epsilon_{el}^{ij}$ stands for the local heterogeneous strain, ϵ^{ij*} signifies the eigenstrain, and ϵ_{pl}^{ij} denotes the plastic strain. Only the eigenstrain resulting from disparities in the lattice parameters of the two phases is accounted for. Crystallographic misfit strain tensor ϵ^{ij*} between phases ϕ_1 , ϕ_2 and ϕ_3 and the total strain ϵ_{tot}^{ij} is calculated from the displacement fields u_j as in [Eshelby \(1957\)](#):

$$\epsilon_{tot}^{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (22)$$

$$\epsilon_{el}^{ij} = \epsilon_{tot}^{ij} - \sum_{\tau=1}^N h^\tau \epsilon^{ij*} \quad (23)$$

Consideration of equilibrium between phases ([Johnson, 1987](#)), interface continuity and no-slip resulted in $\Delta u_i = 0$. The total strain is assumed to be the same in all coexisting phases, $\Delta \epsilon^{ij} = 0$. However, each phase can have different transformation strains denoted as ϵ_i . For the interface, it is taken as a weighted average $\epsilon^* = \sum_{\tau} h^\tau \epsilon^{*\tau}$. This assumption is known as the Voigt–Taylor scheme (VTS), where total strains in each phase are equal, and stress and strain are determined separately in each phase to elastic free energies. On the other hand, the Reuss–Sachs model considers stress to be continuous and same across the phase interface such that $\Delta \sigma_{el}^{ij} = 0$. The Khachaturyan scheme (KHS) ([Khachaturyan, 2013](#)) was used in this work which applies a union of both VTS and Reuss–Sachs in such a way that stress and strains are computed together for deriving the elastic free energy. KHS models ensure kinematic compatibility at the interface by assuming equal total strains in both phases just like VTS [Chatterjee et al. \(2022\)](#), [Durga et al. \(2015\)](#). The global elasticity tensor in KHS model is obtained by interpolation of elasticity tensor and eigenstrain. And the global stiffness tensor (C_{KHS}^{ijkl}) global elastic strain (ϵ_{KHS}^{ij}) is given by ([Simon et al., 2020](#)):

$$C_{KHS}^{ijkl} = \sum_{\tau=1}^N h^\tau (C^{ijkl})^\tau \quad (24)$$

$$\epsilon_{KHS}^{ij} = \epsilon^{ij} - \sum_{\tau=1}^N h^\tau (\epsilon^{*ij})^\tau \quad (25)$$

Now from Eqs. (17) and (19), the elastic stress is uniform, and thus the elastic free energy density in terms of global stiffness tensor and strain is represented as:

$$f_{el}^{KHS} = \frac{1}{2} \epsilon_{KHS}^{ij} C_{KHS}^{ijkl} \epsilon_{KHS}^{kl} \quad (26)$$

3.2. Microstructure evolution kinetics

The phase evolution is explained by a set of two equations. The conserved composition variable (c), is governed by diffusion Eq. (27). Simultaneously, the evolution of phase is elucidated by the diffusion equation of the variational derivative of non-conserved order parameters as expressed in Eq. (28).

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \mathbf{M} \sum_{j=1}^{C-1} \nabla \left(\frac{\partial f_{bulk}}{\partial c_j} + \frac{\partial f_{el}}{\partial c_j} \right) \quad (27)$$

$$\frac{\partial \eta_\tau}{\partial t} = -L(\eta_{11}, \dots, \eta_N) \left(\frac{\partial f_{bulk}}{\partial \eta_\tau} + \frac{\partial f_{el}}{\partial \eta_\tau} + \frac{\partial f_o}{\partial \eta_\tau} - \nabla \cdot \frac{\partial f_{grad}}{\partial (\nabla \eta_\tau)} \right) \quad (28)$$

The time evolution of the phase field η is governed by the kinetic coefficient L , while atomic mobility M controls the kinetics of the composition field.

$$\mathbf{M} = \sum_{i=1}^{N_\phi} (M_o)_i \sum_{j=1}^{N_\chi} h_{ij} + \sum_{k=1}^{N_\phi} \sum_{l=1}^{N_\chi} M g b_{kl} h_{kl} \quad (29)$$

$L(\eta_{11}, \dots, \eta_N)$ is mathematically defined by the following expression:

$$L = \frac{\sum_{ij=1}^N \sum_{kl>ij} (L_{ij,kl} \eta_{ij}^2 \eta_{kl}^2)}{\sum_{ij=1}^N \sum_{kl>ij} \eta_{ij}^2 \eta_{kl}^2} \quad (30)$$

3.3. Phase field simulation setup

The numerical parameters are kept consistent across all elastic schemes to ensure that any variations in model predictions arise solely from differences in the elastic schemes. In this study, the predefined Jacobian-Free Newton–Krylov (PJFNK) solver which is a variant of the Newton–Raphson method is utilized. It employs a Krylov subspace

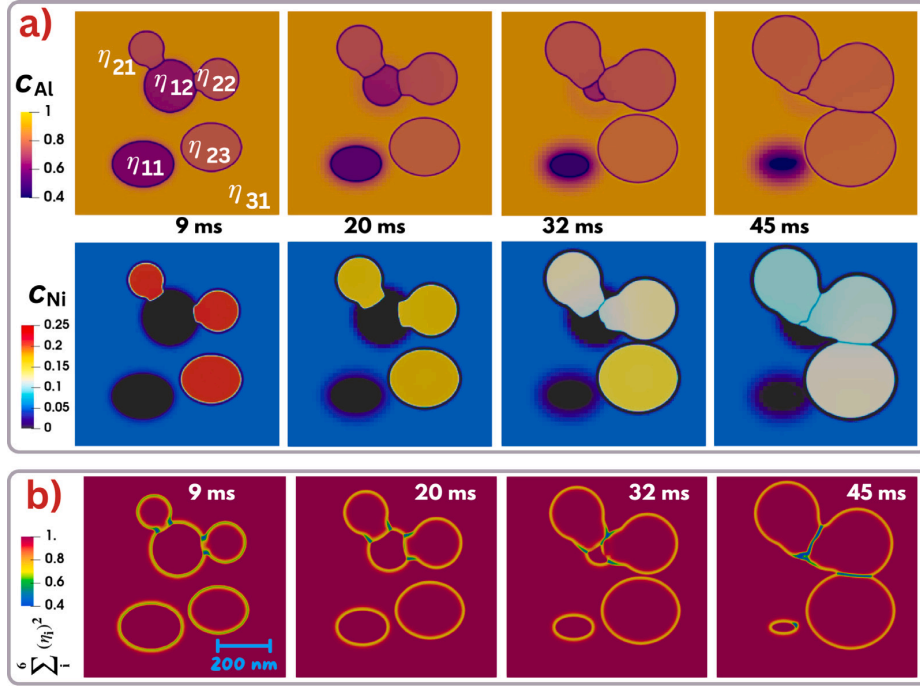


Fig. 2. Case I — Microstructure evolutions driven solely by diffusion: (a) Composition evolution across distinct phases ϕ_1 (AL2CU) and ϕ_2 (AL3NI) within the overarching Al-rich FCC matrix ϕ_3 . Initial Al compositions stand at 0.66 for ϕ_1 , 0.74 for ϕ_2 , and 0.9 for ϕ_3 , while the Ni compositions start at 0.01 for ϕ_1 , 0.25 for ϕ_2 , and 0.05 for ϕ_3 . The third element (Cu) undergoes evolution as a conserved parameter, tied to the compositions of the other two elements. (b) Grain evolution for 5 grains over the Al matrix. Scale bar magnitudes are denoted as 1.0 within grains/phases and are less than 1 at grain/phase boundaries.

Table 2

Phase-field simulation parameters including the corresponding expressions (when applicable) and their respective values employed in the simulations.

Parameters/ Properties	Values	Units	Ref.
Interface width (δ)	35×10^{-9}	m	
Grid space (Δx)	4.411×10^{-9}	m	$\delta \geq 6.65\Delta x$ (Moelans et al., 2008a)
Molar Volume (V_m)	10^{-5}	m^3/mol	Kaptay (2015)
Interfacial energy (σ)	0.5	J/m^2	Kunwar et al. (2020)
κ	13.125×10^{-9}	J/m	Eq. (15)
γ	1.5	—	Kunwar et al. (2022)
m	8.57×10^8	J/m^3	Eq. (15)
L	9.68×10^{-8}	$\text{m}^3/\text{J s}$	Eq. (15)
M_o	2.78×10^{-25}	$\text{m}^5/\text{J s}$	
M_{gb}	2.78×10^{-22}	$\text{m}^5/\text{J s}$	$1000 \times M_o$
T	723	K	

technique to approximate the impact of the Jacobian matrix on a vector, offering cost-effective computation. The simulations are executed with a nonlinear relative tolerance of 10^{-8} and a nonlinear absolute tolerance of 10^{-10} . The specified parameters include a maximum of 10 nonlinear iterations per solve and a maximum of 30 linear iterations. A computational domain with dimensions of 600 nm $\times$ 600 nm is employed unless the grain grows to encompass the entire domain. This domain size is chosen to minimize any significant influence of domain boundaries on the size and morphology of the precipitate. To optimize computational efficiency, adaptive meshing and adaptive time-stepping techniques are utilized, taking advantage of the system's inherent symmetry. Initially, the domain is meshed into elements measuring 34×34 , resulting in an element size of $dx = 17.647$ nm. Gradient jump indicators are applied to variables such as c , η , and three displacement variables (u_i) for determining mesh adaptivity. For adaptive meshing, a single element can be refined up to 2 levels, leading to the finest mesh section with elements of size $\Delta x = 4.411$ nm for precise curvature resolution at the surface, satisfying the condition $\delta \geq 6.65\Delta x$ (Moelans

Table 3

Phases and initial compositions (mole fraction) of the elements in simulations.

Component	ϕ_1 (AL2CU) (η_{11}, η_{12})	ϕ_2 (AL3NI) ($\eta_{21}, \eta_{22}, \eta_{23}$)	ϕ_3 (FCC) (η_{31})
Al	0.66	0.74	0.9
Ni	0.01	0.25	0.05
Cu	0.33	0.1	0.05

et al., 2008a). The phase field model was developed based on the parameters as tabulated in Table 2.

4. Results and discussions

The simulation system maintains a constant temperature and pressure while studying diffusion in alloys. It is characterized by conserved PF parameters (composition) and non-conserved PF fields (order parameter) that illustrate phase transformations. This model utilizes local compositions of Al and Ni, designated as c_{Al} and c_{Ni} , respectively, as conserved fields due to their constant elemental presence in the alloy system. The molar fraction of Cu, represented as c_{Cu} , is derived as a dependent variable: $c_{\text{Cu}} = 1 - c_{\text{Al}} - c_{\text{Ni}}$. Non-conserved order parameters, η_{11}, η_{12} for IMC AL2CU (ϕ_1), $\eta_{21}, \eta_{22}, \eta_{23}$ for IMC AL3NI (ϕ_2), η_{31} for FCC AL (ϕ_3), serve to indicate the local presence of these respective phases. Within the bulk phase regions, $\eta = 1$ within grains/phases, while the order parameters transition diffusely between 0 and 1 at the interface separating the two phases.

This study examines microstructural changes driven by diffusions alone, followed by investigating scenarios that consider the impact of elastic energy. Within the elastic energy scenario, the study highlights the contrast between evolutions based on 0 K elastic constants and those calibrated for the simulation temperature, emphasizing the notable differences observed between the two in subsequent sections.

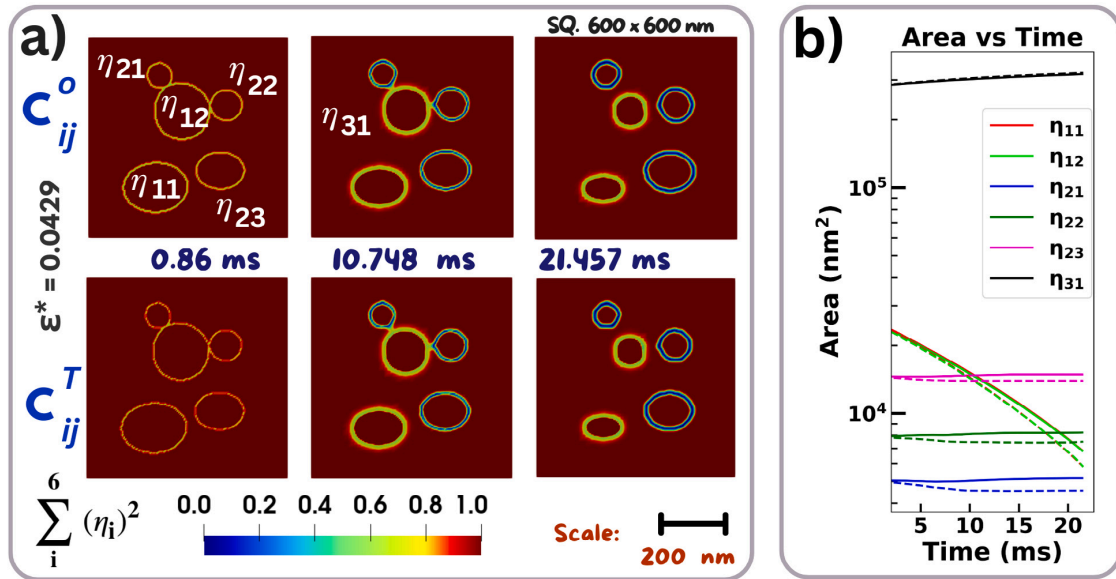


Fig. 3. Highlighting the necessity of incorporating temperature-calibrated elasticity coefficients in microstructure evolutions: (a) Evolution of order parameters with elastic constants at 0 K versus calibrated elastic constants at 723 K. (b) Visualizes the discrepancy in area evolution with dotted lines representing elastic constants at 0 K and solid lines for elastic constants at 723 K. The log-scale presentation emphasizes a substantial difference in area values over time, indicating a significant disparity. It is noteworthy that the area curves of two grains (η_{11}, η_{12}) within the AL2CU phase almost coincide in (b).

4.1. Case I: microstructure evolutions driven solely by diffusion ($\epsilon^* = 0$)

The evolution driven solely by diffusion obeys specific kinetics: Eq. (27) regulates composition changes, while Eq. (28) governs the phase field, excluding elastic free energy effects ($\partial f_{el} = 0$). Fig. 2(b) illustrates the temporal progression of phase evolution in the Al–Cu–Ni system. As time progresses, AL2CU (ϕ_1) contracts, forming a junction with the expanding phase where η_{12} is located. During a 45 ms interval, η_{12} grains dissolve into the enlarging AL3Ni (ϕ_2), while isolated η_{11} steadily decreases in size, taking on a more elliptical shape than its initial form. Simultaneously, Fig. 2(a) portrays the evolution of composition over time for c_{Al} and c_{Ni} . Initially, the compositions of Al stand at 0.66 for ϕ_1 , 0.74 for ϕ_2 , and 0.9 for ϕ_3 , whereas Ni compositions start at 0.01 for ϕ_1 , 0.25 for ϕ_2 , and 0.05 for ϕ_3 as illustrated in Table 3. In the diminishing AL2CU phase (ϕ_1), c_{Al} steadily decreases. Eventually, η_{12} dissolves into the surrounding ϕ_2 as the phase contracts. Similarly, within the Ni-dominant ϕ_2 , there is a slight reduction in c_{Ni} as the phase expands. Please note that significant changes are not visible in ϕ_1 and ϕ_3 as they were initially deficient in c_{Ni} . The detailed quantitative analysis of microstructure evolution for a solely diffusion-driven system is explained in Section 4.3.

4.2. Case II: Influence of elastic energy on microstructure evolution ($\epsilon^* \neq 0$)

The Influence of elastic energy on microstructure evolution is governed by Eq. (27) regulates composition changes, while Eq. (28) governs the phase field with ∂f_{el} from Eq. (26). The elastic energy in the microstructure is accounted for the dilatational eigenstrain generated from atomic clusters, defects, and micro-irregularities that develop residual stress fields (Vizoso et al., 2022). Representing inherent strain from lattice parameter discrepancies, eigenstrain significantly influences stress and composition within a simulated volume. In studying Al–Al₂Cu and Al–Al₃Ni phases, encompassing eigenstrain necessitates insights into their crystallographic structures and orientation relationships. However, complexities arise because of limited measurements of lattice spacings and orientations, and by including temperature-dependent variations, establishing a consistent dataset under simulation conditions is a challenge. In this context, Al–Al₃Ni (Sridhar et al.,

1997) offers a reference for considering mismatch strain, while the 3:2 interface configuration in Al–Cu alloys (Al–Al₂Cu) (Hu et al., 2006) showcases a stress-free strain of 0.0429. Thus, elastic energy in this study is accounted for mismatch strains uniform for all phases at values of 0.01, 0.0245, and 0.0429.

4.2.1. Significance of temperature-calibrated elasticity in phase evolutions

The implementation of temperature-dependent stiffness tensor considerations is fundamental in understanding how elastic energy influences the evolution of phases. In Fig. 3(a), we visually observe how microstructure evolution is impacted by temperature-calibrated elasticity. This observation is based on comparing the growth of areas using elastic constants at 0 K against those calibrated at 723 K, as depicted in Fig. 3(b). Here, the discrepancy in area evolution, stemming from elastic free energy calculated with the elastic constants at 0 K (illustrated as dotted lines), contrasts with the elastic free energy computed using elastic constants calibrated at 723 K (shown as solid lines).

In the initial phase of the simulation, both cases start with equal grain areas. However, as the simulation progresses toward 5 ms (5.03 ms for 0 K and 5.26 ms for 723 K), the deviation in grain area between the two cases of elastic constants for each η (ranging from 1 to 6) is observed. These deviations are initially moderate, with percentages ranging from 1.30%, 1.16%, 4.21%, 4.17%, 3.16%, 0.51%. By the time 21.45 ms is reached, these deviations amplify significantly, escalating to values such as 18.18%, 17.79%, 13.31%, 9.66%, 6.24%, and 1.35% for respective η , signifying a substantial deviation between the grain areas at these temperatures and time points. This observation highlights the trend of deviation in area growth of grain increases as the evolution proceeds for further simulation time. The significant variations in area values over time intervals highlight the impact of temperature-calibrated elasticity as time progresses. This discrepancy in the growth of grains emphasizes the necessity of incorporating temperature-calibrated elasticity in simulations to accurately comprehend how phases evolve. The results presented in this and subsequent sections are for temperature-calibrated elasticity.

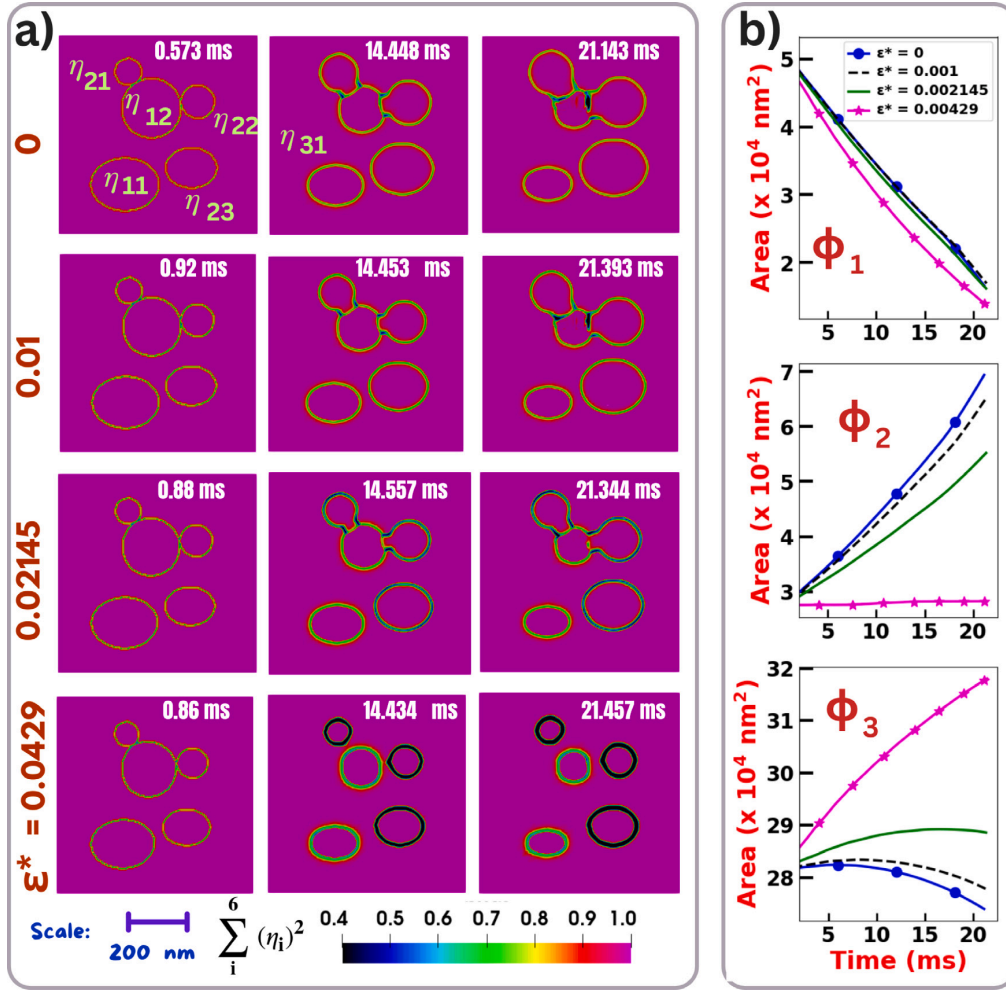


Fig. 4. Case II — Elastic loading and microstructural evolutions: (a) Displays phase transformations both without elastic loading and under sequential elastic loading, varying eigenstrains ($\epsilon^* = 0.01, 0.02145, 0.0429$). While evolution driven solely by diffusion tends to maintain spherical shapes, the influence of elastic energy not only alters grain size but also transforms shrinking grains into rectangular shapes, inducing extended necking in grains surrounded by others. (b) Illustrates the area evolution of η_{11} and η_{12} within ϕ_1 , and $\eta_{21}, \eta_{22}, \eta_{23}$ within ϕ_2 , alongside η_{31} in ϕ_3 . The plot delineates clear trends: absence of elastic loading for ϕ_1 accelerates reduction in area with the introduction of elastic loading. Conversely, in the growing phase ϕ_2 , elastic loading constrains area growth, almost halting at $\epsilon^* = 0.0429$. Simultaneously, the declining area for ϕ_3 with elastic loading begins to increase, influenced by elastic effects from the other two phases.

4.2.2. Elastic loading induced grain evolutions

The results presented in Fig. 4(a) provides an overview of the impacts of elastic loading on microstructural evolution. A comparison between phase transformations solely driven by diffusion ($\epsilon^* = 0$), maintaining spherical shapes within the phases, while slight necking occurs in expanding grains (η_{12}) bordered by shrinking grains (η_{21} and η_{22}). Notably, isolated grain η_{11} assumes a more elliptical shape, concomitant with a reduction in grain size. Sequential elastic loading (at $\epsilon^* = 0.01, 0.02145, 0.0429$) induces significant alterations. It not only modifies grain sizes but also transitions shrinking grains into rectangular shapes, prominently visible in η_{12} for $\epsilon^* = 0.01$ and 0.02145 . At higher ϵ^* values, shrinking grains (η_{11} and η_{12}) adopt square/rectangular shapes. Also, hindering substantial growth in the previously expanding grains (η_{21}, η_{22} and η_{23}).

Fig. 4(b) provides a clear demonstration of the influence of elastic loading on area evolution within specific phase grains (η_{11}, η_{12} in ϕ_1 ; $\eta_{21}, \eta_{22}, \eta_{23}$ in ϕ_2 ; and η_{31} in ϕ_3). In the presence of elastic loading, there is an accelerated reduction in area for ϕ_1 compared without elastic

effects. Conversely, elastic loading in the expanding phase ϕ_2 constrains area growth, nearly halting expansion at $\epsilon^* = 0.0429$. Simultaneously, the diminishing area for ϕ_3 under elastic loading begins to reverse, showing an increase influenced by elastic effects from the other two phases. These outcomes collectively emphasize the qualitative role of elastic loading in shaping microstructural changes. To rigorously quantify the influence of elastic loading, the forthcoming sections will introduce and elaborate on growth kinetics.

4.3. Growth kinetics in multi-phase microstructures and influence of elastic heterogeneity

In a diffusion-driven system, the evolution of the equivalent grain radius follows a parabolic dependence on time ($R \propto t^{0.5}$) (Guan and Moelans, 2015). However, when an elastic driving force is present, this relationship becomes more intricate. In this investigation, the grain area in an elastically loaded system is modeled with the following

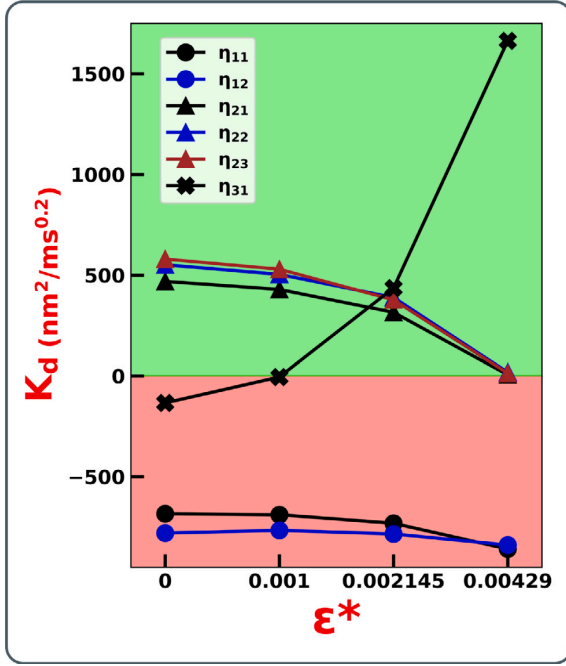


Fig. 5. Influence of elastic heterogeneity on growth kinetics. In phase AL2CU (η_{11} and η_{12}), the introduction of elastic energy results in a further reduction in growth rates. Conversely, AL3NI (η_{21} , η_{22} , and η_{23}) experiences notable constraints on growth rates and almost halting the growth process at higher elastic loading. These distinct effects on two phases are clearly observed in the FCC matrix (η_{31}).

time-dependent relations:

$$A_t = k_d \cdot t^{1/5} + k_e \cdot t + A_0 \quad (31)$$

Here, A_t represents the area at a given time t , and it is derived from the initial area A_0 and growth rate coefficients over time. The equation breaks down into two terms: the first term, $k_d \cdot t^{1/5}$, signifies the evolution of the area due to diffusion processes only. The second term, $k_e \cdot t$, represents the additional increment in area caused by the influence of elastic free energy. To clearly contemplate the growth phenomenon, the fitting is done with consideration of equal magnitudes for k_d and k_e .

The growth kinetics within multi-phase microstructures and the impact of elastic heterogeneity are illustrated in Fig. 5. The color variation in the plot serves to distinguish between positive and negative growth rates. In phase AL2CU, the absence of elastic energy yields highly negative growth rates (-780.56 for η_{11} and -684.75 for η_{12}). Upon introducing elastic loading, these rates further decrease to values -839.90 for η_{11} and -859.52 for η_{12} at $\epsilon^* = 0.0429$. Conversely, in the growing phase AL3NI, diffusion alone results in notably high growth rates (468.62 for η_{21} , 551.21 for η_{22} , and 579.63 for η_{23}). However, with the addition of elastic loading, growth becomes constrained, almost halting at $\epsilon^* = 0.0429$ with rates reduced to 5.42 for η_{21} , 17.77 for η_{22} , and 13.03 for η_{23} . These growth effects are distinctly observed in the FCC matrix. Without elastic loading, the area reduction is evident with a coefficient of $k_d = -134.15$. Sequential addition of elastic loading gradually shifts the rate toward positivity, culminating in a highly positive coefficient (1663.2) at $\epsilon^* = 0.0429$, indicating a sharp growth in the area.

4.4. Stress-patterns for elastic regimes with differing mismatch strain

Investigating stress patterns in different elastic scenarios under varying mismatch strains is crucial to understanding how elastic loading

affects phase grains. The 24 describes the distribution of stress due to elastic loading for the determination of local stress values and von Mises stress in phase grains obtained through simulations.

Fig. 6 shows how stresses evolve in the alloy. The highest normal stresses (σ_{11} and σ_{22}) occur within the grains because of the higher elastic constants in the IMC phases compared to the FCC matrix, as explained in Table 1. The von Mises stress

$\sigma_v = \sqrt{\frac{1}{2} [(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2] + 3(\sigma_{12}^2 + \sigma_{23}^2 + \sigma_{31}^2)}$ follows a similar trend. Plane strain criteria was implemented in the model which has nonzero out-of-plane stress. The conditions of $\sigma_{33} = \nu \cdot (\sigma_{11} + \sigma_{22})$ and equal shear stress i.e., $\sigma_{12} = \sigma_{23} = \sigma_{31}$ was followed in the general expression of σ_v . The shear stress (σ_{12}) is almost negligible in the case of only diffusion-driven but slightly increases at higher strain values.

For an applied eigenstrain of 0.01, the maximum $\sigma_v = 3.409$ GPa with stress component $\langle \sigma_{11}, \sigma_{12}, \sigma_{22} \rangle$ and strain component $\{ \epsilon_{11}, \epsilon_{12}, \epsilon_{22} \} = \langle 1.44, -1.033, 2.77 \rangle$ GPa, $\{ -0.022, -0.0074, -0.014 \}$ at 9.33 mS and $\sigma_v = 4.86$ GPa with $\langle 2.28, -2.44, 3.18 \rangle$ GPa, $\{ -0.018, -0.0177, -0.0124 \}$. Similarly, at slightly higher value of $\epsilon^* = 0.02149$, the maximum von Mises stress along with normal stress increases while there is reduction in magnitude of shear stress with $\sigma_v = 7.47$ GPa with components $\langle 1.93, -1.41, 6.3 \rangle$ GPa, $\{ -0.054, -0.01, -0.026 \}$ at 9.18 mS. And at 21.34 mS, $\sigma_v = 9.45$ GPa characterized by stress components $\langle 4.15, -4.38, 6.11 \rangle$ GPa and corresponding strain components of $\{ -0.042, -0.031, -0.031 \}$. Increasing normal eigenstrain correlates with heightened normal, shear and von Mises stresses, revealing how mismatch strain intricately shapes stress distributions in the alloy system. This is clearly visible for $\epsilon^* = 0.0429$ where maximum $\sigma_v = 15.03$ GPa at 9.148 mS with stress and strain component of $\langle 3.92, -2.96, 12.81 \rangle$ GPa and $\{ -0.108, -0.021, -0.051 \}$. The von-mises slightly reduced to 14.36 GPa at end of simulation with $\langle 3.68, -1.47, 4.34 \rangle$ GPa and $\{ -0.093, -0.01, -0.092 \}$ components.

5. Conclusions

This research explores the evolution of AL2CU and AL3NI IMC phases within an Al-rich FCC matrix. Employing Ab Initio Simulation, temperature-dependent elastic constants were determined, highlighting the critical significance of understanding temperature-calibrated elasticity. Initially, both simulations start with equal grain areas. As time progresses close to 5 ms, the deviation in grain area between 0 K elasticity and temperature-calibrated elasticity for each η ranges from 0.51% to 4.21%, showing moderate differences. However, at 21.45 ms, these deviations escalate significantly, reaching values as high as 18.18% for AL2CU and 13.31% for AL3NI indicating substantial divergence in grain areas between the different sets of elastic constants at this later time point. Variations in area values over time underscored the need for temperature-calibrated elasticity in accurately simulating elastochemical phase evolution. The study further examines microstructure evolutions driven solely by diffusion ($\epsilon^* = 0$) and those affected by elastic loading, exploring diverse mismatch strain values ($\epsilon^* = 0.01, 0.02145, 0.0429$) to gauge the impact of elastic energy on microstructure evolution. These findings emphasize elastic loading's qualitative role in shaping microstructural changes, setting the stage for quantifying its influence through growth kinetics.

The quantitative analyses from numerical simulations and mathematical models explained the influence of elastic loading on growth rates, stress levels, and microstructural evolution. This study underscores the crucial importance of employing temperature-calibrated stiffness values to incorporate elastic free energy accurately in elastochemical phase evolution. These methodologies provide invaluable pathways for optimizing alloy design and structural materials, offering significant implications for a wide array of scientific and industrial applications.

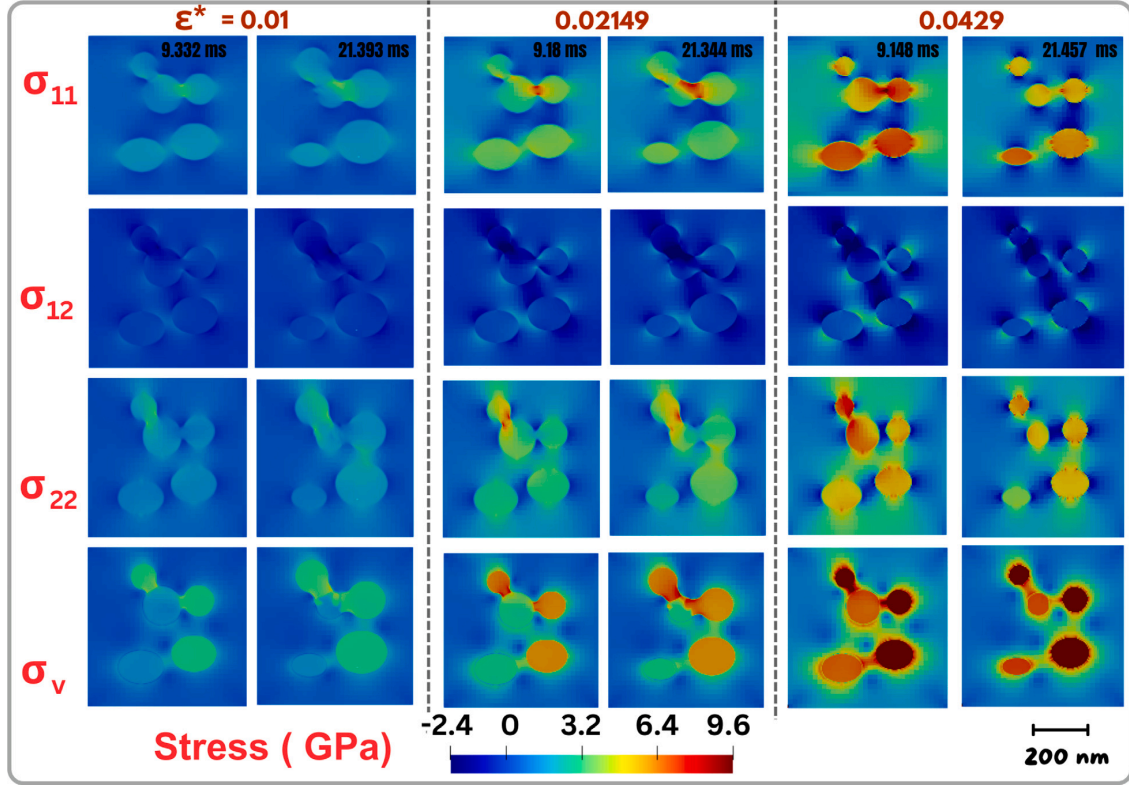


Fig. 6. Illustration of stress evolution within the alloy under varying elastic regimes and mismatch strains. The plot showcases the distribution of normal stresses (σ_{11} and σ_{22}), von Mises stress (σ_v), and shear stress (σ_{12}) across different phases. The higher stresses within phase grains due to elastic loading reflect the influence of mismatch strains on stress distributions in the alloy system. The unit of stress in GPa.

CRediT authorship contribution statement

Sachin Poudel: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nele Moelans:** Writing – review & editing, Validation, Methodology, Formal analysis. **Rubi Thapa:** Writing – review & editing, Visualization, Validation, Software, Formal analysis. **Anna Timofiejczuk:** Writing – review & editing, Validation, Supervision, Methodology. **Dhruba Panthi:** Writing – review & editing, Validation, Formal analysis. **Anil Kunwar:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data and analytic code for this study are available in https://github.com/Sachinscpdl/Al-Cu-Ni_dft_pf.

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Appendix A. Theoretical insights to DFT

A.1. Background of DFT

Density-Functional Theory (DFT) is a theoretical framework used to investigate the electronic structure of atoms, molecules, and solids, based on the adiabatic approximation that separates electronic and nuclear dynamics due to the substantial difference in mass. The many-body Schrödinger equation describes the Al-Cr-Ni system's quantum mechanical properties :

$$\hat{H}\psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_{el}}) = E\psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_{el}}) \quad (\text{A.1})$$

Here, $\hat{H}$ is the Hamiltonian operator, ψ is the electronic wavefunction, and E is the total energy. $\hat{H}$ is defined as:

$$\hat{H} = -\sum_{i=1}^{N_{el}} \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i=1}^{N_{el}} V_{\text{ext}}(\mathbf{r}_i) + \frac{e^2}{8\pi\epsilon_0} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (\text{A.2})$$

Here, $\hbar$ is the reduced Planck constant, m is the electron mass, ∇_i represents the gradient, $V_{\text{ext}}(\mathbf{r}_i)$ is the external potential, e is the elementary charge, and ϵ_0 is the vacuum permittivity.

Hohenberg and Kohn (1964), established a direct link between the ground-state electronic density $\rho(r)$ and the external potential $V_{\text{ext}}(r)$. This correspondence allows the expression of physical properties, particularly the total ground state energy, as functionals of the charge density. The total ground state energy is the expectation value of the Hamiltonian on the ground state $|\Psi_0\rangle$, and it is expressed as a functional of the electronic density.

$$E[\rho(\mathbf{r})] = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = F[\rho(\mathbf{r})] + \int_V V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) d^3r \quad (\text{A.3})$$

The functional $F[\rho(r)]$ encompasses both the kinetic energy and the electronic Coulomb energies and is considered a universal functional, meaning it is independent of V_{ext} and often of unknown form. The integral spans the entire system volume V . The ground-state total energy is determined by minimizing $E[\rho(r)]$ while keeping the number of electrons N_{el} fixed as a constraint.

$$\int_V \rho(\mathbf{r}) d^3r = N_{\text{el}} \quad (\text{A.4})$$

Kohn and Sham (1965) introduced a suitable form of $F[\rho(r)]$ by introducing an auxiliary system of non-interacting electrons with the same ground-state electron density as the interacting system. If we denote $|\psi_i(\mathbf{r})\rangle$ as the single-particle wavefunctions of the non-interacting electrons, which are normalized as:

$$\langle \psi_i(\mathbf{r}) | \psi_j(\mathbf{r}) \rangle = \delta_{ij} \quad (\text{A.5})$$

The electronic density is then expressed as:

$$\rho(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 \quad (\text{A.6})$$

Here, $\rho(\mathbf{r})$ represents the electron density at position $\mathbf{r}$, f_i is the occupation factor for state i , and $|\psi_i(\mathbf{r})|^2$ is the magnitude squared of the single-particle wavefunction $\psi_i(\mathbf{r})$ for the non-interacting electrons. The kinetic energy of non-interacting electrons is written as:

$$T_0 = \sum_i \frac{1}{2} f_i \langle \psi_i(\mathbf{r}) | -\nabla^2 | \psi_i(\mathbf{r}) \rangle \quad (\text{A.7})$$

The Hartree term, representing classical electron–electron interactions, is defined as:

$$E_H = \frac{1}{2} \iint_V \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (\text{A.8})$$

The functional $F[\rho(r)]$ in DFT incorporates these components and the exchange–correlation energy $E_{xc}[\rho(r)]$, which accounts for many-body interactions:

$$F[\rho(r)] = T_0 + E_H + E_{xc}[\rho(r)] \quad (\text{A.9})$$

This leads to the expression of the total energy as:

$$E[\rho(r)] = T_0[\rho(r)] + E_H[\rho(r)] + E_{xc}[\rho(r)] + E_{\text{ext}}[\rho(r)] \quad (\text{A.10})$$

Where E_{ext} is the integral of the external potential, defined as:

$$E_{\text{ext}} = \int_V V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d^3r = \sum_i f_i \langle \psi_i(\mathbf{r}) | V_{\text{ext}} | \psi_i(\mathbf{r}) \rangle \quad (\text{A.11})$$

The electronic wavefunctions are normalized, allowing the minimization of the total energy using the Lagrange multiplier technique, leading to the Kohn–Sham equations:

$$\left(-\frac{1}{2} \nabla^2 + V_{KS}(r) \right) |\psi_i(r)\rangle = \epsilon_i |\psi_i(r)\rangle \quad (\text{A.12})$$

Here, V_{KS} represents the Kohn–Sham potential, a self-consistent mean-field potential that accounts for the external potential of the ions, the Hartree potential V_H , and V_{xc} is the exchange–correlation potential representing the functional derivative of the exchange–correlation energy with respect to electronic density and is defined as :

$$V_{KS}(r) = V_{\text{ext}}(r) + V_H(r) + V_{xc}(r) \quad (\text{A.13})$$

$$V_H(r) = \int_V \frac{\rho(r_0)}{|r - r_0|} d^3r_0 \quad (\text{A.14})$$

$$V_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho} \quad (\text{A.15})$$

The specific form of E_{xc} is typically unknown and requires approximation. One commonly used approach is the local density approximation (LDA), while another is the generalized gradient approximation (GGA). In this work, Al_3Ni is modeled using the LDA, while Al and Al_2Cu utilizes the PBE (Perdew, Burke, Ernzerhof) GGA (Generalized Gradient Approximation) functional.

A.2. Thermal effects and smearing

In the context DFT for metals (e.g. Aluminum), the occupation factors in Eq. (A.6) $f_i \rightarrow f_{kv}$ and is defined as:

$$f_{kv} = \theta(\epsilon_F - \epsilon_{kv}) \quad (\text{A.16})$$

Here, f_{kv} represents the occupation of electronic states, where ϵ_{kv} are eigenvalues, and ϵ_F is the Fermi energy. Here, θ is a step function that equals 0 if the eigenvalues ϵ_{kv} are larger than the Fermi energy ϵ_F and 1 otherwise. This means that only the occupied states are considered. The Fermi energy ϵ_F can be determined by the condition:

$$2 \sum_{kv} \theta(\epsilon_F - \epsilon_{kv}) = N N_{\text{el}} \quad (\text{A.17})$$

Where N represents the total number of unit cells in the solid Al crystal. This step function approach can lead to numerical instability when eigenvalues near ϵ_F fluctuate during iterative calculations. To address this issue, a smeared function with a parameter σ is introduced. A common choice is the Fermi–Dirac distribution:

$$f_{kv} = \frac{1}{2} \left[1 + \text{erf} \left(\frac{\epsilon_{kv} - \epsilon_F}{\sigma} \right) \right] \quad (\text{A.18})$$

The parameter σ is related to the electronic temperature of Al, Al_2Cu , and Al_3Ni resulting in a temperature-dependent charge density.

Incorporating thermal electronic effects, Mermin's extension to DFT (Mermin, 1965) minimizes the Helmholtz free energy $U - TS_{\text{el}}$, where U and S_{el} are computed with Fermi–Dirac occupations at temperature T . This requires self-consistency for each T . The auxiliary electronic free energy F_{el} at temperature T is defined as:

$$F_{\text{el}}(T) = U_{\text{el}} - TS_{\text{el}} \quad (\text{A.19})$$

The parameter $\sigma_{FD} = k_B T$ is associated with the physical broadening at temperature T . Using small Methfessel–Paxton smearing (Methfessel and Paxton, 1989), U is computed to approximate $T = 0\text{ K}$ DFT bands and determine electronic thermal contributions (F_{el}):

$$U_{\text{el}} = \int_{-\infty}^{+\infty} E N(E) f dE - \int_{E_F}^{-\infty} E N(E) dE \quad (\text{A.20})$$

In Eq. (A.20), $f(E, \mu, T)$ represents the Fermi–Dirac occupation, $N(E)$ is the electronic density of states, E_F is the Fermi energy, and μ adjusts for the number of electrons per unit cell (N_{el}). Electronic entropy (S_{el}) is expressed as:

$$S_{\text{el}} = -k_B \int_{-\infty}^{+\infty} [f \ln f + (1 - f) \ln(1 - f)] N(E) dE \quad (\text{A.21})$$

Here, $f(E, \mu, T)$, $N(E)$, and E_F are defined as previously mentioned. The chemical potential μ is determined for each temperature to ensure that the number of electrons per unit cell (N_{el}) satisfies:

$$N_{\text{el}} = \int_{-\infty}^{+\infty} N(E) f(E, T, \mu) dE \quad (\text{A.22})$$

For all the three crystalline structures (Al, Al_2Cu , or Al_3Ni) used in this study, Methfessel–Paxton first-order spreading with a degauss value of 0.02 was applied, offering a spread in electron energies instead of precise levels.

Appendix B. Elastic stability criteria

The Born stability criterion is a key theory in crystal mechanics, revealing insights into the mechanical strength of crystal structures. Analyzing it under normal pressure, fundamental stability criteria for various crystal structures have been unveiled. These criteria, developed for different crystal systems were used for higher temperature elastic constant computations (Mouhat and Coudert, 2014). Liu et al. established a significant connection between these criteria and corresponding Laue classes (Liu et al., 2017). The study encompassed elasticity and positive-definite conditions in various Quasicrystals (QCs). For 1D QCs (Laue

Table B.1

Overview of crystal structures with international space group numbers (SG). It encompasses Born's stability criteria, which illuminate the stability of each structure. Lattice parameters provide insights into their dimensions and orientations. # C_{ij} represents the number of independent second-order elasticity constants. The structural stiffness tensor outlines the behaviors of the crystalline systems with the dot (.) representing zero value. It is to be noted that the phases in our study, namely Al-rich matrix, AL2CU, and AL3NI have cubic, tetragonal-I and orthorhombic structures respectively.

Crystal structure	Born stability criteria	Lattice parameters	# C_{ij}	Stiffness tensor representations
Cubic* SG: 195-230	$C_{11} > 0, C_{44} > 0,$ $C_{11} > C_{12} ,$ $C_{11} + 2C_{12} > 0.$	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	3	$\begin{pmatrix} C_{11} & C_{12} & C_{12} & . & . & . \\ C_{12} & C_{11} & C_{12} & . & . & . \\ C_{12} & C_{12} & C_{11} & . & . & . \\ . & . & . & C_{44} & . & . \\ . & . & . & . & C_{44} & . \\ . & . & . & . & . & C_{44} \end{pmatrix}$
Hexagonal SG: 168-194	$C_{11} > 0, C_{33} > 0,$ $C_{44} > 0, C_{66} > 0,$ $C_{11} > C_{12} ,$ $2C_{13}^2 < C_{33}(C_{11} + C_{12}).$ For Hex: $C_{66} = (C_{11} - C_{12})/2$	$a = b \neq c$ $\alpha = \beta = 90^\circ,$ $\gamma_{hex} = 120^\circ$ $\gamma_{tet-I} = 90^\circ$	5	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & . & . & . \\ C_{12} & C_{11} & C_{13} & . & . & . \\ C_{13} & C_{12} & C_{33} & . & . & . \\ . & . & . & C_{44} & . & . \\ . & . & . & . & C_{44} & . \\ . & . & . & . & . & C_{66} \end{pmatrix}$
Tetragonal I* (4 mm, $\bar{4}2m$, 422, 4/mmm) SG: 89-142	$C_{11} > 0, C_{33} > 0,$ $C_{44} > 0, C_{66} > 0,$ $C_{11} > C_{12} ,$ $2C_{13}^2 < C_{33}(C_{11} + C_{12}),$ $2C_{16}^2 < C_{66}(C_{11} - C_{12}).$	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	7	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & . & . & C_{16} \\ C_{12} & C_{11} & C_{13} & . & . & -C_{16} \\ C_{13} & C_{12} & C_{33} & . & . & . \\ . & . & . & C_{44} & . & . \\ . & . & . & . & C_{44} & . \\ C_{16} & -C_{16} & . & . & . & C_{66} \end{pmatrix}$
Trigonal I (32, 3 m, $\bar{3}m$) SG: 149-167	$C_{11} > 0, C_{44} > 0, C_{66} > 0,$ $C_{11} > C_{12} ,$ $C_{13}^2 < \frac{1}{2}C_{33}(C_{11} + C_{12}),$ $C_{14}^2 < \frac{1}{2}C_{44}(C_{11} - C_{12}) \equiv C_{44}C_{66}.$	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	6	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & . & . \\ C_{12} & C_{11} & C_{13} & -C_{14} & . & . \\ C_{13} & C_{13} & C_{33} & . & . & . \\ C_{14} & -C_{14} & . & C_{44} & . & . \\ . & . & . & . & C_{44} & C_{14} \\ . & . & . & . & . & C_{66} \end{pmatrix}$
Trigonal II (3, $\bar{3}$) SG: 143-148	$C_{11} > 0, C_{44} > 0, C_{66} > 0,$ $C_{11} > C_{12} ,$ $C_{13}^2 < \frac{1}{2}C_{33}(C_{11} + C_{12}),$ $C_{14}^2 + C_{15}^2 < \frac{1}{2}C_{44}(C_{11} - C_{12}) \equiv C_{44}C_{66}.$	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	7	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & . \\ C_{12} & C_{11} & C_{13} & -C_{14} & -C_{15} & . \\ C_{13} & C_{13} & C_{33} & . & . & . \\ C_{14} & -C_{14} & . & C_{44} & . & -C_{15} \\ C_{14} & -C_{15} & . & . & C_{44} & C_{14} \\ . & . & . & . & . & C_{66} \end{pmatrix}$
Orthorhombic* SG: 16-74	$C_{11} > 0, C_{22} > 0, C_{33} > 0,$ $C_{44} > 0, C_{55} > 0, C_{66} > 0,$ $C_{11}C_{22} > C_{12}^2,$ $C_{11}C_{23}C_{33} + 2C_{12}C_{13}C_{23}$ $-C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0.$	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	9	$\begin{pmatrix} C_{11} & C_{12} & C_{13} & . & . & . \\ C_{12} & C_{22} & C_{23} & . & . & . \\ C_{13} & C_{23} & C_{33} & . & . & . \\ . & . & . & C_{44} & . & . \\ . & . & . & . & C_{55} & . \\ . & . & . & . & . & C_{66} \end{pmatrix}$

4–10), these criteria naturally align with the classes, relating stability to periodicity. Likewise, in 2D QCs with periodic symmetry (Lau 6, 8–10), the interplay of elasticity and positive-definite conditions aligns with spatial symmetry, closely linking stability with these classes. This analysis extends to Cubic 3D QCs, where positive-definite conditions emphasize the stability-cubic symmetry relationship. The study delves into aperiodic symmetry in 2D and 3D QCs, detailing point groups and classifying 1D and 3D QCs, enhancing elastic stability considerations.

Appendix C. Bulk free energy in meso-scale simulation

The molar Gibbs free energy (G_m), measured in J/mol, pertains to three distinct phases. For the ternary Al–Cu–Ni system, the mole fraction of any two constituent components can completely represent the global composition. For example, c_{Al} and c_{Cu} can totally depict the composition information of ternary Al–Cu–Ni system. Then, c_{Al}^r and c_{Cu}^r can sufficiently represent the composition description of τ^{th} phase. Thus the composition dependence G_m^r can be assumed to be a paraboloid, and expressed in the following way:

$$G_\tau^m = A^\tau (c_{Al}^\tau - c_{Al}^{\tau_{eq}})^2 + B^\tau (c_{Cu}^\tau - c_{Cu}^{\tau_{eq}})^2 + C^\tau \quad (C.1)$$

The fitted coefficients A^τ , B^τ , and C^τ in Table C.1 were selected to ensure good agreement between the equilibrium compositions and those obtained from the phase diagram calculated with the Al-rich FCC and AL2CU phase (Ansara et al., 1998) database and AL3NI (Ansara et al., 1997). These coefficients are utilized to construct the paraboloid

Table C.1

Coefficients for fitted polynomial Gibbs free energy curve.

Phase	A^τ	B^τ	C^τ
FCC	30	36	−48.64
Al2Cu IMC	48	45	−28.95
Al3Ni IMC	49	50	−66.05

Gibbs free energy curve for the FCC and IMC phases of the Al–Cu–Ni system at a temperature of $T = 723$ K.

For a N-order parameter and C-component model the $\frac{\partial f_{bulk}}{\partial \eta_\tau}$ is expanded as (Bognarova et al., 2023):

$$\frac{\partial f_{bulk}}{\partial \eta_\tau} = \sum_{j=1}^N \frac{\partial h_j(\eta_1, \dots, \eta_N)}{\partial \eta_\tau} f_j + \sum_{i=1}^{C-1} \left(\frac{\partial f_1}{\partial x_{i,1}} \sum_{j=1}^N \frac{\partial h_j(\eta_1, \dots, \eta_N)}{\partial \eta_\tau} x_{i,j} \right) \quad (C.2)$$

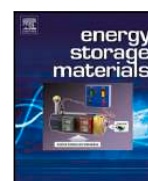
References

- Ainsworth, M., Mao, Z., 2019. Phase field crystal based prediction of temperature and density dependence of elastic constants through a structural phase transition. *Phys. Rev. B* 100 (10), 104101.
- Ansara, I., Dinsdale, A., Rand, M., 1998. Al-Mg COST 507 thermochemical database for light metal alloys. Off. Off. Publ. Eur. Communities.
- Ansara, I., Dupin, N., Lukas, H.L., Sundman, B., 1997. Thermodynamic assessment of the Al-Ni system. *J. Alloys Compd.* 247 (1–2), 20–30.

- Aravind, M., Yu, P., Yau, M.Y., Ng, D.H., 2004. Formation of Al₂Cu and AlCu intermetallics in Al (Cu) alloy matrix composites by reaction sintering. *Mater. Sci. Eng. A* 380 (1–2), 384–393.
- Bai, Q., Zhang, C., Tan, F., Zhang, Z., 2022. High-performance, low-cost nanoporous alloy actuators by one-step dealloying of Al-Ni-Cu precursors. *Intermetallics* 145, 107537.
- Balasubramanian, K., Manna, S., Sankaranarayanan, S.K., 2023. Elastemp—A workflow to compute the quasi-harmonic temperature dependent elastic constants of materials. *Comput. Mater. Sci.* 226, 112223.
- Bognarova, X., Jiang, W., Schwen, D., Tonks, M.R., 2023. A comparative study of two numerical approaches for solving Kim–Kim–Suzuki phase-field models. *Comput. Mater. Sci.* 229, 112375.
- Born, M., 1940. On the stability of crystal lattices. I. In: *Mathematical Proceedings of the Cambridge Philosophical Society*, vol. 36. Cambridge University Press, pp. 160–172.
- Chatterjee, S., Schwen, D., Moelans, N., 2022. An efficient and quantitative phase-field model for elastically heterogeneous two-phase solids based on a partial rank-one homogenization scheme. *Int. J. Solids Struct.* 250, 111709.
- Cui, L., Zhang, Z., Chen, X.-G., 2023. Development of lightweight Al-based entropy alloys for elevated temperature applications. *J. Alloys Compd.* 938, 168619.
- Dal Corso, A., 2014. Pseudopotentials periodic table: From H to Pu. *Comput. Mater. Sci.* 95, 337–350.
- Dal Corso, A., 2017. *Thermo_pw*. https://dalcorso.github.io/thermo_pw. (Accessed 30 August 2023).
- Durga, A., Wollants, P., Moelans, N., 2015. A quantitative phase-field model for two-phase elastically inhomogeneous systems. *Comput. Mater. Sci.* 99, 81–95.
- Durga, A., Wollants, P., Moelans, N., 2020. Phase-field study of IMC growth in Sn–Cu/Cu solder joints including elastoplastic effects. *Acta Mater.* 188, 241–258.
- Eshelby, J.D., 1957. The determination of the elastic field of an ellipsoidal inclusion, and related problems. *Proc. R. Soc. Lond. Ser. A Math. Phys. Sci.* 241 (1226), 376–396.
- Feyen, V., Moelans, N., 2023. Quantitative high driving force phase-field model for multi-grain structures. *Acta Mater.* 119087.
- Fribourg-Blanc, N., Dupoux, M., Guenin, G., Bonnet, R., 1979. Détermination par extensométrie et mesures ultrasonores des six constantes élastiques du cristal Al₂Cu (γ). *Discussion de l'anisotropie. J. Appl. Crystallogr.* 12 (2), 151–155.
- Gao, Y., Liu, H., Shi, R., Zhou, N., Xu, Z., Zhu, Y., Nie, J.F., Wang, Y., 2012. Simulation study of precipitation in an Mg–Y–Nd alloy. *Acta Mater.* 60 (12), 4819–4832.
- Gillan, M., Alfe, D., Brodholt, J., Vočadlo, L., Price, G., 2006. First-principles modelling of earth and planetary materials at high pressures and temperatures. *Reports on progress in physics* 69 (8), 2365.
- Guan, Y., Moelans, N., 2015. Influence of the solubility range of intermetallic compounds on their growth behavior in hetero-junctions. *J. Alloys Compd.* 635, 289–299.
- Hektor, J., Ristinmaa, M., Hallberg, H., Hall, S.A., Iyengar, S., 2016. Coupled diffusion-deformation multiphase field model for elastoplastic materials applied to the growth of Cu₆Sn₅. *Acta Mater.* 108, 98–109.
- Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. *Phys. Rev.* 136 (3B), B864.
- Hou, W., Shen, Z., Huda, N., Oheil, M., Shen, Y., Jahed, H., Gerlich, A.P., 2021. Enhancing metallurgical and mechanical properties of friction stir butt welded joints of Al–Cu via cold sprayed Ni interlayer. *Mater. Sci. Eng. A* 809, 140992.
- Hu, S., Baskes, M., Stan, M., Chen, L., 2006. Atomistic of interfacial energies, nucleus shape and size of θ' precipitates in Al–Cu alloys. *Acta Mater.* 54 (18), 4699–4707.
- Ji, Y., Issa, A., Heo, T., Saal, J., Wolverton, C., Chen, L.-Q., 2014. Predicting θ' precipitate morphology and evolution in Mg–RE alloys using a combination of first-principles calculations and phase-field modeling. *Acta Mater.* 76, 259–271.
- Johnson, W.C., 1987. Precipitate shape evolution under applied stress—thermodynamics and kinetics. *Metall. Mater. Trans. A* 18, 233–247.
- Jokisaari, A.M., Naghavi, S.S., Wolverton, C., Voorhees, P.W., Heinonen, O.G., 2017. Predicting the morphologies of γ precipitates in cobalt-based superalloys. *Acta Mater.* 141, 273–284.
- Kamara, A., Ardell, A., Wagner, C., 1996. Lattice misfits in four binary Ni-base γ/γ' 1 alloys at ambient and elevated temperatures. *Metall. Mater. Trans. A* 27, 2888–2896.
- Kaptay, G., 2015. Approximated equations for molar volumes of pure solid fcc metals and their liquids from zero Kelvin to above their melting points at standard pressure. *J. Mater. Sci.* 50, 678–687.
- Khachatryan, A.G., 2013. *Theory of structural transformations in solids*. Courier Corporation.
- Kim, S.G., Kim, W.T., Suzuki, T., 1999. Phase-field model for binary alloys. *Phys. Rev. E* 60 (6), 7186.
- Kim, S.G., Kim, W.T., Suzuki, T., Ode, M., 2004. Phase-field modeling of eutectic solidification. *J. Cryst. Growth* 261 (1), 135–158.
- Kohn, W., Sham, L.J., 1965. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* 140 (4A), A1133.
- Kundin, J., Pogorelov, E., Emmerich, H., 2015. Phase-field modeling of the microstructure evolution and heterogeneous nucleation in solidifying ternary Al–Cu–Ni alloys. *Acta Mater.* 83, 448–459.
- Kundin, J., Steinbach, I., 2020. Quantum-phase-field: from de broglie-bohm double-solution program to doublon networks. *Zeitschrift für Naturforschung A* 75 (2), 155–170.
- Kundin, J., Wang, P., Emmerich, H., Schmid-Fetzer, R., 2014. Investigation of Al–Cu–Ni alloy solidification: thermodynamics, experiments and phase-field modeling. *Eur. Phys. J. Spec. Top.* 223 (3), 567–590.
- Kunwar, A., Coutinho, Y.A., Hektor, J., Ma, H., Moelans, N., 2020. Integration of machine learning with phase field method to model the electromigration induced Cu₆Sn₅ IMC growth at anode side Cu/Sn interface. *J. Mater. Sci. Technol.* 59, 203–219.
- Kunwar, A., Yousefi, E., Zuo, X., Sun, Y., Seveno, D., Guo, M., Moelans, N., 2022. Multi-phase field simulation of Al₃Ni₂ intermetallic growth at liquid Al/solid Ni interface using MD computed interfacial energies. *Int. J. Mech. Sci.* 215, 106930.
- Li, X., Thornton, K., Nie, Q., Voorhees, P., Lowengrub, J.S., 2004. Two-and three-dimensional equilibrium morphology of a misfitting particle and the Gibbs–Thomson effect. *Acta Mater.* 52 (20), 5829–5843.
- Liu, Z., Li, H., Fan, C., Luo, W., 2017. Necessary and sufficient elastic stability conditions in 21 quasicrystal laue classes. *Eur. J. Mech. A Solids* 65, 30–39.
- Liu, C., Roters, F., Raabe, D., 2023. Finite strain crystal plasticity-phase field modeling of twin, dislocation, and grain boundary interaction in hexagonal materials. *Acta Mater.* 242, 118444.
- Luo, L., Shan, Z., Yang, H., Su, Y., Luo, L., Wang, L., Guo, J., Fu, H., 2022. Optimizing Ni-rich intermetallic and mechanical properties at room and elevated temperatures for Al–Cu–Ni alloys by coupling travelling magnetic fields with sequential solidification. *J. Alloys Compd.* 921, 166069.
- Malica, C., Dal Corso, A., 2020. Quasi-harmonic temperature dependent elastic constants: applications to silicon, aluminum, and silver. *J. Phys.: Condens. Matter.* 32 (31), 315902.
- Malica, C., et al., 2021. From ab-initio thermodynamics to quasi-harmonic thermoelastic properties of crystals: A new workflow and selected applications. *SISSA*.
- Mermin, N.D., 1965. Thermal properties of the inhomogeneous electron gas. *Phys. Rev.* 137 (5A), A1441.
- Methfessel, M., Paxton, A., 1989. High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B* 40 (6), 3616.
- Moelans, N., 2011. A quantitative and thermodynamically consistent phase-field interpolation function for multi-phase systems. *Acta Mater.* 59 (3), 1077–1086.
- Moelans, N., Blanpain, B., Wollants, P., 2008a. Quantitative analysis of grain boundary properties in a generalized phase field model for grain growth in anisotropic systems. *Phys. Rev. B* 78 (2), 024113.
- Moelans, N., Blanpain, B., Wollants, P., 2008b. An introduction to phase-field modeling of microstructure evolution. *CALPHAD* 32 (2), 268–294.
- Mouhat, F., Coudert, F.-X., 2014. Necessary and sufficient elastic stability conditions in various crystal systems. *Phys. Rev. B* 90 (22), 224104.
- Osório, W.R., Peixoto, L.C., Canté, M.V., Garcia, A., 2010. Microstructure features affecting mechanical properties and corrosion behavior of a hypoeutectic Al–Ni alloy. *Mater. Des.* 31 (9), 4485–4489.
- Palumbo, M., Dal Corso, A., 2017. Lattice dynamics and thermophysical properties of hcp Os and Ru from the quasi-harmonic approximation. *J. Phys.: Condens. Matter.* 29 (39), 395401.
- Park, J., Kamachali, R.D., Kim, S.-D., Kim, S.-H., Oh, C.-S., Schwarze, C., Steinbach, I., 2019. First evidence for mechanism of inverse ripening from in-situ TEM and phase-field study of δ' precipitation in an Al–Li alloy. *Sci. Rep.* 9 (1), 3981.
- Parrinello, M., Rahman, A., 1982. Strain fluctuations and elastic constants. *J. Chem. Phys.* 76 (5), 2662–2666.
- Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 77 (18), 3865.
- Perdew, J.P., Wang, Y., 1992. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* 45 (23), 13244.
- Pisutha-Arnond, N., Chan, V., Elder, K., Thornton, K., 2013. Calculations of isothermal elastic constants in the phase-field crystal model. *Phys. Rev. B* 87 (1), 014103.
- Shao, W., Guevara-Vela, J.M., Fernández-Caballero, A., Liu, S., Llorca, J., 2023. Accurate prediction of the solid-state region of the Ni–Al phase diagram including configurational and vibrational entropy and magnetic effects. *Acta Mater.* 253, 118962.
- Shi, D., Wen, B., Melnik, R., Yao, S., Li, T., 2009. First-principles studies of Al–Ni intermetallic compounds. *J. Solid State Chem.* 182 (10), 2664–2669.
- Simon, P.-C.A., Aagesen, L.K., Motta, A.T., Tonks, M.R., 2020. The effects of introducing elasticity using different interpolation schemes to the grand potential phase field model. *Comput. Mater. Sci.* 183, 109790.
- Sridhar, N., Rickman, J., Srolovitz, D., 1997. Microstructural stability of stressed lamellar and fiber composites. *Acta Mater.* 45 (7), 2715–2733.
- Steinbach, I., 2024. Concept of introverted space: is multidimensional, extroverted space an illusion?. *Zeitschrift für Naturforschung A* 79 (3), 207–214.
- Steinbach, I., Salama, H., 2023. *Lectures on Phase Field*. Springer Nature.
- Tan, Q., Zhang, M., 2024. Recent advances in inoculation treatment for powder-based additive manufacturing of aluminium alloys. *Mater. Sci. Eng. R* 158, 100773.
- Vallin, J., Mongy, M., Salama, K., Beckman, O., 1964. Elastic constants of aluminum. *J. Appl. Phys.* 35 (6), 1825–1826.
- Vizoso, D., Deo, C., Dingreville, R., 2022. The effects of dose, dose rate, and irradiation type and their equivalence on radiation-induced segregation in binary alloy systems via phase-field simulations. *J. Nucl. Mater.* 569, 153924.

- Wafula, J.W., Makokha, J.W., Manyali, G.S., 2022. First-principles calculations to investigate structural, elastic, electronic and thermodynamic properties of NbCoSn and VRhSn Half-Heusler compounds. *Results Phys.* 43, 106132.
- Wen, J., Cui, H., Wei, N., Song, X., Zhang, G., Wang, C., Song, Q., 2017. Effect of phase composition and microstructure on the corrosion resistance of Ni-Al intermetallic compounds. *J. Alloys Compd.* 695, 2424–2433.
- Wu, W., Kattner, U.R., Campbell, C.E., Guyer, J.E., Voorhees, P.W., Warren, J.A., Heinonen, O.G., 2022. Co-based superalloy morphology evolution: A phase field study based on experimental thermodynamic and kinetic data. *Acta Mater.* 233, 117978.
- Zhang, M., Wang, J., Wang, B., Xue, C., Liu, X., 2022. Quantifying the effects of Sc and Ag on the microstructure and mechanical properties of Al–Cu alloys. *Mater. Sci. Eng. A* 831, 142355.
- Zhao, P., Low, T.S.E., Wang, Y., Niezgoda, S.R., 2020. Finite strain phase-field microelasticity theory for modeling microstructural evolution. *Acta Mater.* 191, 253–269.
- Zhao, Y., Xing, H., Zhang, L., Huang, H., Sun, D., Dong, X., Shen, Y., Wang, J., 2023. Development of phase-field modeling in materials science in China: A review. *Acta Metallurgica Sinica (English Letters)* 1–27.
- Zuo, X., Moelans, N., 2023. Phase-field study of elastic effects on precipitate evolution in (Al) 0.05 CrFeNi. *Int. J. Mech. Sci.* 247, 108163.

A.4 Publication IV [\[P-IV\]](#): Roadmaps for dendrite suppression in next generation lithium-ion batteries: Toward sustainable energy solutions



Roadmaps for dendrite suppression in next generation lithium-ion batteries: Toward sustainable energy solutions

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ABSTRACT

Dendrite formation remains one of the most pressing challenges in advancing the performance and safety of rechargeable lithium-ion batteries (LiBs). These needle-like structures not only compromise battery capacity but also pose significant safety risks, such as short circuits and thermal runaway. This review explores recent advancements in battery design aimed at overcoming these issues. Key strategies include electrolyte engineering, which focuses on developing stable solid electrolyte interfaces (SEIs) to suppress dendrite growth by optimizing coordination forces and stabilizing nucleation sites. Advanced computational techniques, such as multiscale computational design and battery informatics, provide predictive insights into dendrite suppression. The density functional theory (DFT) studies reveal dendrite formation energies typically ranging from 1.2345–6.7890 eV. Furthermore, optical nucleation site mapping has emerged as a powerful tool for visualizing lithium deposition dynamics, offering new perspectives on dendrite prevention. By addressing challenges in stability criteria and maximizing specific energy densities beyond 300 Wh/kg, this review emphasizes the integration of experimental, computational, and informatics-driven approaches to enable the design of safer, dendrite-free LiBs.

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Nomenclature

Acronyms

3D	Three-dimensional
ANN	Artificial neural network
ASSLMB	All solid state lithium metal batteries
AV	Automated vehicles
BE	Carbonate electrolyte
BPNN	Backpropagation neural network
BTO	BaTiO ₃
CA	Cellular automata
CGCNN	Crystal graph convolutional neural network
CNN	Convolutional neural network
DEC	Diethyl carbonate
DFT	Density functional theory
DEE	1,2diethoxyethane
DMC	Dimethyl carbonate
DME	Dimethoxyethane
DMSO	Dimethyl sulfoxide
DREAMS	DFT-based research engine for agentic materials simulation
EC	Ethylene carbonate
EC+HF	Ethylene carbonate + Hydrogen fluoride
EMC	Ethylene methyl carbonate
EW	Electrochemical window
FEM	Finite Element Method
FEC	Fluoroethylene carbonate
HF	Hydrogen fluoride
IC	Incremental capacity
IL	Ionic liquid
ISC	Internal short circuit
KMC	Kinetic monte carlo
LAGP	Lithium Aluminium Germanium Phosphate: Li _{1+x} Al _x Ge _{2-x} (PO ₄) ₃
LATP	Lithium Aluminium Titanium Phosphate: Li _{1+x} Al _x Ti _{2-x} (PO ₄) ₃
LE	Liquid electrolyte
LFPP	LiSFSI-PET4A-PETMP
LGPS	Li ₁₀ GeP ₂ S ₁₂
LHS	Latin hypercube sampling
LiBOB	Lithium bisoxalate borate
LiBs	Lithium-ion batteries
LiDCTA	Lithium 4,5-dicyano-1,2,3-triazolate
LiDFOB	lithium difluoride (oxalate) borate
LiETFSI	Lithium 2-[2-(2-methoxyethoxy)ethoxy] ethanesulfonyl (trifluoromethanesulfonyl)imide
LiFEA	Lithium 1,1,1-trifluoro -N-[2-(2-methoxyethoxy)ethoxy]ethyl]methanesulfonamide

LiFSI	Lithium bis(fluorosulfonyl)imide
LiI	Lithium iodide
LiMTFSI	Lithium (methanesulfonyl)(trifluoromethanesulfonyl)imide
LiOTf	Lithium trifluoromethanesulfonate
LiSFSI	lithium[(4-styrenesulfonyl)(fluorosulfonyl)imide
LiSTFSI	Lithium (trifluoromethanesulfonyl)imide
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
LLM	Large language model
LLTO	Li _{3+x} La _{(2/3)-x} TiO ₃
LLZO	Li _{3+x} La _{(2/3)-x} TiO ₃
LMB	Lithium metal battery
LPSCI	Li ₆ PS ₅ Cl
LSB	Li-S battery
LSTM	Long short-term memory
MC	Monte carlo
MD	Molecular dynamics
ML	Machine Learning
MLFFs	Machine learning force fields
MOF	Metal organic framework
MOOSE	Multiphysics Object Oriented Simulation Environment
MP	Ethyl propionate
MPEA	Multi-Principal Element Alloy
NDT	N-N-diallyl-2,2,2-trifluoroacetamide
OE	Organic carbonate electrolyte
P2D	Pseudo 2d model
PAN	Polyacrylonitrile
PBO	(poly(p-phenylene benzobisoxazole))
PC	Propylene carbonate
PCA	Principal Component Analysis
PCCPs	Positively charged colloidal particles
PDPs	Partial dependence plots
PEO	Poly(ethylene oxide)
PET	Pentaerythritol tetraacrylate
PETMP	Pentaerythritol tetrakis(2-mercaptoacetate
PF	Phase field
PFM	Phase field model
PFTOS	Polar fluorosilicane
PINN	Physics informed neural network
PLA-Li	Poly(lactic acid-lithium
PTMC	Poly (trimethylene carbonate)
PVCA	Poly(vinylene carbonate)
PVDF	Poly(vinylidene fluoride)
PVDF-HFP	Poly(vinylidene fluoride -co-hexafluoropropylene))
PyBaMM	Python battery mathematical modeling
SEIs	Solid electrolyte interfaces
SHAP	Shapley additive explanations
SISSO	Sure independence screening and sparsity operator
SOC	State of the charge

SOH	State of health
SPE	Solid polymer electrolyte
SPM	Single particle model
SRS	Stimulated raman scattering
SSE	Solid state electrolyte
SS-LPSCB	LPSCB electrolyte synthesized via solid-state sintering
SVR	Support vector regression
TEAN	Tetraethylammonium nitrate
ELYTENG	Electrolyte engineering
TFEO	Tris(2,2,2-trifluoroethyl) or-thoformate
THF	Tetrahydrofuran
TTMS	2,2,2-trifluoroethyl triflu-romethanesulfonate
VASP	Vienna ab initio simulation package
VC	Vinylene carbonate
XCT	X-ray computed tomography
DEE	1,2diethoxyethane

Greek Symbols

κ	Interfacial energy coefficient (J/m ²)
ϕ_i	Phase field variable for phase i
τ	Shear stress (N/m ²)
q	Elementary charge
n	Number of electrons
Ω	Partial molar volume (m ³ /mol)
σ	Electronic conductivity (S/m)
σ_{ion}	Ionic conductivity (S/m)
ϵ	Coulombic efficiency (%)
ζ	Defect density (cm ⁻²)
r_1	Reaction rate constant (C ⁻¹)
δ	Nernst diffusion boundary layer (m)
ξ	Piezoelectric voltage (V)
i	Current density (A/m ²)
i_c	Critical current density (A/m ²)
h_0	Initial SEI thickness (m)
v_{max}	Dendrite growth velocity (m/s)
α_a	Anodic charge transfer coefficient
η	Overpotential (V)
$\eta_p(r, t)$	Order parameter
c	Concentration (mol/m ³)
t	Time (s)
z	Charge number
$\mathbf{v}$	Fluid velocity vector (m/s)
μ	Chemical potential (J/mol)
m	Mass (kg)
ϕ	Electric potential (V)
γ_0	Interfacial energy (J/m ²)
δ_0	Gradient coefficient (J/m ²)
ψ^{mech}	Mechanical free energy density (J/m ³)
a_R, a_P	Activity of reactant/product
α	Charge transfer coefficient
ρ_i	Density (kg/m ³)
ω	Energy density (Wh/kg)
Γ	Areal capacity (mAh/cm ²)
Y	Mechanical modulus (GPa)

Roman Symbols

F	Total free energy (J)
M	Mobility (m ² /J s)
T	Temperature (K)
ΔT	Temperature change/Operating temperature window (°C or K)
ΔP	Laplace pressure term (Pa)
R	Gas constant (J/(mol K))
V	Molar volume (m ³ /mol)
K_c	Mechanical fracture toughness of the SE (Pa m ^{1/2})
F	Faraday constant (C/mol)
D	Diffusion coefficient (m ² /s)

$H_{a\beta}$	Phenomenological coefficient (m ² /(s kg))
J	Diffusion flux (mol/(m ² s))
L	Kinetic coefficient (m ³ /(J s))
W	Gradient energy coefficient (J/m ³)
E	Electric field (V/m)
E_{mech}	Young's modulus of elasticity (GPa)
e	Mechanical strain
$\mathcal{N}$	Cycle life (k-Cycles)

1. Introduction

In essence, the battery consisting of lithium metal at anode is considered a lithium metal battery (LMB). Lithium-ion battery typically consists of graphite anode, but it can also consists of other metals (e.g. Sn, Li, etc. or alloys) as anode. For the purpose of this study, LMB is considered the subset of lithium ion battery. Wherever applicable, LMB represents the battery system with lithium as anode. LiBs will indicate a battery with generic anode materials including but not limited to graphite, Sn, Li, and lithium transitional-metal oxide. Lithium anodes possess the highest theoretical specific capacity ($\approx 3860 \text{ mAh g}^{-1}$) and the lowest reduction potential (-3.04 V vs. standard hydrogen electrode) [1]. The researchers appreciate LMB high energy density and lower redox potential, but expect to solve the low Coulombic efficiency and poor cycle stability. The main reason for these disadvantages is the growth of irregular lithium dendrites during the process of charging and discharging [2]. Unlike lithium graphite batteries, lithium ions can be embedded into the graphite layer structure during charging, thus suppressing dendrite formation in LiBs [3,4]. SEIs, which uses electrolytes during charge and discharge and shortens battery lifespan, is produced quickly by the thermodynamic instability of the liquid electrolyte (LE) and the active lithium electrode in lithium metal batteries [5]. The metal anode will develop defects as a result of the electrode volume change, which will encourage dendritic development and nucleation [4]. Additionally, a steady SEIs interface will successfully prevent dendritic development [6]. Solid electrolyte has several benefits when used in lithium metal batteries [7], including high flexibility, low cost, high lithium ion transfer, high thermal stability and wide operating temperature. These benefits are anticipated to result in high energy density and high safety [8]. On the other hand, dendritic formation and expansion are caused by low mechanical characteristics and uneven contact at ambient temperature [9–13]. High shear modulus and electrolyte additives control dendritic growth [14, 15]. Another important role in dendritic growth is also current density [16], lithium concentration, and electrolyte composition [17]. In summary, over the past several decades, extensive work has advanced in parallel from both mechanistic and engineering perspectives, revealing that dendrite morphology and growth kinetics are coupled and controlled by multiple factors including ion transport, interfacial reactions, SEI structure, local mechanical constraints, and operating conditions (current density, temperature, pressure) [18–20]. To this end, researchers have proposed diverse strategies to mitigate dendrite formation, including rational electrolyte design (e.g., compositional optimization and additive engineering), tailored solid-electrolyte interface construction, and architectural innovation in three-dimensional (3D) current collectors [18,21–23]. In parallel, experimental investigations and computational modeling have significantly contributed to deciphering dendrite growth mechanisms, leveraging in situ electrochemical analysis (e.g., real-time morphological evolution monitoring), high-resolution X-ray tomography (for 3D microstructure visualization), atomistic-scale molecular dynamics simulations (for ion transport dynamics), and mesoscale phase-field modeling (for morphological stability prediction) [24,25]. However, research on lithium battery dendrites still faces challenges. Although phase-field simulations and molecular dynamics simulations have deepened our understanding of dendrite nucleation and stress-driven growth [26], integrating these

strategies for actual batteries remains constrained by parameter uncertainties and computational costs. At the experimental level, microscopy and synchrotron radiation tomography have revealed the nanoscale heterogeneity of whisker crystals and their early formation mechanisms. Establishing a connection between these observations and electrochemical performance remains an urgent challenge. The current body of literature remains deficient in a structured synthesis of the fundamental principles governing dendrite nucleation, the comparative efficacy of suppression methodologies, and the integration of multiscale simulation frameworks. Accordingly, a systematic and critical review is imperative to consolidate interdisciplinary findings, assess the strengths and limitations of existing approaches, and chart future research trajectories toward the safe and high-performance implementation of lithium metal batteries. While numerous reviews have elucidated dendrite nucleation mechanisms, suppression strategies, and characterization techniques in solid-state or liquid-electrolyte systems, they often remain compartmentalized, focusing on isolated aspects such as interface engineering or material innovations without a unified integration of multiscale phenomena, data-driven informatics, or long-term policy-level roadmaps. This creates a critical gap in translating fundamental insights into scalable, dendrite-free designs. The present review bridges this void by: (i) synthesizing dendrite growth as a multiscale process from atomic nucleation to macroscopic failure; (ii) introducing battery informatics as a predictive tool for SEI stability; (iii) proposing the Decathlon of Interfacial Stability and Robustness' as a quantitative benchmark; and (iv) outlining an Autonomous Battery Informatics Chronology' toward absolute dendrite-free interfaces by the early 2040s, aligned with manufacturing automation levels. This holistic framework not only consolidates interdisciplinary advancements but also provides actionable strategies for researchers, engineers, and policymakers.

Against this background, this paper aims to: (i) systematically review the nucleation and growth mechanisms of lithium dendrites in liquid and solid systems; (ii) summarize the design rationale and performance boundaries of suppression strategies; (iii) evaluate the information gain and cross-validation relationship between experimental and simulation methods; and ultimately (iv) propose key research directions and future prospects for multidimensional co-design and comparability testing standards. The discussions on how the dendrite growth at the SEIs and the mechanics and thermodynamics underlying dendrite and whisker formation in lithium-based batteries, highlighting the interplay between electrochemical driving forces and mechanical constraints are provided in Section 2. Dendrite growth as a multiscale phenomenon, spanning from atomic-scale nucleation to mesoscale morphology evolution and cell-level implications are discussed in Section 3. Then the recent endeavours aimed at the goal of producing dendrite-free LiBs are outlined in Section 4. The emerging role of battery informatics in understanding and stabilizing the SEI, emphasizing data-driven modeling and predictive analytics are summarized in Section 5. A consolidated roadmap and future perspectives, outlining key challenges and opportunities for practical implementation are presented in Section 6. Finally, Section 7 concludes the review by summarizing the main insights and proposing directions for future research.

Fig. 1(a)–(b) presents a comprehensive bibliometric analysis of the most relevant keywords with the aim of highlighting hot topics and temporal trends in lithium battery and dendrite research. The keyword searches were carried out using VOSviewer [27] on two major databases ((i) Web of Science and (ii) Scopus) using the same search query (see caption for detailed search syntax). Fig. 1(a) displays the Web of Science (WoS) results, where a minimum occurrence threshold of 20 times per keyword yielded 73 terms classified into 5 clusters. The network visualization reveals “lithium dendrite” as the largest node, indicating its highest occurrence frequency, followed by “solid-state batteries” as the second largest. Notably, “lithium dendrite” exhibits strong co-occurrence connections (edges) with major research themes including “solid-state electrolytes”, “lithium metal anode”, “interface

engineering”, and “critical current density”. The prominence of “critical current density” in this network is particularly significant, as it will be employed later in this work (Section 6) as an influential parameter for design of dendrite suppression strategies roadmap. The temporal results (indicated by node colors) shows that “lithium dendrite” or “li dendrites” maintain strong recency, with peak relevance in 2021 and 2022, reflecting the contemporary importance of this research direction. Fig. 1(b) presents the Scopus database results using the same minimum occurrence filter of 20 times, which yielded 170 keywords classified into 5 clusters. This broader coverage reflects Scopus's extensive indexing. The most frequently occurring term is “lithium metal battery” (365 occurrences) and “lithium dendrites” (227 occurrences) also has a very large node size. Some other prominent keywords in this graph are as “lithium metal battery”, “lithium metal anode”, “lithium sulfur batteries”, “lithium-ion battery”, “li dendrites”, “solid-state electrolyte”, and “interface engineering”. The network structure reveals strong interconnections between dendrite-related research and battery performance metrics, including “cycling stability”, “interfacial resistance”, “transference number”, and “thermal runaway”. The “cycling stability” term will be employed in Section 6 as a significant battery parameter for future batteries. Collectively, these frequently used terms from both databases illustrate that dendrite formation and suppression remain among the most important research directions in the field of lithium batteries.

The publications related to research about dendrites or whiskers in lithium batteries from 2000 onwards is summarized in Fig. 1(c), which is based on a separate, broader Scopus search query conducted on May 17, 2025 (refer Fig. caption for search syntax). This analysis encompasses a more extended period from 2000 to 2025 and employs a streamlined search strategy focusing on the core keywords, thereby capturing a more comprehensive publication landscape with 9514 total documents. The bar chart illustrates the absolute number of annual publications (left axis, red bars), while the superimposed blue dotted line represents the percentage of these publications relative to the total database output (right axis), providing dual perspectives on the field's growth trajectory. The data reveal several distinct phases of research development. From 2000 to approximately 2015, the field experienced modest but steady growth, with annual publications remaining below 200 and representing less than 2% of total publications. A transitional period occurred during 2016–2017, marking the onset of accelerated interest. Beginning around 2018, the field entered a phase of exponential growth, with publication counts approximately doubling between 2017 and 2019, and continuing this rapid ascent through 2024. The peak occurred in 2024, with over 1800 publications representing nearly 20% of the total output in this domain, indicating that dendrite-related research has become an increasingly dominant subfield within battery research. This sustained exponential growth trajectory over the past decade underscores the critical importance of addressing dendrite formation as a fundamental challenge in the development of safe, high energy-density lithium-based batteries. The correlation between this publication surge and the industry's push toward next-generation battery technologies for electric vehicles and grid-scale energy storage suggests that dendrite suppression has emerged as a pivotal research frontier, attracting substantial scientific attention and resources.

2. Mechanics and thermodynamics of dendrites/whiskers in LiBs

Lithium dendrites involve both physical and chemical processes, influenced by a variety of factors, including thermodynamics, [28] kinetics, [29] and electrolyte composition [30]. The nucleation and growth of dendrites is governed by kinetics [31], while thermodynamics influences the stability and morphology of the deposit [32]. There is a feedback loop based interaction between the anode surface morphology and electric field in the battery to cause the “tip effect” at the electrode [33]. The interaction between the electric field

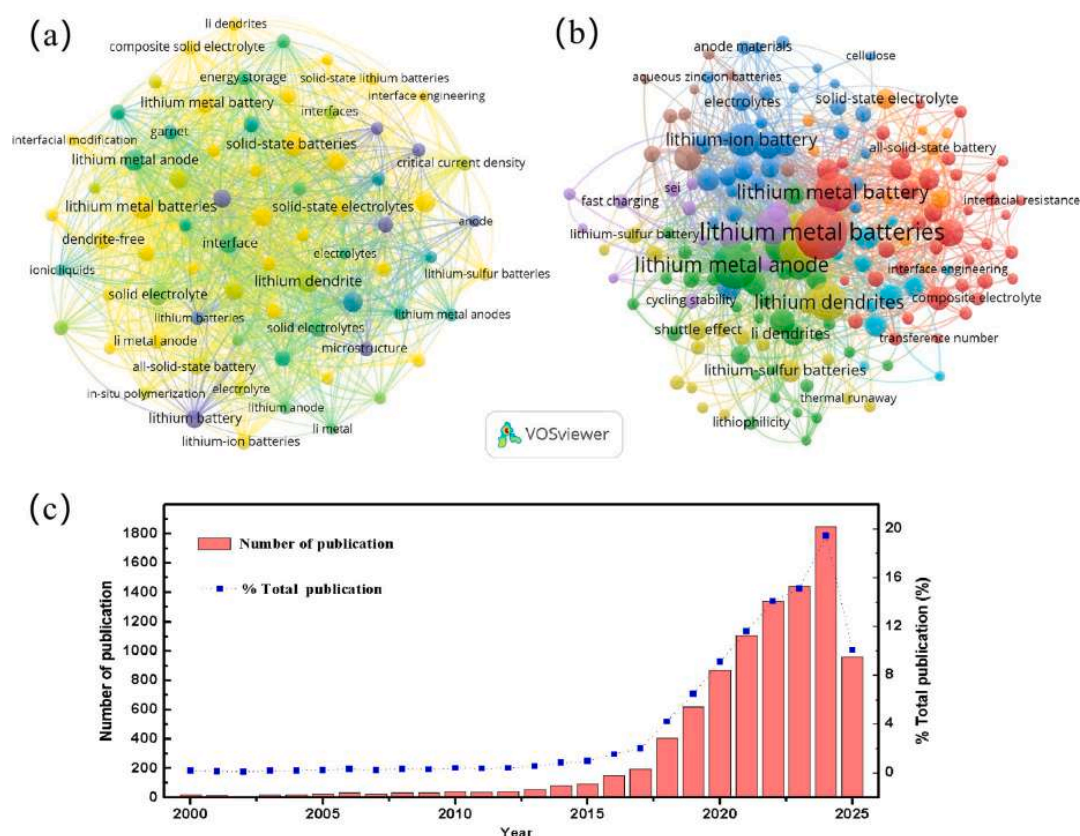


Fig. 1. Bibliometric network visualizations generated using VOSviewer [27] based on searches conducted in the (a) Web of Science and (b) Scopus databases (Search date: January 25, 2025). The same search query was used for both databases in (a)–(b): “(Dendrite OR Whiskers) AND (Lithium ion battery OR Lithium battery OR Lithium metal battery OR Solid state) AND (Electrolyte OR Anode OR Interface OR Simulation OR Algorithm OR Property OR Design OR Application OR Formation OR Grown OR Nucleation OR Cycle OR Capacity)”. (a) Web of Science results: 4397 documents retrieved, refined to 3357 publications from January 2020 onwards. (b) Scopus results: 3171 documents retrieved from January 2020 onwards using the same keywords. (c) Annual publication trends based on a Scopus search conducted on May 17, 2025, covering the period from 2000. The search query for (c) was: “(Dendrite) OR (Whiskers) AND (“Lithium-ion battery” OR “Lithium battery” OR “Lithium metal battery” OR “Solid state””, yielding a total of 9514 publications.

and the microstructure is the topic of focus for the mechanics and thermodynamics study.

Nucleation continues in the process of charging and discharging [34], and the initial nucleation is the key point for research. Surface nucleation is affected by surface energy and diffusion energy. High surface energy [35], low diffusion barriers and migration energy [36] promote uniform deposition rather than aggregation to form dendritic structures. Heterogeneous nucleation mainly describes a process that dissolved thermodynamically unstable embryos develop into thermodynamically stable nuclei when a critical overpotential is exceeded [37]. The size, number and density of the nucleus are related to the overpotential [38]. Effective nucleation inhibition can be achieved by raising the surface energy to decrease the local current density. In space-charge model ion transfer controlled by ion concentration and potential is the key parameter of lithium dendrite. Pei et al. [39] found smaller and more densely distributed lithium nuclei at high current densities. As shown in Fig. 2(a), the model is constructed and the concept of SEIs coverage density is introduced to calculate the rate of SEIs formation by Tafel kinetics, which calculates the rate of dendrite growth by simulating the concentration and potential field in the electrolyte domain. The defect of SEIs itself will encourage nucleation in SEIs-induced nucleation [40]. The nucleation site affects the morphology and direction of dendrite growth. It has been observed in bottom-induced [41] tip-induced nucleation [42], and multidirectional-induced

nucleation [43]. SEIs with low Li-ion transport number and/or conductivity cause a current shift, and the layer at the interface created by the diffusion process of Li-ions through the SEIs promotes nucleation in Fig. 2(d). [44]. In the aftermath of nucleation, lithium deposits develop with multiple patterns, such as needle-like [43,45], mosslike [46,47] and treelike [48,49], depending on a variety of factors including current density [50,51], temperature [52] and pressure [53].

Additionally, the growth rate affected by the migration direction and speed of lithium ions is also different. Lithium ions are driven by electric field and concentration gradient [72,73]. Therefore, parameters such as charging and discharging conditions [74] the viscosity [48] and ionic conductivity of the electrolyte affect dendrite growth after nucleation. Under the control of mass transport, the electrochemical behavior at the interface between SEIs and electrode affects lithium deposition, as shown in Fig. 2(c). When the transport of SEIs is lower, the SEIs are unable to meet the demand of high current density, leading to the activation of lithium ions diffusion process in SEIs and the formation of a layer promoting lithium deposition in the interface [75]. Akolkar et al. [54] controlled the nucleation of lithium dendrites by regulating the temperature or thermodynamic kinetic energy. The paper mainly constructed a thermodynamic model to describe the parameters relaxation time and nucleation overpotential in the nuclear process by the classical Arrhenius equation, which derived that the nucleation rate of lithium improved with the increase of the temperature. Then, the equation combined with the Tafel expression to give

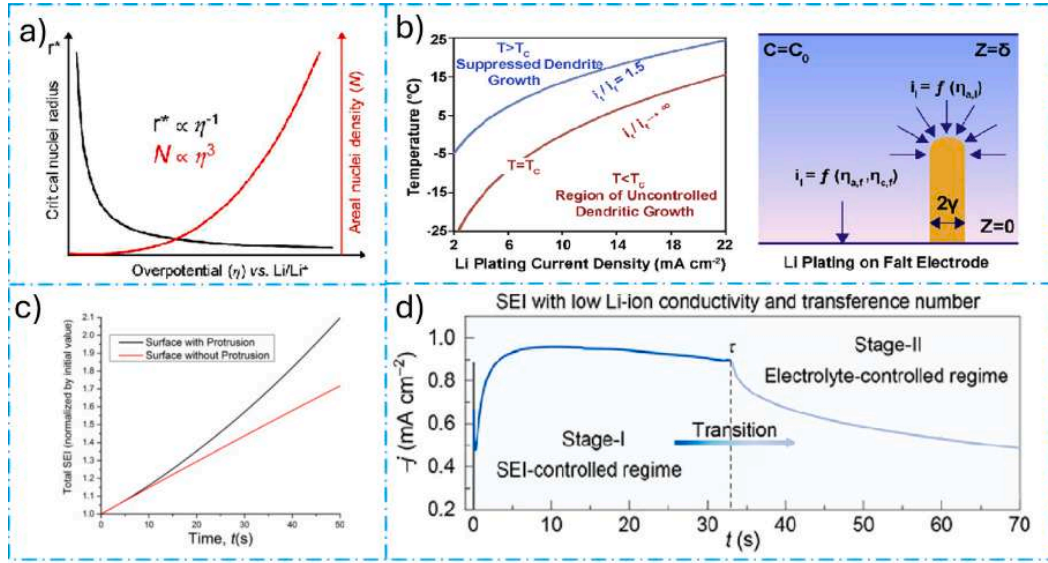


Fig. 2. (a) Relationship between nucleation critical lithium nucleation radius and nucleation density per unit area and overpotential. [38]; (b) The left graph shows the dendrite growth rate at different current densities or temperatures, and the right graph represents the process of lithium deposition, including the activation overpotentials $\eta_{a,f}$ and concentration overpotentials $\eta_{c,f}$, the current density i , the concentration gradient, and the thickness of Nernst diffusion boundary layer δ , etc. [54,55]; (c) The initial SEIs presence of protrusions accelerates the penetration and re-formation of SEIs, emphasizing the importance of controlling the initial SEIs defects [56]; (d) Schematic of the current transient changes, illustrating that when the transmission number of the SEIs is low, the SEIs are unable to satisfy the demand of high current densities, which leads to activation of lithium ions diffusion process in the SEIs, and formation of a space charge layer at the interface of the electrode and the SEIs thus promoting the lithium space charge layer thereby promoting lithium deposition [44].

the effect of the temperature on the diffusion and charge transfer. it calculated the critical temperature T_c under the special current density. (as shown in Fig. 2(b)). Comparing the different temperature situation, the conclusion is that the transport capacity of lithium ions decreases leading to an increase in the rate of dendrite growth at low temperatures because of the increase in the viscosity of the electrolyte.

In order to study the growth and nucleation of lithium dendrites, models were constructed to analyze the diffusion and deposition of lithium ions from different directions. Physical factors include potential differences driving the accumulation of metal cations, which is a prerequisite for dendrite formations, high current density consuming large amounts of cations on the surface of the metal electrodes, the concentration gradient [76], mechanical stress [77] developed during charging and discharging of the cell, leading to instability at the SEIs interface and increased tension [56]. Primary chemical factors are the electrolyte composition and SEIs formed by the decomposition of solvent molecules on the electrode surface. The additives present in the electrolyte significantly influence the composition and metal deposition kinetics of the SEIs [78]. Stability and conductivity of SEIs have been shown to inhibit dendrite growth. Temperature plays an important role. Higher temperature increases the side reaction between the electrode and the electrolyte, and the “dead lithium” by-product will be produced, which will eventually form dendrites. Low temperatures increase the viscosity of electrolytes and limit mass transfer, thus accelerating dendrite growth [52,79,80]. Experimental reports [81–83] indicated that von Mises stress is detrimental to batteries in relation to the health of solid state electrolyte. External pressure and high temperature on the system lead to higher von Mises stress which will generate dendrite broken and form dead lithium. The mechanism and mathematical model related to the cause–effect relationship between mechanical loading and dendrite formation can be interpreted using the phase field method and other computational models. In order to describe the detail, more on this topic will be discussed later in Section 3. Researchers have found that a piezoelectric/ferroelectric material nanofiber has a certain effect on the growth of lithium dendrites, as shown

in Fig. 3. The piezoelectric effect can reduce the driving force for the growth of lithium dendrites at the high-curvature electrode–electrolyte interface, and the addition of $\text{BaTiO}_3(\text{BTO})$ can reduce the internal resistance and polarization overpotential of the battery [57–59].

Aslam et al. [86] conducted a comprehensive literature review and provided a chronological overview of the most widely accepted theoretical frameworks and models describing dendrite growth in rechargeable batteries, including lithium-ion systems. The most influential contributions include the Wranglen Theory, Barton–Bockris Model, Kim–Jorne Theory, Chazalviel Model, Deposition–Dissolution Model, Heterogeneous Nucleation Model, Stress-Driven Dendrite Growth Model, Akolkar Model, and the Monroe–Newman Model. These frameworks collectively aim to elucidate the fundamental electrochemical and physical mechanisms governing dendrite initiation and propagation. More recently, Choobar et al. [87] expanded this body of work by incorporating newer theoretical perspectives. Building upon these efforts, the present study further extends the existing list by including the most recent *Preferential Growth Model* [71], which introduces the concept of preferential lithium transport or expulsion rate (θ) along grain boundaries of solid electrolytes (e.g., LLZO), as opposed to the slower diffusion within the inner grains. The key features and governing equations associated with these models are summarized in Table 1. Collectively, these models provide valuable chronological insights into the electrochemical, physical, and mechanical factors driving dendrite nucleation and evolution. The Wranglen Theory (1960) [60] first introduced the concept of a critical current density (j_c) for dendrite initiation in aqueous systems, expressed as $j_{\text{global}} > j_c$ or $j_{\text{local}} > j_c$. However, its applicability to solid electrolytes is limited, in contrast to the Preferential Growth Model, which emphasizes electron accumulation at grain boundaries ($\theta = \frac{4\pi r^3 \eta_{Li} \rho_{Li}}{3A}$). The Barton–Bockris Model (1962), later extended by Diggle et al. (1969) [61,62], correlates dendrite growth velocity in ionic solutions with applied current density ($v_{\text{max}} = j_0 \frac{v_n}{RT}$), yet remains primarily applicable to liquid electrolytes rather than solid-state systems. The Kim–Jorne Theory (1980) [63] describes mass transport at the edge of a rotating disk electrode ($c_s = c_b(1 - \frac{j}{j_l})$), which is also

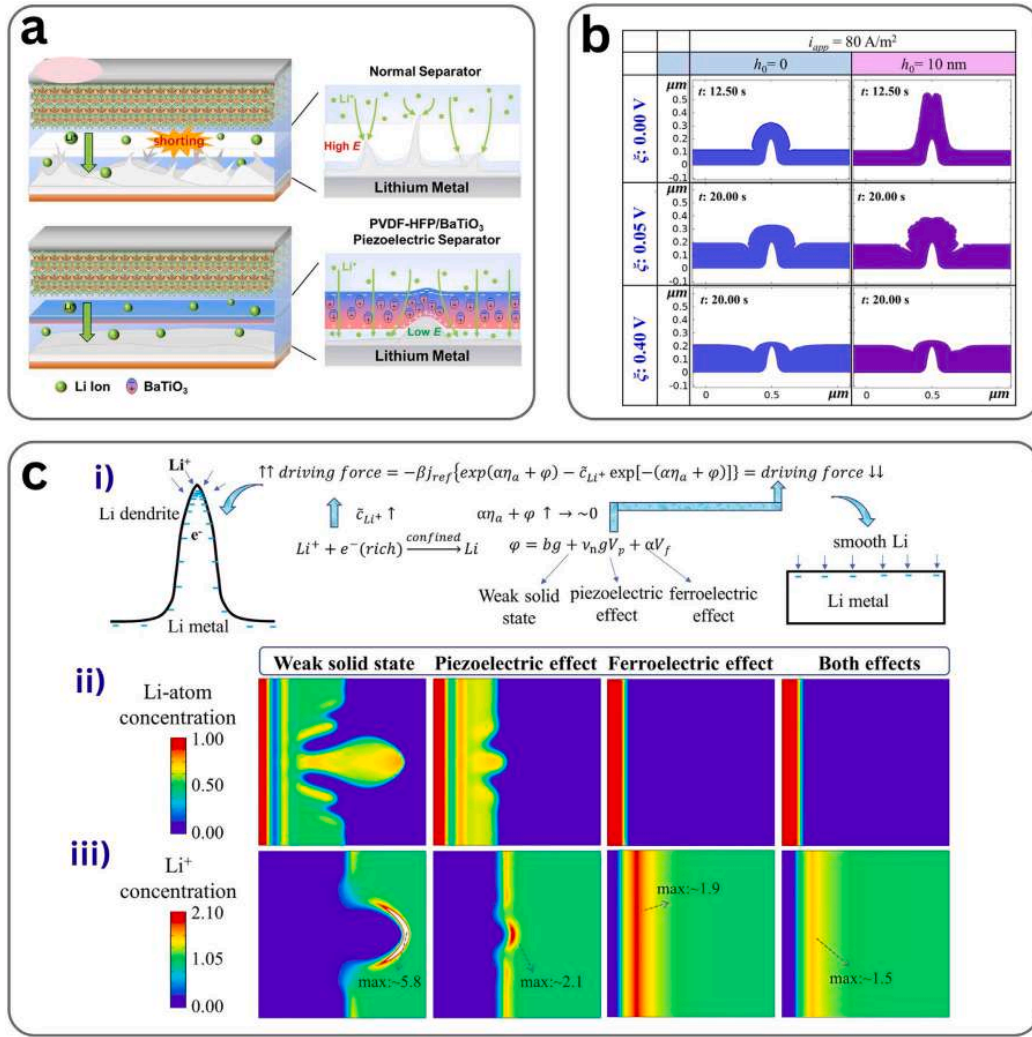


Fig. 3. (a) Schematic illustration of the working mechanism of a piezoelectric separator in a battery [57]. (b) Interactive effects of piezoelectric voltage (ξ), applied current density (i_{app}), and initial SELs thickness (h_0) on Li morphology, showing negligible SELs influence at $\xi = 0.4 \text{ V}$ [58]. (c) Schematic of Li deposition in ASSLBs with Li-atom dimensionless concentration and Li⁺ concentration distribution after 86 s under 1 mA cm⁻², comparing weak solid-state, piezoelectric, ferroelectric, and combined piezo-/ferroelectric effects [59].

specific to liquid-phase conditions, whereas the Preferential Growth Model accounts for lithium expulsion along solid electrolyte grain boundaries. The Chazalviel Model (1990) [64] addresses dendritic growth under high-field conditions by considering ion transport imbalance, formulated as $\nabla \cdot (D_a \nabla c_a + \mu_a c_a \nabla \phi - v_a c_a) = 0$. This electrochemical model differs fundamentally from the electron transport focus of solid-state systems. The Whisker (Deposition–Dissolution) Model (1998) [65] attributes growth to competition between deposition and dissolution processes, represented by the Laplace pressure term $\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$, yet neglects the role of grain boundaries central to the Preferential Growth Model. The Monroe–Newman Model (2003) [66], developed for lithium/polymer interfaces, quantifies the limiting current as $j_L = \frac{c_0 D F}{(1 - i_0^0) L}$, making it suitable for polymer electrolytes rather than solid systems. Similarly, the Internal Resistance Theory (2008) [67] correlates dendrite growth with internal resistance and thermal effects ($\tau = \frac{\pi D (C_0 q_0)^2}{(2 J_0)^2}$, $J^* = \frac{8 \tau J_0^2 I_0}{\pi C_0 q_0 L}$), diverging from the electron-driven framework of the Preferential Growth Model. The Heterogeneous Nucleation Model (2013) [68] considers the preferential nucleation of

lithium at heterointerfaces but lacks an explicit quantitative formulation, in contrast to the Preferential Growth Model's well-defined kinetics. The Akolkar Model (2013) [69] quantifies current distribution at dendrite tips through $\frac{j_L}{j_f} = \left\{ \frac{-1}{b C_0} \ln \left(e^{-b C_0} + \frac{j_f}{j_{L,f}} (1 - e^{-b C_0}) \right) \right\}^{-\frac{c_0}{a}}$, again formulated primarily for liquid electrolyte environments. The Stress-Driven Dendrite Growth Model (2018) [70] introduced mechanical coupling by linking growth to residual stress ($\mu_m = \mu_0 - \sigma \Omega$, $\sigma_0 = \frac{R T}{F D} j r$), offering an important mechanical perspective absent in earlier electrochemical models. The Preferential Growth Model [71], in contrast to its predecessors, uniquely addresses solid-state lithium dendrite formation. It highlights grain boundary electron trapping and quantifies the lithium expulsion rate as $\frac{d\theta}{dt} = r_1 \sigma E$, where σ is the ionic conductivity, E is the electric field strength, and r_1 is a constant associated with charge transfer resistance. Notably, experimental observations indicate that the lithium expulsion rate at grain boundaries ($\frac{d\theta}{dt}_{GB} = 0.0399 \mu\text{g nm}^{-2} \text{ s}^{-1}$) is approximately 2.35 times higher than within the inner grains, thereby providing a quantifiable mechanistic understanding of dendrite initiation in solid electrolytes.

Table 1

Theoretical models to expand the understanding of the mechanisms of dendrite formation and growth in metal (Li, Zn, Na, etc.) ion batteries. The applications and limitations of these models are provided in [Metal Deposition Mechanisms Web App](#).

S.N.	Models (Year)	Mechanisms or concepts	Mathematical expression	Reference
1	Wranglen Theory (1960)	Concept of critical current density (j_c) in aqueous solutions	Condition for dendrite growth: $j_{global} > j_c$ or $j_{local} > j_c$	G. Wranglen [60]
2	Barton and Bockris Model (1962), Extended as Diggle, Despic & Bockris model (1969)	Maximum velocity of dendrite growth in ionic solutions	$v_{max} = j_0 \frac{V\eta}{RT}$	Barton & Bockris [61], Diggle et al. [62]
3	Kim and Jorne Theory (1980)	Dendrite growth mechanism at edge of rotating disc	$c_s = c_b(1 - \frac{j}{j_l})$ where, c_s = surf. conc. c_b = bulk conc. j_l = limiting j	Kim and Jorne [63].
4	Chazalviel Model (1990)	Theory of the ramified metallic deposits growth via electrodeposition in presence of high electric field	$\nabla \cdot (D_a \nabla c_a + \mu_a c_a \nabla \phi - v_a c_a) = 0$, where v_a is filament growth velocity at anode	J. N. Chazalviel [64]
5	Whisker Model (1998)	Resulting from the competition between deposition & dissolution currents	Deformation caused by pressure difference $\Delta P = \gamma \left(\frac{1}{R_i} + \frac{1}{R_s} \right)$	Yamaki et al. [65]
6	Monroe and Newman Model (2003)	Dendrite growth in parallel-electrode lithium/polymer cell	$j_L = \frac{2c_0 DF}{(1-\phi_0)L}$	Monroe and Newman [66]
7	Internal resistance theory (2008)	Current rate and temperature effects, critical current density	Sand's time (τ) = $\frac{\pi D(C_0 q_0)^2}{(2J_c)^2}$ $J^* = \frac{8\pi J_c^2 V_a}{\pi C_0 q_0 L}$	Park et al. [67].
8	Growth via Heterogeneous Nucleation (2013)	Nucleation at heterointerfaces	$\Delta G_c = \frac{16\pi\gamma_{ij}^3(2 + \cos\theta)\sin^4(\theta/2)}{3(\Delta G_f)^2(1 + \eta)^2}$	Ely and Garcia [68].
9	Akolkar Model (2013)	quantification of j at dendrite tip (j_t) and flat surface (j_f)	$\frac{j_t}{j_f} = \left\{ \frac{-1}{\beta C_0} \ln \left(e^{-\beta C_0} + \frac{j_f}{j_{t,f}} (1 - e^{-\beta C_0}) \right) \right\} - \frac{\eta}{\alpha}$	R. Akolkar [69]
10	Stress-driven dendrite growth (2018)	Role of residual stress during electrodeposition; Concept of stress relaxation	Chemical potential of metallic filament $\mu_m = \mu_0 - \sigma\Omega$ Critical stress $\sigma_0 = \frac{RT}{FD_a} j r$	Wang et al.[70]
11	Preferential growth model (2023)	Dendrite growth pathway along GBs in solid electrolytes	$\theta = \frac{4\pi r^2 n_{Li} \rho_{Li}}{3A}$	Zhu et al. [71]

Stable electrodeposition is directly related to the size of the interfacial defect, fracture toughness, and molar volume of the solid electrolyte. The critical condition equations for stable electrode deposition can be obtained by integrating electrochemical and mechanical changes. The following Eq. (1). shows that a smaller interfacial defect size and a larger fracture toughness and molar volume result in a lower critical current density required to stabilize electrodeposition [88].

$$\ln \left(\frac{i_{critical}}{i_0} \right) \leq \frac{b\alpha_a}{a\pi RT} \cdot \frac{K_c}{\sqrt{\pi a}} |V_{VI} - V_{VI}^{2+}| \quad (1)$$

Liu et al. [56] construct models to illustrate the effects of current density, SEIs resistivity, and SEIs defects on the growth of lithium dendrites. As shown in Eq. (2), reaction current density i_{Li} is described by the Butler-Volmer equation associated with the exchange current density $i_0 = FK(c_{Li})^{(1-\alpha)}$ and the overpotential η . Many factors influence the overpotential including temperature, charge rate, materials, and electrolyte. The side reaction should also be considered when the value of overpotential is defined [89]. Overpotential mainly represent the kinetic resistance such as diffusion or charge transfer. The value of the overpotential is the difference between the real voltage and the Equilibrium Potential ($\eta = E_{real} - E_{eq}$). A better method is to determine the parameter values related and limited to the overpotential value range. The real voltage is restricted by an electrochemical window. The value of the electrochemical window is relevant only to the electrolyte. The table below summarizes the window voltages and ionic conductivities of some common solid electrolytes (Table 2) [90] and liquid electrolytes (Table 3) [91]. Another parameter K is the lithium deposition rate coefficient and α is the charge transfer coefficient for lithium deposition. They found that at low current density, protrusions on the surface of lithium would grow dendrites by penetrating the SEIs,

high current density would be accompanied by a much dendrite tip, and an increase in the resistivity of the SEIs would round the dendrites and reduce the risk. The flat initial lithium surface and uniform low resistance SEIs layer help to reduce dendrite formation and growth and improve Coulomb efficiency.

$$i_{Li} = i_0 \left(\exp\left(\frac{(1-\alpha)F\eta}{RT}\right) - \exp\left(-\frac{\alpha F\eta}{RT}\right) \right) \quad (2)$$

The kinetics of electrochemical immersion was studied by means of the Butler-Volmer Eq. (2), which describes the lithium deposition process at the interface of the two phases of the electrolyte and the electrolyte as including mechanical forces due to viscous and deformation stresses, as well as changes in the local concentration at the electrode. Charles et al. [14] used a modified version of the Butler-Volmer equation to study the effect of elastic mechanics on the stability of the electrode. The Nernst-Planck equation [121]

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(D \nabla c + \frac{zF D c}{RT} \nabla \phi \right) + \mathbf{v} \cdot \nabla c \quad (3)$$

serves as a fundamental electrochemical formulation that describes the transport of lithium ions through an electrolyte, driven by diffusion, migration, and convection [2]. Dreger builds on the Nernst-Planck equation, bridging some of the model's shortcomings in describing the electrolyte system, and the Dreger model adds a link between the conservation of mass and momentum balance equations, taking into account diffusion and thermodynamic consistency [122].

$$J_a = - \sum_{\beta=1}^{N-1} H_{a\beta} \left(\frac{\nabla \mu_\beta - \nabla \mu_N}{T} + \frac{e_0}{T} \left(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N} \right) \nabla \phi \right), \quad a \in \{1, 2, \dots, N-1\} \quad (4)$$

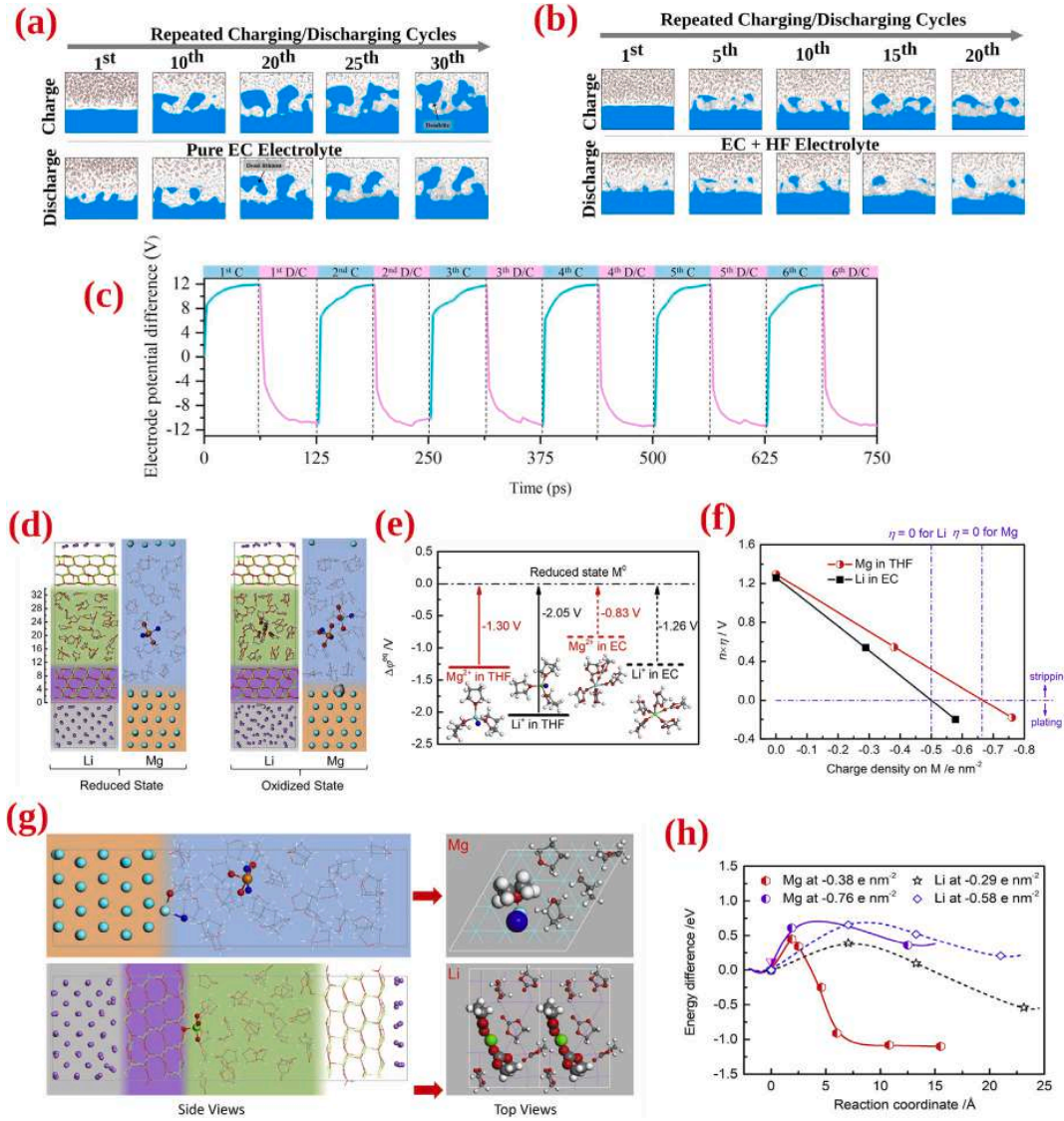


Fig. 4. Atomic scale simulations of electrochemical systems. The images (a)–(c) represent the Li dendrite evolution kinetics study via reactive MD simulations [84]. The dendrite growth rate during charging stage is lower for system containing (b) EC+HF(hydrogen fluoride) electrolyte as compared to the (a) pure EC electrolyte. Dead lithium is formed during the discharge cycle. The total time for the 6 charge + discharge cycles as shown in (c) is 750 ps. The images (d)–(h) are associated with the DFT study of Li and Mg based systems [85]. In the comparative study between these two systems, the Li based system uses EC electrolyte whereas Mg based system utilizes THF electrolyte. The explicit half-cell models, namely, Li/Li₂CO₃/EC (Model 1) and Mg/THF (Model 2) of (d) are at the reduced and oxidized states with one Li atom (for Model 1) and Mg atom (for Model 2) stripped. The associated equivalent potentials and driving forces for these models are quantified at (e) and (f) respectively. The desolvated states of Model 2 and Model 1 are shown as sideviews and top views in (g). The graph (h) depicts the calculated energetic coordinates for Mg²⁺ ion (Model 2) or Li⁺ ion (Model 1) transport.

The classical equations of Allen-Cahn [146] (Eq. (6)) and Cahn-Hilliard [147] (Eq. (5)) of the phase field model (PFM) are mainly used in modified forms, to numerically track the interfacial phenomena associated with the distribution of ion concentration and evolution of lithium dendrites. Lin et al. [148] create a model of lithium dendrite growth and this model considering the mechanical and chemical effects based on the Allen-Cahn function. The model function (Eq. (7)) describes the driving force for the phase field evolution. The migration of the interface consists of two main components: mechanical driving force and electrodeposition driving force. In the system, the crack extension is primarily driven by stress concentration and elastic energy

release and lithium deposition kinetics affected by overpotential and stress chemical potentials (see Box I).

$$\frac{\partial c_i(\mathbf{r}, t)}{\partial t} = \nabla \cdot \left(M_{ij} \nabla \frac{\delta F}{\delta c_j(\mathbf{r}, t)} \right) + \mathbf{v} \cdot \nabla c \quad (5)$$

$$\frac{\partial \eta_p(\mathbf{r}, t)}{\partial t} = -L_{pq} \frac{\delta F}{\delta \eta_q(\mathbf{r}, t)} \quad (6)$$

Table 2

Electrochemical window (EW) and ion conductivity for some common solid electrolyte materials. The successful deployment of dendrite inhibition strategies (e.g. electrolyte engineering, SEIs design) in the experimental, computational and machine learning models of all solid state batteries largely depends on such databases of EW and ion conductivity.

SN	Electrolyte	EW (V)	Ion-conductivity (mS cm ⁻¹)	Ref.
1.	Poly(ethylene oxide) (PEO)	3.8	0.25	[92,93]
2.	Polyacrylonitrile (PAN)	>4	3	[94]
3.	Poly(trimethylene carbonate) (PTMC)	>5	10 ⁻⁴	[95]
4.	Poly(vinylene carbonate) (PVCA)	>4.5	0.078	[96]
5.	Poly(vinylidene fluoride) (PVDF)	>4	0.6	[97]
6.	Li _{1+x} Al _x Ti _{2-x} (PO ₄) ₃ (LATP)	2.65–4.6	1	[98,99]
7.	Li _{1+x} Al _x Ge _{2-x} (PO ₄) ₃ (LAGP)	1.85–4.9	5.08	[98,100]
8.	Li _{3+x} La _{(2/3)-x} TiO ₃ (LLTO)	1.75–3.71	1.5	[101]
9.	Li ₃ PS ₄	0.6–3.7	0.164	[102]
10.	Li ₇ P ₃ S ₁₁	2.28–2.31	0.63	[103,104]
11.	Li ₇ La ₃ Zr ₂ O ₁₂ (LLZO)	0.05–2.91	1	[105,106]
12.	Li ₆ PS ₅ Cl (LPSCl)	1.71–2.01	0.22	[104,107]
13.	Li ₁₀ GeP ₂ S ₁₂ (LGPS)	1.71–2.14	12	[104,106]
14.	Li ₃ YCl ₆	0.62–4.21	2.2	[108]
15.	Li ₃ YBr ₆	0.59–3.15	1	[108]
16.	Li _{0.388} Ta _{0.238} La _{0.475} Cl ₃	2.01–4.27	3.02	[109]
17.	1.6 Li ₂ O–TaCl ₅	2.20–4.15	6.6	[110]
18.	1.5 Li ₂ O–HfCl ₄	2.10–4.10	1.97	[110]
19.	Li _{1.75} ZrCl _{4.75} O _{0.5}	1.79–4.0	2.42	[111]
20.	Li _{0.94} Zr _{1.94} Sb _{0.06} (PO ₄) ₃	>4.8	0.065	[112]
21.	Li ₃ PW ₁₂ O ₄₀	0–4.8	0.89	[113]
22.	Li ₂ BaSnS ₄	1.70–2.17	0.72	[114]
23.	Li ₂ SrSi ₄	1.33–2.33	0.72	[114]
24.	Li ₁₇ P ₃ S _{7.5} O _{3.5}	1.93–3.02	0.458	[115]
25.	Li-ion-conducted hydrogen-bonded organic framework	>5.05	0.22	[116]
26.	Polyhedral oligomeric silsesquioxane-based covalent organic frameworks	1.7–4.5	0.123	[117]
27.	Organic molecular porous solid cucurbit[7]uril	0–4.65	0.245	[115]
28.	Lithium hexafluorophosphate (LiPF ₆)+Porous polymer/EC/DMC/EMC	–0.5–5	0.4	[118]
29.	Polybutylacrylate/succinonitrile	>4.5	>1.1	[119]
30.	PEO/PBO(poly(p-phenylene benzobisoxazole))	≈5	0.028	[120]

$$\begin{aligned} \frac{\partial \phi}{\partial t} = & -L_{\text{int}} \left(W \frac{\partial g(\phi)}{\partial \phi} - \gamma_0 \delta_0 \left(\eta^2 \nabla^2 \phi - \frac{\partial}{\partial x} \left(\eta \frac{\partial \eta}{\partial \theta} \frac{\partial \phi}{\partial y} \right) + \frac{\partial}{\partial y} \left(\eta \frac{\partial \eta}{\partial \theta} \frac{\partial \phi}{\partial x} \right) \right) - \frac{\partial h(\phi)}{\partial \phi} \left(-\frac{\partial \psi^{\text{mech}}}{\partial \phi} \right) \right) \\ & + \frac{\partial h(\phi)}{\partial \phi} L_{\text{bulk}} \left(a_R \exp \left(\frac{(1-\alpha)(\mu_R^{\text{ex}} - \mu_P^{\text{ex}})}{RT} \right) - a_P \exp \left(-\frac{\alpha(\mu_R^{\text{ex}} - \mu_P^{\text{ex}})}{RT} \right) \right) \end{aligned} \quad (7)$$

Box I.

In the Cahn–Hilliard-advection equation, the advection velocity [149] expressed as

$$\mathbf{v} = -\frac{i_{\text{Li}}}{2F} \cdot \frac{M_i}{\rho_i} \cdot 10^{-2} \quad (8)$$

The Allen-Cahn equation [150] is used primarily to analyze the stability of the interface by describing the dynamic evolution of the interface during the growth of dendrites. David et al. [151] did some work on the growth mechanism of lithium dendrites under different currents

and the effect of different contact angles on the morphology of dendrite. In addition, Peng et al. [20] described that at current density exceeding the diffusion limit, the salt concentration in the electrolyte approaches zero, the initiated ions are deposited in the protrusions and the dendrites begin to grow by the sand equation. Here, Sand's time and Sand's capacity are applied as critical values to inhibit dendrite growth, the relationship $\tau = \pi D \left(\frac{C_0 c}{2J_d} \right)^2$ holds, with t_a defined as $\frac{\mu_a}{\mu_a + \mu_c}$, representing relevant physical quantities. It is usually used to predict

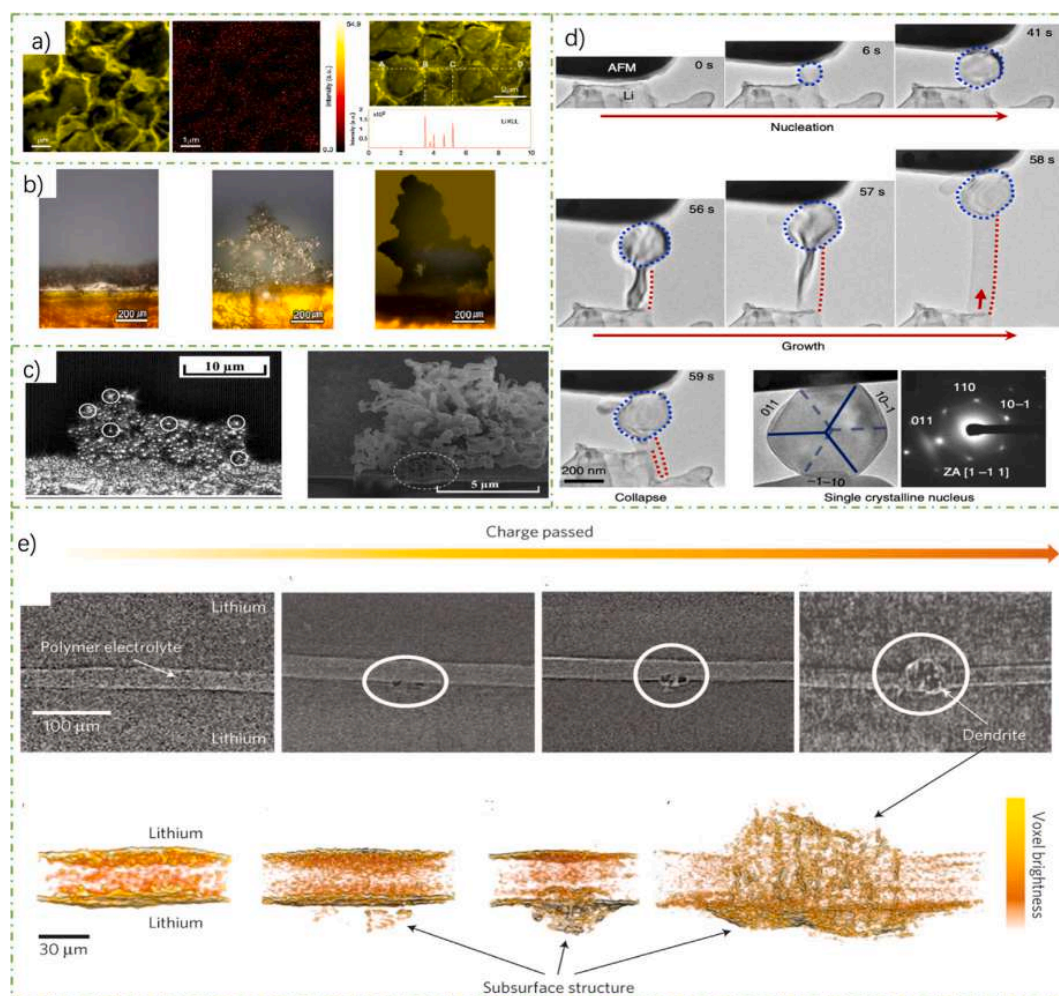


Fig. 5. Lithium metal morphologies in different states and at multiscale. (a) Needle-like structures, using AES-SEM chemical analyzing method, and proving the lithium ion gathering and the lithium filaments distributed on grain boundary in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ structure solid state electrolyte [45]. (b) Moss-like deposits, no perfect direction and lithium bush building with a strong random component superimposed to the overall expansion [47]. (c) Tree-like structural pattern, using different kinds of electrolyte [48]. (d) Sequential TEM snapshots of lithium nucleation, growth process and lithium dendrite collapse. The last two images is a single lithium nucleus in electron diffraction pattern [123]. (e) X-ray tomography slices show the dendrite growth of symmetric lithium cell in charge and discharge state. The last three layers on the upper part clearly show the dendrites between the electrodes and the electrolyte. The dendrites have clearly penetrated the electrolyte and have reached the prerequisite condition for causing a short circuit accident in the last figure on the upper part. The lower part shows the 3D model and illustrates the process of lithium ion gathering in electrodes and growth through the electrolyte. This system uses lithium metal electrodes and the polystyrene-block-poly (ethylene oxide) copolymer electrolyte. From left to right, the charge rate increases from low to high (0 C cm^{-2} , 9 C cm^{-2} , 84 C cm^{-2} , 296 C cm^{-2}) [124].

the time of dendrite growth, revealing distinct growth morphologies under varying current densities.

The processes of lithium nucleation and growth are influenced by surface energy and chemical potential. Recently, Pant et al. [152] used phase field simulation to find the formation mechanism of dead lithium in the process of charging and discharging and further illustrate the importance of SEIs. The development of lithium dendrite increased significantly at high current densities, resulting in a higher interface impedance and contact loss. Dendrite growth can be inhibited and interface stability can be demonstrated by introducing lithium alloys or polymer electrolytes [153–155]. Iriyama et al. [156] explored the effect of current density on the morphology of deposited lithium in LiPON electrolyte. Sakamoto et al. [157] proposed the critical current density in the $\text{Li}/\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ system, which was used to evaluate the maximum available ions transport and charge-transfer capacity per unit

area and time. The critical current density value is determined by the interfacial lithium chemistry.

Another factor that inevitably affects the formation of dendrites within the battery is defects. Liquid electrolytes, in the hydraulic state, can fill the interfacial pores and become homogeneous, whereas solid electrolytes have defects such as grain boundaries, scratches, pores, and surface roughness, which substantially contribute to the growth of dendrite nucleation. Defects in the electrolyte develop different dendrite morphologies under the control of various current densities [3]. For example, lithium filaments growing along crystals in garnet [45], tree-like dendrites in sulfide electrolytes [158,159]. Interfacial lithium chemical processes include lithium kinetics, evolution of interfacial morphology, and interfacial degradation and failure. Lithium kinetics are based on liquid electrolyte lithium deposition. Models such as non-homogeneous nucleation [68], interphase-induced dendrite growth,

Table 3

Summarized data for EW and ion conductivity in common liquid electrolytes. In contrary to the solid electrolyte, the liquid electrolyte needs solvent as environment. The database of EW and ion conductivity of the liquid electrolytes are the pillar to developing experimental, computational and AI models related for dendrite mitigation strategies.

SN	Electrolyte (Solute)	Solvent/Environment	EW(V)	Ion-conductivity (mS cm ⁻¹)	Ref.
1.	Lithium perchlorate (LiClO ₄)	EC (ethylene carbonate)/DMC (dimethyl carbonate)	0.2–4	8.4	[125]
		PC (propylene carbonate)	≈2	5.6	[126,127]
		PEO (poly(ethylene oxide))	<4.45	0.57	[128]
2.	Lithium hexafluorophosphate (LiPF ₆)	EC/DMC	0.2–4	10.7	[125]
		PC	2.5–4.2	5.8	[78,126,129]
3.	Lithium tetrafluoroborate (LiBF ₄)	EC/DMC	2.5–5.9	4.9	[130]
		PC	4.2	3.4	[78,126,129]
		poly(1,3-dioxolane)/fluoroethylene carbonate(FEC)	4.7	1.76	[131]
4.	Lithium hexafluoroarsenate (LiAsF ₆)	EC/DMC	4.5	11.1	[132]
		PC	–	5.7	[78,126]
5.	Lithium nitrate (LiNO ₃)	Dimethyl sulfoxide/PC	≈4.4	3.19	[132]
6.	Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)	PVDF-HFP (Poly(vinylidene fluoride-co-hexafluoropropylene))	0.05	0.46	[133]
		EC/DEC (diethyl carbonate)	–	0.43	[134]
7.	Lithium (methanesulfonyl) (trifluoromethanesulfonyl) imide (LiMTFSI)	EC/DEC	–	0.21	[134]
8.	Lithium 1,1,1-trifluoro-N-[2-(2-methoxyethoxy)ethoxy]ethyl methanesulfonamide (LiFEA)	EC/DEC	>4.3	0.013	[135]
9.	Lithium 2-[2-(2-methoxyethoxy)ethoxy]ethanesulfonyl (trifluoromethanesulfonyl)imide (LiETFSI)	BE (carbonate electrolyte)	≈4.8	0.24	[136]
10.	Lithium (trifluoromethanesulfonyl)imide (LiSTFSI)	DME (dimethoxyethane)	3.75	10	[137]
11.	Lithium bis(fluorosulfonyl)imide (LiFSI)	MP (ethyl propionate)/FEC	>4.2	9.73	[138,139]
		TFEO (tris(2,2,2-trifluoroethyl) orthoformate)/DME	>4.4	3	[140]
		DEE (1,2-diethoxyethane)	4.4	5.01	[141]
12.	Lithium trifluoromethanesulfonate (LiOTf)	TTMS (2,2,2-trifluoroethyl trifluoromethanesulfonate)/TM	5.2	2.99	[142]
13.	Lithium difluoride (oxalate) borate (LiDFOB)	EC/DMC	≈4.4	≈4.6	[143]
14.	Lithium bisoxalate borate (LiBOB)	γ-valerolactone	5.5	>4.9	[144]
15.	Lithium 4,5-dicyano-1,2,3-triazolate (LiDCTA)	EC/DMC	4.8	6.5	[145]

etc. are suitable for solid electrolytes. However, solid electrolytes have unique chemical and mechanical states [66]. The formation/consumption models of lithium ion/atom and interfacial morphology, including interfacial defect formation and atomic diffusion [38] are predicted by studying key parameters such as shear modulus and molar volume ratio [160], and interfacial degradation and failure [68,161]. Interfacial degradation and failure, on the other hand, involve the increase in interfacial impedance and contact loss.

3. Dendrite growth as a multiscale phenomenon

The mechanistic and thermodynamic principles outlined in Section 2 encompassing nucleation kinetics, overpotential-driven heterogeneous nucleation, SEI-induced space-charge effects, stress-mediated growth, temperature-dependent mass transport, and the competition between electrochemical driving forces and mechanical constraints—collectively demonstrate that lithium dendrite formation and propagation are inherently multiscale processes. These phenomena span

atomic-scale ion desolvation and interface reactions, mesoscale morphological instability and stress accumulation, and macroscopic cell-level performance degradation. Consequently, a single-scale description is insufficient to capture the full complexity and feedback loops involved.

A multiscale approach is needed to understand the growth of dendrites in batteries. The molecular dynamics (MD) and DFT frameworks effectively predict molecular behavior and mechanisms, revealing insights into Li-ion diffusion influenced by solvation shells and the thermodynamic processes governing dendrite growth morphology [31, 162]. In other words, MD and DFT methods can provide detailed insights of dendrite growth at atomic scale. Lee et al. [84] conducted a series of reactive MD simulations (refer Fig. 4(a)–(c)) to explore the electrochemical dynamic reactions occurring at the electrode/electrolyte interface, providing insights into the mechanisms involved in these critical interactions. The duration of a single charge cycle in their simulation is maintained around 125 ps. The results of the dynamic growth of dendrite(at charge cycle) and dead lithium (at discharge cycle) during repeated charging-discharging cycles for an EC electrolyte

is shown in Fig. 4(a). Huang et al. [163] employed DFT to investigate the adsorption and diffusion of lithium atoms by calculating the binding energy and potential map. The adsorption and diffusion mechanism are considered as the critical factors influencing dendrite growth. Despite the ability of MD and DFT to detail dendrite growth mechanisms at the atomic level, simulating dendrite formation throughout the entire charging process of LiBs remains challenging due to the extremely short timeframes (picoseconds to nanoseconds) of molecular simulations [164]. It is necessary to upscale these methods and integrate them with continuum-level simulations to understand the mechanisms during the entire battery charging or discharging process. In their study, Liu et al. [85] developed a comprehensive multiscale model that effectively links atomic-level charge transfer physics with the mesoscale phase-field method, incorporating transition state theory to describe the electrodeposition process within a half-cell system. For DFT computations in Li based half cell model (Model 1), they have considered organic EC electrolyte, whereas the half cell model based on Mg uses tetrahydrofuran (THF) electrolyte. As can be seen from Fig. 4(d)–(h), the quantities such as equivalent potentials, driving forces and energetic coordinates for ion transports have been computed by the researchers for the two models: Li/Li₂CO₃/EC (Model 1) and Mg/THF (Model 2). The knowledge obtained from DFT computation is then exported to mesoscale phase field simulations. Another way to overcome the time scale related limitations of MD and DFT method is to combine them with the kinetic Monte Carlo (KMC) simulations. Lee et al. [165] utilized a high-fidelity KMC simulation to observe dendrite formation over extended time scales of 5 to 10 min, or even longer. Their KMC model utilizes the diffusion constants and activation energies obtained from MD and DFT frameworks. Zhang et al. [166] employed large-scale molecular dynamics simulations to reproduce the dynamic process of dendrite nucleation and penetration, revealing that dynamically generated lithium depositions lead to a continuous accumulation of internal stress, ultimately causing a fracture of the solid electrolyte at dendrite tips.

At continuum scale, the phase field method is the most robust as well as most widely utilized to study the spatiotemporal dynamics of dendrites in the batteries [167–170]. Earlier Guyer [171] PFM studied the equilibrium state of electrodeposition, constructed the minimal components of the electrochemical interface model, and the dynamic solutions of the phase field equations. Arguello et al. [172] simulated the growth rate and morphology of the dendrites in 2- and 3-dimensions and investigated the electrodeposition process of dendrite formation in metal anode batteries and deduced a free energy functional describing the partial differential equation of phase field, lithium ion concentration and potential. Chen et al. [173] and Qi et al. [170] used a nonlinear PFM to describe the growth characteristics of different types of dendrites and the effects of temperature and anisotropy on lithium deposition. Hong et al. [167] studied dendrite growth simulations, concentration gradients, overpotentials, and electrochemical reactions on growth patterns. The broken lithium dendrites at the root form dead lithium because of the von Mises stress, when external pressure is applied to the system. As outlined earlier in Section 2, the partial differential equations are very important in explaining the cause–effect relationship between mechanical stress and dendrite morphology. Yang et al. [81] considered the plastic behavior of lithium dendrite by adding the coupling of the heat transfer model and PFM. The model combined the diffusion coefficient of Li⁺, temperature and overpotential generation and described high von Mises stress leading to broken dendrite and dead lithium. The plastic part of free energy density can be expressed as the function of strain (ϵ) and moduli (E_{mech} and K):

$$f_{pls} = (1 - \xi)^2 \left(\frac{1}{2} E_{mech} \epsilon_y^2 + \sigma_y (e_{ij}^T - e_y) + \frac{1}{2} K_1 (e_{ij}^T - e_y)^2 \right) \quad (9)$$

Zhang et al. [174] simulated the formation of dead lithium and combined the experimental results to reveal the discharge electrochemical performance of lithium metal batteries. Of course, some researchers

have also studied the inhibition methods of lithium dendrites, such as Cao et al. [175] who studied elastic modulus and the electrolyte nanochannel width controlled to the growth of lithium dendrites, and added the mechanical energy (the electrostatic energy density f_{mech}) as an additional driving force for the evolution of lithium dendrites.

$$\frac{\partial \xi}{\partial t} = -L_\xi \left[\frac{\partial f_{ch}}{\partial \xi} - \kappa_\xi \nabla^2 \xi + \frac{\partial f_{mech}}{\partial \xi} \right] - L_\eta h'(\xi) \left\{ \exp \left[\frac{\alpha \Delta G(r, t)}{RT} \right] - c_i^* \exp \left[-\frac{\beta \Delta G(r, t)}{RT} \right] \right\} \quad (10)$$

Some other macroscale simulations methods for tracking the spatio-temporal evolution of current density, voltage and state of the charge (SOC) in rechargeable LiBs are pseudo 2D model (P2D) model and single particle model (SPM). These electrochemical models can also be used to perform thermal runaway simulations. The P2D model, while effective, has a high computational load; therefore, it is often simplified into a one-dimensional electrochemical model known as the SPM to reduce simulation time and complexity [176]. The lightweight SPM model has already been implemented in Python Battery Mathematical Modelling (PyBaMM), which is an open-source battery simulation package [177]. SPM is not built with the capability to describe the moving interfaces, and thus it is not possible for using it as standalone method to geometrically describe the profiles of the evolving dendrites. Sahu and Foster [178] have implemented the SPM based continuum model for studying lithium plating and dendrite formation in LiBs. With the existing capabilities of the electrochemical model, they have been able to accurately quantify the concentration, voltage, reaction rate etc. Although the temporal values of lithium metal have been quantified through their model, the spatial profile information regarding dendrite formation remains unaddressed in their work. As the magnitude of electric field strength at the tip is different from the base of the dendrites [69], it is necessary to quantify the spatial information of these structures in the numerical model. To describe the spatio-temporal evolution of Li dendrites, SPM has to be integrated with another method characterized by capabilities to track the spatio-temporal information of bulk and interfacial features. Lee et al. have successfully integrated the SPM [165] with atomistically-informed KMC to describe the evolving dendrites.

Some researchers focused on the simulation of dendrite nucleation and growth processing and some paid more attention on experiments. Many relevant papers exhibited multiscale dendrite morphologies. In Fig. 5, it shows the lithium dendrite in different states. Needle-like, moss-like and branch-like morphologies could be observed in Fig. 5(a)–(c). Researchers used some advanced electron microscopes. He et al. [123] observed the nucleation and growth of lithium dendrite on a nano scale by coupling an atomic force microscopy cantilever into a solid open-cell setup in environmental transmission electron microscopy. Harry et al. [124] observed lithium dendrite growing in different charge rate states by using X-ray tomography slices technology. When the symmetric lithium cell works in a higher charge rate situation, lithium dendrite will grow rapidly and penetrating the electrolyte. Shen et al. [179] observe the pore property of solid state electrolyte. Different sintered temperatures cause different densities and this kind of inhomogeneous electrolyte has great impact on dendrite growth. The experiment showed that the size distribution of dendrites changed in electrolytes with continuous or discontinuous pores. The influence of the related defects was studied by Porz et al. [180]. The lithium plating depends on defects such as surface crack by doing tests on Amorphous 70/30 percentage mol Li₂S – P₂S₅, polycrystalline β -Li₃PS₄, and polycrystalline and single-crystalline Li₆La₃ZrTaO₁₂ garnet. Lithium ions accumulate at the crack tip and generate stress that promoted crack propagation. The voids created by the crack propagation then facilitate the accumulation of more lithium ions, which eventually pass through the entire electrolyte.

4. Suppression of the dendrite growths: scientific approaches

Addressing lithium dendrite formation requires a multifaceted strategy that spans experimental innovation, theoretical insight, and data-driven discovery. This section synthesizes current scientific approaches into three complementary frameworks: (i) experimental and empirical methods that establish foundational suppression protocols, (ii) multiscale computational models that elucidate mechanistic origins and enable virtual screening, and (iii) intelligent data-driven techniques that accelerate high-throughput optimization. Ultimately, integrated approaches that bridge these paradigms offer the most promising pathway towards dendrite-free, commercially viable lithium-metal batteries.

4.1. Experimental and empirical methods

This section reports the work that are solely focused on the experimental approaches for dendrite suppression in LiBs. Works that employ deduction- or induction-based computational methods along with the experiments will be included in Section 4.4. Interface modification and structural design of electrodes/electrolytes are the straightforward approaches to prevent the dendrite formation problems in LiBs [181]. Researchers have proposed some feasible methods to inhibit dendrite growth, summarized in Table 4.

4.1.1. Design of solid electrolyte interphase

The understanding of the interactions between SEIs and dendrites is crucial for developing sustainable electrochemical devices such as batteries [239]. Zhong et al. [240] designed and synthesized a novel artificial SEIs layer, named LiFSI-PET4A-PETMP (LFPP) SEIs. This layer was created in situ on lithium metal surfaces through a one-step click reaction using lithium[(4-styrenesulfonyl)(fluorosulfonyl)imide] (LiFSI), pentaerythritol tetraacrylate (PET), and pentaerythritol tetrakis(2-mercaptoacetate) (PETMP). The resulting LFPP-SEIs featured a controllable 3D cross-linked network structure with high ionic conductivity and a lithium-ion transference number close to unity. These properties effectively prevented lithium dendrite nucleation, thereby suppressing dendrite formation at its source. Patino et al. [74] demonstrated a practical cell operation approach to reinforce the SEIs in lithium anodes through a refined formation protocol that is governed by the redox reactions characteristic of lithium-sulfur systems. Cheng et al. [241] incorporated Li_2S into the SEIs, resulting in a polycrystalline, mosaic film with poor crystallinity. As the nanoparticles of Li_2S , Li_2O , Li_3N , Li_3NO_3 , and LiF were embedded, the Li metal anode was subsequently protected. The sulfurized SEIs achieved a very high ionic conductivity of $3.1 \times 10^{-7} \text{ S cm}^{-1}$, an order of magnitude higher than the routine SEIs ($4.2 \times 10^{-8} \text{ S cm}^{-1}$). This sulfurized SEIs enabled uniform Li plating or stripping, thereby preventing the dendrite formation. Moreover, the coulombic efficiency of the battery with the sulfurized SEIs were larger than that of the device with the routine SEIs. Pokharel et al. [242] developed a scalable solution-processed method to construct a phase-pure, crystalline Li_3N -rich artificial SEI on lithium metal, achieving both high mechanical strength and low Li^+ diffusion barrier. Compared to conventional polycrystalline Li_3N layers, the single-crystalline SEI enhanced Li^+ transport kinetics and electrode stability. Combined experimental and phase-field simulation analyses revealed the coupling between Li^+ transference, diffusion behavior, and interfacial mechanics, leading to improved reversibility and cycling performance in both symmetric and full cells.

Rather than altering the chemistry of SEIs, some researchers have floated the idea of using the mechanical design approach. Cheng et al. [243] constructed an implantable SEIs and then placed it on a lithium-metal battery device to prevent or suppress the appearance of dendrite. The design was found to work in $\text{Li} - \text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ and Li|S batteries containing ether and ester electrolytes, respectively.

4.1.2. Engineering the electrolytic medium

Electrolyte engineering (ELYTENG) deals with the topics of bringing out innovations in the chemistry and composition of the electrolytes [244,245]. Among many many approaches, the study with ionic liquid electrolytes, metal organic framework (MOF)-modified electrolytes and electrolyte additives are some examples that can be considered well within the scope of ELYTENG [244]. It has been recognized as one of the most effective strategies to develop a stable SEIs for eventual suppression of the growth of lithium dendrites [246]. The ELYTENG includes both chemical- and physical-method-based engineering designs of the electrolytes. While the chemical method is utilized for both liquid and solid states electrolyte, the physical technique is dominantly utilized for solid state electrolytes. Chemical-methods are generally intended to alter the reaction kinetics at the electrolyte domain that ultimately favors the inhibition of dendrites while maintaining or even increasing the Coulombic efficiency. The main roadmap of chemical-method based electrolyte engineering is associated with the search of functional additives for electrolytes that can coordinate with the Li^+ and contribute to the creation of a stable SEIs film [246,247]. In this perspective, ELYTENG is a branch of SEIs design, that focuses solely on modifying the composition of electrolytes via introduction of functional additives.

Chen et al. [248] systematically elucidated the correlation between electrolyte solvation structure, SEI formation, and lithium deposition morphology using a single-salt, single-solvent model system. Through cryo-EM and computational analyses, they revealed that high-concentration electrolytes with Li^+ -anion-dominated solvation favor anion decomposition, yielding inorganic-rich amorphous SEI layers with high interfacial energy and uniform granular Li deposition. In contrast, solvent-dominated solvation in dilute electrolytes promotes solvolysis, forming organic-rich mosaic SEI with low interfacial energy that drives whisker-like dendritic growth. Their work provides mechanistic insights into dendrite formation and highlights strategies for electrolyte concentration design in lithium metal batteries. Wang et al. [249] proposed that incorporating an optimal amount of lithium iodide (LiI) as a functional additive in ether-based electrolytes enables dendrite-free lithium deposition (Fig. 6(a)). They have described that LiI induces electrolyte polymerization, forming an in-situ robust and elastic oligomer-enriched SEIs on the lithium surface. Subsequently, this SEIs enhances ionic conductivity and facilitates lithium-ion migration, leading to uniform lithium deposition at the Li/electrolyte interface while effectively suppressing dendrite growth. In their experimental study, Pham et al. [250] proposed N-N-diallyl-2,2,2-trifluoroacetamide (NDT) as an electrolyte additive to inhibit dendrite growth on an ultrathin Li anode (20 μm). Through its preferential reduction and involvement in the primary Li^+ solvation shell, the NDT facilitated the formation of a Li_3N -enriched, uniform SEIs layer on the Li metal. Through electrolyte engineering, Ye et al. [251] have discovered the synergistic effect of an Al-containing solid electrolyte interphase layer and Al-based colloidal particles in achieving a stable lithium metal anode. In their work, a controllable AlCl_3 was used as an efficient electrolyte additive for dendrite-free Li deposition, reacting with trace water to form an Al_2O_3 -rich SEIs layer and Al-based positively charged colloidal particles (PCCPs). The PCCPs were found to create an electrostatic shield around protruding Li, guiding uniform deposition and preventing dendrite formation. Li|Se and $\text{Li|Li}_4\text{Ti}_5\text{O}_{12}$ batteries showed improved dendrite suppression and improved performance due to synergism between the SEIs layer and PCCPs.

Wu et al. [252] introduced a facile approach to induce the growth of detrimental dendritic lithium, causing cells to short frequently and consistently. Using this protocol of intentional dendrite induction, they revisited various electrolytes, comparing and quantifying the resulting SEIs. Although their work is focused on different electrolytes and not electrolyte additives, their methodology could be expanded to measure

Table 4
Highlighted strategies for inhibiting dendrite growth in typical batteries.

SN	Strategy/Method	Key ingredients/processes	Battery systems	Ref.
1.	Electrolyte additives	FEC	LiBs	[182,183]
		Vinylene carbonate (VC)		[183,184]
		Nitrates: KNO_3 , LiNO_3 , AgNO_3		[185–189]
		Anhydrides: succinic anhydride	LMB	[190–192]
		Heptafluorobutyric anhydride		[193]
		Lithium salts: $\text{Li}[\text{N}(\text{SO}_2\text{F})_2]\text{--Li}[\text{N}(\text{SO}_2\text{CF}_3)_2]$, LiTFSI--LiBOB , $\text{Li}[(\text{FSO}_2)(\text{n-C}_4\text{F}_9\text{SO}_2)\text{N}]$		[194–196]
		Organic reagents: $\text{Py}_{13}\text{TFSI}$, 1,4-dioxane		[197,198]
		ethyl α -cyanoacrylate, methyl viologen		[199,200]
		1,3-propanesulfonate		[189]
		Other: AlCl_3 , Li halides		[187,201]
		Lithium polysulfide	LSB (Li-S battery)	[202]
		LiNO_3		[202,203]
		Tetraethylammonium nitrate (TEAN)		[204]
		CsNO_3		[205]
		LiODFB		[206]
		LiBOB		[207]
		$\text{La}(\text{NO}_3)_3$		[208]
		$\text{PYR}_{1,14}\text{TFSI}$		[209]
2.	Artificial SEIs	Cu_3N + SBR	LiBs/LMB	[210]
		AlI_3		[211]
		Al_2O_3		[212]
		Fluorinated polysulfonamide		[200]
		Li_3PO_4 layer		[213,214]
		LiSFSI		[200,215]
		Polyvinylidene difluoride	LSB	[216,217]
		Nafion		[218,219]
3.	Super-concentrated electrolyte	Gas processing (N_2)	LMB/LSB	[220,221]
		Dimethyl sulfoxide (DMSO)-based electrolyte	Li–O ₂	[222]
		LiFSI-DME electrolyte	LMB	[223]
4.	Solid-State Electrolyte	Highly porous glass fiber	LMB	[224]
		Solid inorganic electrolytes (PEO + LiTFSI), Li_3N	SSB	[225,226]
		Gel polymer electrolyte		[227]
5.	Nanostructured Electrolyte	Inorganic solid electrolytes (composites, coating)		[228,229]
		Nanocomposite electrolytes	LMB	[230,231]
		SiO_2 composite electrolyte		[232]
6.	Main material modification	Ionic liquid electrolytes		[233,234]
		Structured anode	LMB	[235]
		Polyolefin separator		[6]
7.	Cell operation	Cathode modification		[236]
		Charging/discharging rate	LMB	[74]
		Pulse plating		[237]
		Convection cell		[238]

the behavior of electrolytes with different additives. Hwang et al. [253] found that the electrolyte of ionic liquid can inhibit the accumulation of dead Li (Fig. 6(b)). Especially, this kind of system has great cycle properties as shown in Fig. 6(c) [254].

In the context of the use of the novel electrolytic additives for dendritic suppression, it is necessary to equally focus on maintaining or if possible improving Coulombic efficiency [240,255]. The advances made in the area of electrolyte engineering in other battery types such

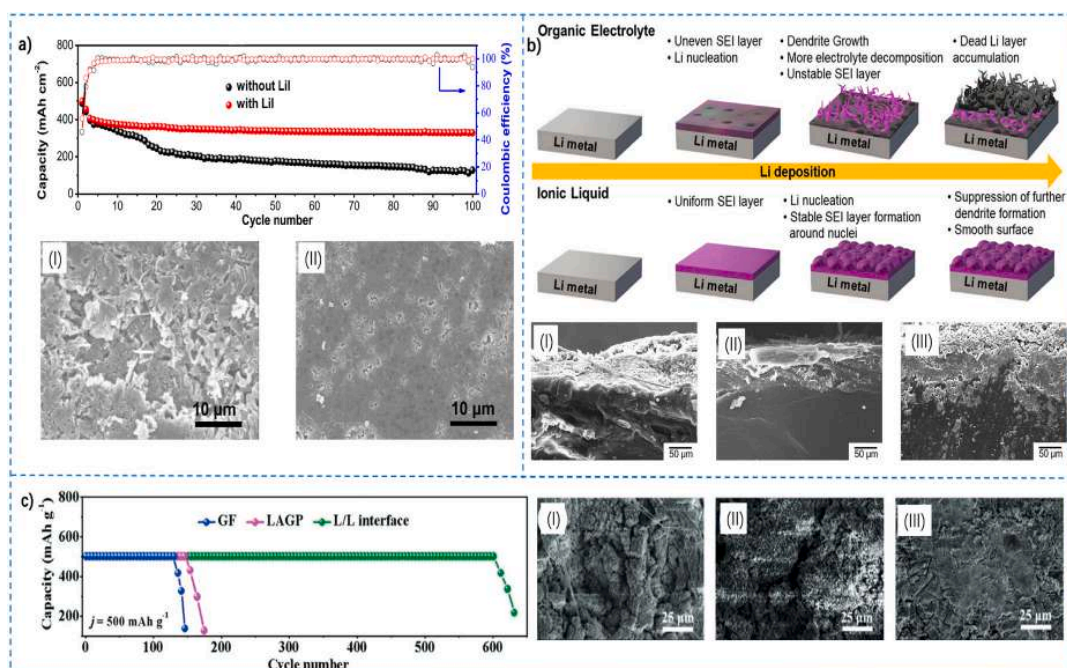


Fig. 6. Liquid electrolyte engineering strategies: Modifying liquid electrolytes to achieve controlled lithium ion deposition and suppression of dendrite growth. (a) The addition of the functional additive LiI to ether-based electrolytes enables a substantial increase in cycle life without compromising coulombic efficiency. The additive system (II) promotes uniform lithium-ion deposition, resulting in a smoother metal surface. Current density is 0.1 C (1 C=678 mA g⁻¹). Voltage is 0.8–3 V. Material is Li-Se battery system with LiTFSI electrolyte [249]. (b) 30 mol% Li[FSA]-[1-ethyl-3-methylimidazolium] [FSA] ionic liquid (IL) electrolyte contrasted with traditional organic carbonate electrolyte of 1 mol dm⁻³ Li[PF6]-EC/DMC (1:1 vol/vol) (OE) has great properties of dendrite suppression and dead Li accumulation. There are irregular lithium dendrites on the surface by using organic electrolyte OE (I). On the contrary, IL system has smooth surface under 25 °C (II) and lower dendrite density of surface under 90 °C (III) [253]. (c) Polarity difference in liquid electrolytes protects lithium electrodes and inhibits lithium dendrite growth. This liquid electrolyte system made by non-polar fluorosilicane (PFTOS) and conventionally polar dimethyl sulfoxide solvents. PFTOS has excellent wettability towards electrodes, and this character promotes Li uniform deposition. Comparing glass fiber (I) and Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ (II), it is observed that the surface of liquid/liquid two phase electrolyte is smoother [254].

as Zn-ion batteries [256–258] and Na-ion batteries [259–261] can be translated and implemented for the development of dendrite-free LIBs.

On the other hand, the physical-method based ELYTENG comprises of employing different manufacturing routes or processing variables to produce electrolyte with desirable microstructures (e.g. grains with preferable orientation and size distribution, reduced porosity) that are resistant to dendrite growth. Using solid-state electrolyte instead of liquid ones is the most studied physical approach to tame the unwanted growth of dendrites. In fact, solid polymer electrolyte (SPE)-based all-solid-state lithium batteries [262] are emerging as the next-generation energy storage devices in terms of their desirability for safety and performance aspects. Liu et al. [263] have performed manufacturing route based design of electrolytes in all solid state lithium metal battery (ASSLMB). They identified a novel cube-shaped microstructure in the Li_{5.3}PS_{4.3}ClBr_{0.7} argyrodite electrolyte, synthesized via a high-speed mechanical milling followed by annealing method (BMAN-LPSCB), through comparisons of various synthesis routes. They have shown schematic sketches (refer Fig. 7(a)–(b)) to compare the microstructures of LPSCB electrolyte synthesized via solid-state sintering (SS-LPSCB) and BMAN-LPSCB. While the SS-LPSCB has non-uniform microstructure with larger porosity, the BMAN-LPSCB is characterized by uniformity and a very low degree of porosity. This lack of defects in the latter enables it to inhibit dendrite growth even at larger values of current density. Additionally, they have found out that the ASSLMB utilizing the BMAN-LPSCB electrolyte showed excellent

durability, retaining 96% capacity over 1000 cycles at a 1C rate. Their study highlighted the critical role of the sulfide electrolyte's microstructure in influencing mechanically-driven Li dendrite propagation in all-solid-state batteries. Han et al. [75] have implied that high electronic conductivity (>10⁻⁴ S cm⁻¹) of solid electrolytes such as LLZO, LIPON and amorphous Li₃PS₄, is the main cause behind dendrite formation in all solid state batteries. They have proposed that lowering the overall electronic conductivity of the SEs is a better solution than increasing the ionic conductivity in suppressing the dendrite formation.

4.1.3. Electrode engineering

Electrode engineering focuses on improving the properties and functionalities of electrodes, such as their conductivity, stability, and surface characteristics, to facilitate better electrochemical reactions. Increment of the areal capacity of the electrode is one of the milestones in relation to the design of resilient and electrochemically efficient batteries, and the discussion about this parameter will be provided later in Section 6. However, achieving higher areal capacity amplifies dendrite risks through uneven deposition and volume stress, yet it drives innovations in suppression strategies, such as 3D hosts that promote uniform plating. The stress-associated challenges arising from the uncontrollable volume expansion of Li-metal anodes during battery cycling, account for the mechanical damages such as dendritic growth, electrode cracking and SEIs degradation. Utilization of porous 3D structures as electrodes or use of some coating layer on electrodes can be

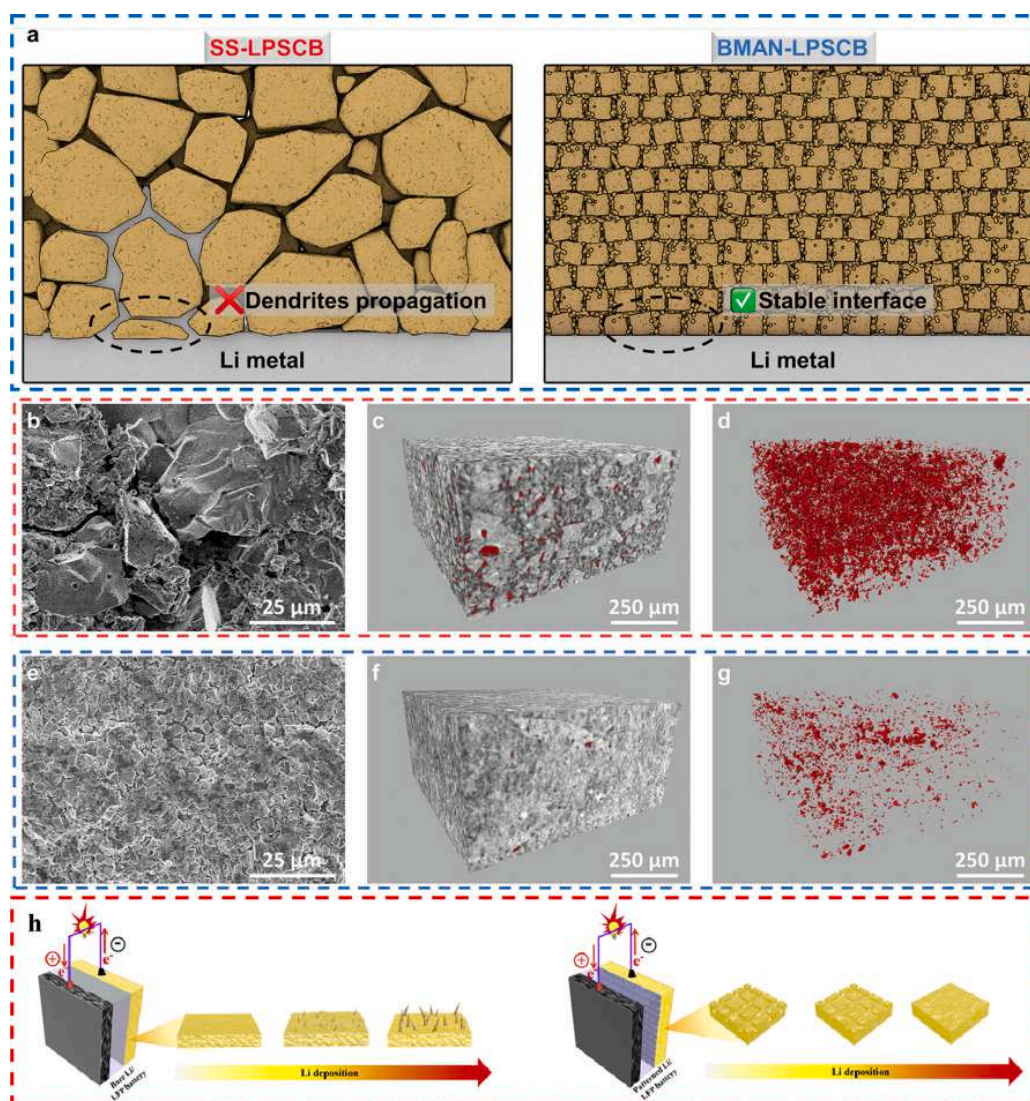


Fig. 7. Solid electrolyte engineering strategy illustrated in (a)–(g): Solid state electrolytes with more uniform grain microstructure and low porosity are more resistant to dendrite growth. From the cross-sectional SEM images of (b) SS-LPSCB and (e) BMAN-LPSCB cold-pressed pellets, it can be inferred that the mechanical processing route has an influence on the grain morphology and relative porosity content. The 3D volume rendered synchrotron X-ray computed tomography (XCT) image of SS-LPSCB pellet with inside voids is shown in (c) whereas that of BMAN-LPSCB pellet with inside voids is presented in (f). The 3D rendered synchrotron XCT image of voids only for pellet (c) is presented in (d) whereas that for pellet (f) is shown in (g). From these characterizations, it is evident that the BMAN-LPSCB electrolyte produced via mechanical alloy milling + annealing, has more uniform grain microstructure and lower degree of porosity as compared to SS-LPSCB fabricated via solid state sintering method. This inference is presented in (a) as schematic sketches [263]. (h) Schematic comparison of lithium dendrite growth after pattern design in solid state battery [15].

some common examples related to electrode engineering of LiBs. Both electrolyte and electrode engineering aim to establish the stable SEIs and can be categorized as the two different fields of SEIs design. The physical design of electrodes is of great interest to researchers. Yang et al. [264] constructed a freestanding three-dimensional Li metal foam which was accompanied by an inherent SEIs encapsulation formed through template-free chemical etching. Unlike planar Li metal foil, a 3D porous Li matrix can effectively buffer volume changes and allow Li deposition within its porous structure. So, their designed 3D porous electrode promoted uniform lithium deposition and contributed to the suppression the growth of dendritic Li. A 3D $\text{Li}_2\text{O}@\text{CuNA}/\text{CF}$ skeleton with superior lithiophilic properties has been fabricated by

Tan et al. [265]. The CuO nanowire (CuNA) array on Cu foam caused the enhancement in the Li wettability through in-situ formation of Li_2O , thereby enabling the Li pre-storage through thermal infusion mechanism. This type of multilevel 3D structure can flexibly accommodate volume changes during Li plating/stripping, and by aiding the formation of stable SEIs caused a suppression of the dendrite growth. $\text{MoO}_2/\text{Mo}_2\text{C}$ heteronanotubes change the electrode structure and have great impact on dendrite suppression (Fig. 8(a)) [266]. There are some different type of surface modification such as flower-like LiFePO_4 micropheres [267] (Fig. 8(b)), LiMn_2O_4 microtube [268], hierarchical $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{TiO}_2$ tube [269], hierarchical Si with carbon coating [270], SnO_2 thin films [271] and bimodal porous carbon [272]. During lithium

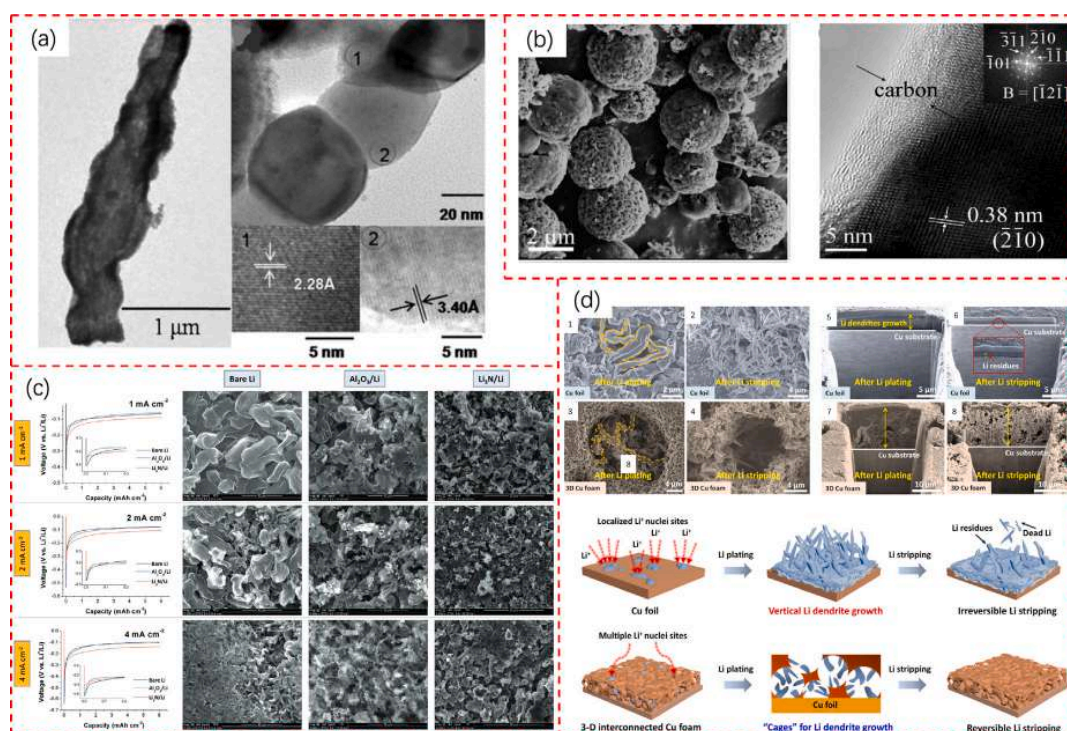


Fig. 8. Different electrode modification methods are employed to suppress dendrite growth on surfaces. (a) The mesoporous material containing nanotubes forms a hierarchical structure with a three-dimensional porous network, which facilitates the penetration of electrolyte and lithium ions into the electrode interior. $\text{MoO}_2/\text{Mo}_2\text{C}$ heteronanotubes can be clearly observed in TEM images [266]. (b) Overall morphology of walnut-shape LiFePO_4 microspheres shows in SEM and TEM images [267]. (c) Compared to Al_2O_3 -modified electrodes, Li_3N -modified electrodes exhibit superior voltage curves and a dendrite-free surface state [273]. (d) Lithium nucleation and deposition/stripping behavior on different copper electrodes show in schematic diagrams and SEM Images [274].

plating through a Li_3N particle bed, dendritic crystal grows into a 3D lithium network formed by particle surface wetting, whereas direct plating through Li_3N particles does not exhibit dendritic crystal nucleation. During electrodeposition through a Li_3N particle bed, lithium ions wet the particle surfaces to form a three-dimensional lithium network, thereby converting dendritic crystal growth into this network structure. In contrast, direct electrodeposition through Li_3N particles does not result in dendritic crystal nucleation. Li_3N -modified electrodes have more excellent superior voltage curves and lower density surface (Fig. 8(c)) [273]. Kim et al. [274] designed a “lithium dendrite cage” structure for anode-less lithium metal batteries. This system employs a three-dimensional interconnected porous copper foam electrode synthesized via electrodeposition. The numerous pores within the electrode constrain lithium dendrite growth while accommodating lithium dendrite deposition, thereby suppressing vertical lithium growth and mitigating swelling failure during battery cycling. The structures show in Fig. 8(d) [274].

Multiphysics guided strategy has been implemented by Chang et al. [275] to stabilize the Lithium metal anodes in batteries. They have implemented an adaptive piezoelectric effect to successfully control the stress-variations induced side effects at the Lithium anode. The stress-harnessing innovative approach leverages the piezoelectric effect to transform potentially hazardous stress variations in lithium-metal batteries into an adaptive built-in electric field. The polylactic acid-lithium (PLA-Li) anode was designed for multisystem batteries. Remarkably, this inherent electric field spontaneously adjusts its intensity to accommodate different battery systems, enhancing ion migration, ensuring uniform distribution across the entire anode and reducing the stress concentration. The reduction of stress concentration via

the multiphysics field decoupling strategy was responsible for minimizing the dendrite formation. Attempts have been made to design next-generation substrated for anode-less batteries. Grain boundary engineering have been performed by Aota et al. [276] to control the lithiation of solid solution substrates and thereafter reduce the dendrite formation in Li-metal batteries. The Li-Ag diffusion couple is utilized as the substrate in their work. The results showed that lithiation was primarily driven by grain boundary diffusion, leading to the localized formation of Li-rich regions with lithium content exceeding 93.8 at.%. Within the grain interiors, lithiation and phase transformations were hindered by kinetic and possibly chemo-mechanical factors. This suggests that the previously reported high lithium diffusivities in silver were due to intense lithiation occurring at grain boundaries or surfaces, as observed in this study. Random high-angle grain boundaries were found to be favorable sites for the nucleation of Li-rich regions. Controlling the grain size and grain boundary structure has been postulated as a key design strategy for developing futuristic anode-less battery substrates.

Lithium methyl carbonate coating formed on the lithium metal through the reaction of lithium iodide with dimethyl carbonate can enable dendrite-free lithium cycling in symmetric Li-Li cells at a high current density of $3 \text{ mA}/\text{cm}^2$ [277]. As shown in Fig. 7(h), the structural design of solid-state batteries is also one of the effective ways to suppress dendrites. Bare lithium anode has uneven surface because of irregular pothole defects during the production process. These kind of defects influence the stability of anodes and electrolytes. It is very easy to promote dendrite growth, pierce the electrolytes and eventually cause a short circuit during the charging and discharging process. However, the treated grid shaped non-smooth unit lithium anode can effectively suppress the formation of dendrites and increase the cycle life.

4.2. Multiscale computational methods (Virtual framework based on deduction methods)

Computational models at the multiscale level, spanning from atomistic to continuum scales, are strategically designed to accurately identify and optimize dendrite suppression strategies by elucidating the underlying electrochemical, mechanical, and kinetic mechanisms that govern lithium deposition and growth. However, it is noteworthy that the number of computational models specifically focused on dendrite suppression remains significantly lower compared to those dedicated to dendrite growth modeling, highlighting a critical gap in the literature that prioritizes understanding formation over proactive mitigation.

4.2.1. Atomistic scale modeling

Atomistic modeling methods, such as DFT and MD, provide foundational insights into the atomic-scale interactions at the electrode-electrolyte interface, enabling the virtual screening of additives and materials that can stabilize the SEI and inhibit dendrite nucleation. Lee et al. [84] have demonstrated via reactive MD simulations that the use of the hydrogen fluoride (HF) additive in the organic EC electrolyte can aid in the suppression of dendrite growths. For example, pure EC electrolyte leads to dead lithium during the charging and discharging process (Fig. 4(b)). This virtual ELYTENG approach is safer and more cost-effective as compared to the experimental approaches described in Section 4.1.2. Moreover, the images, namely Fig. 4(a)–(c), illustrate that beneficial decomposition reactions between electrolyte components generate a protective film on the anode surface, reducing interphase volume changes and preventing unnecessary degradation. Liu et al. [85] have employed DFT calculations in Li and Mg based systems with different electrolytes, and presented the comparative studies as shown in Fig. 4(d)–(h). The images show that the disparity in cation desolvation-induced exchange current is primarily responsible for the markedly different dendritic Li plating and smooth magnesium plating. The authors have combined atomistic charge-transfer calculations with a mesoscale phase-field model to understand and predict the morphological evolution of metal electrodeposition processes. The study by Liu et al. [85] thus presents a multiscale modeling strategy, combining phase-field and atomistic calculations, to guide the design of dendrite-free Li-ion battery anodes.

4.2.2. Continuum level material modeling

Continuum-level material modeling, particularly through PFM, bridges mesoscale phenomena to macroscopic battery performance by simulating the interplay between mechanical stresses, ion transport, and electrochemical driving forces, thereby offering predictive tools for evaluating dendrite suppression under realistic operating conditions. Phase field method has been implemented by Ren et al. [175] to study the role of ELYTENG in suppression of lithium dendrites. The aluminum oxide nanofiber embedded polyvinylidene fluoride-co-hexafluoropropylene constituted the microstructure of the solid electrolyte and the mechanical effects of these electrolyte is investigated in their model. Specifically, the influence of the elastic modulus and width of the electrolyte channel has been outlined. Mechanistic insights were obtained from the computational model regarding the competitive roles between mechanical and electrochemical driving forces to determine the fate of the dendrites. It was found from the model that an additional mechanical driving force is induced by the difference in Young's modulus between the Li metal and the solid electrolyte, partially offsetting the electrochemical driving force and influencing dendrite growth. The confinement of Li-ion transport along the vertical direction, the reduction of the concentration gradient at the metal/electrolyte interface, and the inhibition of Li dendrite growth are achieved by the introduction of 1D nanofiber arrays. The piezoelectric effect (Fig. 3) offers a promising mechanism to suppress dendrite growth in lithium-metal batteries by generating localized electric fields that counteract ion deposition at protrusion sites. When lithium deposition creates

surface protrusions, mechanical stress from dendrite growth stretches adjacent piezoelectric materials (e.g., PVDF or BTO composites in separators/coatings). This deformation generates a local piezoelectric overpotential (up to 100 V in simulations) [58]. Reduces lithium-ion flux to dendrite tips by creating an opposing electric field. Redirects ions to flatter regions, promoting uniform deposition.

While these deductive methods provide detailed mechanistic insights into dendrite suppression such as identifying optimal electrolyte additives for SEI stabilization or mechanical reinforcements to counteract protrusion growth, their standalone application is often slow and computationally intensive, thereby limiting their ability to rapidly screen vast material spaces for effective dendrite control strategies. This necessitates integration with induction-based learning approaches, such as machine learning, to accelerate high-throughput screening and optimization of suppression techniques, including tailored interfacial coatings and microstructure designs, as discussed in subsequent sections. In conclusion, multiscale deductive modeling lays a robust foundation for dendrite suppression strategies by elucidating nucleation barriers and growth kinetics but underscores the need for hybrid frameworks to address computational bottlenecks and enhance predictive efficiency in achieving dendrite-free battery interfaces.

4.3. Intelligent data-driven techniques (Virtual framework based on inference methods)

Recent advancements in deep learning methods [278–280] have showcased the strength of these techniques in establishing process-property connections and accelerating the search for optimal processing routes. These capabilities have turned the attention of the renewable energy community toward the use of advanced data-driven and generative AI models in the design of improved LiBs [281–283]. Several design factors for LiBs, ranging from thermal management [284] to battery health status [285] have been included in data-driven assisted designs. Zhai et al. [286] have provided a review paper focused on machine learning studies of LiBs lifecycle management. In their paper, advancements in machine learning methods for material selection, life prediction, and cascade utilization related to LiBs lifecycle are discussed. These works attest to the computational advantages that data-driven methods provide in battery design efforts.

The large space of parameters affecting Li dendrite formation and the multiscale nature of this process necessitate the use of data-driven techniques. Machine learning studies on Lithium dendrite formation have so far focused on screening candidate materials with the ability to suppress dendrite initiation and growth or predicting properties that control stability criteria. In a review paper on modeling the nucleation and growth of Li dendrites in solid electrolytes, Esmizadeh et al. [287] briefly discussed dendrite nucleation modeling studies, including the use of machine learning models. Ahmad et al. [288] developed a crystal graph convolutional neural network (CGCNN) to predict shear and bulk moduli, and gradient boosting regression and kernel ridge regression models to predict elastic constants of inorganic solid electrolytes—properties that have been shown to control dendrite initiation [289]. These properties are usually obtained from first-principles models, while the machine learning models are trained on structural features without the need for first-principles calculations, reducing the high computational cost of screening a large space of candidate materials. These predictions are then used in a theoretical framework that evaluates dendrite initiation with a lithium metal anode. Using this framework, the authors were able to screen over 12000 organic solids and found 20 interfaces that can suppress dendrite formation [288]. Due to their high energy density and promising energy storage capability, the design of LMB has been a focus of accelerated material discovery efforts [290,291]. Satpati et al. [292] applied several machine learning models to establish the structure-property correlation of solid electrolytes by predicting their mechanical properties and interphases. The models were trained on more than 9000

materials and used to predict the properties of over 49000 materials. In addition to shortlisting promising compounds with a lower propensity for dendrite formation, their study investigates the implementation and performance of several machine learning tools for structure–property connections. Liu et al. [293] studied the stabilization of the lithium metal anode with cation doping and utilized a machine learning approach to classify candidate Li|LLZOM (where M is the dopant) based on its interface thermodynamic stability and predict the Li|LLZOM interface reaction energy. They initially performed a feature selection investigation to reveal the underlying mechanisms of interface stability. Their machine learning technique yielded accurate predictions of interface stability, and their combined high-throughput automated reaction screening and machine learning approach revealed that the M–O chemical bond strength controls the Li|LLZOM interface stability.

Charge transport properties can also affect the Li dendrite formation. Ma et al. [294] developed an Artificial Neural Network (ANN) model to reveal the effects of ion concentration and surface curvature on the lithium growth rate. In their study, Stimulated Raman Scattering (SRS) Microscopy was used to obtain the ion concentration in the electrolyte. The analysis of SRS images provided information on lithium surface curvature, concentration and gradient of Li ions, as well as the Li dendrite growth rate. Additionally, a sensitivity analysis was performed to quantitatively show the impact of each network feature on the dendrite growth rate. Permatasari et al. [295] developed a Support Vector Regression (SVR) model that serves as a non-destructive estimator for the factors affecting Li dendrite growth. This model identifies the variables controlling the current distribution within a LiBs. A subsequent analysis of the working potential at the anode and dendrite precipitation enabled the investigation of two different cells and three separator structures with regard to their sensitivity to Li dendrite precipitation. Similarly, Ma et al. [296] introduced a real-time method to estimate the LiBs anode potential. Random Forest, Back-propagation Neural Network (BPNN), and Long Short-Term Memory (LSTM) models were developed based on nine anode potential features. In their work, feature engineering and machine learning models contribute to establishing the linkage between operating conditions and Li plating. Agentic battery-materials simulations and autonomous battery informatics are the most trendy fields in connections to the candidate selection, reliability design and controls of dendrites. More details on these two popular intelligent data-driven methods will be provided in Sections 5 and 6.

4.4. Integrated approaches

Wang et al. [247] used DFT and molecular dynamics simulation to analyze the strong coordination between 15-c-5 and Li⁺ ions in detail, and the mechanism to inhibit the growth of lithium dendrites was explained. Electrolyte additives were used in the experiments to suppress dendrite formation and increase battery life. There are some traditional analytical models and numerical simulation methods, such as MD, phase field(PF), Monte Carlo(MC) and cellular automata(CA), etc. These methods have made some headway in the simulation branches, but there are still challenges of accuracy and complexity. Zhao et al. [297] combined machine learning and computational methods for multiscale modeling to simulate dendrite growth in the mechanism and reveal the influence of physical factors, focusing on selecting a variety of different parameters to improve the robustness of the system, including temperature, concentration gradient, electric field intensity, ion concentration, dendrite surface energy, solution mobility, and number of lattice defects. The VASP (Vienna Ab initio Simulation Package) software was used to describe the microscopic interactions of dendrite growth by the First Principle Thinking. Machine learning methods also have obvious advantages in accelerating material selection. Ahmal et al. [288] used CGCNN to predict the shear modulus and bulk modulus of crystalline solid electrolytes and calculate

the stability parameters (Eq. (11)), to select electrolytes that inhibit dendrite growth.

$$\chi(k) = \frac{\Delta\mu_e(k)}{f_1(k)\cos(kx) + f_2(k)\sin(kx)} \quad (11)$$

Choi et al. [301] have conducted in-silico design to study the role of the mechanical seed mechanism in inducing homogeneous lithium metal growth in batteries. The total energy in amorphous Li and disordered-phase was computed using DFT method, whereas the effective cluster interaction was predicted with the DFT-assisted machine learning model. Then the concept of mechanical seeds was employed in the classical MD computations of compressive strains in disordered phase transition. By using the integrated in-silico approaches, they have elaborated the way how the mechanical seed concept could be applicable to the system for the prevention of the dendrite growth. Liu et al. combined DFT and phase field methods to achieve dendrite-free deposition of lithium metal anodes. By comparing the Mg electrodeposition morphology, they found that the difference in cation desolvation-induced exchange current was the main reason for the difference in electrodeposition morphology. Through experiments, they verified that the low intrinsic exchange current density of Mg during electrodeposition was the main reason for its non-dendritic deposition, providing support for the dendrite-free electrodeposition of Li metal electrodes [85].

Integrating machine learning approaches with ab initio and physics-based methods is another way to mitigate the accuracy/computational efficiency trade-off. In recent years, there have been several studies on LiBs design that utilized machine learning models either to accelerate the ab initio simulations or to further establish the process-property linkage from first-principles results [302–305]. Han and Lin [306] combined a high-throughput phase field model with a machine learning approach in the study of performance evolution during lithium battery cycling. Utilizing a step function to distinguish between dead and active states of local Li metal, phase field simulations revealed the effects of current density and ion diffusion coefficient on Li dendrite growth. Subsequently, by combining phase field simulation results, Lasso regression, and feature engineering, the relationship between battery parameters and performance under cycling conditions was established. Similarly, Ren et al. [307] used the phase field method to connect the elastic modulus and yield strength of both solid electrolyte and metal anode to Li dendrite morphology. Subsequently, a machine learning approach was developed to reveal the relative importance of electrode and electrolyte mechanical properties in dendrite growth. For this purpose, a Sure Independence Screening and Sparsity Operator (SISSO) was utilized to provide interpretable correlations between material mechanical properties and dendrite morphology. Based on phase field and machine learning results, the authors concluded that solid electrolytes with high elastic modulus and yield strength better inhibit Li dendrite growth. Wang et al. [308] have developed the Density Functional Theory Based Research Engine for Agentic Materials Simulation (DREAMS) framework that integrates DFT with a hierarchical, multi-agent Large Language Model (LLM) system to establish L3-level (Level 3 Autonomy) automation in computational materials discovery. This framework has been validated as a generic materials simulation tool for achieving expert-level accuracy in complex challenges like predicting adsorption energies and quantifying functional-driven uncertainties. Crucially, the autonomous, high-fidelity nature of DREAMS provides a blueprint for future integrated computational platforms capable of accelerating complex electrochemical research, including but not limited to the simulation of SEIs formation, the prediction of ionic transport properties in novel electrolytes, and the rational, high-throughput design of materials and coatings for effective Li dendrite suppression in next-generation batteries.

One of the main aspects of Li battery design that can benefit from data-driven techniques is the simulation of the microstructure

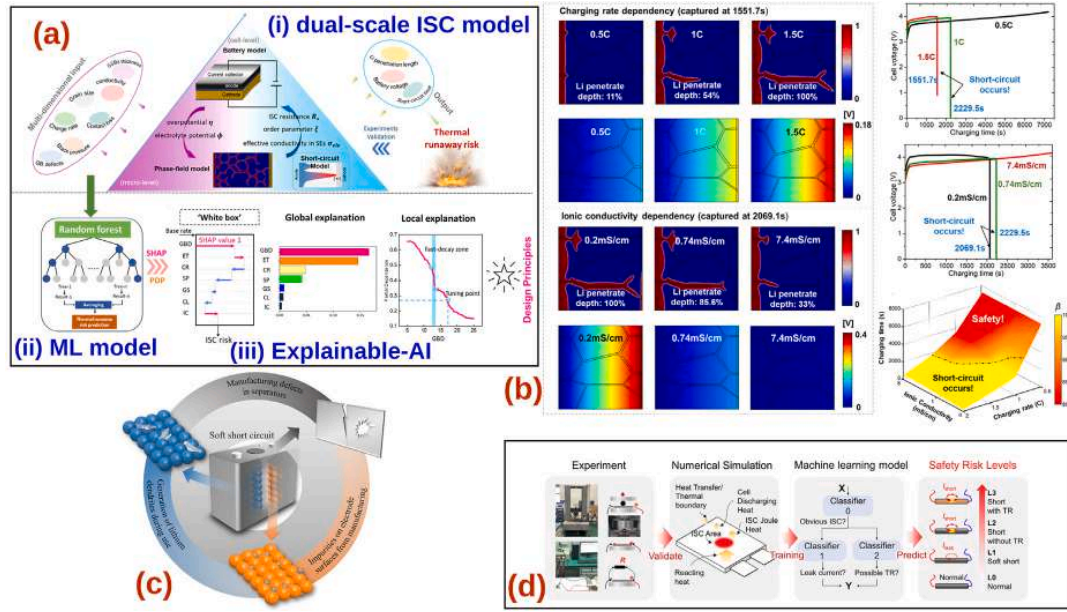


Fig. 9. Integrated methods serve as the strong tools in preventing dendrite induced short circuit in lithium metal batteries. As illustrated in (a), (i) a dual-scale short circuit model combined with (ii) ML-model and (iii) explainable AI enables transparent prediction and interpretation of battery thermal runaway risk based on key material and design features. The phase field model for dendrite evolution along grain boundaries of solid electrolyte as shown in (b) is the core aspect within the dual-scale model of (a) (i), that interacts with battery model. The mechanisms of short-circuit in battery is elaborated schematically in (c), and dendrites growth are highlighted as the cause of such safety risks in the batteries. The images (d) present the battery safety model by combining experimental battery models with numerical simulation and ML model. (The images (a)–(b) are reproduced with permission from [298], and (c) is reproduced with permission from [299] and (d) is reproduced with permission from [300]).

and morphology evolution of Li dendrites. Dendrite formation is an interfacial phenomenon that involves a wide range of length scales. Despite the accuracy of first-principles methods, they fail to provide a complete picture of Li dendrite formation, as these methods are limited to a simulation domain of a few nanometers and a few hundred picoseconds [309,310]. On the other hand, the computational advantages of machine learning models can bridge this gap. In this regard, machine learning force fields (MLFF) have been utilized in recent studies on Li dendrite formation. MLFFs are trained on relevant accurate data obtained from *ab initio* methods and are expected to capture the underlying quantum mechanics relationships [311]. Tawfik et al. [312] introduced a graph neural network, called the direct integration of the external potential (DIEP) model, that demonstrated enhanced accuracy in predicting the potential energy surface for materials. In a subsequent work, they applied the DIEP model, trained on the 188k-sample large MPF.2021.2.8 dataset [313], to simulate Li dendrite initiation in SEIs [314]. With this method, they were able to simulate relatively large domains, including over 35000 atoms and up to 50 ps. This powerful approach allowed for the investigation of the mechanisms behind dendrite initiation in several well-known solid state electrolyte (SSE) materials, revealing the role of nanoscopic dendrite initiation that occurs on some material interfaces without existing grain boundaries or cracks [314].

Zhang et al. [315] introduced an MLFF with an active learning strategy consisting of sampling, labeling, and training stages, which allowed for cross-scale morphology simulation. In this scheme, the local configurations that significantly change during MLFF simulations are sampled and calculated using the DFT method. The DFT results are concatenated with existing data and used for retraining the MLFF model. Using this approach, they studied the Li dendrite morphology evolution influenced by surface energy, internal domain energy, and grain boundary energy. It is shown that the dendrite morphology

consists of two stages: first, the dendrite is divided into domains with different orientations; subsequently, the top domain migrates to heal the initial grain boundary and stabilizes the dendrite. Based on this Li dendrite evolution mechanism, the authors provided suggestions for designing a more stable Li metal anode.

Su et al. [298] have proposed dual-scale short circuit model integrated with an explainable AI framework for battery safety assessment. As shown in (i) of Fig. 9, the dual-scale model links Li dendrite formation to internal short circuit (ISC) risk using seven key features (e.g., grain size, electrolyte thickness) as machine learning inputs. A thermal runaway risk metric is then derived from battery voltage and short-circuit time. The phase field model, which takes the information about overpotential and electrolyte potential from the experimental model, and returns the data about ISC resistance, order parameter and solid electrolyte's conductivity to it, is illustrated in Fig. 9(b). Subsequently, a random forest ML model (refer (ii) of Fig. 9(a)) is trained on 400 simulation datasets generated via Latin Hypercube Sampling (LHS). In context of explainable AI ((iii) of Fig. 9(a)), SHapley Additive exPlanations (SHAP) analysis and Partial Dependence Plots (PDPs) are utilized to identify key features driving thermal runaway risk. The authors have mentioned that the physics informed explainable data-driven framework is readily customizable to several batteries as well as other energy systems. Zhao et al. [299] have provided a concise summary regarding the Battery short circuit mechanism. Among several other causes, dendrite growth and penetration has been regarded as the cause of ISC related safety risk in the batteries. As shown in Fig. 9(c) they have explained the mechanism of short circuit in batteries. Lithium dendrites formed during regular operation may puncture the separator, causing acute internal shorts, or remain within the separator, leading to soft shorts. Manufacturing defects in separators (e.g., pinholes, scratches, surface particles) or contamination (e.g., metal particles on electrodes) increase the risk of soft shorts under prolonged operating

conditions. Understanding this mechanism is crucial in the development of Battery safety models. Jia et al. [300] have developed a classifier type machine learning model that categorizes the safety risk level of different batteries (refer Fig. 9(d)). In other words, the battery safety risk classification is performed using an electrochemomechanical surrogate model combined with decision tree and support vector classifiers. This machine learning takes datasets from experiments and numerical simulations, and thus is an example of integrated approach.

In lithium (ion/metal) battery research, the “simulation–experiment” closed loop is increasingly emerging as an efficient paradigm for dendrite suppression and interfacial regulation. On the one hand, phase-field/continuum models and electrochemical–mechanical coupling frameworks can integrate the thermodynamic driving forces discussed in the previous section (overpotential, interfacial energy anisotropy, chemical potential differences) with stress concentration and defect amplification effects into a unified computational framework. This enables prediction of dendrite morphological evolution and failure pathways under varying current densities, stack pressures, and pore/grain-boundary defect distributions, and directly informs which experimental variables should be prioritized from both safety and electrochemical perspectives [316,317] (e.g., critical current density testing windows, stack pressure ranges, ceramic electrolyte densification and grain-boundary engineering, interfacial roughness and contact evolution characterization protocols). On the other hand, atomistic-to-mesoscale simulations such as DFT/AIMD/kMC can elucidate, at the molecular level, the reduction and decomposition pathways of electrolytes/additives, the formation tendencies of key SEI components [318,319] (e.g., LiF, Li₂CO₃, Li₃N), and their impacts on ionic transport and mechanical stability. These insights guide experimental selection of additive systems and the design of salt/solvent coordination structures, which can then be cross-calibrated against model parameters and mechanisms using XPS/ToF-SIMS and operando optical or electron microscopy observations. Particularly in solid-state systems, operando observations of lithium filament penetration morphologies and propagation trajectories can constrain defect sensitivity and fracture criteria in phase-field and fracture models [160,320]. In this way, the closed loop of “model-derived testable predictions toward targeted experimental validation followed by feedback refinement of the model” is concretely established, ultimately translating simulation outputs into actionable experimental design rules (material microstructure, interfacial layer formulations, and pressure–current–temperature operating windows).

5. Battery informatics for SEI stability

Battery informatics is the intersection of battery science and informatics, with a strong emphasis on machine learning for data-driven insights and advancements in battery technology [325]. It is a research field that utilizes artificial intelligence as the main technique or relies on machine learning as a major tool for data analysis and interpretation in the context of batteries. This area focuses on utilizing advanced data-driven methods to analyze, interpret, and optimize battery performance, design, and management. It is now understandable that the enormous strength of AI and informatics can be implemented in the design of dendrite-resistant lithium-ion batteries. In context of this current review study, battery informatics bridges the gap between fundamental mechanisms of dendrite formation and practical strategies for their suppression, using machine learning and data-driven methods to accelerate the design of stable, dendrite-resistant lithium-ion batteries. Building on the mechanistic insights from Sections 2 and 3, where dendrite nucleation and growth are linked to overpotential, SEI heterogeneity, and stress evolution, and the suppression strategies outlined in Section 4 (such as electrolyte formulation and interfacial engineering via experiments, multiscale modeling etc.), battery informatics offers a powerful approach to integrate these complex factors. By applying machine learning and data analytics, battery informatics

translates physical and chemical understanding into predictive models and actionable design rules for SEI stability and dendrite suppression.

In fact there are multi-variate factors influencing dendrite nucleation and growth, and it is essential to quantify their relative presence or significance using materials informatics approach. The active material weight, electrolyte quantity, porosity, drying temperature, electrode coating, formulation etc. largely impact the SEI stability during operation stage. Fortunately, these factors can be controlled or optimized during the cell production stage. Haghi et al. [321] have implemented the processes-variables-algorithms methods to study the Lithium-ion battery cell production. In their comprehensive process mapping studies for data pool, the electrode coating has been outlined as the most investigated process (39%), and drying is the least mentioned process (5%) in the overall process chain. In the diagram of Fig. 10(a), the width of the links between any two attributes is equal to the number of studies conducted. This network diagram highlights the need to increase studies on processes or variables that are critical to battery health/reliability but have links with thinner width. Such types of informatics knowledge base will be very useful in precisely locating the control strategies of defects and dendrites in the batteries. Zhao et al. [322] have performed web-scraping task to obtain the battery dendrite related data and then built convolutional neural network (CNN) models CNN-1/CNN mode 1 and CNN-2/CNN mode 2 upon these datasets. The authors have used the Python Selenium library for web-scraping the dendrite datasets, and then training the machine learning models (visual results presented in upper half of Fig. 10(b)). While the CNN-1 model is simple, the model CNN-2 is physics informed. The CNN-2 was supplied to with seven physical parameters (temperature, concentration gradient, electric field strength, ion concentration, surface energy of dendrites, fluidity of the solution, and the number of lattice defects) relevant to the dendritic growth and electrochemical dynamics. The R^2 value for the train and validation data in CNN-1 and CNN-2 models are 0.38 and 0.93 respectively, thereby implying that the reinforcement of the machine learning model with physical parameters rendered it more accurate. The data-driven model is accompanied with DFT models (shown in the bottom half of Fig. 10(b)). The methodology presented by the Zhao et al. [322] can be expanded to incorporating principal physical parameters associated with the suppression of dendrites in Lithium-ion batteries.

Physics informed neural network (PINN) has been utilized by Deng et al. [323] to study the state of health (SOH) of Lithium based batteries. The battery aging datasets were first featurized, and then fed as input to back propagation neural network (BPNN) as illustrated in Fig. 10(c). The monotonic relationship between incremental capacity (IC) and SOH has been incorporated into the architecture of BPNN via the monotonicity loss term or monotonicity constraint. The PINN, which predicts the SOH, is augmented with a multilayer perceptron to model battery degradation dynamics from both empirical and state-space perspectives. This machine learning model is trained upon datasets of small size - first type consists data of just eight LiCoO₂ pouch batteries whereas the second type consists of the data of 55 lithium-ion batteries subjected to six different charging and discharging strategies. For models trained upon such smaller datasets, it is impossible to make generic or broader inferences on degradation kinetics or dendrite-induced damage at the SEI and electrolytes beyond the compositions of the training data. This highlights the context of data scarcity as one of the most significant hurdle in the field of battery informatics. Olabi et al. [324] have highlighted ANNs as one of the most useful machine learning models for study of the Lithium-Ion battery states. As depicted in Fig. 10(d), ANN could be implemented for the prediction of state of charge, state of health, remaining useful life, thermal state and other battery parameters. These LiB states prediction is deeply associated with reliability and stability of SEI, and thus has relevance with the design of dendrite resistant batteries.

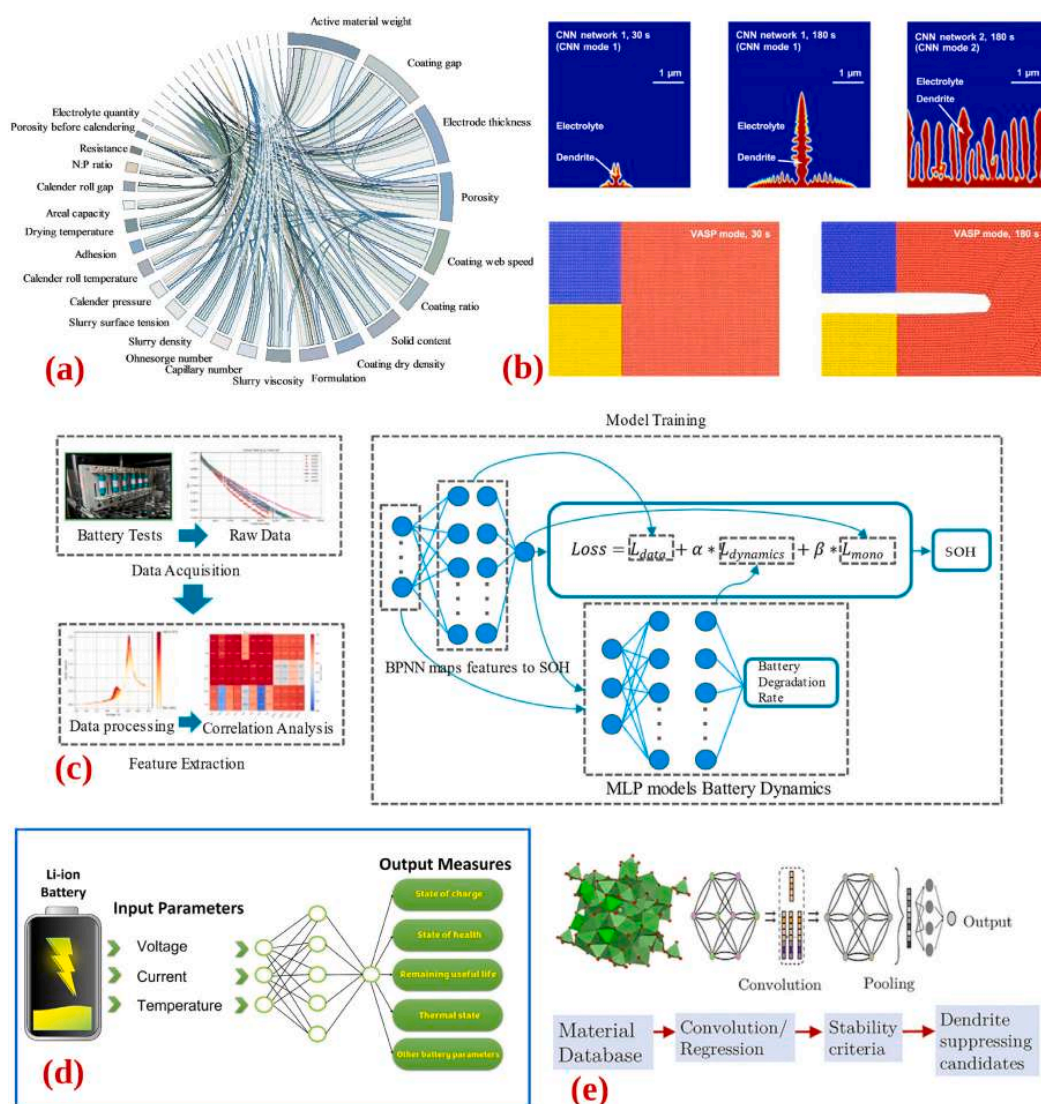


Fig. 10. Informatics and AI are robust tools that can be utilized for designing reliable and dendrite resistant batteries. The informatics techniques can be implemented at the (a) cell production stage to outline the product and process parameters [321] that are crucial to the overall state of health. The machine learning models (CNN mode 1 and CNN mode 2) of (b), were built upon datasets obtained via web-scraping technique [322]. These models were validated with computational technique to enable in the efficient prediction of interfacial dynamics during dendrite formation. The (c) PINN [323] and (d) ANN [324] are very practically viable when it comes to estimation of several factors related to the battery health, performance and reliability. Interestingly, ML techniques are also employed in (e) computational screening of candidate solid electrolytes [288] that can suppress the dendrite growth.

Informatics and machine learning approach can be utilized for candidate materials design for next generation batteries. Ahmad et al. [289] have performed computational screening of over 12000 inorganic solids to evaluate their ability to suppress dendrite initiation at Li interfaces. The stepwise procedure of their integrated computational and machine learning pipeline is presented in Fig. 10(e). They used a large material database and machine-learning models (graph convolution and regression) to predict mechanical properties, apply stability criteria, and screen solid electrolytes that can suppress dendrite growth. It should be noted however that their approach is limited to candidate design at DFT scale and thus is not transferrable to practical battery devices. Though the atomistic scale battery informatics can obtain sufficient datasets

from high throughput DFT computations, it is not always possible to upscale the inferences to continuum scale. However, the autonomous battery informatics needs to be applied at all length scales and so the major challenge in it is the lack of abundance of datasets at microscale or macroscale.

The main bottleneck in the utilization of autonomous battery informatics for the prevention and control of dendrites and the design of stable SEI is the scarcity of data [325]. Addressing data scarcity through synthetic data, transfer learning, collaboration, and smart experimentation is essential for realizing the full potential of informatics in designing robust, dendrite-resistant batteries. These complementary strategies

provide synergistic solutions to limited battery performance data. Synthetic data uses simulations, computational models, and generative AI [326] to supplement scarce experimental data, enabling robust model training, exploration of rare conditions, and accelerated early-stage development. Transfer learning [327] allows models from related battery chemistries or domains to reduce new data requirements, speed model convergence, and efficiently exploit existing knowledge, particularly for novel materials or architectures. Collaborative sharing fosters partnerships and data consortia among academia and industry, creating larger, standardized datasets that enhance model generalizability while distributing costs and risks. Smart experimental design maximizes information per test through approaches like active learning, Bayesian optimization, and design-of-experiments, reducing overall experiments while improving statistical power and decision-making.

6. Roadmap toward sustainable energy solutions in lithium-ion batteries

The shift from fundamental multiscale modeling and laboratory experiments to commercially viable, dendrite-free systems necessitates a transition from descriptive science to prescriptive informatics. While the preceding sections established the mechanistic origins of dendrite growth through atomistic and continuum lenses, the following roadmap synthesizes these insights into a unified chronological framework. By bridging the gap between isolated material properties and system-level manufacturing, we translate the complex interplay of electrochemical kinetics into a decathlon of interfacial stability and a structured path toward agentic discovery.

Fig. 11(a) is a 3D logarithmic bar graph that visualizes the visionary milestones and policy-level targets for key physical parameters aimed at suppressing dendrite formation in batteries, particularly in lithium-based systems where dendrites pose safety and performance risks. The graph emphasizes progressive improvements from 2025–2030 (initial milestones) to 2035–2040 (advanced targets), reflecting a roadmap for scientific and technological advancements to achieve dendrite-free batteries. The timeline is represented in one of the horizontal axes. Another of the horizontal axes lists the ten most significant battery design parameters: critical current density (i_c in mA/cm²), cycle life to 0.8 capacity retention (N in k cycles), Coulombic efficiency (ϵ in %), energy density (ω in Wh/kg), areal capacity (Γ in mAh/cm²), operating temperature window (ΔT in °C), shear modulus (Y in GPa), ionic conductivity (σ_{ion} in S/cm), electronic conductivity (σ in S/cm), and defect density or crack density (ζ in cm⁻²). The vertical axis uses a logarithmic scale spanning from 10^{-10} to 10^{+2} , enabling the comparison of parameters with diverse units and magnitudes. The bars, colored in a gradient from deep blue (left) to teal, green, and yellow (right), represent target values labeled at either bottom for 2025–2030 or the top for 2035–2040. In 2025–2030, it is estimated that i_c , N , ϵ , ω , Γ , ΔT , Y , σ_{ion} (polymer electrolyte), σ and ζ will respectively have the values of 3 mA/cm², 0.1 k cycles, 99.5%, 350 Wh/kg, 3.0 mAh/cm², 50 °C, 10 GPa, 1×10^{-4} S/cm, 1×10^{-10} S/cm and 3%. The parameters will reach the values in the range 10 mA/cm² for i_c , 1.5 k cycles for N , 0.999% for ϵ (equivalent to 99.9%), 500 Wh/kg for ω , 5.0 mAh/cm² for Γ , 100 °C for ΔT , 20 GPa for Y , 1×10^{-2} S/cm for σ_{ion} in polymer electrolyte, 1×10^{-12} S/cm for σ , and 1% for ζ . Higher targets for parameters like i_c [328–332], N [333–336], ϵ [337,338], ω [339], Γ [340,341], ΔT [342–344], Y [345–348], and σ_{ion} [349] indicate aims to enhance stability, efficiency, and performance, while lower targets for σ (to minimize short-circuit risks) [350] and ζ (to reduce initiation sites for dendrites) [351–353] highlight suppression strategies. These values are inferred based upon the analysis of these parameters as independent attributes, and the detailed presentation is provided in Appendix. While the bar graph in Fig. 11(a) characterizes each of the ten parameters as independent metrics, strategies for dendrite control and mitigation must also capture the interrelationships and

correlations among them. In other words, achieving dendrite-free, high-energy-density LiBs demands a holistic roadmap that unites electrolyte engineering, anode surface design, electrode architecture optimization, battery chemistry innovations ML & AI integration and in-situ monitoring & feedback. The conceptual “Dendrite-mitigation tree” presented in Fig. 11(b) addresses precisely this need by mapping the interdependent attributes into a unified framework of synergistic scientific efforts. In this tree, each branch integrates multiple parameters (e.g., high σ_{ion} must be paired with sufficient shear modulus Y to prevent both nucleation and penetration), thereby linking the interrelated physical, chemical, and interfacial attributes to the common goal of comprehensive, dendrite-free battery operation. The tree features a central trunk labeled “Dendrite-mitigation tree” in red, branching into six interconnected ovals, each representing a core area of innovation. *Electrolyte Engineering* focuses on tailoring electrolyte composition to simultaneously maximize ionic conductivity (σ_{ion}) while driving electronic conductivity (σ) toward zero, thereby eliminating the pathways for internal lithium plating. *Anode Surface Design* engineers robust interfaces through coatings and nanostructures that raise the shear modulus (Y) and suppress defect density (ζ), ensuring uniform lithium plating and stripping. *Electrode Architecture Optimization* employs advanced structural designs to increase areal capacity (Γ) and critical current density (i_c), distributing current and mechanical stress uniformly to prevent localized hot spots. *Battery Chemistry Innovations* pursues next-generation solid-state and alloy anodes that simultaneously boost energy density (ω) and Coulombic efficiency (ϵ), fundamentally reshaping reaction kinetics. *ML & AI Integration* harnesses data-driven modeling to predict and optimize cycle life (N) and operating temperature window (ΔT), accelerating discovery across all other branches. Finally, *In-situ Monitoring & Feedback* (graph icon) provides real-time diagnostics that close the loop, allowing dynamic adjustment of any parameter as soon as deviations appear. Collectively, these six branches form a synergistic ecosystem in which no parameter is treated in isolation; each advance in one domain is deliberately coupled with complementary improvements in the others. The tree thereby embodies the policy-level vision-international collaborations, targeted funding programs, and industrial standards-required to move dendrite suppression from laboratory demonstrations to scalable, safe, high-performance batteries for electric vehicles, renewable storage, and grid applications.

From a fundamental standpoint, the lack of comprehensive mechanistic understanding limits the rational design of battery systems [354]. The development of novel solid-state electrolytes represents the most favored research direction in electrolyte engineering in Branch 1 of Fig. 11(b). The successful development of solid electrolytes with high energy density [355], low defect [356], crack-free [357], and uniform nucleation and growth of dendrites would significantly reduce nucleation and growth. Ionic liquids and additives are a safer alternative electrolyte for lithium-ion batteries but finding a suitable separator material for ionic liquids is a great challenge [358,359]. Lithium metal anodes with advanced surfaces are considered the most promising anode material for next-generation batteries [360]. To address issues such as lithium dendrite formation and interface instability, various effective strategies have been proposed, including artificial SEI [361], three-dimensional nanostructure design [362], and coating [363]. The anode surface mentions in Branch 2 of Fig. 11. The architectural design of lithium metal electrodes plays a pivotal role in mitigating dendrite growth and accommodating severe volume fluctuations during cycling. It is mentioned in Branch 3 of Fig. 11(b). Lithophilic surface engineering—such as heteroatom doping or coating with Li-affine materials—significantly lowers nucleation barriers and promotes homogeneous plating [364]. Coupling flexible and self-healing components with advanced manufacturing techniques and digital design tools will accelerate the transition from lab-scale prototypes to practical batteries. Ultimately, achieving dendrite free will require synergistic optimization of electrode architecture, electrolyte chemistry, and interfacial

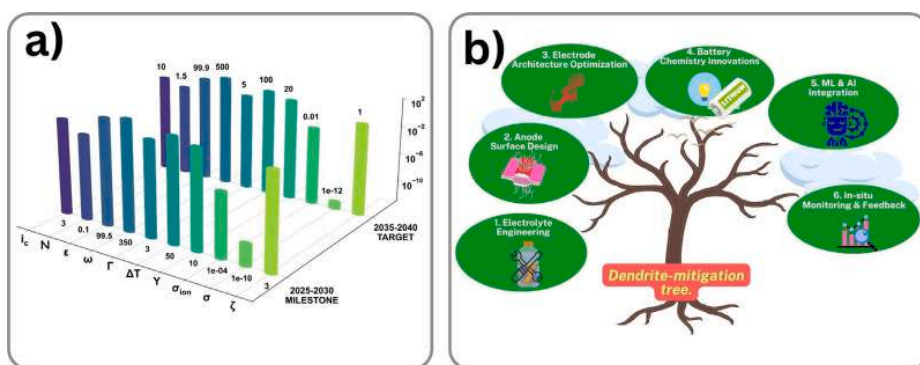


Fig. 11. Strategies for dendrite control and mitigation must include both independent parameter quantification followed by capturing the interrelationships and correlations among these parameters. (a) Logarithmic bar diagram illustrating independent physical, chemical, and interfacial parameters (e.g., i_c in mA/cm², ϵ in %, ω in Wh/kg) as standalone metrics for dendrite control, with visionary milestones from 2025–2040; (b) Dendrite-mitigation tree emphasizing interrelationships among scientific efforts (e.g., electrolyte engineering, AI integration) for synergistic suppression of dendrite growth in lithium batteries.

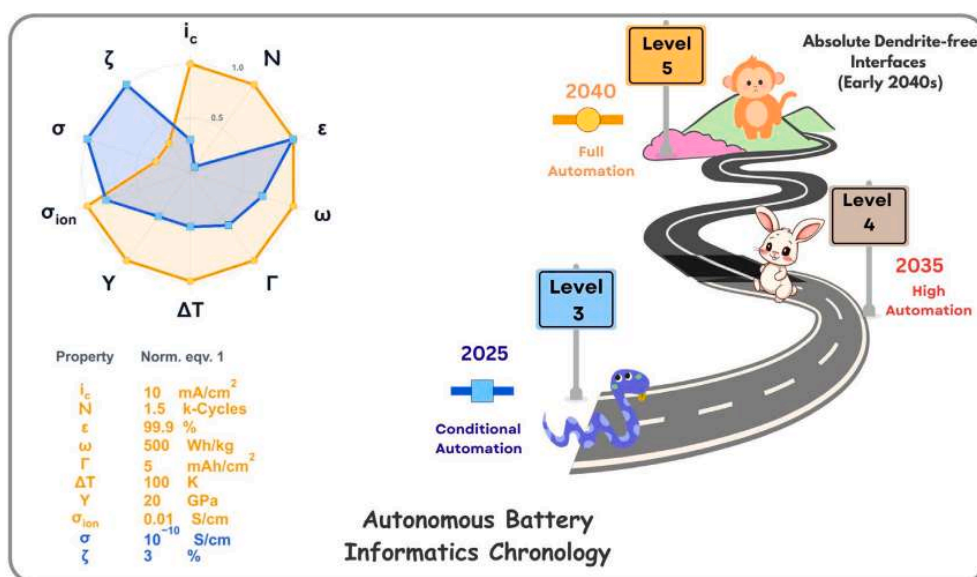


Fig. 12. The decathlon of interfacial stability and the chronological path to agentic discovery are inextricably intertwined in this visionary trajectory for the realization of absolute dendrite-free battery interfaces by the early 2040s. In this Autonomous Battery Informatics Chronology, the decathlon of design and interfacial parameters (left panel) provides the quantitative foundation of the futuristic robust battery, defining the necessary expansion of the ten-parameter design space: i_c , N , ϵ , ω , Γ , ΔT , Y , σ_{ion} , σ , and ζ (quantified in non-dimensionalized format), required to reach industrial viability. These metrics serve as the source material for the progression on the right, where manufacturing maturity evolves from human-supervised “Conditional Automation” (2025) to “Full Automation” (2040s). The coloring/legend styles used in the left panel is associated with the corresponding styles in the right panel. The transition from the considerable risks stage of 2025 to the risk-free summit of the 2040s illustrates a shift from trial-and-error discovery to an agentic regime where AI-driven manufacturing autonomously satisfies the stringent requirements of the battery systems decathlon chart. This integrated roadmap serves as a strategic blueprint for policy-level actions across the global lithium-ion battery ecosystem, guiding the transition to dendrite-free operation in **electric vehicles (EVs)**, **consumer electronics** (smartphones, laptops, wearables), **grid energy storage**, **aerospace** (drones, satellites), **renewable integration** (solar/wind backup), **medical devices**, **industrial equipment**, and **IoT infrastructure**. The autonomous battery informatics chronology applied to the ten attributes can help achieve the sustainable energy solutions.

stability [365]. Of course, different electrochemical systems also play a crucial role in dendrite formation. Alloy electrode systems [366], Li-S [367], and Li-air systems [368,369] are key research areas exhibited in Branch 4 of Fig. 11. Visually monitoring dendrite growth through experiments is an essential process for future modifications to battery materials showed in Branch 6 of Fig. 11(b). In-situ monitoring and feedback systems – combining advanced imaging, real-time sensors, and AI-driven adaptive control – promise autonomous operation and enhanced safety for next-generation lithium metal batteries [370–374].

Agentic assistant [375] that combine physics-aware simulation and automated informatics could speed up the finding of materials and methods that restrict the dendrite growth [376]. The agentic simulation approach has been categorized under Branch 5. ML & AI Integration of the Dendrite-mitigation strategy tree in Fig. 11(b). Simple decision agents (like reinforcement-learning controllers [377]) can pick simulation settings relevant to dendrite growth such as: current, microstructure, or additive levels. Fast, physics-informed surrogate models then let those agents explore many options without always running slow,

full-scale simulations [378]. When experiments and characterization data are fed back quickly, the models learn where they are least certain and suggest the best next tests [379]. Adding safety checks and physical limits prevents the system from proposing unsafe or impossible experiments. Battery informatics has been indicated in the same Branch 5 of Fig. 11(b), and is one of the most robust techniques to establish solution measures that guarantee the dendrite-free batteries. The hurdle to the creation of self-sufficient and perfect informatics pipelines is the scarcity of battery datasets [325]. The challenges related to lack of dataset can be overcome by using either conditional automation (Level 3) technique [308] to obtain lithium ion battery datasets from DFT/other computational method or by using web-scraping methods to download text based datasets and train transformers models [380].

At 2025, the battery design sector has already embraced the conditional automation [308]. Since the battery reliability design is less vulnerable to ethical concerns than the automated vehicles (AV), the high automation (Level 4) or full automation (Level 5) can be achieved potentially quite earlier than those of AV. However, the intensity of inputs in this field is proportional to the events happening in the AV sector. Once the moderating effects of contextual factors related to Level 4 (high automation) and Level 5 (full automation) are adequately addressed in the sector of automated vehicles, the people's propensity to use AVs will also increase [381]. The increasing attention to automated design of AVs will then impact many other areas including the materials design of Lithium-ion batteries. The battery reliability sector focusing on dendrite suppression or minimization, also will also see the use of high level automation by 2035 and full automation by 2040 [382]. To translate the static performance metrics represented by ten parameters (decathlon of interfacial stability) into a actionable temporal trajectory, Fig. 12 presents the *Autonomous Battery Informatics Chronology*. This roadmap frames the achievement of absolute dendrite-free interfaces as a multi-dimensional expansion of the battery's performance envelope, driven by the increasing maturity of manufacturing automation and agentic AI. The left panel of Fig. 12 utilizes a dual-radar informatics plot to visualize the “design space” required to overcome dendrite growth issues while maintaining excellent battery performance such as high energy density and mechanical stability. To enable direct comparison between diverse physical quantities across disparate units and magnitudes, each parameter P_i is normalized to a non-dimensional value $\bar{P}_i \in [0, 1]$ relative to its **maximum observed value** across the chronology:

$$\bar{P}_i = \frac{P_i}{P_{i,\max}} \quad (12)$$

where $P_{i,\max}$ represents the highest observed (or projected) value of parameter $i = i_c, N, \epsilon, \omega, \Gamma, \Delta T, Y, \sigma_{\text{ion}}, \sigma$, and ζ , across the 2025–2040 timeline—set to 1.0 by definition. A companion index is provided within the figure, mapping the normalized coordinates to their absolute physical magnitudes and units to ensure quantitative transparency across the chronology. The **blue polygon (2025–2030)** represents the current frontier of Level 3 (Conditional Automation). At this stage, research is primarily focused on stabilizing the Solid Electrolyte Interface (SEI) using human-supervised simulations, pushing the critical current density (i_c) initially toward 3 mA cm⁻² (normalized value of 0.3 in radar chart), and progressively toward 5 mA cm⁻² (normalized value of 0.5, not shown in the chart). The detailed datasets of i_c for different electrolytes of present and future are shown in the Table A.1 of Appendix A.1. However, the transition to the **orange target envelope (Early 2040s)** represents a paradigm shift. Achieving Level 5 (Full Automation) requires a simultaneous optimization of ten decisive parameters (a.k.a. decathlon of interfacial stability and battery performance) to reach the “ideal” convergence zone, such as mechanical fortification, conductivity paradox resolution and operational resolution. Scaling the shear modulus (Y) to ≥ 20 GPa to satisfy the Monroe-Newman criterion for both elastic and inelastic regimes [383–385] while suppressing microstructural defect density (ζ)

to $< 1\%$ are the primary objectives related to mechanical fortification of battery materials and devices. Conductivity Paradox Resolution, involves optimizing the design of battery's solid electrolyte material between the electrical ability to stop the growth of dendrites and the mechanical capacity to suppress them if they grow by chance. Engineering electrolytes that achieve high ionic conductivity ($\sigma_{\text{ion}} \geq 10^{-2}$ S cm⁻¹) while maintaining near-insulating electronic conductivity ($\sigma_e \leq 10^{-12}$ S cm⁻¹) to prevent internal lithium plating, are the ideal choice. Operational Robustness focuses of life cycle and temperature windows. Extending the cycle life (N) to 1.5 k-cycles and the thermal window (ΔT) to 100 K, ensuring stability from -20 to 80 °C, will be the primary aims in connection with the operational aspects. More information about the tabular datasets of the quantities discussed here can be obtained in the Appendix section.

The right panel of Fig. 12, also referred to as the path to agentic discovery, illustrates the “winding road” from experimental risks to autonomous certainty. This chronology maps the evolution of the six mitigation branches (shown in the tree of Fig. 11(b)) from electrolyte engineering to AI-driven discovery, onto three pivotal milestones named on the levels of automation. The **2025 (Level 3 - Conditional Automation)** stage acknowledges the prevalence of existing dendrite risks. Informatics relies on DFT and web-scraping to manage “hot spots” at the anode interface. The **2035 (Level 4 - High Automation)**: milestone in the mid-journey marks the acceleration phase. High-throughput experimentation and phase-field modeling on top of advanced AI algorithms enable the rapid iteration of composite electrolytes with $Y > 10$ GPa. The **2040+ (Level 5 - Full Autonomy)**: signifies the realization of **Absolute Dendrite-free Interfaces**. Here, agentic manufacturing systems autonomously tune the interdependencies of all ten parameters, delivering industrially viable batteries with energy densities (ω) exceeding 500 Wh kg⁻¹ (refer the table in Appendix A.4) This informatics chronology serves as the quantitative blueprint for the next two decades, ensuring that the quest for dendrite-free energy storage moves beyond trial-and-error toward a regime of guaranteed electrochemical safety. Ultimately, this roadmap converges on a unified vision for sustainable energy solutions powered by dendrite-free lithium-ion batteries. Among the ten interfacial stability parameters, energy density (ω), cycle life (N), Coulombic efficiency (ϵ), areal capacity (Γ), and operating temperature window (ΔT) are directly tied to sustainable energy outcomes respectively in term of governing storage capacity, resource longevity, energy retention, practical deployment, and climate resilience in renewable integration. The remaining parameters: critical current density (i_c), shear modulus (Y), ionic conductivity (σ_{ion}), electronic conductivity (σ), and defect density (ζ), indirectly but critically enable sustainability by ensuring mechanical integrity, kinetic efficiency, and failure resistance that underpin the reliable operation of the direct metrics. Together, this decathlon of parameters, orchestrated through agentic informatics and cross-disciplinary innovation, charts a definitive path toward safe, scalable, and circular battery ecosystems for a carbon-neutral future.

7. Conclusions

7.1. Summary of key insights

This review synthesizes the current scientific landscape regarding lithium dendrite formation and suppression, identifying them as a fundamental bottleneck in high-energy battery development. Keyphrase analysis underscores that dendrite kinetics remain a premier research priority, with significant progress made in delineating the mechanisms of nucleation and growth. It is now established that dendrite initiation is influenced by a multivariable set of factors, including overpotential, surface and diffusion energies, ion concentration, and SEI structural defects. Subsequent growth is primarily governed by lithium-ion diffusion and migration, driven by electric fields and concentration gradients. To navigate this multiscale phenomenon, current research employs a

hierarchical approach: atomic-scale density functional theory (DFT) provides the parameters for SEI stability; mesoscale phase-field models (PFM) simulate morphological evolution and growth orientation; and macroscale experimental designs validate failure behaviors and performance enhancements. Integrating these with multiphysics modeling and the proposed **Autonomous Battery Informatics Chronology** allows for more accurate forecasting of interfacial behavior. The diverse array of suppression methods—ranging from electrode surface coatings and interface engineering to electrolyte modification and separator design—demonstrates a robust effort to improve safety and cycle life. However, critical challenges remain, notably the trade-off between ionic conductivity and mechanical strength, the “Conductivity-Modulus Paradox”, and the chemical instability of interfaces. This review introduces the **Decathlon of Interfacial Stability and Robustness** as a quantitative benchmark to resolve these issues. By aligning material selection and structural modification with the 2040 research roadmap, future developments can move toward prescriptive, agentic design. Achieving these milestones not only enables absolute dendrite suppression but also provides the theoretical and practical foundation for specialized battery systems capable of operating in extreme environments.

7.2. Proposed directions for future research

Based on the current situations and challenges outlined above, several critical gaps remain that require in-depth investigation. Future research on lithium dendrites should continue to prioritize a combined approach of **mechanistic simulation and experimental validation**. Integrating a multiscale framework—which harmonizes atomic-level interactions, mesoscale phase-field simulations, and continuum-scale models with machine learning, is essential to enhance prediction accuracy across disparate length scales. Establishing advanced, comprehensive battery diagnostic databases and standardized keyphrase maps will facilitate the tracking of battery metrics and the accurate forecasting of operational lifespans. Furthermore, the **dynamic modeling of the SEI formation process**, coupled with advanced *in-situ* and *operando* analysis techniques, will enable the direct observation of interfacial stability and dendrite kinetics during cycling. The design of next-generation battery systems must incorporate holistic suppression strategies, such as multifunctional electrode coatings, interfacial gradient modifications, composite electrolytes, and targeted mechanical reinforcement to simultaneously address dendrite propagation and cycle-life degradation. In this endeavor, **advanced AI-assisted technologies and data-driven approaches** are indispensable; these tools accelerate the R&D lifecycle, optimize complex manufacturing workflows, and facilitate the discovery of entirely new battery architectures. Achieving these objectives will not only realize the vision of an absolute dendrite-free battery but will also drive simultaneous improvements in energy density, power performance, and safety. Ultimately, these advancements provide a solid theoretical and practical foundation for developing specialized battery systems tailored for extreme and diverse environments.

CRediT authorship contribution statement

Yi Li: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Software. **Sachin Poudel:** Writing – review & editing, Visualization, Validation, Methodology, Investigation, Formal analysis. **Sweta Kumari:** Writing – review & editing, Validation, Methodology. **Erfan Azqadan:** Writing – review & editing, Validation, Methodology. **Anil Kunwar:** Writing – review & editing, Visualization, Validation, Methodology, Data curation, Conceptualization, Formal analysis, Investigation, Software. **Nele Moelans:** Writing – review & editing, Visualization, Validation, Methodology, Data curation, Conceptualization, Formal analysis.

Table A.1

Assessment and chronological roadmap for critical current density (i_c).

(a) i_c for different technical conditions and the assessments.		
Technical stage	CCD (mA/cm ²)	Influence
Liquid electrolyte	0.5–1	Dendrite formation
Advanced liquid electrolyte	1–3	Partially dendrite-free
Solid-state electrolyte	1–5	Unstable interface
Advanced SSE + interface energy	5–10	Approaching practicality
2035+ target	>10	Fast-charging level

(b) Chronological design roadmap for i_c .		
Timeframe	Research priority	Target values
2025–2030	Stable SEI design	CCD > 5 mA/cm ²
2035–2040	Industrial LMB	CCD > 10 mA/cm ²

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix. The decathlon of interfacial stability-technical metrics for sustainable energy solutions and dendrite-free battery design

To provide a rigorous quantitative foundation for the sustainable energy solutions roadmap presented in Section 6, this appendix details the **Decathlon of Interfacial Stability and Robustness**—a multivariate framework of ten physico-chemical hallmarks carefully selected for their decisive role in determining the thermodynamic and kinetic fate of solid-electrolyte interfaces. These metrics are strategically categorized into three operational pillars: **Electrochemical Flux and Efficiency**, comprising i_c , ϵ , I , and σ_{ion} to govern ion transport and plating uniformity; **Mechanical and Structural Integrity**, encompassing Y , σ , and ζ to dictate dendrite penetration resistance and internal short-circuit prevention; and **System-Level Performance**, involving N , ω , and ΔT to ensure the long-term industrial viability and environmental resilience of the battery system. For clarity, the numbering of **Tables A.1–A.10** is intentionally synchronized with parameters **A.1–A.10**, such that each table reports the quantitative evaluation of its correspondingly numbered metric, irrespective of its placement within the appendix.

A.1. Critical Current Density (CCD)

Critical Current Density, assigned the symbol i_c , represents the maximum current flux an electrolyte can sustain before localized ion depletion triggers the onset of dendritic ramification.

Reliable, high-power batteries must operate at elevated i_c values to bridge the gap between laboratory curiosities and commercial fast-charging requirements [328–332]. Within the 2040 roadmap, achieving a tenfold increase in i_c is categorized as a primary objective for ensuring that lithium-metal systems can match or exceed the power density of modern liquid-electrolyte lithium-ion counterparts.

Table A.2Technological readiness and sustainability goals for cycle life (N).

(a) Correlation between technical level and cycle life capacity.		
Technical level	N (Cycles)	Remarks
Traditional Li metal	<100	Unstable interface
Lab system	100–300	Laboratory scale
Advanced solid-state system	300–1000	Approaching practicality
2035+ target	800–1500+	Industrial grade

(b) Chronological research focus and target milestones for N .		
Timeframe	Research focus	Targets/Goals
2025–2030	Interface stabilization	>300 cycles
2035–2040	Industrial LMB	>1500 cycles

Table A.3Quantification of ϵ in different systems.

Technical level	CE	Remarks
Traditional Li metal	95%–98%	Sharp decline
Lab system	98–99.5%	Controllable
Advanced system	99.5–99.8%	Approaching practicality
2035+ target	$\geq 99.9\%$	High level

A.2. Cycle life to 0.8 capacity retention

The parameter N denotes the number of charge–discharge cycles a cell can undergo before its capacity degrades to 80% of the initial value. A larger value of cycle life N signifies a highly stable electrode–electrolyte interface capable of resisting cumulative mechanical strain and chemical degradation [333–336]. In the context of the 2040 vision, extending N beyond 1500 cycles is essential for ensuring the longevity required for second-life applications and minimizing the lifecycle carbon footprint of the global battery ecosystem.

A.3. Coulombic efficiency

The pursuit of dendrite-free operation is inextricably linked to the maximization of Coulombic Efficiency (ϵ), which serves as a proxy for the reversibility of lithium plating and stripping. In the context of all-solid-state batteries, even a marginal deficit in ϵ leads to the rapid depletion of the active lithium inventory and the accumulation of electrochemically “dead” lithium, which can accelerate interfacial failure [337,338]. Achieving the 2040 target of $\epsilon \geq 99.9\%$ is therefore a prerequisite for minimizing the required lithium excess, thereby maximizing both the specific energy and the economic viability of the cell.

A.4. Energy density

Denoted as ω , this parameter is the most significant metric for determining the practical utility and market competitiveness of next-generation energy storage. Enhancing ω for lithium-metal batteries remains the primary motivation for researchers, as it offers the only viable pathway to significantly extend the range of electric vehicles and the runtime of portable electronics. Near-term development targets aim for 350–400 Wh/kg at the cell level, while long-term commercialization requires ≥ 500 Wh/kg to surpass the performance ceiling of conventional lithium-ion technology [339]. Realizing these targets by 2040 necessitates a holistic design strategy that minimizes the weight and volume of inactive components – such as separators and current collectors – while maximizing the utilization of the high-capacity lithium anode.

Table A.4

Greater energy density in dendrite-free batteries are the goals in 2040 + batteries.

Type	Energy density (Wh/kg)
Traditional lithium battery	50–300
Laboratory scale battery	350–450
2035+ target	450–500+

Table A.5

Increment in areal capacity is a necessity for future batteries.

Timeframe	Areal capacity (mAh/cm ²)
2025–2030	≥ 3
2035–2040	≥ 5

Table A.6Thermal reliability zones and chronological expansion of the operating window (ΔT).

(a) Thermal zones and their impact on battery reliability.	
Temperature range	Effect
<0 °C	Rapid dendrite growth
0–25 °C	Laboratory standard range
25–45 °C	Most stable operational range
>60 °C	Thermal failure and decomposition risk

(b) Target operating temperature window across future timelines.		
Timeframe	Temperature Range	ΔT Milestone
2025–2030	0 to 50 °C	50 °C
2035–2040	–20 to 80 °C	100 °C

A.5. Areal capacity

The areal capacity, Γ , is a critical engineering parameter reflecting the practical mass loading of the electrode per unit area. Near-term research aims to achieve ≥ 3 mAh cm^{–2}, while commercial lithium-metal batteries require ≥ 5 mAh cm^{–2} to meet industrial energy density targets [340,341]. Increasing Γ is essential for reducing the weight fraction of inactive current collectors and separators; however, higher loading levels significantly intensify the local flux of lithium ions. This necessitates the use of advanced architectural designs to ensure uniform current distribution and prevent the formation of localized “hot spots” that act as precursors for dendritic nucleation.

A.6. Operating temperature window ΔT

Operating temperature window is a critical reliability metric governing dendrite kinetics and interfacial stability. The dendrite growth is more pronounced at lower temperature, whereas the risk lowers as the temperature is larger than 60 °C. However, thermal failure and decrease in efficiency are again observed at higher temperature. Hence, the choice of optimal temperature window is very important in the devices that use batteries. Near-term targets aim for stable cycling between 0–50 °C, while long-term industrial deployment requires a wide operating range from –20 °C to 80 °C [342–344]. Thus, the batteries of 2040s will be thermomechanically robust to be able to operate in such a large temperature window.

Table A.7

Shear modulus estimated for solid electrolytes at nearby and distant future design timelines.

Timeframe	Mechanical modulus (GPa)
2025–2030	≥ 5 –10
2035–2040	≥ 20

A.7. Mechanical modulus of electrolyte

Mechanical modulus or shear modulus (Y) is a key parameter governing dendrite penetration resistance. The shear modulus (Y_{Li}) of bulk Li metal is 3.4 GPa, and this is an order of magnitude higher than the one of a typical polymer electrolyte [384]. In accordance with the Monroe-Newman criterion [383], the solid electrolytes' shear modulus needs to be at least twice that of Li metal ($Y_{electrolyte} \geq 2.0Y_{Li}$) in order to mechanically suppress dendrite growth. Based on this criterion, it can be inferred that polymer electrolyte can never be able to suppress the dendrite growth. Dendrite free lithium metal batteries require electrolytes with shear modulus exceeding 10 GPa. Near-term targets focus on achieving 5–10 GPa composite electrolytes, while long-term development aims for ≥ 20 GPa tailored new inorganic electrolyte materials with enhanced fracture tolerance [345–348].

It is to be noted that Monroe-Newman criterion considers only the elastic processes. In future, there is also a need to extend the Monroe-Newman criterion to include the possibilities of inelastic processes such as shear relaxation in Li metal [385].

A.8. Ionic conductivity

Low ionic conductivity (σ_{ion}) is favorable in terms of overall battery performance [349]. While higher σ_{ion} is generally a primary goal for solid-state batteries (SSBs), its relationship with dendrite suppression is more complex than “higher is always better”. High ionic conductivity ensures that lithium ions move quickly and uniformly through the electrolyte. This prevents “hot spots” or local ion depletion at the anode interface, which is where dendrite nucleation typically begins. Better conductivity reduces the internal resistance of the cell. This keeps the overpotential low during charging; high overpotentials are a major driving force for dendrite growth. But again there is the “Ionic Conductivity Paradox”. Even with high ionic conductivity, dendrites can still pierce through a solid electrolyte due to the major two factors: (a) non-zero σ_e , and (b) lack of synergy between mechanical properties and ion transport. Firstly, for a material to be a good electrolyte, it must have high ionic conductivity but near-zero electronic conductivity. If the electrolytic material allows even a tiny amount of electrons to pass through, lithium ions can meet those electrons inside the electrolyte rather than at the electrode. This causes lithium to plate internally within the pores or grain boundaries of the electrolyte, eventually forming a bridge (dendrite) that shorts the battery. Secondly, there is often a trade-off between how fast ions move and how “stiff” the electrolyte material is. Most of the polymer electrolytes with good ionic conductivity have a small value of shear modulus. Thus, the current material design will have to focus on a set of attributes rather than considering σ_{ion} as a standalone parameter.

The ideal scenario for favorable dendrite suppression, a high σ_{ion} candidate must also possess High Li-ion Transference Number, dense microstructure with ideally zero defect density and good interfacial stability. A candidate electrolyte is only truly favorable if that high conductivity is paired with negligible electronic leakage and a dense, defect-free structure.

Table A.8

The physical state and composition of electrolytes along mapped with the range of values for σ_{ion} .

Electrolyte type	Ionic conductivity (S/cm)
Liquid electrolyte	10^{-2}
Polymer electrolyte	10^{-5} – 10^{-4}
Composite electrolyte	10^{-4} – 10^{-3}
Excellent solid sulfide	10^{-3} – 10^{-2}
Ideal target	$\geq 10^{-2}$

Table A.9

Lowering σ is a key priority in the pursuit of resilient batteries.

Timeframe	Electronic conductivity (S/cm)
2025–2030	$\leq 10^{-10}$
2035–2040	$\leq 10^{-12}$

Table A.10

Porosity (a component of ζ vector) is an issue of concern in battery manufacturing sector.

Electrolyte state	Defect level
Conventional sintering SSE	5%–10% porosity
Optimized process	<3% porosity
High-end dense SSE	<1% porosity
Ideal target	Approaching 0

A.9. Electronic conductivity

σ or σ_e must remain extremely low to prevent internal lithium plating within the electrolyte. Near-term targets aim for $\sigma_e \leq 10^{-10}$ S cm $^{-1}$, while long-term industrial electrolytes require $\sigma_e \leq 10^{-12}$ S cm $^{-1}$ to ensure dendrite-free operation [350].

A.10. Defect density

The term ζ represents the microstructural quantities challenging the structural integrity of the batteries device, such as void fraction (%), crack density (mm $^{-2}$), grain boundary density, and defects per μm^3 . Microstructural defect density critically determines dendrite nucleation sites. Near-term targets aim to reduce electrolyte porosity below 3%, while long-term industrial benchmarks require sub-1% porosity and crack-free interfaces to eliminate defect-driven dendrite initiation [351–353].

Notes and remarks on the data and estimations

It is imperative to note the disparity in the data sources used for these forecasts; while the projections for liquid electrolyte systems are derived from mature, market-scale battery datasets, the estimates for all-solid-state batteries are primarily extrapolated from emerging laboratory-scale results. Currently, these estimations treat the ten “Decathlon” parameters as independent attributes to establish a baseline for future milestones. However, a truly predictive informatics framework must account for the complex correlations and inherent trade-offs between these variables. For instance, the “Ionic Conductivity-Shear Modulus Paradox” illustrates that solid electrolytes optimized for high ionic conductivity (σ_{ion}) often exhibit increased ductility and lower shear modulus (Y). While high σ_{ion} is beneficial for suppressing the electrochemical nucleation of dendrites, a reduced Y renders the material mechanically vulnerable to dendrite penetration should growth initiate. Future iterations of this roadmap will utilize multi-variate

agentic models to resolve these interdependencies and optimize the design space for absolute interfacial stability.

Data availability

The data and codes for this study are available in https://github.com/anilkunwar/dendritefree_interfaces2025.

References

- [1] K. Xu, Electrolytes and interphases in Li-ion batteries and beyond, *Chem. Rev.* 114 (23) (2014) 11503–11618.
- [2] M.D. Tikekar, S. Choudhury, Z. Tu, L.A. Archer, Design principles for electrolytes and interfaces for stable lithium-metal batteries, *Nat. Energy* 1 (9) (2016) 1–7.
- [3] N.A. Kaskhedikar, J. Maier, Lithium storage in carbon nanostructures, *Adv. Mater.* 21 (25–26) (2009) 2664–2680.
- [4] X. Su, F. Dogan, J. Ilavsky, V.A. Maroni, D.J. Gosztola, W. Lu, Mechanisms for lithium nucleation and dendrite growth in selected carbon allotropes, *Chem. Mater.* 29 (15) (2017) 6205–6213.
- [5] R. Fang, P. Dong, H. Ge, J. Fu, Z. Li, J. Zhang, Capacity plunge of lithium-ion batteries induced by the suppression of lithium dendrites for rechargeable high-energy batteries, *Mater. Horizons* 8 (1) (2021) 12–32.
- [6] Z. Hao, Q. Zhao, J. Tang, Q. Zhang, J. Liu, Y. Jin, H. Wang, Functional separators towards the suppression of lithium dendrites for rechargeable high-energy batteries, *Mater. Horizons* 8 (1) (2021) 12–32.
- [7] Y. Zhao, T. Ma, L. Hu, X. Ren, X. Sun, X. Yu, Supramolecular interaction chemistry in polymer electrolytes towards stable lithium metal batteries, *J. Energy Chem.* 107 (2025) 154–169.
- [8] G. Cen, X. Zhang, H. Yu, L. Ben, R. Qiao, X. Shen, J. Zhu, J. Hao, Q. Sun, X. Huang, Interface evolution of lithium metal anodes in all-solid-state batteries via mechanical–electrochemical investigations, *Solid State Ion.* 411 (2024) 116557.
- [9] J. Zhang, J. Yang, T. Dong, M. Zhang, J. Chai, S. Dong, T. Wu, X. Zhou, G. Cui, Aliphatic polycarbonate-based solid-state polymer electrolytes for advanced lithium batteries: advances and perspective, *Small* 14 (36) (2018) 1800821.
- [10] H. Zhang, J. Zhang, J. Ma, G. Xu, T. Dong, G. Cui, Polymer electrolytes for high energy density ternary cathode material-based lithium batteries, *Electrochem. Energy Rev.* 2 (2019) 128–148.
- [11] J. Liang, J. Luo, Q. Sun, X. Yang, R. Li, X. Sun, Recent progress on solid-state hybrid electrolytes for solid-state lithium batteries, *Energy Storage Mater.* 21 (2019) 308–334.
- [12] H. Huo, J. Sun, X. Meng, M. He, N. Zhao, X. Guo, et al., Flexible interfaces between Si anodes and composite electrolytes consisting of poly(propylene carbonates) and garnets for solid-state batteries, *J. Power Sources* 383 (2018) 150–156.
- [13] S.-J. Tan, X.-X. Zeng, Q. Ma, X.-W. Wu, Y.-G. Guo, Recent advancements in polymer-based composite electrolytes for rechargeable lithium batteries, *Electrochem. Energy Rev.* 1 (2018) 113–138.
- [14] C. Monroe, J. Newman, The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces, *J. Electrochem. Soc.* 152 (2) (2005) A396.
- [15] X. Yang, X. Gao, C. Zhao, Q. Sun, Y. Zhao, K. Adair, J. Luo, X. Lin, J. Liang, H. Huang, et al., Suppressed dendrite formation realized by selective Li deposition in all-solid-state lithium batteries, *Energy Storage Mater.* 27 (2020) 198–204.
- [16] K. Deng, J. Qin, S. Wang, S. Ren, D. Han, M. Xiao, Y. Meng, Effective suppression of lithium dendrite growth using a flexible single-ion conducting polymer electrolyte, *Small* 14 (31) (2018) 1801420.
- [17] O. Crowther, A.C. West, Effect of electrolyte composition on lithium dendrite growth, *J. Electrochem. Soc.* 155 (11) (2008) A806.
- [18] D. Lin, Y. Liu, Y. Cui, Reviving the lithium metal anode for high-energy batteries, *Nature Nanotechnology* 12 (3) (2017) 194–206.
- [19] W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang, J.-G. Zhang, Lithium metal anodes for rechargeable batteries, *Energy Environ. Sci.* 7 (2) (2014) 513–537.
- [20] P. Bai, J. Li, F.R. Brushett, M.Z. Bazant, Transition of lithium growth mechanisms in liquid electrolytes, *Energy Environ. Sci.* 9 (10) (2016) 3221–3229.
- [21] Y. Zheng, F.A. Soto, V. Ponce, J.M. Seminario, X. Cao, J.-G. Zhang, P.B. Balbuena, Localized high concentration electrolyte behavior near a lithium–metal anode surface, *J. Mater. Chem. A* 7 (43) (2019) 25047–25055.
- [22] C. Yan, Y.-X. Yao, X. Chen, X.-B. Cheng, X.-Q. Zhang, J.-Q. Huang, Q. Zhang, Lithium nitrate solvation chemistry in carbonate electrolyte sustains high-voltage lithium metal batteries, *Angew. Chem. Int. Ed.* 57 (43) (2018) 14055–14059.
- [23] F. Flatscher, M. Philipp, S. Ganschow, H.M.R. Wilkening, D. Rettenwander, The natural critical current density limit for Li 7 La 3 Zr 2 O 12 garnets, *J. Mater. Chem. A* 8 (31) (2020) 15782–15788.
- [24] Y. Qi, L.-Q. Chen, X. Xiao, Q.-Z. Zhang, Dendrite Growth Morphology Modeling in Liquid and Solid Electrolytes, Technical Report, Michigan State Univ., East Lansing, MI (United States); Pennsylvania State ..., 2020.
- [25] S. Nahm, J. Kim, H. Kim, M. Kim, H. Yim, K. Oh, M. Kim, J. Hong, J.-W. Choi, S.-H. Yu, et al., Investigation of early stage lithium growth behaviors using cryo-TEM, *Microsc. Microanal.* 30 (2024).
- [26] A. Jana, S.I. Woo, K. Vikrant, R.E. García, Electrochemomechanics of lithium dendrite growth, *Energy Environ. Sci.* 12 (12) (2019) 3595–3607.
- [27] N.J. van Eck, L. Waltman, Software survey: Vosviewer, a computer program for bibliometric mapping, *Scientometrics* 84 (2) (2010) 523–538.
- [28] J.-i. Yamaki, S.-i. Tobishima, K. Hayashi, K. Saito, Y. Nemoto, M. Arakawa, A consideration of the morphology of electrochemically deposited lithium in an organic electrolyte, *J. Power Sources* 74 (2) (1998) 219–227.
- [29] Y. Lu, Z. Tu, L.A. Archer, Stable lithium electrodeposition in liquid and nanoporous solid electrolytes, *Nat. Mater.* 13 (10) (2014) 961–969.
- [30] F. Ding, W. Xu, G.L. Graff, J. Zhang, M.L. Sushko, X. Chen, Y. Shao, M.H. Engelhard, Z. Nie, J. Xiao, et al., Dendrite-free lithium deposition via self-healing electrostatic shield mechanism, *J. Am. Chem. Soc.* 135 (11) (2013) 4450–4456.
- [31] A. Hagopian, M.-L. Doublet, J.-S. Filhol, Thermodynamic origin of dendrite growth in metal anode batteries, *Energy Environ. Sci.* 13 (2020) 5186–5197.
- [32] R. Fang, Y.-X. Li, W.-W. Wang, Y. Gu, B.-W. Mao, Kinetic understanding of lithium metal electrodeposition for lithium anodes, *Phys. Chem. Chem. Phys.* 26 (36) (2024) 23544–23560.
- [33] D. Qiao, X. Wei, J. Zhu, X. Wang, B. Jiang, W. Fan, G. Wei, G. Han, X. Lai, Y. Zheng, H. Dai, Unraveling the mechanism of non-uniform lithium deposition in liquid electrolytes, *Cell Rep. Phys. Sci.* 5 (5) (2024) 101961.
- [34] L. Lin, H. Zheng, Q. Luo, J. Lin, L. Wang, Q. Xie, D.-L. Peng, J. Lu, Regulating lithium nucleation at the electrolyte/electrode interface in lithium metal batteries, *Adv. Funct. Mater.* 34 (24) (2024) 2315201.
- [35] C. Ling, D. Banerjee, M. Matsui, Study of the electrochemical deposition of Mg in the atomic level: Why it prefers the non-dendritic morphology, *Electrochim. Acta* 76 (2012) 270–274.
- [36] Y. Ozhobes, D. Gunceler, T. Arias, Stability and surface diffusion at lithium–electrolyte interphases with connections to dendrite suppression, 2015.
- [37] D.R. Ely, R.E. García, Heterogeneous nucleation and growth of lithium electrodeposits on negative electrodes, *J. Electrochem. Soc.* 160 (4) (2013) A662.
- [38] A. Pei, G. Zheng, F. Shi, Y. Li, Y. Cui, Nanoscale nucleation and growth of electrodeposited lithium metal, *Nano Lett.* 17 (2) (2017) 1132–1139.
- [39] V. Fleury, J.-N. Chazalviel, M. Rosso, B. Sapoval, The role of the anions in the growth speed of fractal electrodeposits, *J. Electroanal. Chem. Interfacial Electrochem.* 290 (1–2) (1990) 249–255.
- [40] K. Guo, R. Kumar, X. Xiao, B.W. Sheldon, H. Gao, Failure progression in the solid electrolyte interphase (SEI) on silicon electrodes, *Nano Energy* 68 (2020) 104257.
- [41] A. Cipolla, C. Barchasz, B. Mathieu, B. Chavillon, S. Martinet, Effect of electrochemical and mechanical properties of SEI on dendritic growth during lithium deposition on lithium metal electrode, *J. Power Sources* 545 (2022) 231898.
- [42] A. Wang, Q. Deng, L. Deng, X. Guan, J. Luo, Eliminating tip dendrite growth by Lorentz force for stable lithium metal anodes, *Adv. Funct. Mater.* 29 (25) (2019) 1902630.
- [43] J. Steiger, D. Kramer, R. Mönig, Mechanisms of dendritic growth investigated by in situ light microscopy during electrodeposition and dissolution of lithium, *J. Power Sources* 261 (2014) 112–119.
- [44] Y. Gu, H. Yan, W.-W. Wang, X.-G. Zhang, J. Yan, B.-W. Mao, Unraveling the mechanism of very initial dendritic growth under lithium ion transport control in lithium metal anodes, *Nano Lett.* 23 (21) (2023) 9872–9879.
- [45] E.J. Cheng, A. Sharafi, J. Sakamoto, Intergranular Li metal propagation through polycrystalline Li₆ 25Al₀ 25La3Zr2O12 ceramic electrolyte, *Electrochim. Acta* 223 (2017) 85–91.
- [46] J.K. Zheng, J. Yin, T. Tang, L.A. Archer, Moss-like growth of metal electrodes: On the role of competing faradaic reactions and fast charging, *ACS Energy Lett.* 8 (5) (2023) 2113–2121.
- [47] J. Steiger, D. Kramer, R. Mönig, Microscopic observations of the formation, growth and shrinkage of lithium moss during electrodeposition and dissolution, *Electrochim. Acta* 136 (2014) 529–536.
- [48] M.S. Park, S.B. Ma, D.J. Lee, D. Im, S.-G. Doo, O. Yamamoto, A highly reversible lithium metal anode, *Sci. Rep.* 4 (1) (2014) 3815.
- [49] C. Wang, X. Wu, W. Yuan, X. Zhang, S. Jiang, B. Zhao, Y. Chen, G. Zhang, Y. Zeng, Q. Liu, et al., New understanding toward lithium morphologic evolution in lithium metal batteries, *Adv. Funct. Mater.* 34 (48) (2024) 2408758.
- [50] Y. Liu, X. Xu, M. Sudd, O.O. Kapitanova, V.A. Krivchenko, J. Ban, J. Wang, X. Jiao, Z. Song, J. Song, et al., Insight into the critical role of exchange current density on electrodeposition behavior of lithium metal, *Adv. Sci.* 8 (5) (2021) 2003301.
- [51] I.W. Seong, C.H. Hong, B.K. Kim, W.Y. Yoon, The effects of current density and amount of discharge on dendrite formation in the lithium powder anode electrode, *J. Power Sources* 178 (2) (2008) 769–773.

- [52] X. Gao, Y.-N. Zhou, D. Han, J. Zhou, D. Zhou, W. Tang, J.B. Goodenough, Thermodynamic understanding of Li-dendrite formation, *Joule* 4 (9) (2020) 1864–1879.
- [53] C. Monroe, J. Newman, Dendrite growth in lithium/polymer systems: A propagation model for liquid electrolytes under galvanostatic conditions, *J. Electrochem. Soc.* 150 (10) (2003) A1377.
- [54] R. Akolkar, Modeling dendrite growth during lithium electrodeposition at sub-ambient temperature, *J. Power Sources* 246 (2014) 84–89.
- [55] X. Gao, Y.-N. Zhou, D. Han, J. Zhou, D. Zhou, W. Tang, J.B. Goodenough, Thermodynamic understanding of Li-dendrite formation, *Joule* 4 (9) (2020) 1864–1879.
- [56] G. Liu, W. Lu, A model of concurrent lithium dendrite growth, SEI growth, SEI penetration and regrowth, *J. Electrochem. Soc.* 164 (9) (2017) A1826.
- [57] Y. Ji, B. Yuan, J. Zhang, Z. Liu, S. Zhong, J. Liu, Y. Liu, M. Yang, C. Wang, C. Yang, et al., A single-layer piezoelectric composite separator for durable operation of Li metal anode at high rates, *Energy & Environ. Mater.* 7 (1) (2024) e12510.
- [58] T. Gao, C. Rainey, W. Lu, Piezoelectric mechanism and a compliant film to effectively suppress dendrite growth, *ACS Appl. Mater. Interfaces* 12 (46) (2020) 51448–51458.
- [59] J. Tao, Y. Chen, A. Bhardwaj, L. Wen, J. Li, O.V. Kolosov, Y. Lin, Z. Hong, Z. Huang, S. Mathur, Combating Li metal deposits in all-solid-state battery via the piezoelectric and ferroelectric effects, *Proc. Natl. Acad. Sci.* 119 (41) (2022) e2211059119.
- [60] G. Wranglén, Dendrites and growth layers in the electrocrystallization of metals, *Electrochim. Acta* 2 (1–3) (1960) 130–132.
- [61] J.L. Barton, J.O. Bockris, A.R.J.P. Ubbelohde, The electrolytic growth of dendrites from ionic solutions, *Proc. R. Soc. Lond. Ser. A. Math. Phys. Sci.* 268 (1335) (1962) 485–505.
- [62] J.W. Diggle, A.R. Despic, J.O. Bockris, The mechanism of the dendritic electrocrystallization of zinc, *J. Electrochem. Soc.* 116 (11) (1969) 1503.
- [63] J.T. Kim, J. Jormé, The kinetics and mass transfer of zinc electrode in acidic zinc-chloride solution, *J. Electrochem. Soc.* 127 (1) (1980) 8.
- [64] J.-N. Chazalviel, Electrochemical aspects of the generation of ramified metallic electrodeposits, *Phys. Rev. A* 42 (1990) 7355–7367.
- [65] J. ichi Yamaki, S. ichi Tobishima, K. Hayashi, Keiichi Saito, Y. Nemoto, M. Arakawa, A consideration of the morphology of electrochemically deposited lithium in an organic electrolyte, *J. Power Sources* 74 (2) (1998) 219–227.
- [66] C. Monroe, J. Newman, Dendrite growth in lithium/polymer systems : A propagation model for liquid electrolytes under galvanostatic conditions, *J. Electrochem. Soc.* 150 (10) (2003) A1377.
- [67] H.E. Park, C.H. Hong, W.Y. Yoon, The effect of internal resistance on dendritic growth on lithium metal electrodes in the lithium secondary batteries, *J. Power Sources* 178 (2) (2008) 765–768, Selected Papers Presented at the 3rd INTERNATIONAL CONFERENCE ON POLYMER BATTERIES FUEL CELLS(PBFC 2007) on the occasion of Professor Bruno Scrosati's 70th birthday.
- [68] D.R. Ely, R.E. García, Heterogeneous nucleation and growth of lithium electrodeposits on negative electrodes, *J. Electrochem. Soc.* 160 (4) (2013) A662.
- [69] R. Akolkar, Mathematical model of the dendritic growth during lithium electrodeposition, *J. Power Sources* 232 (2013) 23–28.
- [70] X. Wang, W. Zeng, L. Hong, W. Xu, H. Yang, F. Wang, H. Duan, M. Tang, H. Jiang, Stress-driven lithium dendrite growth mechanism and dendrite mitigation by electroplating on soft substrates, *Nat. Energy* 3 (3) (2018) 227–235.
- [71] C. Zhu, T. Fuchs, S.A.L. Weber, F.H. Richter, G. Glasser, F. Weber, H.-J. Butt, J. Janek, U. Berger, Understanding the evolution of lithium dendrites at Li₆25Al_{0.25}La₃Zr₂O₁₂ grain boundaries via operando microscopy techniques, *Nat. Commun.* 14 (1) (2023) 1300.
- [72] R. Akolkar, Mathematical model of the dendritic growth during lithium electrodeposition, *J. Power Sources* 232 (2013) 23–28.
- [73] H. Yang, C. Guo, A. Naveed, J. Lei, J. Yang, Y. Nuli, J. Wang, Recent progress and perspective on lithium metal anode protection, *Energy Storage Mater.* 14 (2018) 199–221.
- [74] D. Patino, B. Dong, F. Villalobos, S. Herrera, J. Bell, M. Ozkan, C.S. Ozkan, Beyond cell parameters: Exploiting cell operation towards optimizing the SEI and suppressing dendrite growth on lithium metal anodes, *Energy Storage* 2 (5) (2020) e188.
- [75] F. Han, A.S. Westover, J. Yue, X. Fan, F. Wang, M. Chi, D.N. Leonard, N.J. Dudney, H. Wang, C. Wang, High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes, *Nat. Energy* 4 (3) (2019) 187–196.
- [76] I. Jang, A. Yethiraj, Effect of diffusion constant on the morphology of dendrite growth in lithium metal batteries, *J. Chem. Phys.* 154 (23) (2021).
- [77] J. Becherer, D. Kramer, R. Mönig, The growth mechanism of lithium dendrites and its coupling to mechanical stress, *J. Mater. Chem. A* 10 (10) (2022) 5530–5539.
- [78] S.S. Zhang, A review on electrolyte additives for lithium-ion batteries, *J. Power Sources* 162 (2) (2006) 1379–1394.
- [79] J. Wang, W. Huang, A. Pei, Y. Li, F. Shi, X. Yu, Y. Cui, Improving cyclability of Li metal batteries at elevated temperatures and its origin revealed by cryo-electron microscopy, *Nat. Energy* 4 (8) (2019) 664–670.
- [80] C.T. Love, O.A. Baturina, K.E. Swider-Lyons, Observation of lithium dendrites at ambient temperature and below, *ECS Electrochem. Lett.* 4 (2) (2015) A24.
- [81] H. Yang, Z. Wang, Effects of pressure, temperature, and plasticity on lithium dendrite growth in solid-state electrolytes, *J. Solid State Electrochem.* 27 (10) (2023) 2607–2618.
- [82] Y. Li, K. Zhang, B. Zheng, F. Yang, Effect of local deformation on the coupling between diffusion and stress in lithium-ion battery, *Int. J. Solids Struct.* 87 (2016) 81–89.
- [83] X. Zhang, Q.J. Wang, K.L. Harrison, K. Jungjohann, B.L. Boyce, S.A. Roberts, P.M. Attia, S.J. Harris, Rethinking how external pressure can suppress dendrites in lithium metal batteries, *J. Electrochem. Soc.* 166 (15) (2019) A3639–A3652.
- [84] H.G. Lee, S.Y. Kim, J.S. Lee, Dynamic observation of dendrite growth on lithium metal anode during battery charging/discharging cycles, *Npj Comput. Mater.* 8 (1) (2022) 103.
- [85] Z. Liu, Y. Li, Y. Ji, Q. Zhang, X. Xiao, Y. Yao, L.-Q. Chen, Y. Qi, Dendrite-free lithium based on lessons learned from lithium and magnesium electrodeposition morphology simulations, *Cell Rep. Phys. Sci.* 2 (1) (2021).
- [86] M.K. Aslam, Y. Niu, T. Hussain, H. Tabassum, W. Tang, M. Xu, R. Ahuja, How to avoid dendrite formation in metal batteries: Innovative strategies for dendrite suppression, *Nano Energy* 86 (2021) 106142.
- [87] B.G. Chooabar, H. Hamed, S. Yari, M. Safari, Theoretical and experimental insights into dendrite growth in lithium-metal electrode, *ChemElectroChem* 11 (23) (2024) e202400441.
- [88] Y. Liu, J. Zhang, B. Zhang, H. Gao, D. Chen, M. Wang, C. Wang, Stability criterion for electrodeposition in solid-state batteries with metallic anodes, *PRX Energy* 3 (2024) 013010.
- [89] R. Suresh, R. Rengaswamy, Modeling and control of battery systems. Part I: Revisiting Butler–Volmer equations to model non-linear coupling of various capacity fade mechanisms, *Comput. Chem. Eng.* 119 (2018) 336–351.
- [90] C. Bai, Y. Li, G. Xiao, J. Chen, S. Tan, P. Shi, T. Hou, M. Liu, Y.-B. He, F. Kang, Understanding the electrochemical window of solid-state electrolyte in full battery application, *Chem. Rev.* (2025).
- [91] S. Wang, L. Zhang, Z. Hu, B. Zhang, N. Li, Y.-B. Tong, D. Cao, X. Zheng, W.-Y. Lai, Z. Jin, et al., Intrinsic structural and coordination chemistry insights of Li salts in rechargeable lithium batteries, *Adv. Mater.* 37 (11) (2025) 2420428.
- [92] Y. Xia, T. Fujieda, K. Tatsumi, P.P. Prossini, T. Sakai, Thermal and electrochemical stability of cathode materials in solid polymer electrolyte, *J. Power Sources* 92 (1–2) (2001) 234–243.
- [93] K. Fu, Y. Gong, J. Dai, A. Gong, X. Han, Y. Yao, C. Wang, Y. Wang, Y. Chen, C. Yan, et al., Flexible, solid-state, ion-conducting membrane with 3D garnet nanofiber networks for lithium batteries, *Proc. Natl. Acad. Sci.* 113 (26) (2016) 7094–7099.
- [94] G. Appetecchi, P. Romagnoli, B. Scrosati, Composite gel membranes: a new class of improved polymer electrolytes for lithium batteries, *Electrochem. Commun.* 3 (6) (2001) 281–284.
- [95] B. Sun, J. Mindemark, K. Edström, D. Brandell, Polycarbonate-based solid polymer electrolytes for Li-ion batteries, *Solid State Ion.* 262 (2014) 738–742.
- [96] X. Huang, J. Wu, X. Wang, Y. Tian, F. Zhang, M. Yang, B. Xu, B. Wu, X. Liu, H. Li, In situ synthesis of a Li₆. 4La₃Zr₁. 4Ta₀. 6O₁₂/poly (vinylene carbonate) hybrid solid-state electrolyte with enhanced ionic conductivity and stability, *ACS Appl. Energy Mater.* 4 (9) (2021) 9368–9375.
- [97] K. Yang, L. Chen, J. Ma, C. Lai, Y. Huang, J. Mi, J. Biao, D. Zhang, P. Shi, H. Xia, et al., Stable interface chemistry and multiple ion transport of composite electrolyte contribute to ultra-long cycling solid-state LiNi₀. 8Co₀. 1Mn₀. 1O₂/lithium metal batteries, *Angew. Chem. Int. Ed.* 60 (46) (2021) 24668–24675.
- [98] Y. Benabed, M. Rioux, S. Rousselot, G. Hautier, M. Dollé, Assessing the electrochemical stability window of NASICON-type solid electrolytes, *Front. Energy Res.* 9 (2021) 682008.
- [99] T. Hupfer, E.C. Bucharsky, K.G. Schell, A. Senyshyn, M. Monchak, M.J. Hoffmann, H. Ehrenberg, Evolution of microstructure and its relation to ionic conductivity in Li_{1+x}Al_xTi_{2-x}(PO₄)₃, *Solid State Ion.* 288 (2016) 235–239.
- [100] J.S. Thokchom, B. Kumar, Composite effect in superionically conducting lithium aluminium germanium phosphate based glass-ceramic, *J. Power Sources* 185 (1) (2008) 480–485.
- [101] Y. Inaguma, L. Chen, M. Itoh, T. Nakamura, Candidate compounds with perovskite structure for high lithium ionic conductivity, *Solid State Ion.* 70 (1994) 196–202.
- [102] Y. Yang, Q. Wu, Y. Cui, Y. Chen, S. Shi, R.-Z. Wang, H. Yan, Elastic properties, defect thermodynamics, electrochemical window, phase stability, and Li⁺ mobility of Li₃PS₄: insights from first-principles calculations, *ACS Appl. Mater. Interfaces* 8 (38) (2016) 25229–25242.
- [103] C. Yu, S. Ganapathy, E.R. van Eck, L. van Eijck, N. de Klerk, E.M. Kelder, M. Wagemaker, Investigation of Li-ion transport in Li₇P₃S₁₁ and solid-state lithium batteries, *J. Energy Chem.* 38 (2019) 1–7.
- [104] Y. Zhu, X. He, Y. Mo, Origin of outstanding stability in the lithium solid electrolyte materials: insights from thermodynamic analyses based on first-principles calculations, *ACS Appl. Mater. Interfaces* 7 (42) (2015) 23685–23693.

- [105] T. Binninger, A. Marcolongo, M. Mottet, V. Weber, T. Laino, Comparison of computational methods for the electrochemical stability window of solid-state electrolyte materials, *J. Mater. Chem. A* 8 (3) (2020) 1347–1359.
- [106] S. Yu, R.D. Schmidt, R. Garcia-Mendez, E. Herbert, N.J. Dudney, J.B. Wolfenstine, J. Sakamoto, D.J. Siegel, Elastic properties of the solid electrolyte $\text{Li}_7\text{La}_3\text{Zr}_{20}\text{Li}_{12}\text{O}_{42}$ (LLZO), *Chem. Mater.* 28 (1) (2016) 197–206.
- [107] F. Ahmed, A. Chen, M.V.P. Altoé, G. Liu, Argyrodite- $\text{Li}_6\text{PS}_5\text{Cl}$ /polymer-based highly conductive composite electrolyte for all-solid-state batteries, *ACS Appl. Energy Mater.* 7 (5) (2024) 1842–1853.
- [108] S. Wang, Q. Bai, A.M. Nolan, Y. Liu, S. Gong, Q. Sun, Y. Mo, Lithium chlorides and bromides as promising solid-state chemistries for fast ion conductors with good electrochemical stability, *Angew. Chem. Int. Ed.* 58 (24) (2019) 8039–8043.
- [109] Y.-C. Yin, J.-T. Yang, J.-D. Luo, G.-X. Lu, Z. Huang, J.-P. Wang, P. Li, F. Li, Y.-C. Wu, T. Tian, et al., A LaCl_3 -based lithium superionic conductor compatible with lithium metal, *Nature* 616 (7955) (2023) 77–83.
- [110] S. Zhang, F. Zhao, J. Chen, J. Fu, J. Luo, S.H. Alahakoon, L.-Y. Chang, R. Feng, M. Shakouri, J. Liang, et al., A family of oxychloride amorphous solid electrolytes for long-cycling all-solid-state lithium batteries, *Nat. Commun.* 14 (1) (2023) 3780.
- [111] L. Hu, J. Wang, K. Wang, Z. Gu, Z. Xi, H. Li, F. Chen, Y. Wang, Z. Li, C. Ma, A cost-effective, ionically conductive and compressible oxychloride solid-state electrolyte for stable all-solid-state lithium-based batteries, *Nat. Commun.* 14 (1) (2023) 3807.
- [112] X. Pu, X. Cheng, Q. Yan, Y. Lin, R. Yan, B. Li, R. Yang, X. Zhu, Rhombohedral $\text{Li}_1\text{-xZr}_2\text{-xSb}_x(\text{PO}_4)_3$ electrolytes with improved Li^+ conductivity for high-performance solid-state Li-metal battery, *J. Energy Storage* 101 (2024) 113959.
- [113] D.-H. Guan, X.-X. Wang, L.-N. Song, C.-L. Miao, J.-Y. Li, X.-Y. Yuan, X.-Y. Ma, J.-J. Xu, Polyoxometalate $\text{Li}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Li}_3\text{PMo}_{12}\text{O}_{40}$ electrolytes for high-energy all-solid-state lithium batteries, *Angew. Chem. Int. Ed.* 63 (5) (2024) e202317949.
- [114] H. Mao, X. Zhu, G. Li, J. Pang, J. Hao, L. Wang, H. Yu, Y. Shi, F. Wu, S. Pan, et al., Moisture-stable chalcogenide solid electrolytes in Li_2BMQ_4 ($\text{B}=\text{Ca}$, Sr , and Ba ; $\text{M}=\text{Si}$, Ge , and Sn ; $\text{Q}=\text{O}$, S , and Se) systems, *ACS Energy Lett.* 9 (10) (2024) 4827–4834.
- [115] H. Li, Q. Lin, J. Wang, L. Hu, F. Chen, Z. Zhang, C. Ma, A cost-effective sulfide solid electrolyte $\text{Li}_7\text{P}_3\text{S}_7 \cdot 5\text{O}_3$ with low density and excellent anode compatibility, *Angew. Chem. Int. Ed.* 63 (37) (2024) e202407892.
- [116] Y. Wang, L.-N. Song, X.-X. Wang, Y.-F. Wang, J.-J. Xu, Hydrogen-bonded organic frameworks-based electrolytes with controllable hydrogen bonding networks for solid-state lithium batteries, *Angew. Chem. Int. Ed.* 63 (41) (2024) e202401910.
- [117] G.-Y. Qiao, X. Wang, X. Li, J. Li, K. Geng, E. Jin, J.-J. Xu, J. Yu, Unlocking synthesis of polyhedral oligomeric silsesquioxane-based three-dimensional polycubane covalent organic frameworks, *J. Am. Chem. Soc.* 146 (5) (2024) 3373–3382.
- [118] J. Zou, A. Trewin, T. Ben, S. Qiu, High uptake and fast transportation of LiPF_6 in a porous aromatic framework for solid-state Li-ion batteries, *Angew. Chem.* 132 (2) (2020) 779–784.
- [119] M.J. Lee, J. Han, K. Lee, Y.J. Lee, B.G. Kim, K.-N. Jung, B.J. Kim, S.W. Lee, Elastomeric electrolytes for high-energy solid-state lithium batteries, *Nature* 601 (7892) (2022) 217–222.
- [120] A. Du, H. Lu, S. Liu, S. Chen, Z. Chen, W. Li, J. Song, Q.-H. Yang, C. Yang, Breaking the trade-off between ionic conductivity and mechanical strength in solid polymer electrolytes for high-performance solid lithium batteries, *Adv. Energy Mater.* 14 (31) (2024) 2400808.
- [121] J. Newman, K.E. Thomas-Alyea, *Electrochemical Systems*, John Wiley & Sons, 2012.
- [122] R. Jiwari, S. Singh, et al., Finite element method for the numerical simulation of modified Poisson-Nernst-Planck/Navier-Stokes model, 2024, arXiv preprint arXiv:2409.08746.
- [123] Y. He, X. Ren, Y. Xu, M.H. Engelhard, X. Li, J. Xiao, J. Liu, J.-G. Zhang, W. Xu, C. Wang, Origin of lithium whisker formation and growth under stress, *Nature Nanotechnology* 14 (11) (2019) 1042–1047.
- [124] K.J. Harry, D.T. Hallinan, D.Y. Parkinson, A.A. MacDowell, N.P. Balsara, Detection of subsurface structures underneath dendrites formed on cycled lithium metal electrodes, *Nat. Mater.* 13 (1) (2014) 69–73.
- [125] R. Marom, O. Haik, D. Aurbach, I.C. Halalay, Revisiting LiClO_4 as an electrolyte for rechargeable lithium-ion batteries, *J. Electrochem. Soc.* 157 (8) (2010) A972.
- [126] M. Ue, S. Mori, Mobility and ionic association of lithium salts in a propylene carbonate-ethyl methyl carbonate mixed solvent, *J. Electrochem. Soc.* 142 (8) (1995) 2577.
- [127] D. Zhou, R. Zhou, C. Chen, W.-A. Yee, J. Kong, G. Ding, X. Lu, Non-volatile polymer electrolyte based on poly (propylene carbonate), ionic liquid, and lithium perchlorate for electrochromic devices, *J. Phys. Chem. B* 117 (25) (2013) 7783–7789.
- [128] L. Zou, K. Shi, H. Liu, Y. Wu, T. Xu, Q. Wang, Z. Chen, Z. Yang, R. Song, J. Su, et al., Polybenzimidazole-reinforced polyethylene oxide-based polymer-in-salt electrolytes enabling excellent structural stability and superior electrochemical performance for lithium metal batteries, *Chem. Eng. J.* 465 (2023) 142794.
- [129] S. Hwang, D.-H. Kim, J.H. Shin, J.E. Jang, K.H. Ahn, C. Lee, H. Lee, Ionic conduction and solution structure in LiPF_6 and LiBF_4 propylene carbonate electrolytes, *J. Phys. Chem. C* 122 (34) (2018) 19438–19446.
- [130] S. Borisevich, E.Y. Evshchik, M. Il'ina, E. Khamitov, T. Mel'nikova, R.Y. Rubtsov, O. Bushkova, Y.A. Dobrovolskii, Algorithm for theoretical assessment of the electrochemical stability of electrolytes in lithium-ion batteries by the example of LiBF_4 in the EC/DMC mixture, *Russ. J. Electrochem.* 58 (11) (2022) 1008–1019.
- [131] X. Chen, C. Qin, F. Chu, F. Li, J. Liu, F. Wu, Contriving a gel polymer electrolyte to drive quasi-solid-state high-voltage Li metal batteries at ultralow temperatures, *Energy Environ. Sci.* 18 (2) (2025) 910–922.
- [132] K. Xu, Nonaqueous liquid electrolytes for lithium-based rechargeable batteries, *Chem. Rev.* 104 (10) (2004) 4303–4418.
- [133] X. He, Y. Ni, Y. Hou, Y. Lu, S. Jin, H. Li, Z. Yan, K. Zhang, J. Chen, Insights into the ionic conduction mechanism of Quasi-solid polymer electrolytes through multispectral characterization, *Angew. Chem.* 133 (42) (2021) 22854–22859.
- [134] P. Zhou, Y. Ou, Q. Feng, Y. Xia, H. Zhou, W.-h. Hou, X. Song, Y. Lu, S. Yan, W. Zhang, et al., Tuning the nucleophilicity of anion in lithium salt to enable an anion-rich solvation sheath for stable lithium metal batteries, *Adv. Funct. Mater.* 35 (10) (2025) 2416800.
- [135] Y. Xia, P. Zhou, X. Kong, J. Tian, W. Zhang, S. Yan, W.-h. Hou, H.-Y. Zhou, H. Dong, X. Chen, et al., Designing an asymmetric ether-like lithium salt to enable fast-cycling high-energy lithium metal batteries, *Nat. Energy* 8 (9) (2023) 934–945.
- [136] P. Zhou, H. Zhou, Y. Xia, Q. Feng, X. Kong, W.-h. Hou, Y. Ou, X. Song, H.-y. Zhou, W. Zhang, et al., Rational lithium salt molecule tuning for fast charging/discharging lithium metal battery, *Angew. Chem.* 136 (19) (2024) e202316717.
- [137] Y. Lu, Q. Cao, W. Zhang, T. Zeng, Y. Ou, S. Yan, H. Liu, X. Song, H. Zhou, W. Hou, et al., Breaking the molecular symmetry of sulfonamide anions for high-performance lithium metal batteries under extreme cycling conditions, *Nat. Energy* 10 (2) (2025) 191–204.
- [138] H.-B. Han, S.-S. Zhou, D.-J. Zhang, S.-W. Feng, L.-F. Li, K. Liu, W.-F. Feng, J. Nie, H. Li, X.-J. Huang, et al., Lithium bis (fluorosulfonyl) imide (LiFSI) as conducting salt for nonaqueous liquid electrolytes for lithium-ion batteries: Physicochemical and electrochemical properties, *J. Power Sources* 196 (7) (2011) 3623–3632.
- [139] Z. Li, Y.-X. Yao, M. Zheng, S. Sun, Y. Yang, Y. Xiao, L. Xu, C.-B. Jin, X.-Y. Yue, T. Song, et al., Electrolyte design enables rechargeable LiFePO_4 /graphite batteries from -80°C to 80°C , *Angew. Chem.* 137 (2) (2025) e202409409.
- [140] C.M. Efav, Q. Wu, N. Gao, Y. Zhang, H. Zhu, K. Gering, M.F. Hurley, H. Xiong, E. Hu, X. Cao, et al., Localized high-concentration electrolytes get more localized through micelle-like structures, *Nat. Mater.* 22 (12) (2023) 1531–1539.
- [141] N. Li, X. Han, X. Cui, C. Xu, C. Mao, X. Dai, W. Xue, Recent progress in liquid electrolytes for high-energy lithium-metal batteries: From molecular engineering to applications, *Adv. Funct. Mater.* 35 (1) (2025) 2409431.
- [142] J. Zhang, H. Zhang, S. Weng, R. Li, D. Lu, T. Deng, S. Zhang, L. Lv, J. Qi, X. Xiao, et al., Multifunctional solvent molecule design enables high-voltage Li-ion batteries, *Nat. Commun.* 14 (1) (2023) 2211.
- [143] Z. Liu, W. Hou, H. Tian, Q. Qiu, I. Ullah, S. Qiu, W. Sun, Q. Yu, J. Yuan, L. Xia, et al., An ultralow-concentration and moisture-resistant electrolyte of lithium difluoro (oxalato) borate in carbonate solvents for stable cycling in practical lithium-ion batteries, *Angew. Chem.* 136 (19) (2024) e202400110.
- [144] K.S. Teoh, M. Melchiorre, S. Darlami Magar, M. Hermesdorf, D. Leistschneider, M. Oschatz, F. Ruffo, J.L. Gómez Urbano, A. Balducci, Fluorine-free lithium-ion capacitor with enhanced sustainability and safety based on bio-based γ -valerolactone and lithium bis (oxalato) borate electrolyte, *Adv. Mater.* 36 (18) (2024) 2310056.
- [145] D. Flachard, J. Rolland, M. Obadia, A. Serghei, R. Bouchet, E. Drockenmüller, A. 1, 2, 3-triazolate lithium salt with ionic liquid properties at room temperature, *Chem. Commun.* 54 (65) (2018) 9035–9038.
- [146] J.W. Cahn, S.M. Allen, A microscopic theory for domain wall motion and its experimental verification in Fe-Al alloy domain growth kinetics, *J. Phys. Colloq.* 38 (C7) (1977) C7–51.
- [147] J.W. Cahn, On spinodal decomposition, *Acta Metall.* 9 (9) (1961) 795–801.
- [148] C. Lin, H. Ruan, Mechano-electrochemical modeling of lithium dendrite penetration in a solid-state electrolyte: Mechanism and suppression, *J. Energy Storage* 65 (2023) 107389.
- [149] L. Chen, H.W. Zhang, L.Y. Liang, Z. Liu, Y. Qi, P. Lu, J. Chen, L.-Q. Chen, Modulation of dendritic patterns during electrodeposition: A nonlinear phase-field model, *J. Power Sources* 300 (2015) 376–385.
- [150] N. Moelans, B. Blanpain, P. Wollants, Quantitative analysis of grain boundary properties in a generalized phase field model for grain growth in anisotropic systems, *Phys. Rev. B—Condensed Matter Mater. Phys.* 78 (2) (2008) 024113.

- [151] D.R. Ely, A. Jana, R.E. García, Phase field kinetics of lithium electrodeposits, *J. Power Sources* 272 (2014) 581–594.
- [152] B.R. Pant, Y. Ren, Y. Cao, Dendrite growth and dead lithium formation in lithium metal batteries and mitigation using a protective layer: A phase-field study, *ACS Appl. Mater. Interfaces* 16 (42) (2024) 56947–56956.
- [153] Y. Lu, C.-Z. Zhao, H. Yuan, X.-B. Cheng, J.-Q. Huang, Q. Zhang, Critical current density in solid-state lithium metal batteries: mechanism, influences, and strategies, *Adv. Funct. Mater.* 31 (18) (2021) 2009925.
- [154] A. Kato, H. Kowada, M. Deguchi, C. Hotehama, A. Hayashi, M. Tatsumisago, XPS and SEM analysis between Li/Li3PS4 interface with Au thin film for all-solid-state lithium batteries, *Solid State Ion.* 322 (2018) 1–4.
- [155] F. Sun, K. Dong, M. Osenberg, A. Hilger, S. Risse, Y. Lu, P.H. Kamm, M. Klaus, H. Markötter, F. García-Moreno, et al., Visualizing the morphological and compositional evolution of the interface of InLi-anode|thio-LiSION electrolyte in an all-solid-state Li-S cell by in operando synchrotron X-ray tomography and energy dispersive diffraction, *J. Mater. Chem. A* 6 (45) (2018) 22489–22496.
- [156] F. Sagane, K.-i. Ikeda, K. Okita, H. Sano, H. Sakaebe, Y. Iriyama, Effects of current densities on the lithium plating morphology at a lithium phosphorus oxynitride glass electrolyte/copper thin film interface, *J. Power Sources* 233 (2013) 34–42.
- [157] A. Sharafi, H.M. Meyer, J. Nanda, J. Wolfenstine, J. Sakamoto, Characterizing the Li–Li7La3Zr2O12 interface stability and kinetics as a function of temperature and current density, *J. Power Sources* 302 (2016) 135–139.
- [158] Y. Shi, J. Wan, G.-X. Liu, T.-T. Zuo, Y.-X. Song, B. Liu, Y.-G. Guo, R. Wen, L.-J. Wan, Interfacial evolution of lithium dendrites and their solid electrolyte interphase shells of quasi-solid-state lithium-metal batteries, *Angew. Chem. Int. Ed.* 59 (41) (2020) 18120–18125.
- [159] X.-B. Cheng, C. Yan, X. Chen, C. Guan, J.-Q. Huang, H.-J. Peng, R. Zhang, S.-T. Yang, Q. Zhang, Implantable solid electrolyte interphase in lithium-metal batteries, *Chem* 2 (2) (2017) 258–270.
- [160] E. Kazyak, R. Garcia-Mendez, W.S. LePage, A. Sharafi, A.L. Davis, A.J. Sanchez, K.-H. Chen, C. Haslam, J. Sakamoto, N.P. Dasgupta, Li penetration in ceramic solid electrolytes: operando microscopy analysis of morphology, propagation, and reversibility, *Matter* 2 (4) (2020) 1025–1048.
- [161] X.-B. Cheng, R. Zhang, C.-Z. Zhao, F. Wei, J.-G. Zhang, Q. Zhang, A review of solid electrolyte interphases on lithium metal anode, *Adv. Sci.* 3 (3) (2016) 1500213.
- [162] S. Angarita-Gomez, P.B. Balbuena, Insights into lithium ion deposition on lithium metal surfaces, *Phys. Chem. Chem. Phys.* 22 (2020) 21369–21382.
- [163] K. Huang, Y. Liu, H. Liu, First-principles study of the adsorption and diffusion mechanisms of lithium dendrite growth, *Mol. Simul.* 49 (3) (2023) 284–291.
- [164] L.A. Selis, J.M. Seminario, Dendrite formation in Li-metal anodes: an atomistic molecular dynamics study, *RSC Adv.* 9 (2019) 27835–27848.
- [165] H. Lee, N. Sitapure, S. Hwang, J.S.-I. Kwon, Multiscale modeling of dendrite formation in lithium-ion batteries, *Comput. Chem. Eng.* 153 (2021) 107415.
- [166] B. Zhang, B. Yuan, X. Yan, X. Han, J. Zhang, H. Tan, C. Wang, P. Yan, H. Gao, Y. Liu, Atomic mechanism of lithium dendrite penetration in solid electrolytes, *Nat. Commun.* 16 (1) (2025).
- [167] Z. Hong, V. Viswanathan, Phase-field simulations of lithium dendrite growth with open-source software, *ACS Energy Lett.* 3 (7) (2018) 1737–1743.
- [168] W. Mu, X. Liu, Z. Wen, L. Liu, Numerical simulation of the factors affecting the growth of lithium dendrites, *J. Energy Storage* 26 (2019) 100921.
- [169] M.E. Arguello, N.A. Labanda, V.M. Calo, M. Gumulya, R. Utikar, J. Derksen, Three-dimensional experimental-scale phase-field modeling of dendrite formation in rechargeable lithium-metal batteries, *J. Energy Storage* 62 (2023) 106854.
- [170] G. Qi, X. Liu, R. Dou, Z. Wen, W. Zhou, L. Liu, A three-dimensional multiphysics field coupled phase field model for lithium dendrite growth, *J. Energy Storage* 101 (2024) 113899.
- [171] J.E. Guyer, W.J. Boettinger, J.A. Warren, G.B. McFadden, Phase field modeling of electrochemistry. I. Equilibrium, *Phys. Rev. E* 69 (2) (2004) 021603.
- [172] M.E. Arguello, N.A. Labanda, V.M. Calo, M. Gumulya, R. Utikar, J. Derksen, Dendrite formation in rechargeable lithium-metal batteries: Phase-field modeling using open-source finite element library, *J. Energy Storage* 53 (2022) 104892.
- [173] H.-W. Zhang, Z. Liu, L. Liang, L. Chen, Y. Qi, S.J. Harris, P. Lu, L.-Q. Chen, Understanding and predicting the lithium dendrite formation in Li-ion batteries: Phase field model, *ECS Trans.* 61 (8) (2014) 1.
- [174] R. Zhang, X. Shen, Y.-T. Zhang, X.-L. Zhong, H.-T. Ju, T.-X. Huang, X. Chen, J.-D. Zhang, J.-Q. Huang, Dead lithium formation in lithium metal batteries: A phase field model, *J. Energy Chem.* 71 (2022) 29–35.
- [175] Y. Ren, Y. Zhou, Y. Cao, Inhibit of lithium dendrite growth in solid composite electrolyte by phase-field modeling, *J. Phys. Chem. C* 124 (23) (2020) 12195–12204.
- [176] C. Hong, H. Cho, D. Hong, S.-K. Oh, Y. Kim, An improved thermal single particle model and parameter estimation for high-capacity battery cell, *Electrochim. Acta* 439 (2023) 141638.
- [177] V. Sulzer, S.G. Marquis, R. Timms, M. Robinson, S.J. Chapman, Python battery mathematical modelling (PyBaMM), *J. Open Res. Softw.* 9 (1) (2021) 14.
- [178] S. Sahu, J.M. Foster, A continuum model for lithium plating and dendrite formation in lithium-ion batteries: Formulation and validation against experiment, *J. Energy Storage* 60 (2023) 106516.
- [179] F. Shen, M.B. Dixit, X. Xiao, K.B. Hatzell, Effect of pore connectivity on Li dendrite propagation within LLZO electrolytes observed with synchrotron X-ray tomography, *ACS Energy Lett.* 3 (4) (2018) 1056–1061.
- [180] L. Porz, T. Swamy, B.W. Sheldon, D. Rettenwander, T. Frömling, H.L. Thaman, S. Berends, R. Uecker, W.C. Carter, Y.-M. Chiang, Mechanism of lithium metal penetration through inorganic solid electrolytes, *Adv. Energy Mater.* 7 (20) (2017) 1701003.
- [181] X. Xu, S. Wang, H. Wang, C. Hu, Y. Jin, J. Liu, H. Yan, Recent progresses in the suppression method based on the growth mechanism of lithium dendrite, *J. Energy Chem.* 27 (2) (2018) 513–527.
- [182] X.-Q. Zhang, X.-B. Cheng, X. Chen, C. Yan, Q. Zhang, Fluoroethylene carbonate additives to render uniform Li deposits in lithium metal batteries, *Adv. Funct. Mater.* 27 (10) (2017) 1605989.
- [183] A.L. Michan, B.S. Parimalam, M. Leskes, R.N. Kerber, T. Yoon, C.P. Grey, B.L. Lucht, Fluoroethylene carbonate and vinylene carbonate reduction: understanding lithium-ion battery electrolyte additives and solid electrolyte interphase formation, *Chem. Mater.* 28 (22) (2016) 8149–8159.
- [184] H. Sano, H. Sakaebe, H. Matsumoto, Observation of electrodeposited lithium by optical microscope in room temperature ionic liquid-based electrolyte, *J. Power Sources* 196 (16) (2011) 6663–6669.
- [185] S. Liu, G.-R. Li, X.-P. Gao, Lanthanum nitrate as electrolyte additive to stabilize the surface morphology of lithium anode for lithium–sulfur battery, *ACS Appl. Mater. Interfaces* 8 (12) (2016) 7783–7789.
- [186] K. Peng, X. Wang, X. Yan, Converting LiNO3 additive to single nitrogenous component Li2N2O2 SEI layer on Li metal anode in carbonate-based electrolyte, *Chin. Chem. Lett.* 35 (9) (2024) 109274.
- [187] J. Jiang, M. Li, X. Liu, J. Yi, Y. Jiang, C. Wu, H. Liu, B. Zhao, W. Li, X. Sun, et al., Multifunctional additives to realize dendrite-free lithium deposition in carbonate electrolytes toward low-temperature Li metal batteries, *Adv. Energy Mater.* 14 (27) (2024) 2400365.
- [188] M. Wang, Q. Sun, Y. Liu, Z. Yan, Q. Xu, Y. Wu, T. Cheng, Impact of lithium nitrate additives on the solid electrolyte interphase in lithium metal batteries, *Chin. J. Struct. Chem.* 43 (2) (2024) 100203.
- [189] L. Deng, J. You, W. Wang, Y. Li, Y. Cao, B. Zhang, X. Gao, Z. Xu, Cyclosulfate additive constructs stable interface to limit dendrites and realize stable cycle of LMBs, *J. Energy Storage* 89 (2024) 111683.
- [190] Y.-X. Xie, Y.-X. Huang, X.-H. Wu, C.-G. Shi, L.-N. Wu, C. Song, J.-J. Fan, P. Dai, L. Huang, Y.-J. Hua, et al., Succinic anhydride as a deposition-regulating additive for dendrite-free lithium metal anodes, *J. Mater. Chem. A* 9 (32) (2021) 17317–17326.
- [191] S. Yang, G. Li, X. Lin, C. Mo, X. Zhou, L. Quan, K. Zhou, S. Li, H. Wang, W. Li, Highly improved cyclic stability of Ni-rich/Li batteries with succinic anhydride as electrolyte additive and underlying mechanism, *J. Energy Chem.* 78 (2023) 80–90.
- [192] J. Jeong, J.-N. Lee, J.-K. Park, M.-H. Ryou, Y.M. Lee, Stabilizing effect of 2-(triphenylphosphoranylidene) succinic anhydride as electrolyte additive on the lithium metal of lithium metal secondary batteries, *Electrochim. Acta* 170 (2015) 353–359.
- [193] W.-W. Han, R.E.A. Ardhi, G.-C. Liu, Dual impact of superior SEI and separator wettability to inhibit lithium dendrite growth, *Rare Met.* 41 (2) (2022) 353–355.
- [194] R. Miao, J. Yang, X. Feng, H. Jia, J. Wang, Y. Nuli, Novel dual-salts electrolyte solution for dendrite-free lithium-metal based rechargeable batteries with high cycle reversibility, *J. Power Sources* 271 (2014) 291–297.
- [195] H. Xiang, P. Shi, P. Bhattacharya, X. Chen, D. Mei, M.E. Bowden, J. Zheng, J.-G. Zhang, W. Xu, Enhanced charging capability of lithium metal batteries based on lithium bis (trifluoromethanesulfonyl) imide-lithium bis (oxalato) borate dual-salt electrolytes, *J. Power Sources* 318 (2016) 170–177.
- [196] Z. Fang, Q. Ma, P. Liu, J. Ma, Y.-S. Hu, Z. Zhou, H. Li, X. Huang, L. Chen, Novel concentrated Li [(FSO2)(n-C4F9SO2) N]-based ether electrolyte for superior stability of metallic lithium anode, *ACS Appl. Mater. Interfaces* 9 (5) (2017) 4282–4289.
- [197] N.-W. Li, Y.-X. Yin, J.-Y. Li, C.-H. Zhang, Y.-G. Guo, Passivation of lithium metal anode via hybrid ionic liquid electrolyte toward stable Li plating/stripping, *Adv. Sci.* 4 (2) (2016) 1600400.
- [198] R. Miao, J. Yang, Z. Xu, J. Wang, Y. Nuli, L. Sun, A new ether-based electrolyte for dendrite-free lithium-metal based rechargeable batteries, *Sci. Rep.* 6 (1) (2016) 21771.
- [199] Z. Hu, S. Zhang, S. Dong, W. Li, H. Li, G. Cui, L. Chen, Poly (ethyl α -cyanoacrylate)-based artificial solid electrolyte interphase layer for enhanced interface stability of Li metal anodes, *Chem. Mater.* 29 (11) (2017) 4682–4689.
- [200] Y. Zhong, J. Zhang, S. Wang, D. Han, M. Xiao, Y. Meng, Effective suppression of lithium dendrite growth using fluorinated polysulfonamide-containing single-ion conducting polymer electrolytes, *Mater. Adv.* 1 (4) (2020) 873–879.
- [201] Y. Lu, Z. Tu, J. Shu, L.A. Archer, Stable lithium electrodeposition in salt-reinforced electrolytes, *J. Power Sources* 279 (2015) 413–418.

- [202] W. Li, H. Yao, K. Yan, G. Zheng, Z. Liang, Y.-M. Chiang, Y. Cui, The synergetic effect of lithium polysulfide and lithium nitrate to prevent lithium dendrite growth, *Nat. Commun.* 6 (1) (2015) 7436.
- [203] X. Liang, Z. Wen, Y. Liu, M. Wu, J. Jin, H. Zhang, X. Wu, Improved cycling performances of lithium sulfur batteries with LiNO₃-modified electrolyte, *J. Power Sources* 196 (22) (2011) 9839–9843.
- [204] C. Liu, H. Wu, J. Wu, Y. Xiao, Y. Deng, Dual-functional electrolyte additive for lithium–sulfur batteries limits lithium dendrite formation and increases sulfur utilization rate, *Batteries* 9 (9) (2023) 444.
- [205] J.-S. Kim, D.-J. Yoo, J. Min, R.A. Shakoor, R. Kahraman, J.W. Choi, Poreless separator and electrolyte additive for lithium–sulfur batteries with high areal energy densities, *ChemNanoMat* 1 (4) (2015) 240–245.
- [206] F. Wu, J. Qian, R. Chen, J. Lu, L. Li, H. Wu, J. Chen, T. Zhao, Y. Ye, K. Amine, An effective approach to protect lithium anode and improve cycle performance for Li–S batteries, *ACS Appl. Mater. Interfaces* 6 (17) (2014) 15542–15549.
- [207] S. Xiong, X. Kai, X. Hong, Y. Dia, Effect of LiBOB as additive on electrochemical properties of lithium–sulfur batteries, *Ionics* 18 (2012) 249–254.
- [208] W. Jia, C. Fan, L. Wang, Q. Wang, M. Zhao, A. Zhou, J. Li, Extremely accessible potassium nitrate (KNO₃) as the highly efficient electrolyte additive in lithium battery, *ACS Appl. Mater. Interfaces* 8 (24) (2016) 15399–15405.
- [209] G. Ma, Z. Wen, J. Jin, M. Wu, X. Wu, J. Zhang, et al., The enhanced performance of Li–S battery with P14YRTFSI-modified electrolyte, *Solid State Ion.* 262 (2014) 174–178.
- [210] Y. Liu, D. Lin, P.Y. Yuen, K. Liu, J. Xie, R.H. Dauskardt, Y. Cui, An artificial solid electrolyte interphase with high Li-ion conductivity, mechanical strength, and flexibility for stable lithium metal anodes, *Adv. Mater.* 29 (10) (2016).
- [211] L. Ma, M.S. Kim, L.A. Archer, Stable artificial solid electrolyte interphases for lithium batteries, *Chem. Mater.* 29 (10) (2017) 4181–4189.
- [212] H.-K. Jing, L.-L. Kong, S. Liu, G.-R. Li, X.-P. Gao, Protected lithium anode with porous Al₂O₃ layer for lithium–sulfur battery, *J. Mater. Chem. A* 3 (23) (2015) 12213–12219.
- [213] N.-W. Li, Y.-X. Yin, C.-P. Yang, Y.-G. Guo, An artificial solid electrolyte interphase layer for stable lithium metal anodes, *Adv. Mater.* 28 (9) (2016) 1853–1858.
- [214] L. Wang, Q. Wang, W. Jia, S. Chen, P. Gao, J. Li, Li metal coated with amorphous Li₃PO₄ via magnetron sputtering for stable and long-cycle life lithium metal batteries, *J. Power Sources* 342 (2017) 175–182.
- [215] K. Li, Y. Wang, W. Jia, S. Qu, Z. Yao, R. Cui, W. Zou, F. Zhou, J. Li, Polymer electrolyte film as robust and deformable artificial protective layer for high-performance lithium metal anode, *ACS Appl. Mater. Interfaces* 12 (2) (2019) 2285–2292.
- [216] R. Xu, X.-Q. Zhang, X.-B. Cheng, H.-J. Peng, C.-Z. Zhao, C. Yan, J.-Q. Huang, Artificial soft–rigid protective layer for dendrite-free lithium metal anode, *Adv. Funct. Mater.* 28 (8) (2018) 1705838.
- [217] J. Luo, C.-C. Fang, N.-L. Wu, High polarity poly (vinylidene difluoride) thin coating for dendrite-free and high-performance lithium metal anodes, *Adv. Energy Mater.* 8 (2) (2018) 1701482.
- [218] R. Xu, Y. Xiao, R. Zhang, X.-B. Cheng, C.-Z. Zhao, X.-Q. Zhang, C. Yan, Q. Zhang, J.-Q. Huang, Dual-phase single-ion pathway interfaces for robust lithium metal in working batteries, *Adv. Mater.* 31 (19) (2019) 1808392.
- [219] J. Luo, R.-C. Lee, J.-T. Jin, Y.-T. Weng, C.-C. Fang, N.-L. Wu, A dual-functional polymer coating on a lithium anode for suppressing dendrite growth and polysulfide shuttling in Li–S batteries, *Chem. Commun.* 53 (5) (2017) 963–966.
- [220] G. Ma, Z. Wen, M. Wu, C. Shen, Q. Wang, J. Jin, X. Wu, A lithium anode protection guided highly-stable lithium–sulfur battery, *Chem. Commun.* 50 (91) (2014) 14209–14212.
- [221] S.L. Koch, B.J. Morgan, S. Passerini, G. Teobaldi, Density functional theory screening of gas-treatment strategies for stabilization of high energy-density lithium metal anodes, *J. Power Sources* 296 (2015) 150–161.
- [222] N. Togasaki, T. Momma, T. Osaka, Enhanced cycling performance of a Li metal anode in a dimethylsulfoxide-based electrolyte using highly concentrated lithium salt for a lithium–oxygen battery, *J. Power Sources* 307 (2016) 98–104.
- [223] J. Qian, W.A. Henderson, W. Xu, P. Bhattacharya, M. Engelhard, O. Borodin, J.-G. Zhang, High rate and stable cycling of lithium metal anode, *Nat. Commun.* 6 (1) (2015) 6362.
- [224] B. Wu, J. Lochala, T. Taverne, J. Xiao, The interplay between solid electrolyte interface (SEI) and dendritic lithium growth, *Nano Energy* 40 (2017) 34–41.
- [225] H. Liu, X.-B. Cheng, J.-Q. Huang, H. Yuan, Y. Lu, C. Yan, G.-L. Zhu, R. Xu, C.-Z. Zhao, L.-P. Hou, et al., Controlling dendrite growth in solid-state electrolytes, *ACS Energy Lett.* 5 (3) (2020) 833–843.
- [226] U.v. Alpen, A. Rabenau, G. Talat, Ionic conductivity in Li₃N single crystals, *Appl. Phys. Lett.* 30 (12) (1977) 621–623.
- [227] J. Song, Y. Wang, C.C. Wan, Review of gel-type polymer electrolytes for lithium-ion batteries, *J. Power Sources* 77 (2) (1999) 183–197.
- [228] D. Lin, W. Liu, Y. Liu, H.R. Lee, P.-C. Hsu, K. Liu, Y. Cui, High ionic conductivity of composite solid polymer electrolyte via in situ synthesis of monodispersed SiO₂ nanospheres in poly (ethylene oxide), *Nano Lett.* 16 (1) (2016) 459–465.
- [229] C. Wang, Y. Gong, B. Liu, K. Fu, Y. Yao, E. Hitz, Y. Li, J. Dai, S. Xu, W. Luo, et al., Conformal, nanoscale ZnO surface modification of garnet-based solid-state electrolyte for lithium metal anodes, *Nano Lett.* 17 (1) (2017) 565–571.
- [230] Z. Tu, P. Nath, Y. Lu, M.D. Tikekar, L.A. Archer, Nanostructured electrolytes for stable lithium electrodeposition in secondary batteries, *Acc. Chem. Res.* 48 (11) (2015) 2947–2956.
- [231] J.H. Yoon, W.-J. Cho, T.H. Kang, M. Lee, G.-R. Yi, Nanostructured polymer electrolytes for lithium-ion batteries, *Macromol. Res.* 29 (8) (2021) 509–518.
- [232] D. Zhou, R. Liu, Y.-B. He, F. Li, M. Liu, B. Li, Q.-H. Yang, Q. Cai, F. Kang, SiO₂ hollow nanosphere-based composite solid electrolyte for lithium metal batteries to suppress lithium dendrite growth and enhance cycle life, *Adv. Energy Mater.* 6 (7) (2016) 1502214.
- [233] Y. Lu, S.K. Das, S.S. Mogganty, L.A. Archer, Ionic liquid-nanoparticle hybrid electrolytes and their application in secondary lithium-metal batteries, *Adv. Mater.* (Deerfield Beach Fla.) 24 (32) (2012) 4430–4435.
- [234] Y. Li, K.W. Wong, Q. Dou, K.M. Ng, A single-ion conducting and shear-thinning polymer electrolyte based on ionic liquid-decorated PMMA nanoparticles for lithium-metal batteries, *J. Mater. Chem. A* 4 (47) (2016) 18543–18550.
- [235] H.T. Duong, N.T. Duong, S. Nithiananth, V. Soundharajan, D.T. Pham, et al., Two in one: The use of hexagonal copper sulfide (CuS) nanoparticles as a bifunctional high-performance cathode and as a reinforced electrolyte additive for an all-solid-state lithium battery, *J. Electroanal. Chem.* 961 (2024) 118227.
- [236] H. Ling, L. Shen, Y. Huang, J. Ma, L. Chen, X. Hao, L. Zhao, F. Kang, Y.-B. He, Integrated structure of cathode and double-layer electrolyte for highly stable and dendrite-free all-solid-state Li-metal batteries, *ACS Appl. Mater. Interfaces* 12 (51) (2020) 56995–57002.
- [237] T. Melsheimer, M. Morey, A. Cannon, E. Ryan, Modeling the effects of pulse plating on dendrite growth in lithium metal batteries, *Electrochim. Acta* 433 (2022) 141227.
- [238] D.A. Dornbusch, R. Hilton, S.D. Lohman, G.J. Suppes, Experimental validation of the elimination of dendrite short-circuit failure in secondary lithium-metal convection cell batteries, *J. Electrochem. Soc.* 162 (3) (2014) A262.
- [239] Y. Wang, F. Hao, Interactions between solid electrolyte interphase and lithium dendrite, *J. Electrochem. Energy Convers. Storage* 19 (4) (2022) 040801.
- [240] Y. Zhong, J. Zhang, S. Wang, D. Han, M. Xiao, Y. Meng, Effective suppression of lithium dendrite growth using fluorinated polysulfonamide-containing single-ion conducting polymer electrolytes, *Mater. Adv.* 1 (2020) 873–879.
- [241] X.-B. Cheng, C. Yan, H.-J. Peng, J.-Q. Huang, S.-T. Yang, Q. Zhang, Sulfurized solid electrolyte interphases with a rapid Li⁺ diffusion on dendrite-free Li metal anodes, *Energy Storage Mater.* 10 (2018) 199–205.
- [242] J. Pokhare, A. Cresce, B. Pant, M.Y. Yang, A. Gurung, W. He, A. Baniya, B.S. Lamsal, Z. Yang, S. Gent, X. Xian, Y. Cao, W.A. Goddard, K. Xu, Y. Zhou, Manipulating the diffusion energy barrier at the lithium metal electrolyte interface for dendrite-free long-life batteries, *Nat. Commun.* 15 (1) (2024).
- [243] X.-B. Cheng, C. Yan, X. Chen, C. Guan, J.-Q. Huang, H.-J. Peng, R. Zhang, S.-T. Yang, Q. Zhang, Implantable solid electrolyte interphase in lithium-metal batteries, *Chem* 2 (2) (2017) 258–270.
- [244] P. Hundekar, R. Jain, A.S. Lakhot, N. Koratkar, Recent advances in the mitigation of dendrites in lithium-metal batteries, *J. Appl. Phys.* 128 (1) (2020) 010903.
- [245] J. Deng, X. Chen, Y. Bai, J. Mo, X. Yu, Data2010driven electrolyte design for advanced rechargeable lithium batteries †, *Chin. J. Chem.* 44 (3) (2025) 403–418.
- [246] S. Zhang, Suppressing Li dendrites via electrolyte engineering by crown ethers for lithium metal batteries, *Nano-Micro Lett.* 12 (1) (2020) 158.
- [247] H. Wang, J. He, J. Liu, S. Qi, M. Wu, J. Wen, Y. Chen, Y. Feng, J. Ma, Electrolytes enriched by crown ethers for lithium metal batteries, *Adv. Funct. Mater.* 31 (2) (2021) 2002578.
- [248] Y. Chen, M. Li, Y. Liu, Y. Jie, W. Li, F. Huang, X. Li, Z. He, X. Ren, Y. Chen, X. Meng, T. Cheng, M. Gu, S. Jiao, R. Cao, Origin of dendrite-free lithium deposition in concentrated electrolytes, *Nat. Commun.* 14 (1) (2023).
- [249] G. Wang, X. Xiong, D. Xie, X. Fu, X. Ma, Y. Li, Y. Liu, Z. Lin, C. Yang, M. Liu, Suppressing dendrite growth by a functional electrolyte additive for robust Li metal anodes, *Energy Storage Mater.* 23 (2019) 701–706.
- [250] T.H. Pham, V.-C. Ho, G.-H. Son, J. Mun, J.-G. Kim, Suppressing the growth of dendrites on ultrathin lithium metal anodes by an amide electrolyte additive, *J. Electrochem. Soc.* 171 (2) (2024) 020525.
- [251] H. Ye, Y.-X. Yin, S.-F. Zhang, Y. Shi, L. Liu, X.-X. Zeng, R. Wen, Y.-G. Guo, L.-J. Wan, Synergism of Al-containing solid electrolyte interphase layer and Al-based colloidal particles for stable lithium anode, *Nano Energy* 36 (2017) 411–417.
- [252] B. Wu, J. Lochala, T. Taverne, J. Xiao, The interplay between solid electrolyte interface (SEI) and dendritic lithium growth, *Nano Energy* 40 (2017) 34–41.
- [253] J. Hwang, H. Okada, R. Haraguchi, S. Tawa, K. Matsumoto, R. Hagiwara, Ionic liquid electrolyte for room to intermediate temperature operating Li metal batteries: Dendrite suppression and improved performance, *J. Power Sources* 453 (2020) 227911.
- [254] X. He, X. Liu, Q. Han, P. Zhang, X. Song, Y. Zhao, A liquid/liquid electrolyte interface that inhibits corrosion and dendrite growth of lithium in lithium-metal batteries, *Angew. Chem.* 132 (16) (2020) 6459–6467.
- [255] H. Yang, C. Guo, A. Naveed, J. Lei, J. Yang, Y. Nuli, J. Wang, Recent progress and perspective on lithium metal anode protection, *Energy Storage Mater.* 14 (2018) 199–221.

- [256] S. Bai, Z. Huang, G. Liang, R. Yang, D. Liu, W. Wen, X. Jin, C. Zhi, X. Wang, Electrolyte additives for stable Zn anodes, *Adv. Sci.* 11 (4) (2024) 2304549.
- [257] C. Zhai, D. Zhao, Y. He, H. Huang, B. Chen, X. Wang, Z. Guo, Electrolyte additive strategies for suppression of zinc dendrites in aqueous zinc-ion batteries, *Batteries* 8 (10) (2022) 153.
- [258] W. Feng, Z. Liang, W. Zhou, X. Li, W. Wang, Y. Chi, W. Liu, D. Gengzang, G. Zhang, Q. Chen, P. Wang, W. Chen, S. Zhang, Dendrite-free zinc metal anodes enabled by electrolyte additive for high-performing aqueous zinc-ion batteries, *Dalton Trans.* 52 (2023) 7457–7463.
- [259] B. Lee, E. Paek, D. Mitlin, S.W. Lee, Sodium metal anodes: emerging solutions to dendrite growth, *Chem. Rev.* 119 (8) (2019) 5416–5460.
- [260] H. Xu, Y. Xiang, X. Xu, Y. Liang, Y. Li, Y. Qi, M. Xu, A polysulfides-defensive, dendrite-suppressed, and flame-retardant separator with lean electrolyte for room temperature sodium–sulfur batteries, *Adv. Funct. Mater.* 34 (40) (2024) 2403663.
- [261] S. Lee, B. Koo, S. Kang, H. Lee, H. Lee, Hydrofluoroether-assisted dilution of na-ion concentrated ionic liquid electrolyte for safe, stable cycling of high-voltage na-metal batteries, *Chem. Eng. J.* 425 (2021) 130612.
- [262] X. Yang, X. Gao, C. Zhao, Q. Sun, Y. Zhao, K. Adair, J. Luo, X. Lin, J. Liang, H. Huang, L. Zhang, S. Lu, R. Li, X. Sun, Suppressed dendrite formation realized by selective Li deposition in all-solid-state lithium batteries, *Energy Storage Mater.* 27 (2020) 198–204.
- [263] Y. Liu, H. Su, Y. Zhong, M. Zheng, Y. Hu, F. Zhao, J.T. Kim, Y. Gao, J. Luo, X. Lin, J. Tu, X. Sun, Inhibiting dendrites by uniformizing microstructure of superionic lithium argyrodites for all-solid-state lithium metal batteries, *Adv. Energy Mater.* 14 (31) (2024) 2400783.
- [264] T. Yang, Y. Sun, T. Qian, J. Liu, X. Liu, F. Rosei, C. Yan, Lithium dendrite inhibition via 3D porous lithium metal anode accompanied by inherent SEI layer, *Energy Storage Mater.* 26 (2020) 385–390.
- [265] L. Tan, X. Li, M. Cheng, T. Liu, Z. Wang, H. Guo, G. Yan, L. Li, Y. Liu, J. Wang, In-situ tailored 3D Li₂O@Cu nanowires array enabling stable lithium metal anode with ultra-high coulombic efficiency, *J. Power Sources* 463 (2020) 228178.
- [266] H.-J. Zhang, K.-X. Wang, X.-Y. Wu, Y.-M. Jiang, Y.-B. Zhai, C. Wang, X. Wei, J.-S. Chen, MoO₂/Mo₂C heteronanotubes function as high-performance Li-ion battery electrode, *Adv. Funct. Mater.* 24 (22) (2014) 3399–3404.
- [267] C. Sun, S. Rajasekhara, J.B. Goodenough, F. Zhou, Monodisperse porous LiFePO₄ microspheres for a high power Li-ion battery cathode, *J. Am. Chem. Soc.* 133 (7) (2011) 2132–2135.
- [268] Y. Wu, Z. Wen, H. Feng, J. Li, Hollow porous LiMn₂O₄ microcubes as rechargeable lithium battery cathode with high electrochemical performance, *Small* 8 (6) (2012) 858–862.
- [269] Y.-M. Jiang, K.-X. Wang, H.-J. Zhang, J.-F. Wang, J.-S. Chen, Hierarchical Li₄Ti₅O₁₂/TiO₂ composite tubes with regular structural imperfection for lithium ion storage, *Sci. Rep.* 3 (1) (2013) 3490.
- [270] B.M. Bang, J.-I. Lee, H. Kim, J. Cho, S. Park, High-performance macroporous bulk silicon anodes synthesized by template-free chemical etching, *Adv. Energy Mater.* 2 (2012).
- [271] Y. Yu, C.-H. Chen, Y. Shi, A tin-based amorphous oxide composite with a porous, spherical, multideck-cage morphology as a highly reversible anode material for lithium-ion batteries, *Adv. Mater.* 19 (7) (2007) 993–997.
- [272] G.S. Chai, I.S. Shin, J.S. Yu, Synthesis of ordered, uniform, macroporous carbons with mesoporous walls templated by aggregates of polystyrene spheres and silica particles for use as catalyst supports in direct methanol fuel cells, *Adv. Mater.* 16 (22) (2004) 2057–2061.
- [273] K. Park, J.B. Goodenough, Dendrite-suppressed lithium plating from a liquid electrolyte via wetting of Li₃N, *Adv. Energy Mater.* 7 (19) (2017) 1700732.
- [274] S. Kim, M. Lee, S. Oh, W.-H. Ryu, Li-dendrite cage electrode with 3-D interconnected pores for anode-free lithium-metal batteries, *Chem. Eng. J.* 474 (2023) 145447.
- [275] C. Chang, M. Zhang, Z. Lao, X. Xiao, G. Lu, H. Qu, X. Wu, H. Fu, G. Zhou, Achieving stable lithium anodes through leveraging inevitable stress variations via adaptive piezoelectric effect, *Adv. Mater.* 36 (19) (2024) 2313525.
- [276] L.S. Aota, C. Jung, S. Zhang, Ö.K. Büyüksulu, A. Sakseena, E. Hatipoglu, P. Yadav, M.P. Singh, X. Chen, E. Woods, C. Scheu, S.-H. Kim, D. Raabe, B. Gault, Grain boundaries control lithiation of solid solution substrates in lithium metal batteries, *Adv. Sci.* 12 (2025) 2409275.
- [277] H. Liu, H. Zhou, B.-S. Lee, X. Xing, M. Gonzalez, P. Liu, Suppressing lithium dendrite growth with a single-component coating, *ACS Appl. Mater. Interfaces* 9 (36) (2017) 30635–30642.
- [278] J. Schmidt, M.R.G. Marques, S. Botti, M.A.L. Marques, Recent advances and applications of machine learning in solid-state materials science, *Npj Comput. Mater.* 5 (2019) 83.
- [279] S.S. Chong, Y.S. Ng, H.-Q. Wang, J.-C. Zheng, Advances of machine learning in materials science: Ideas and techniques, *Front. Phys.* 19 (2024) 13501.
- [280] A. Jain, Machine learning in materials research: Developments over the last decade and challenges for the future, *Curr. Opin. Solid State Mater. Sci.* 33 (2024) 101189.
- [281] C.H. Liow, H. Kang, S. Kim, M. Na, Y. Lee, A. Baucour, K. Bang, Y. Shim, J. Choe, G. Hwang, S. Cho, G. Park, J. Yeom, J.C. Agar, J.M. Yuk, J. Shin, H.M. Lee, H.R. Byon, E. Cho, S. Hong, Machine learning assisted synthesis of lithium-ion batteries cathode materials, *Curr. Opin. Solid State Mater. Sci.* 98 (2022) 107214.
- [282] A. Dave, J. Mitchell, K. Kandasamy, H. Wang, S. Burke, B. Paria, B. Póczos, J. Whitacre, V. Viswanathan, Autonomous discovery of battery electrolytes with robotic experimentation and machine learning, *Cell Rep. Phys. Sci.* 1 (12) (2020) 100264.
- [283] Y. Zhang, X. He, Z. Chen, Q. Bai, A.M. Nolan, C.A. Roberts, D. Banerjee, T. Matsunaga, Y. Mo, C. Ling, Unsupervised discovery of solid-state lithium ion conductors, *Nat. Commun.* 10 (2019) 5260.
- [284] F. Kolodziejczyk, B. Mortazavi, T. Rabczuk, X. Zhuang, Machine learning assisted multiscale modeling of composite phase change materials for Li-ion batteries' thermal management, *Int. J. Heat Mass Transfer* 172 (2021) 121199.
- [285] G. Sun, Y. Liu, X. Liu, A method for estimating lithium-ion battery state of health based on physics-informed machine learning, *J. Power Sources* 627 (2025) 235767.
- [286] Q. Zhai, H. Jiang, N. Long, Q. Kang, X. Meng, M. Zhou, L. Yan, T. Ma, Machine learning for full lifecycle management of lithium-ion batteries, *Renew. Sustain. Energy Rev.* 202 (2024) 114647.
- [287] S. Esmizadeh, L. Cabras, M. Serpelloni, T. Dev, V. Oancea, E. Knobbe, M. Lachner, A. Salvadori, A review on modeling of nucleation and growth of Li dendrites in solid electrolytes, *J. Energy Storage* 97 (Part B) (2024) 112897.
- [288] Z. Ahmad, T. Xie, C. Maheshwari, J.C. Grossman, V. Viswanathan, Machine learning enabled computational screening of inorganic solid electrolytes for suppression of dendrite formation in lithium metal anodes, *ACS Central Sci.* 4 (8) (2018) 996–1006.
- [289] Z. Ahmad, V. Viswanathan, Stability of electrodeposition at solid-solid interfaces and implications for metal anodes, *Phys. Rev. Lett.* 119 (5) (2017) 056003.
- [290] K. Li, J. Wang, Y. Song, Y. Wang, Machine learning-guided discovery of ionic polymer electrolytes for lithium metal batteries, *Nat. Commun.* 14 (2023) 2789.
- [291] F. Li, X. Cheng, L.-L. Lu, Y.-C. Yin, J.-D. Luo, G. Lu, Y.-F. Meng, H. Mo, T. Tian, J.-T. Yang, W. Wen, Z.-P. Liu, G. Zhang, C. Shang, H.-B. Yao, Stable all-solid-state lithium metal batteries enabled by machine learning simulation designed halide electrolytes, *Nano Lett.* 22 (16) (2022) 2461–2469.
- [292] A. Satpati, G.R. Kandregul, K. Ramanujam, Machine learning enabled high-throughput screening of inorganic solid electrolytes for regulating dendritic growth in lithium metal anodes, *New J. Chem.* 46 (2022) 14227–14238.
- [293] B. Liu, J. Yang, H. Yang, C. Ye, Y. Mao, J. Wang, S. Shi, J. Yang, W. Zhang, Rationalizing the interphase stability of Li/doped-Li₇La₃Zr₂O₁₂ via automated reaction screening and machine learning, *J. Mater. Chem. A* 7 (34) (2019) 19961–19969.
- [294] Y. Ma, T. Jin, R. Choudhury, Q. Cheng, Y. Miao, C. Zheng, W. Min, Y. Yang, Understanding the correlation between lithium dendrite growth and local material properties by machine learning, *J. Electrochem. Soc.* 168 (9) (2021) 090523.
- [295] A. Permatasari, Y. Mori, M. So, V.L. Nguyen, G. Inoue, Simulation study of ionic current distribution and Li dendrite growth on the anode in lithium-ion batteries using support vector regression machine learning, *J. Energy Storage* 92 (2024) 112115.
- [296] S. Ma, B. Sun, X. Chen, X. Zhang, X. Zhang, W. Zhang, H. Ruan, X. Zhao, Machine learning and feature engineering-based anode potential estimation method for lithium-ion batteries with application, *J. Energy Storage* 103 (B) (2024) 114387.
- [297] Z. Zhao, J. Xia, S. Wu, X. Wang, G. Xu, Y. Zhu, J. Sun, H.-F. Li, Insights into dendritic growth mechanisms in batteries: A combined machine learning and computational study, *Batter. Energy* (2025) e70015.
- [298] J. Su, H. Yan, Y. Xiao, W. Yang, Z. Wang, X. Yao, H. Abbasi, L. Chen, Dual-scale model enabled explainable-AI toward decoding internal short circuit risk of lithium metal batteries, *Energy Storage Mater.* 78 (2025) 104286.
- [299] J. Zhao, X. Feng, Q. Pang, M. Fowler, Y. Lian, M. Ouyang, A.F. Burke, Battery safety: Machine learning-based prognostics, *Prog. Energy Combust. Sci.* 102 (2024) 101142.
- [300] Y. Jia, J. Li, W. Yao, Y. Li, J. Xu, Precise and fast safety risk classification of lithium-ion batteries based on machine learning methodology, *J. Power Sources* 548 (2022) 232064.
- [301] G. Choi, Y. Kim, J. Choi, D. Kim, Mechanical seed mechanism to facilitate homogeneous Li metal growth, *Adv. Energy Mater.* 13 (34) (2023) 2300816.
- [302] R. Jaleem, K. Kanamori, I. Takeuchi, M. Nakayama, H. Yamasaki, T. Saito, Bayesian-driven first-principles calculations for accelerating exploration of fast ion conductors for rechargeable battery application, *Sci. Rep.* 8 (2018) 5845.
- [303] Q. Sun, Y. Xiang, Y.L. and Liang Xu, T. Leng, Y. Ye, A. Fortunelli, W.A.G. III, T. Cheng, Machine learning predicts the X-ray photoelectron spectroscopy of the solid electrolyte interface of lithium metal battery, *J. Phys. Chem. Lett.* 13 (34) (2022) 8047–8054.
- [304] P. C.V., A.K. Lakshminarayanan, B. Ramasubramanian, S. Ramakrishna, Progress of machine learning in materials design for Li-ion battery, *Next Mater.* 2 (2024) 100145.

- [305] R. Li, W. Zhao, R. Li, C. Gan, L. Chen, Z. Wang, X. Yang, Leveraging machine learning for accelerated materials innovation in lithium-ion battery: a review, *J. Energy Chem.* 106 (2025) 44–62.
- [306] D. Han, C. Lin, Combination of high-throughput phase field modeling and machine learning to study the performance evolution during lithium battery cycling, *Energy Storage Mater.* 74 (2025) 103982.
- [307] Y. Ren, K. Zhang, Y. Zhou, Y. Cao, Phase-field simulation and machine learning study of the effects of elastic and plastic properties of electrodes and solid polymer electrolytes on the suppression of Li dendrite growth, *ACS Appl. Mater. Interfaces* 14 (27) (2022) 30658–30671.
- [308] Z. Wang, H. Huang, H. Zhao, C. Xu, S. Zhu, J. Janssen, V. Viswanathan, DREAMS: Density functional theory based research engine for agentic materials simulation, 2025, arXiv preprint arXiv:2507.14267.
- [309] Y. Mo, S.P. Ong, G. Ceder, First principles study of the Li₁₀GeP₂S₁₂ lithium super ionic conductor material, *Chem. Mater.* 24 (1) (2012) 15–17.
- [310] T. Cheng, B.V. Merinov, S. Morozov, W.A. Goddard, Quantum mechanics reactive dynamics study of solid Li-electrode/Li₆PS₅Cl-electrolyte interface, *ACS Energy Lett.* 2 (6) (2017) 1454–1459.
- [311] O.T. Unke, S. Chmiela, H.E. Sauceda, M. Gastegger, I. Poltavsky, K.T. Schütt, A. Tkatchenko, K.-R. Müller, Machine learning force fields, *Chem. Rev.* 121 (16) (2021) 10142–10186.
- [312] S.A. Tawfik, T.M. Nguyen, S.P. Russo, T. Tran, S. Gupta, S. Venkatesh, Embedding material graphs using the electron-ion potential: application to material fracture, *Digit. Discov.* 3 (12) (2024) 2618–2627.
- [313] C. Chen, S.P. Ong, A universal graph deep learning interatomic potential for the periodic table, *Nat. Comput. Sci.* 2 (2022) 718–728.
- [314] S.A. Tawfik, L. La, T.M. Nguyen, T. Tran, S. Gupta, S. Venkatesh, Scale matters: simulation of nanoscopic dendrite initiation in lithium solid electrolyte interphases using a machine learning potential, *J. Mater. Chem. A* 13 (2025) 6357–6363.
- [315] W. Zhang, M. Weng, M. Zhang, Y. Ye, Z. Chen, S. Li, S. Li, F. Pan, L. Wang, Revealing morphology evolution of lithium dendrites by large-scale simulation based on machine learning force field, *Adv. Energy Mater.* 13 (4) (2023) 2202892.
- [316] R. Zhao, J. Liu, J. Gu, Simulation and experimental study on lithium ion battery short circuit, *Appl. Energy* 173 (2016) 29–39.
- [317] Y. Ye, Y. Shi, N. Cai, J. Lee, X. He, Electro-thermal modeling and experimental validation for lithium ion battery, *J. Power Sources* 199 (2012) 227–238.
- [318] F. Meng, X. Jia, H. Kang, W. Qin, In-situ construction of Li₃N/Li₂CO₃ hybrid SEI to improve interface stability of quasi-solid-state lithium metal batteries, 2026, Available At SSRN 6161218.
- [319] P. Dong, Z. Xie, F. Li, S. Hou, D. Zhang, W. Gao, Y. Lei, B. Yang, F. Liang, Li₃N/Li₂O-rich artificial SEI formed by in-situ dielectric barrier discharge plasma for lithium metal batteries, *Chem. Eng. J.* (2026) 173130.
- [320] X. Jiao, X. Wang, X. Xu, Y. Wang, H.-H. Ryu, J. Park, J.-Y. Hwang, S. Xiong, Y.-K. Sun, Z. Song, et al., Multi-physical field simulation: A powerful tool for accelerating exploration of high-energy-density rechargeable lithium batteries, *Adv. Energy Mater.* 13 (39) (2023) 2301708.
- [321] S. Haghi, M.F.V. Hidalgo, M.F. Niri, R. Daub, J. Marco, Machine learning in lithium-ion battery cell production: A comprehensive mapping study, *Batter. & Supercaps* 6 (7) (2023) e202300046.
- [322] Z. Zhao, J. Xia, S. Wu, X. Wang, G. Xu, Y. Zhu, J. Sun, H.-F. Li, Insights into dendritic growth mechanisms in batteries: A combined machine learning and computational study, *Batter. Energy* 4 (5) (2025) e70015.
- [323] Y. Deng, C. Du, Z. Ren, A novel method for estimating the state of health of lithium-ion batteries based on physics-informed neural network, *Batteries* 11 (2) (2025) 49.
- [324] A. Olabi, A.A. Abdelghafar, B. Soudan, A.H. Alami, C. Semeraro, M. Al Radi, M. Al-Murisi, M.A. Abdelkareem, Artificial neural network driven prognosis and estimation of lithium-ion battery states: Current insights and future perspectives, *Ain Shams Eng. J.* 15 (2) (2024) 102429.
- [325] C. Ling, A review of the recent progress in battery informatics, *Npj Comput. Mater.* 8 (2022) 33.
- [326] J. Sun, A. Gu, J. Kainz, A solution framework for the experimental data shortage problem of lithium-ion batteries: Generative adversarial network-based data augmentation for battery state estimation, *J. Energy Chem.* 103 (2025) 476–497.
- [327] A. Valizadeh, M.H. Amirhosseini, Machine learning in lithium-ion battery: Applications, challenges, and future trends, *SN Comput. Sci.* 5 (6) (2024).
- [328] Y. Lu, et al., Critical current density in solid-state lithium metal batteries: mechanism, influences, and strategies, *Adv. Funct. Mater.* 31 (18) (2021) 2009925.
- [329] G. Liu, et al., Densified Li₆PS₅Cl nanorods with high ionic conductivity and improved critical current density for all-solid-state lithium batteries, *Nano Lett.* 20 (9) (2020) 6660–6665.
- [330] T. Fuchs, et al., Evaluating the use of critical current density tests of symmetric lithium transference cells with solid electrolytes, *Adv. Energy Mater.* 13 (45) (2023) 2302383.
- [331] M. Gao, et al., Constructing a multifunctional interlayer toward ultra-high critical current density for garnet-based solid-state lithium batteries, *Adv. Funct. Mater.* 33 (22) (2023) 2300319.
- [332] B. Pang, et al., Ag nanoparticles incorporated interlayer enables ultrahigh critical current density for Li₆PS₅Cl-based all-solid-state lithium batteries, *J. Power Sources* 563 (2023) 232836.
- [333] X. Yao, et al., High-energy all-solid-state lithium batteries with ultralong cycle life, *Nano Lett.* 16 (11) (2016) 7148–7154.
- [334] Z. Zhang, et al., An advanced construction strategy of all-solid-state lithium batteries with excellent interfacial compatibility and ultralong cycle life, *J. Mater. Chem. A* 5 (32) (2017) 16984–16993.
- [335] F. Wu, et al., Liquid-in-solid and solid-in-liquid electrolytes with high rate capacity and long cycling life for lithium-ion batteries, *Chem. Mater.* 28 (3) (2016) 848–856.
- [336] S.S. Choi, H.S. Lim, Factors that affect cycle-life and possible degradation mechanisms of a Li-ion cell based on LiCoO₂, *J. Power Sources* 111 (1) (2002) 130–136.
- [337] F. Yang, et al., A study of the relationship between coulombic efficiency and capacity degradation of commercial lithium-ion batteries, *Energy* 145 (2018) 486–495.
- [338] J. Xiao, et al., Understanding and applying coulombic efficiency in lithium metal batteries, *Nat. Energy* 5 (8) (2020) 561–568.
- [339] J. Li, et al., Toward low-cost, high-energy density, and high-power density lithium-ion batteries, *JOM* 69 (9) (2017) 1484–1496.
- [340] A.M. Gaikwad, et al., A high areal capacity flexible lithium-ion battery with a strain-compliant design, *Adv. Energy Mater.* 5 (3) (2015) 1401389.
- [341] K.G. Gallagher, et al., Optimizing areal capacities through understanding the limitations of lithium-ion electrodes, *J. Electrochem. Soc.* 163 (2) (2016) A138–A149.
- [342] S. Ma, et al., Temperature effect and thermal impact in lithium-ion batteries: A review, *Prog. Nat. Sci.: Mater. Int.* 28 (6) (2018) 653–666.
- [343] A.M. Aris, B. Shabani, An experimental study of a lithium ion cell operation at low temperature conditions, *Energy Procedia* 110 (2017) 128–135.
- [344] Z. Lu, et al., A comprehensive experimental study on temperature-dependent performance of lithium-ion battery, *Appl. Therm. Eng.* 158 (2019) 113800.
- [345] J. Wolfenstine, et al., Mechanical behavior of Li-ion-conducting crystalline oxide-based solid electrolytes: a brief review, *Ionics* 24 (5) (2018) 1271–1276.
- [346] F. Gucci, et al., Electrical and mechanical characterisation of poly(ethylene) oxide-polysulfone blend for composite structural lithium batteries, *Polymers* 15 (11) (2023) 2581.
- [347] S.K. Tripathi, A. Gupta, M. Kumari, Studies on electrical conductivity and dielectric behaviour of PvdF–HFP–PMMA–NaI polymer blend electrolyte, *Bull. Mater. Sci.* 35 (6) (2012) 969–975.
- [348] L. Yue, et al., All solid-state polymer electrolytes for high-performance lithium ion batteries, *Energy Storage Mater.* 5 (2016) 139–164.
- [349] R. Shang, T. Nelson, T.V. Nguyen, C. Nelson, H. Antony, B. Abaoag, M. Ozkan, C.S. Ozkan, A comprehensive review of solid-state lithium batteries: Fast charging characteristics and in-operando diagnostics, *Nano Energy* 142 (2025) 111232.
- [350] V. Thangadurai, W. Weppner, Recent progress in solid oxide and lithium ion conducting electrolytes research, *Ionics* 12 (1) (2006) 81–92.
- [351] Z. Gao, et al., Promises, challenges, and recent progress of inorganic solid-state electrolytes for all-solid-state lithium batteries, *Adv. Mater.* 30 (17) (2018) 1705702.
- [352] A. du Baret de Limé, et al., Impact of electrode defects on battery cell performance: a review, *Batter. Supercaps* 5 (10) (2022) e202200239.
- [353] J.H. Yin, et al., Recent advances of LATP and their NASICON structure as a solid-state electrolyte for lithium-ion batteries, *Adv. Eng. Mater.* 25 (20) (2023) 2300566.
- [354] P. Li, Q. Wang, Novel structural janus hydrogels for battery applications: Structure design, properties, and prospects, *Colloids Interfaces* 9 (4) (2025) 48.
- [355] X. Lu, Y. Wang, X. Xu, B. Yan, T. Wu, L. Lu, Polymer-based solid-state electrolytes for high-energy-density lithium-ion batteries–review, *Adv. Energy Mater.* 13 (38) (2023) 2301746.
- [356] L. Xia, J. Tang, Y. Chen, X. Zhou, Z. Ma, Y. Pei, Exploring the effects of defect concentrations and distribution on Li diffusion in Li₃OBr solid-state electrolyte using a deep potential model, *J. Mater. Chem. A* 12 (11) (2024) 6724–6732.
- [357] C. Yuan, X. Gao, Y. Jia, W. Zhang, Q. Wu, J. Xu, Coupled crack propagation and dendrite growth in solid electrolyte of all-solid-state battery, *Nano Energy* 86 (2021) 106057.
- [358] M. Hasanpoor, M. Eftekharnia, T. Pathirana, U. Pal, R. Kerr, M. Forsyth, P.C. Howlett, Understanding the role of separator and electrolyte compatibility on lithium metal anode performance using ionic liquid-based electrolytes, *ACS Appl. Energy Mater.* 4 (6) (2021) 6310–6323.
- [359] C.F. Francis, I.L. Kyratzis, A.S. Best, Lithium-ion battery separators for ionic-liquid electrolytes: a review, *Adv. Mater.* 32 (18) (2020) 1904205.
- [360] C. Wang, C. Yang, Z. Zheng, Toward practical high-energy and high-power lithium battery anodes: present and future, *Adv. Sci.* 9 (9) (2022) 2105213.
- [361] C. Chen, Q. Liang, G. Wang, D. Liu, X. Xiong, Grain-boundary-rich artificial SEI layer for high-rate lithium metal anodes, *Adv. Funct. Mater.* 32 (4) (2022) 2107249.

- [362] Y. Luo, S. Huang, J. Liao, Z. Wu, L. Chen, Three-dimensional nanostructured composite lithium soap fibers for constructing high-performance lithium metal anode interfacial layers, *Chem. Sci.* 16 (21) (2025) 9366–9374.
- [363] T. Kang, Y. Wang, F. Guo, C. Liu, J. Zhao, J. Yang, H. Lin, Y. Qiu, Y. Shen, W. Lu, et al., Self-assembled monolayer enables slurry-coating of Li anode, *ACS Central Sci.* 5 (3) (2019) 468–476.
- [364] X. He, K. Zhang, Z. Zhu, Z. Tong, X. Liang, 3D-hosted lithium metal anodes, *Chem. Soc. Rev.* 53 (1) (2024) 9–24.
- [365] Z. Chen, C. Zhang, Engineering electrode microstructures for advanced lithium-ion batteries, *Microstructures* 4 (3) (2024) N–A.
- [366] W. Yuan, Y. Li, T. Ding, L. Zhang, J. Shu, Dendrite-free NaK alloy anodes: Electrodes preparation and interfacial reaction, *Chem. Eng. J.* 432 (2022) 134353.
- [367] W. Yao, J. Xu, L. Ma, X. Lu, D. Luo, J. Qian, L. Zhan, I. Manke, C. Yang, P. Adelhelm, et al., Recent progress for concurrent realization of shuttle-inhibition and dendrite-free lithium–sulfur batteries, *Adv. Mater.* 35 (32) (2023) 2212116.
- [368] B. Ge, L. Hu, X. Yu, L. Wang, C. Fernandez, N. Yang, Q. Liang, Q.-H. Yang, Engineering Triple2010Phase interfaces around the anode toward practical alkali Metal2013Air batteries, *Adv. Mater.* 36 (27) (2024).
- [369] J.-S. Lee, S. Tai Kim, R. Cao, N.-S. Choi, M. Liu, K.T. Lee, J. Cho, Metal–air batteries with high energy density: Li–air versus Zn–air, *Adv. Energy Mater.* 1 (1) (2011) 34–50.
- [370] Y. Liang, D. Song, W. Wu, Y. Yu, J. You, Y. Liu, Review of the real-time monitoring technologies for lithium dendrites in lithium-ion batteries, *Molecules* 29 (9) (2024) 2118.
- [371] T. Foroozan, S. Sharifi-Asl, R. Shahbazian-Yassar, Mechanistic understanding of Li dendrites growth by in-situ/operando imaging techniques, *J. Power Sources* 461 (2020) 228135.
- [372] C.-E. Dutoit, M. Tang, D. Gourier, J.-M. Tarascon, H. Vezin, E. Salager, Monitoring metallic sub-micrometric lithium structures in Li-ion batteries by in situ electron paramagnetic resonance correlated spectroscopy and imaging, *Nat. Commun.* 12 (1) (2021) 1410.
- [373] J. Mohammadi Moradian, A. Ali, X. Yan, G. Pei, S. Zhang, A. Naveed, K. Shehzad, Z. Shahnavaaz, F. Ahmad, B. Yousaf, Sensors innovations for smart lithium-based batteries: Advancements, opportunities, and potential challenges, *Nano-Micro Lett.* 17 (1) (2025) 279.
- [374] C. Zhang, Z. Liu, Z. Lao, Y. Zhou, X. Xiao, T. Feng, C. Chang, R. Wang, G. Zhou, X. Guan, Operando spatiotemporal super-resolution of thermal events monitoring in lithium metal batteries, *Natl. Sci. Rev.* 12 (5) (2025) nwaf088.
- [375] R. Feng, Y. Liang, T. Yin, P. Gao, W. Wang, Agentic assistant for materials scientists, *Electrochem. Soc. Interface* 34 (2) (2025) 45.
- [376] Y.-C. Gao, X. Chen, Y.-H. Yuan, Y.-P. Chen, Y.-L. Niu, N. Yao, Y.-B. Gao, W.-L. Li, Q. Zhang, Accelerating battery innovation: AI-powered molecular discovery, *Chem. Soc. Rev.* (2025).
- [377] C. Karpovich, E. Pan, E.A. Olivetti, Deep reinforcement learning for inverse inorganic materials design, *Npj Comput. Mater.* 10 (1) (2024) 287.
- [378] K. Luo, J. Zhao, Y. Wang, J. Li, J. Wen, J. Liang, H. Soekmadji, S. Liao, Physics-informed neural networks for PDE problems: A comprehensive review, *Artif. Intell. Rev.* 58 (10) (2025) 1–43.
- [379] H. Taghavian, V. Vanoppen, E. Berg, P. Broqvist, J. Sjölund, Navigating chemical design spaces for metal-ion batteries via machine-learning-guided phase-field simulations, *Npj Comput. Mater.* 11 (1) (2025) 243.
- [380] Y. Wang, Application-oriented design of machine learning paradigms for battery science, *Npj Comput. Mater.* 11 (2025) 89, Received: 16 August 2024; Accepted: 06 March 2025; Published: 02 April 2025.
- [381] H.O. Khogali, S. Mekid, The blended future of automation and AI: Examining some long-term societal and ethical impact features, *Technol. Soc.* 73 (2023) 102232.
- [382] L. Duboz, I.C. Raileanu, J. Krause, A. Norman-López, M. Weitzel, B. Ciuffo, Scenarios for the deployment of automated vehicles in Europe, *Transp. Res. Interdiscip. Perspect.* 32 (2025) 101530.
- [383] C. Monroe, J. Newman, The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces, *J. Electrochem. Soc.* 152 (2) (2005) A396.
- [384] K.D. Owensby, R. Sahore, W.-Y. Tsai, X.C. Chen, Understanding and controlling lithium morphology in solid polymer and gel polymer systems: mechanisms, strategies, and gaps, *Mater. Adv.* 4 (23) (2023) 5867–5881.
- [385] Z. Tang, S. Li, Y. Li, H. Xu, Y. Yu, Y. Huang, J. Li, Lithium metal electrode protected by stiff and tough self-compacting separator, *Nano Energy* 69 (2020) 104399.

A.5 Publication V [P-V]: Physics-Guided Machine Learning for Enhanced Piezoelectric Performance in Electrospun PVDF/SnO₂ Nanofibers



Physics-Guided Machine Learning for Enhanced Piezoelectric Performance in Electrospun PVDF/SnO₂ Nanofibers

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ABSTRACT

Sustainable piezoelectric design linking processing and microstructure with device performance is needed for wearable energy harvesters and soft actuators. NLP was used for gap analysis to identify SnO₂ as a high-potential yet underexplored filler for PVDF. To address the literature data scarcity, we developed a Physics-Guided Machine Learning (PGMLpiezo) model that provides property predictions for multiscale FEM device simulations. Using optimized electrospinning (18 w/v% PVDF), SnO₂ doping reduced fiber diameter from 680 nm to 290 nm. The β -phase fraction increased from 0.3456 (powder) to 0.5725. The PGMLpiezo model predicts a d_{33} increase from 18 to 28.91 pC/N after the addition of SnO₂ in PVDF. Using these predicted properties, FEM simulations were performed to evaluate device-level performance, showing thickness-mode harvesting with open-circuit voltages of 4.7 V and nano-watt range power outputs. Similarly, a lateral-clamp actuation gives strokes up to 69.6 nm with an effective $d_{33}^{\text{eff}} = 45.95$ pm/V.

1. Introduction

Poly(vinylidene fluoride) (PVDF) is a semicrystalline, flexible piezoelectric fluoropolymer whose polar β -phase enables efficient conversion between mechanical and electrical energy, making it an excellent candidate for self-powered Internet-of-Things (IoT) devices, wearables, and micro-actuators [1–3]. PVDF offers a high dielectric constant alongside strong mechanical and thermal stability [4]. PVDF is also increasingly used for optical [5] and sensing technologies [6]. PVDF is a better choice in energy harvesting [7] and various nanotechnology applications [8,9]. Beyond piezoelectricity, PVDF-based composite electrolytes are gaining traction in all-solid-state lithium-metal batteries [10,11]. Their high polarity and electrochemical stability enable salt dissociation and ion transport, while tunable morphology allows for the integration of functional fillers that maintain mechanical strength and interfacial compatibility [12,13]. These advancements position PVDF as a soft material link between energy harvesting and next-generation storage [14]. This motivates strategies to increase the β -phase fraction and thereby improve macroscopic piezoelectric properties and device-level output in PVDF polymers. Electric-field-driven phase transitions among α , δ , and β have been observed under very high fields ($\approx$

100–500 MV m⁻¹), offering one route to increase polarization but imposing significant energetic and processing costs [15–17]. Therefore, sustainable, low-energy routes to increase β -phase fraction and enhance piezoelectric performance are desirable.

Among the available approaches, nanoparticle doping combined with electrospinning is one of the most scalable routes for enhancing β -phase formation. The strong elongational forces during electrospinning promote chain alignment, while nanoparticle inclusions act as interfacial nucleation sites and locally modify dielectric and electrostatic conditions [18,19]. However, existing studies are still largely empirical and do not yet establish a general relationship between composition, processing, microstructure, and device-level response [19, 20]. In particular, current machine-learning models for piezoelectric polymers often treat composites as homogeneous systems, overlooking the coupled crystalline-amorphous dynamics and interfacial effects that govern electromechanical behavior in semicrystalline electrospun architectures [21–24].

In this work, we focus on SnO₂ as a filler because it offers a favorable balance of functional and processing advantages. SnO₂ nanoparticles provide a chemically active surface with hydroxyl groups that

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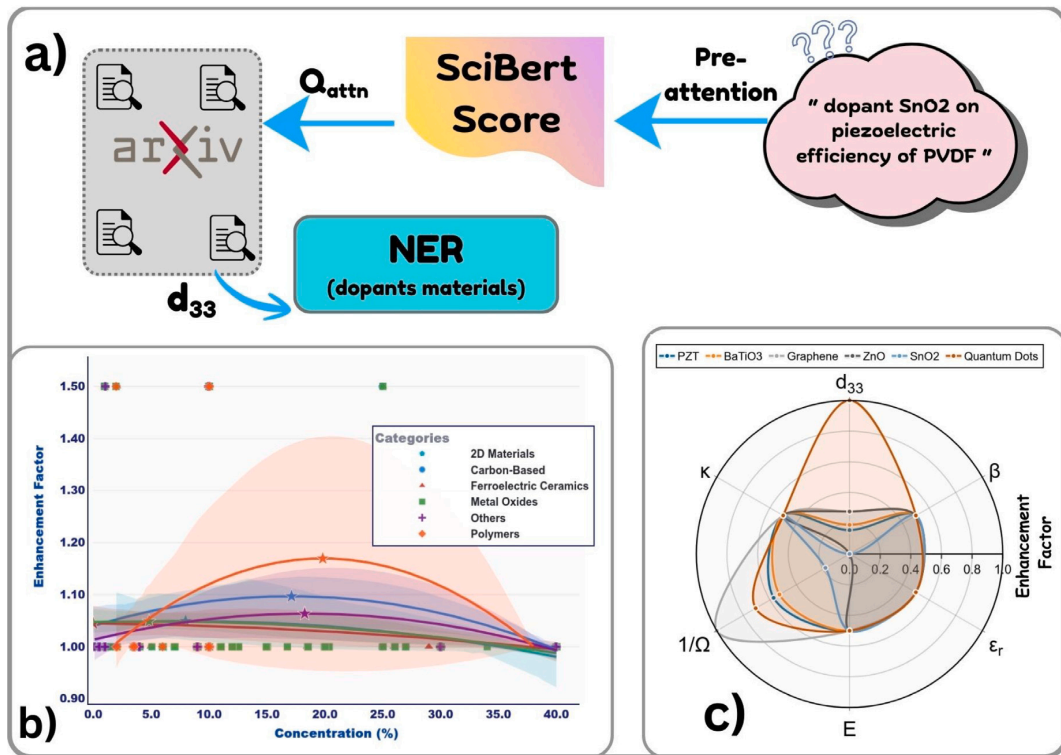


Fig. 1. Knowledge extraction and trend analysis. (a) Multi-stage NLP framework transforms arXiv scientific data into structured knowledge. Functional properties and dopant compositions are extracted via NER, followed by SciBERT-based semantic scoring of document embeddings. (b) Enhancement factors across six material categories ($N = 733$). **Metal Oxides** exhibit a localized performance peak ($1.049\times$) at 4.82% concentration (*), whereas **Polymers** and **Carbon-Based** materials show broader optima at $\sim 20\%$. (c) Performance enhancement across six physical parameters, min-max scaled to a [0, 1] range. Parameters and their respective raw value intervals include: piezoelectric (d_{33} , [1.00, 1.07]); β -phase (β , [0.90, 1.10]); dielectric (ϵ_r , [0.90, 1.10]); mechanical (E , [0.90, 1.10]); electrical ($1/\Omega$, [1.02, 1.09]); and thermal (κ , [0.90, 1.10]).

can interact with PVDF chains and promote β -phase formation [25,26], while also contributing beneficial changes in interfacial polarization, stiffness, hydrophobicity, and optical transparency [27]. This makes SnO₂ a promising yet underexplored additive for multifunctional PVDF nanocomposites and a suitable candidate for soft actuators and energy harvesters [28,29]. To better identify such opportunities, we use an NLP as a meta-analysis tool to extract dopant–property relationships and research trends from the published PVDF literature. We then combine this with a physics-guided machine-learning framework and finite-element simulations.

2. Natural language processing of doped PVDF literature

The NLP workflow is designed to perform structured literature meta-analysis. It semantically searches the PVDF piezoelectric literature, identifies recurring dopant–property associations, and ranks studies according to relevance to the target design problem. This provides a way to relate the current state of the field, identify underexplored filler chemistries such as SnO₂, and motivate subsequent physics-guided modeling and device-level studies. This section describes this literature-driven analysis and the insights it provides.

2.1. Literature mining pipeline

The Fig. 1(a) presents a material informatics pipeline designed to discover and analyze scientific literature on the piezoelectric properties of PVDF from the arXiv repository. This combines natural language processing (NLP) techniques with specialized scoring methods to enable

scalable exploration of relevant studies. The pipeline uses semantic understanding to map dopant–performance connections, informing research trends in nanoenergy systems. The query ("dopant SnO₂ on piezoelectric efficiency of PVDF") guides the retrieval of $N_{db} = 145$ papers from arXiv based on subject areas like materials science and publication dates. Each paper's title and abstract are analyzed using SciBERT to generate contextual representations. These representations allow the system to measure similarity to both the query and a set of key domain terms, including PVDF variants, dopants like SnO₂, ZnO etc., indicators of the β -phase, and piezoelectric concepts. A weighted scoring function aggregates these similarities (70% for the query and 30% for key terms) to rank papers, with a threshold of 30% to ensure only the most pertinent ones advance. By highlighting query-relevant text like SnO₂ boosting PVDF performance, SciBERT's attention provides an interpretable rationale for paper prioritization.

In addition to semantic search, rule-based filtering identifies specific dopants and β -phase features. The pipeline then extracts text from retrieved PDFs by prioritizing initial sections for efficiency before calculating a final relevance score based on the full content. All data (metadata, extracted texts, and derived flags) are stored in interconnected databases (db) to support quick querying and multi-format exports. This structure not only preserves the corpus for ongoing analysis but also enables targeted searches, such as extracting reported values of the piezoelectric coefficient d_{33} from the stored literature. For instance, by querying the database for " d_{33} coefficient", the system retrieves and summarizes instances across papers, linking them to dopant strategies like SnO₂ incorporation.

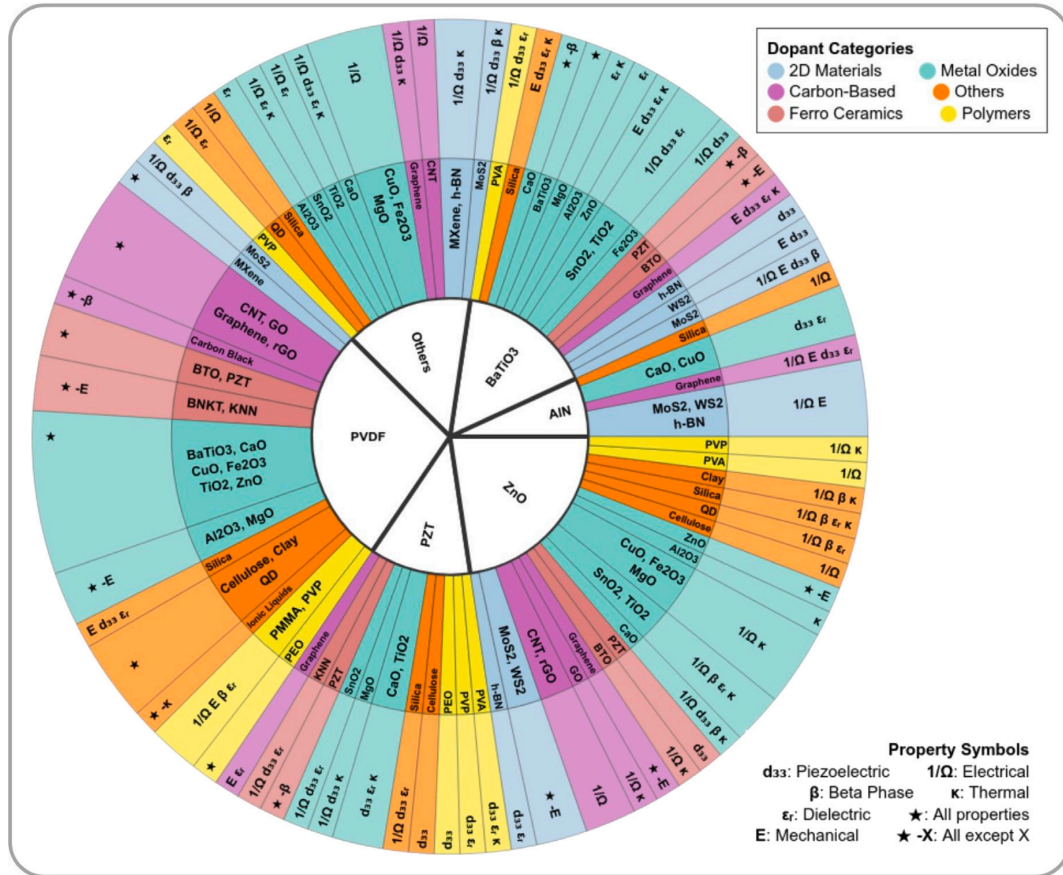


Fig. 2. Host-dopant synergies and functional properties. The hierarchical visualization (derived from $N_{db}=145$ arXiv papers) illustrates the relationships between material components and performance. **Inner Ring:** Primary host materials. **Middle Ring:** Dopant classifications categorized into six distinct chemical families (see color legend). **Outer Ring:** Specific functional property improvements achieved through hybridization. The star ($\star$) notation indicates enhancement across all listed properties, while ($\star-X$) denotes improvement in all properties except X. Although the query specifically targeted SnO_2 and PVDF, the multi-head self-attention mechanism of SciBERT facilitates a broader inclusion of papers. The model identifies relevant dopants and piezoelectric bases beyond exact matches by capturing the latent semantic relationships between keywords like ‘piezoelectric’, ‘PVDF’, and ‘efficiency’.

2.2. Dopant synergies in piezoelectric composites

Hierarchical mapping of host matrices, dopant chemistry, and functional performance (Fig. 2) identifies PVDF as a primary host matrix. Integration strategies vary by filler type: carbon-based fillers (CNTs, graphene) and 2D materials (MXenes, MoS_2) primarily improve electrical conductivity ($1/\Omega$) and mechanical reinforcement (E). Conversely, adding ferroelectric ceramics (BTO, PZT) and metal oxides (ZnO , TiO_2) to the PVDF matrix enhances the piezoelectric coefficient (d_{33}) and dielectric constant (ϵ_r). This highlights the emergence of multifunctional enhancements where all properties are optimized simultaneously (denoted by the $\star$ symbol) achieved through precise tuning of the filler-matrix interface. We extracted key descriptors from $N = 733$ piezoelectric samples using a SciBERT-based Named Entity Recognition (NER) framework. Data synthesis reveals distinct optimization thresholds across material categories (Fig. 1b). While the average performance enhancement is $1.04 \times \pm 0.14$, metal oxides reach their peak ($1.049\times$) at a concentration of only 4.82%. This threshold is much lower than those for polymers (19.82% peak, $1.170\times$ enhancement) and Carbon-based materials (17.12% peak, $1.097\times$ enhancement). The early saturation in oxides suggests that rigid inorganic structures are highly sensitive to internal strain and defects when filler levels increase. Consequently, while the global maximum enhancement ($1.5\times$)

was found at 10% loading, designing reliable metal oxide structures requires staying within a narrow zone to avoid the performance drop-off seen beyond the $\sim 5\%$ threshold. Although metal oxides are widely utilized as dopants, the specific influence of SnO_2 on PVDF’s functional landscape remains poorly defined. SnO_2 is a compelling candidate not merely for d_{33} enhancement, but for its ability to integrate secondary functional benefits into the polymer matrix. Fig. 1(c) shows SnO_2 to enhance the mechanical flexibility and tensile strength of PVDF and also increase the surface hydrophobicity. The high ϵ_r of SnO_2 -doped PVDF makes it suitable for optical applications. This filler also preserves high optical transparency (around 80%–90% in the visible spectrum), making the composite suitable in optical devices and systems where light transmission is essential [30], flexible electronics [31], biomedical implants [32], and IoT devices [33], even when the piezoelectric enhancement is not the highest among dopants.

3. Fabrication and experimental characterization

3.1. Materials and electrospinning

Electrospinning creates nanofibers with high surface-area-to-volume ratios, requiring less material for functional applications. The process

Table 1
Parameters of spinning solution and electrospinning process.

Parameter	Value
SnO ₂ concentration	1.5 wt%
PVDF concentration	10 w/v%, 15 w/v%, 18 w/v%
Flow rate	1.4 ml/h
Distance between electrodes	15 cm
Voltage	21 kV

runs at moderate temperatures and allows solvent recovery. This reduces waste compared with many bulk casting routes [34,35]. The strong electric field during electrospinning stretches polymer chains and aligns molecular dipoles. This produces partial *in situ* poling and raises the β -phase fraction. The experiments quantify how poling and SnO₂ doping change the β -phase area fraction f^β . The following chemicals were used without further purification to prepare spinning solutions: polyvinylidene fluoride (PVDF, purity 99%), N, N-Dimethylformamide (DMF, purity 99.9%), acetone (99.5%), and SnO₂ nanoparticles. All reagents were supplied by Sigma-Aldrich. The fabrication workflow for pure PVDF solution and PVDF with SnO₂ solution is presented in Fig. 3 (a). The first step was to prepare the spinning solution. For this purpose, 1.5 wt % of SnO₂ nanoparticles was added to 14 ml of DMF and sonicated for 30 min to break down agglomerates. SnO₂ nanoparticles improve electrospinning by increasing solution conductivity and promoting jet stretching, while their hydroxyl-rich surface supports β -phase nucleation in PVDF. The 1.5 wt.% loading was selected as the best balance between morphology and phase enhancement [28,36]. Then, a certain amount of PVDF was added and left for 1 h on a heated magnetic stirrer set to 50 °C to obtain a homogeneous solution (Table 1). Subsequently, acetone was added to the solution so that the volume ratio of DMF to acetone was 7:3. After 30 min of mixing, the solution was placed directly in the pump of the DOXA Microfluidics Electrospinning StartUp Machine. The morphology of electrospun PVDF nanofibers and PVDF nanofibers containing SnO₂ nanoparticles was examined using a scanning electron microscope (SEM; Zeiss Supra 35). The chemical structure, including the presence of characteristic bonds and functional groups, was analyzed by Fourier transform infrared (FTIR) spectroscopy in attenuated total reflectance (ATR) mode using a Nicolet 6700 spectrometer (Thermo Scientific). The parameters of the electrospinning process and the solution are shown in Table 1. Samples without the addition of SnO₂ were prepared in the same way, omitting the nanoparticles. The electrospun fiber networks collected on the substrate were dried under ambient conditions prior to analysis. Based on fiber morphology, 18 w/v% PVDF was chosen as the optimized base for composite samples.

3.2. Results from the experiments

The analysis of the morphology of PVDF and PVDF/SnO₂ nanofibers was performed based on SEM images which show a clear link between solution concentration and fiber morphology. Low concentrations (10 and 15 w/v%) produce bead-on-string structures. This behavior is visible in Fig. 3(d). These undesirable beads degrade the piezoelectric properties. Beads form when surface tension overcomes jet viscoelasticity [37]. At low polymer concentration chain entanglement is weak and the jet breaks into beads. Higher concentration increases chain entanglement and viscosity. This suppresses bead formation and yields continuous fibers [38,39]. The 18 w/v% solution therefore produces smooth, long, bead-free fibers (Fig. 3(e)). Based on these morphology results, 18 w/v% PVDF was selected as the optimized base for composites. SEM of the PVDF/SnO₂ composite confirms uniform fiber formation and clear nanoparticle incorporation. SnO₂ aggregates appear inside fibers and on the surface (Fig. 3(f)). This distribution indicates good embedding of particles during jet solidification.

Fiber diameters were measured from 100 independent fibers and the statistical results are shown in Fig. 3(b). The mean diameter of the pure

Table 2

Absorbance intensities a_α (763 cm⁻¹) and a_β (840 cm⁻¹) extracted from FTIR spectra in Fig. 3 and the corresponding calculated β -phase fraction f^β for different PVDF-based samples.

Sample	a_α	a_β	f^β
PVDF powder (no electrospinning)	0.0903	0.0602	0.3456
PVDF fiber (electrospun)	0.0370	0.0570	0.5496
PVDF fiber (electrospun) + SnO ₂ (1.5 wt%)	0.0710	0.1200	0.5725

18 w/v% PVDF fibers is 680 nm, while the mean for the PVDF/SnO₂ composite is 290 nm. The composite also shows a tighter size distribution on the log scale (Fig. 3(b, right)). The diameter drop on adding SnO₂ is due to changes in solution electrical and flow properties. SnO₂ raises solution conductivity and local charge density, which increases electrostatic stretching of the jet and yields thinner fibers [28]. Well-dispersed particles also alter viscosity and surface charge distribution, stabilizing the jet and reducing diameter scatter. Faster solvent loss around particle-rich regions can further lock smaller diameters during solidification. Together, these effects explain the smaller mean and the narrower log-scale distribution seen in the composite. Fig. 3(c,e,f) shows the FTIR spectra for the PVDF powder, the optimized 18 w/v% fibers, and the PVDF/SnO₂ composite, respectively. At 612 cm⁻¹ and 763 cm⁻¹, bands characteristic of bending and wagging vibrations of CF₂ and rocking vibrations in the PVDF chain α phase are observed, respectively. The absorbance intensity at 762 cm⁻¹ originates from bending of CF₂, which is a characteristic feature of α -PVDF. On the other hand, the absorbance peak at 840 cm⁻¹ can be attributed to the stretching of C–C skeleton and as well as CF₂ and to rocking of CH₂, and so this peak corresponds to β -PVDF. The relative growth of the 840 cm⁻¹ band compared with the 763 cm⁻¹ band is visible when comparing the powder (Fig. 3(c)) to the fibers (Fig. 3(e)) and to the composite (Fig. 3(f)). The recorded spectra also show two absorbance bands at 1188 cm⁻¹ and 1412 cm⁻¹, which can be assigned to the CF₂ functional group. Moreover, at 2797 cm⁻¹, the presence of a band originating from stretching vibrations of C–H bonds was found. The presence of these bands confirms that each of the samples produced is composed of PVDF polymer in the α and β phases. No broad absorption appears around 3000–3400 cm⁻¹, so there is no detectable OH-related water adsorption on the fiber surface.

Wu et al. [31] have shown that the absorbance intensities at two characteristic wavenumbers associated with the α and β crystalline phases of PVDF can be used to quantify the fraction of the electroactive β phase (f^β). Accordingly, the β -phase fraction was calculated using the De Gregorio relation [31,40]:

$$f^\beta = \frac{a_\beta K_\alpha}{K_\alpha a_\beta + K_\beta a_\alpha} \quad (1)$$

In Eq. (1), a_α and a_β denote the absorbance intensities measured at 763 and 840 cm⁻¹, which are characteristic of the α and β phases, respectively. The absorption coefficients are $K_\alpha = 6.1 \times 10^4$ cm²/mol and $K_\beta = 7.7 \times 10^4$ cm²/mol [41]. The measured absorbance values and the corresponding calculated β -phase fractions for all samples are summarized in Table 2. The PVDF powder, which has not undergone electrospinning or electrical poling, exhibits a relatively low β -phase fraction of 0.3456. In contrast, the electrospun PVDF fibers show a substantial increase in f^β to 0.5496, while the incorporation of SnO₂ nanoparticles further increases the β -phase content to 0.5725.

3.3. Structural information

As discussed above, the electrospinning and the incorporation of SnO₂ nanoparticles increased the β -phase fraction of PVDF. To interpret this result, it is useful to recall five distinct polymorphic phases of PVDF (α , β , γ , δ , and ϵ), which arise from different conformations of the polymer backbone and packing arrangements of adjacent chains [42].

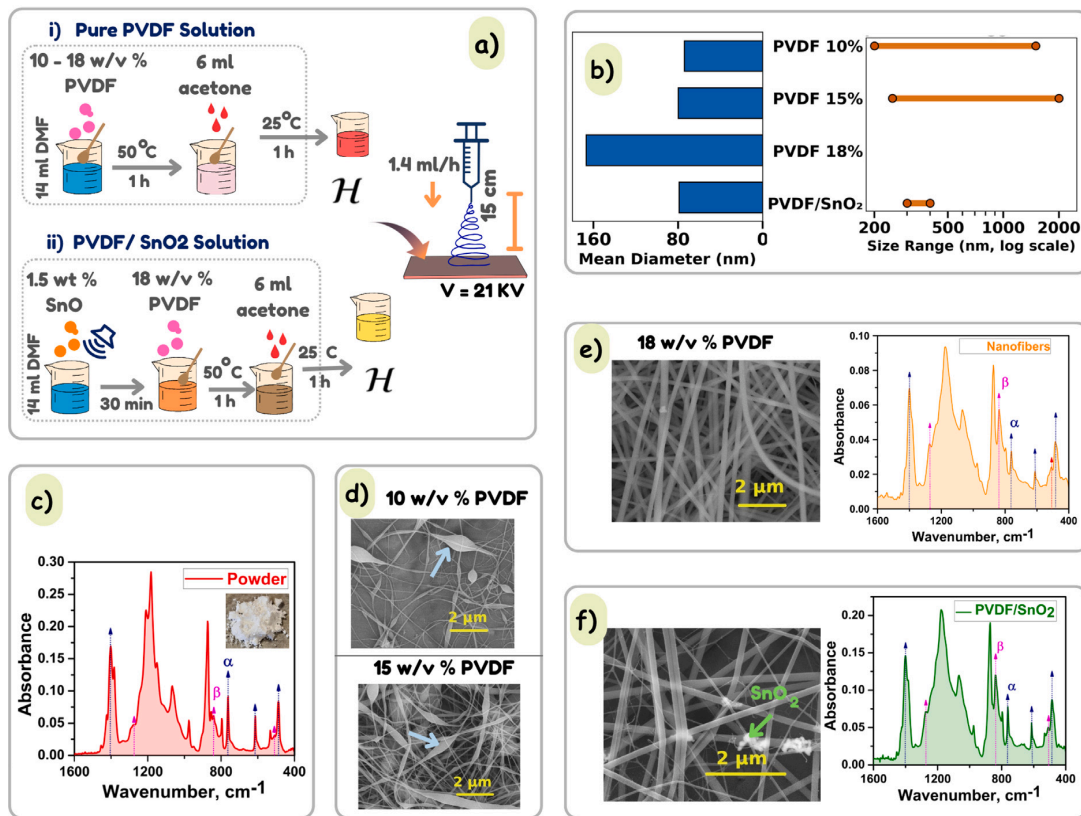


Fig. 3. Fabrication workflow and multiscale characterization of nanofibers. (a) Schematic illustration of solution preparation and electrospinning: (i) Pure PVDF solutions prepared in a DMF/acetone solvent. (ii) PVDF/SnO₂ nanocomposite (1.5 wt.% SnO₂) prepared via 30 min sonication. (b) Statistics of the mean fiber diameter (left) and log-scale size distribution range (right). The mean diameters for the optimized 18 w/v% PVDF and the PVDF/SnO₂ composite were found to be 680 nm and 290 nm, respectively. (c) FTIR absorbance spectrum of the raw PVDF powder precursor identifying the characteristic α -phase (763 cm⁻¹) and β -phase (840 cm⁻¹) peaks. (d) SEM micrographs of 10 w/v% and 15 w/v% PVDF showing the formation of bead-on-string morphologies (indicated by blue arrows). (e) SEM micrograph and FTIR spectrum of the optimized 18 w/v% PVDF nanofibers exhibiting a smooth, bead-free morphology. (f) SEM micrograph and FTIR spectrum of the PVDF/SnO₂ composite; the green arrow indicates the successful integration of SnO₂ nanoparticle aggregates within the fiber network.

The molecular chains adopt combinations of trans (T) and gauche (G) conformations, and variations in these torsional states lead to different dipole arrangements and macroscopic properties. Although several phases are known, the α -, β -, and γ -phases are the most commonly encountered under practical processing conditions, while the δ - and ϵ -phases typically require strong electric fields or specific thermal-mechanical treatments to stabilize [43]. The β -phase possesses an all-trans (TTTT) planar zigzag conformation and crystallizes in an orthorhombic structure with point group symmetry $mm2$, previously categorized as PG5 (Class B) in our earlier **PiezoTensorNet** work [44]. The symmetry restrictions of the $mm2$ class define the non-zero piezoelectric tensor components, which are represented in Voigt notation in Eq. (4). This aligns the C–F dipoles in the same direction along the polymer chain, resulting in a large net spontaneous polarization [45]. This molecular arrangement explains the enhanced piezoelectric and ferroelectric properties of β -PVDF compared to the non-polar α -phase, where antiparallel dipole orientations cancel out the macroscopic polarization. Consequently, maximizing the β -phase content is a central objective in PVDF-based energy harvesting and sensing devices [46].

The increase in f^β after electrospinning in the experiment confirms that the strong elongation forces and high electric fields inherent to the process induce partial in situ poling and favor the formation of the all-trans conformation. Furthermore, the additional enhancement of the β -phase fraction in the PVDF/SnO₂ composite can be rationalized by nanoparticle-polymer interfacial interactions, which locally constrain

chain rotations and promote β -phase nucleation. Similar stabilization mechanisms have been reported for PVDF composites containing metal oxide nanoparticles, where surface charges and interfacial polarization lower the energy barrier for β -phase formation. Poled β -PVDF films retain strong piezoelectric activity over a wide temperature range [47]. This thermal resilience, combined with the high polarization density intrinsic to the all-trans chain conformation, makes β -PVDF particularly suitable for flexible electromechanical devices operating under varying environmental conditions. For completeness, the crystallographic parameters, molecular conformations, and electroactive characteristics of all five PVDF polymorphs are summarized in Supplementary Information (Sec. S1: Table S1). Although the present study focuses primarily on the α - and β -phases identified experimentally, inclusion of the remaining polymorphs provides a structural reference and highlights the unique advantages of the β -phase for piezoelectric performance.

4. Quantitative link between β -phase enrichment and piezoelectricity

The fabrication, molecular and structural analysis above shows that filler composition and processing (via the measured increase in the β -phase fraction) influence PVDF's piezoelectric potential. To effectively design and assess the device, we need a quantitative value like the piezoelectric coefficient. The **PGMLpiezo** toolkit bridges the gap from microscopic characterization to device performance by predicting

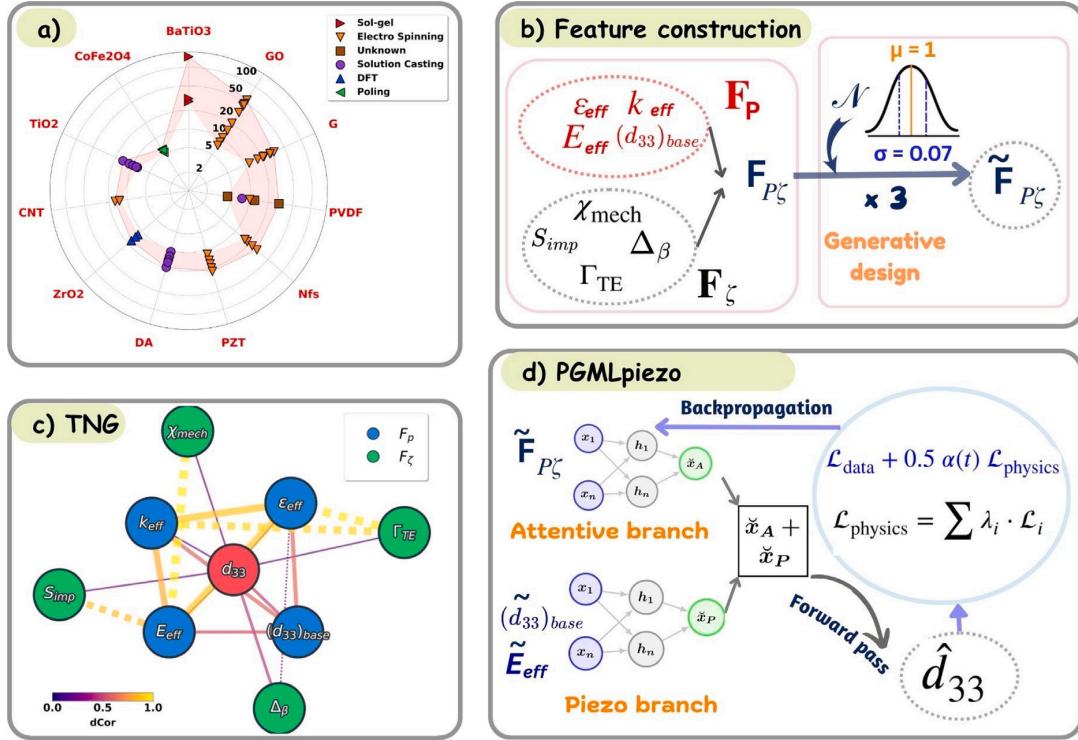


Fig. 4. (a) d_{33} (pC/N) across various dopants (represented by multiple axis) and fabrication methods (represented by different shapes of the markers). (b) **Featurization:** Homogenized (F_p) and Engineered interfacial and coupling (F_ζ) features forming the input $F_{P\zeta}$. To overcome data scarcity, a generative design approach uses Gaussian perturbation to expand the dataset (3 $\times$) while preserving physical feature-target relationships resulting in $\tilde{F}_{P\zeta}$. (c) **Topological network graph (TNG):** Distance correlations ($dCor$) between d_{33} , with primary (F_p) and secondary (F_ζ) features. Edge thickness and color represent the strength of non-linear coupling (Refer Supplementary Information Fig S1 for detailed correlation analysis). (d) **PGMLpiezo architecture and training:** The model integrates an attentive branch and a piezoelectric branch, optimized via a composite loss that balances numerical accuracy and physics constraints.

piezoelectric properties based on composition and processing inputs. Since the recorded data is available for d_{33} piezoelectric coefficients mostly, the model is trained for d_{33} , and with reference to this value, other coefficients were approximated. The PGMLpiezo training set included a diverse range of filler categories to ensure model generalizability. These include Ferroelectric Ceramics (BaTiO₃, PZT), Conductive Fillers (Graphene, CNTs), Metal Oxides (ZnO, Fe₃O₄, TiO₂, SnO₂), and other novel materials (Borophene, MoS₂). This broad chemical space ensures that the attentive network learns generalized features of filler–polymer interactions, rather than over-fitting to SnO₂ specifically. While only SnO₂ is used for the multiscale analysis in this work, the model is capable of predicting properties across this wider material spectrum. The experimentally measured β -phase fraction ($f^\beta = 0.5725$) serves as a direct input to this model. Here, the experimentally measured results refer to morphology, fiber diameter, and β -phase fraction, whereas the piezoelectric coefficient used for tensor reconstruction and FEM simulations is obtained from the PGMLpiezo model and should be interpreted as a predicted property.

4.1. Featurization based on homogenization and interfacial descriptors

The training dataset comprises experimental data from the literature for PVDF composites. After cleaning and consistency checks, the working dataset contains fifty-two unique samples spanning filler fractions up to 20%. The d_{33} values across 10 filler compositions on the PVDF matrix for six fabrication/computation methods are presented in Fig. 4(a). Because the PVDF composite properties are governed not only by constituent chemistry but also from processing-induced interfacial and

phase-formation effects, composition-based feature vector and crystal-structure descriptors which are common in the study of ceramics and alloys [44,48] are less suitable. To address this, we construct a high-dimensional feature space that integrates **Homogenized Composite Baselines** (F_p), and the **Engineered Interfacial and Coupling Descriptors** (F_ζ). The Piezoelectric Feature Ensemble is structured as a composite feature matrix $F_{P\zeta}$, which captures both intrinsic constituent properties and emergent interfacial phenomena. Continuous features ($F_{P\zeta}$) are standardized using training-set statistics and categorical fabrication descriptors are one-hot encoded. The PGMLpiezo is designed for small materials datasets. The input feature matrix is constructed by concatenating physics-derived and interaction features as represented in Fig. 4(b). In matrix form:

$$F_{P\zeta} = [F_\zeta | F_p] \in \mathbb{R}^{n \times (p+q)}, \quad (2)$$

where $n = 52$ denotes the sample size, $p = 4$ represents the F_p , and $q = 4$ represents the F_ζ . Full definitions of the features used in the PGMLpiezo training are presented in Table 3.

4.2. Hybrid physics-guided machine learning

The model has two branches (Fig. 4d). The principal branch is a dense feedforward network with a multi-head attention for adaptive re-weighting of feature interactions. The auxiliary branch processes piezo-relevant inputs (E_{eff} and $(d_{33})_{base}$). These branches are fused to produce a point estimate ($\hat{d}_{33}$) and an ensemble-derived uncertainty. During training, physical constraints are recomputed inside the physics loss so that model predictions remain consistent with known relations

Table 3

Hierarchical featurization architecture for PGMLpiezo. The framework combines (I) Homogenization limits, (II) Multi-physics descriptors (Interfacial [I] and Coupling [C]), and (III) nodes interrelationship, (IV) stochastic/auxiliary features to balance physical consistency. The PVDF matrix is represented by subscript m , and dopants by δ , while ϕ represents the dopants fractions.

Feature (Model)	Definition	* In Topological Network graph Fig. 4	Ref.
I. Homogenized Composite Baselines (F_p), as  in TNG Fig. 4(c)			
Dielectric (Yamada)	$\epsilon_{\text{eff}} = \epsilon_m \left[1 + \frac{3\phi(\epsilon_\delta - \epsilon_m)}{3\epsilon_m + (1 - \phi)(\epsilon_\delta - \epsilon_m)} \right]$	Optical and electrostatic contrib.	[49,50]
Thermal Cond. (Maxwell-Eucken)	$k_{\text{eff}} = k_m \frac{2k_m + k_\delta + 2\phi(k_\delta - k_m)}{2k_m + k_\delta - \phi(k_\delta - k_m)}$	Thermal contrib.	[51,52]
Stiffness (Halpin-Tsai)	$E_{\text{eff}} = E_m \frac{1 + \xi\eta\phi}{1 - \eta\phi}$ $\eta = \frac{(E_\delta/E_m) - 1}{(E_\delta/E_m) + \xi}$ $(d_{33})_{\text{base}} = (1 - \phi)d_{33}^m + L\phi d_{33}^\delta$	Composite mechanical contrib.	[53,54]
Piezo-Base (Hybrid Law)	$L = \frac{3\epsilon_m}{\epsilon_\delta + 2\epsilon_m}$	Electro-mechanical contrib.	[55,56]
II. Engineered Interfacial (I) & Coupling (C) Descriptors (F_c), as 			
Γ_{TE}	$\Gamma_{\text{TE}} = k_{\text{eff}} \times \epsilon_{\text{eff}}$	Hybrid thermo-electric and optical (I).	—
χ_{mech}	$\chi_{\text{mech}} = E_{\text{eff}} / E_m$	Strain-transfer efficiency (I).	—
S_{imp}	$S_{\text{imp}} = \phi \times E_\delta$	wt. % dopants' impact on stiffness (C)	—
Δ_β	$\Delta_\beta = F_\beta - F_{\beta,\text{ref}}$	β -phase calibration (I).	—
III. Interrelationship between nodes			
Edge type I	$d_{\text{cor}} > 0.5 (F_p^i \leftrightarrow F_p^j)$	Primary (Solid/Thick)	[]
Edge type II	$d_{\text{cor}} < 0.5 (F_p^i \leftrightarrow F_p^j)$	Primary (Solid/Thin)	[]
Edge type III	$d_{\text{cor}} > 0.5 (F_p^i \leftrightarrow F_c^j)$	Secondary (Dashed)	[]
IV. Stochastic & Auxiliary ML Features (present in PGMLpiezo but not sketched in TNG).			
Fourier (ϕ)	$\{\sin(2\pi\phi f_i), \cos(2\pi\phi f_i)\}_{i=1}^N$	Non-linear/scale-dependent effects modeling.	—
Embeddings	$\mathcal{E}_{\text{dopant}} \in \mathbb{R}^d$	Latent chemical similarity indexing.	—

* Readers are advised to refer to Fig. 4 (c) Topological Network Graph (TNG) to identify the features and their relations.

even when inputs are perturbed by augmentation. Data augmentation (3 $\times$) applies multiplicative Gaussian or uniform noise to composition and effective properties within physically meaningful bounds to increase data diversity and improve robustness. To avoid learning non-physical patterns, physics-informed loss terms act as regularizers that anchor predictions to expected behavior. The training objective used in reported results is:

$$\mathcal{L}_{\text{total}} = \mathcal{L}_{\text{data}} + 0.5\alpha(t)\mathcal{L}_{\text{physics}}, \quad (3)$$

where $\alpha(t)$ is a slowly increasing annealing factor that lets the model first fit measured data and then progressively emphasize physical consistency.

We trained the physics-constrained network with three random seeds (42, 150, 220). Each run used 500 training epochs followed by 100 fine-tuning epochs. Model performance varied with initialization; the average validation MAE across runs was 10.25. The best-performing model, evaluated on the original (non-augmented) dataset, achieved $R^2 = 0.85$. The PGMLpiezo predicts $\hat{d}_{33} \approx 28.91$ pC/N for the 1.5 wt.% SnO₂-PVDF composite. Details of the PGMLpiezo architecture and training outcomes are provided in the Supplementary Information (Sec. S2.2).

4.3. Piezoelectric tensor estimation in PVDF/SnO₂ composites

To obtain a complete electromechanical description for finite-element simulation, the PGMLpiezo-predicted longitudinal coefficient, $\hat{d}_{33}$, is converted into a full piezoelectric strain tensor using a coupling-factor-based reconstruction. For the electrospun 1.5 wt.% SnO₂ specimen, which exhibits a β -phase fraction of 0.5725, the PGMLpiezo

ensemble predicts $|\hat{d}_{33}| = 28.91$ pC/N. This corresponds to an increase of approximately 60% relative to the baseline electrospun PVDF value of $|\hat{d}_{33}| \approx 18$ pC/N.

The increase in β -phase fraction is nominal and should be interpreted as one of the many contributing factor. Although the effective permittivity changes only slightly ($\epsilon_r \approx 10$), the SnO₂ addition can still influence the device-level response through interfacial charge separation, local polarization effects, and changes in electromechanical coupling at the polymer-filler interface. The reconstructed piezoelectric strain tensor in Voigt notation is written as:

$$\mathbf{d}_{ij} = \begin{pmatrix} 0 & 0 & 0 & 0 & -24.12 & 0 \\ 0 & 0 & 0 & -20.55 & 0 & 0 \\ 18.07 & 1.36 & -28.91 & 0 & 0 & 0 \end{pmatrix}. \quad (4)$$

Fig. 5 compares the piezoelectric tensor values evaluated from PGMLpiezo for pure PVDF and doped sample. The characteristic anisotropy of PVDF is preserved with $|d_{31}/d_{33}| \approx 0.625$ and $|d_{15}/d_{33}| \approx 0.83$. The reconstruction assumes quasi-isotropic composite behavior together with PVDF-like anisotropy, which is appropriate for low filler loadings (≤ 5 wt.%) of metal-oxide dopants. Further details of the tensor reconstruction procedure are provided in Supplementary Information Sec. S2.3.

To facilitate broader use of the workflow, the PGMLpiezo is deployed as an interactive web-based application (Refer to data availability section). This illustrates that the SnO₂ case studied here is a representative application of a broader predictive architecture for rapid material screening.

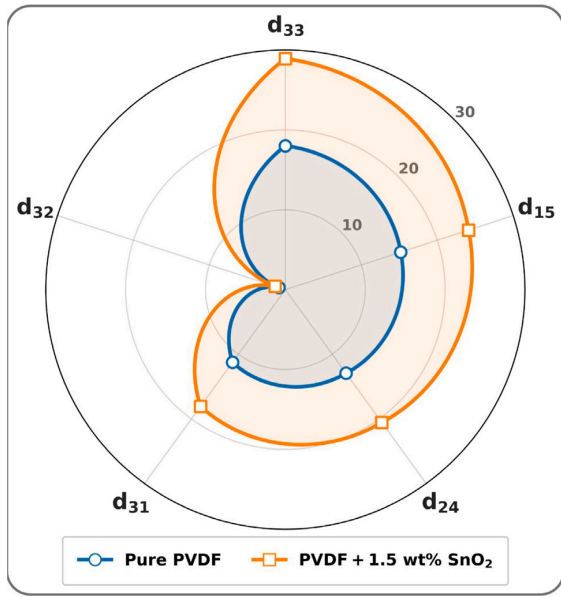


Fig. 5. Reconstructed magnitudes $|d_{ij}|$ (pC/N) for pure PVDF and the 1.5 wt.% SnO_2 -PVDF sample. Baseline pure PVDF values are $|d_{33}| = 18.00$ and $|d_{31}| = 11.25$ pC/N. Tensor components are estimated from the PGMLpiezo prediction $|\hat{d}_{33}|$ and effective medium properties.

5. Finite-element modeling of piezoelectric SnO_2 /PVDF nanocomposites

The piezoelectric properties predicted from PGMLpiezo were used in the finite-element simulations to evaluate device-level performance under realistic boundary conditions. We used finite-element simulations, built based on the FERRET piezoelectric module [57,58] within the open-source MOOSE framework [59,60]. FERRET is designed to solve the coupled electro-mechanical constitutive equations governing ferroelectric and piezoelectric systems. By utilizing this validated solver, we evaluated two operating modes: (i) energy harvesting under mechanical excitation and electrical loading, and (ii) actuation under imposed electric potential. The model employs the linear piezoelectric constitutive relations in strain-charge form within the small-strain, small-field regime; strain-charge coefficients (d_{ij}) supplied to the solver are converted internally to stress-charge form (e_{ij}) for assembly. The weak form is discretized by standard Galerkin finite elements and solved fully coupled, with typical boundary conditions consisting of prescribed displacement on mechanical and electrical boundaries. Elasticity constants are drawn from the literature [61] and dielectric constants from effective property estimates used in featurization as explained in Table 3. The piezoelectric tensors used as input to the FEM are those predicted by the PGMLpiezo pipeline: the ML estimate $\hat{d}_{33}$ is expanded to a full tensor (As in Section 4.3) and supplied to the solver in Voigt form. Because the FEM model treats the composite as a homogenized linear piezoelectric continuum, it does not explicitly account for structural anisotropy, inter-fiber interactions, or mesoscale porosity present; therefore, the results should be interpreted as representative of an idealized PVDF/ SnO_2 architecture under small-strain operating conditions. The governing equations and material tensor transformations are detailed in our previous work [44] and summarized in the Supplementary Information (Sec. S3) Piezoelectric FEM Model.

5.1. Thickness-mode energy harvester

The energy harvesting devices constructed from PVDF/ SnO_2 nanocomposites convert mechanical vibrations into electrical energy, powering wearables or sensors. This leads to efficient harvesting from

low-frequency sources like human motions. Studies show that 2D SnO_2 nanosheets in PVDF create flexible nanogenerators with stable output, suitable for self-powered monitoring systems [27]. These benefits make the material suitable in ultra-low-capacitance setups where reactive compensation via circuits like parallel synchronized-switch harvesting on inductor (P-SSHI) amplifies performance [62,63]. A $200 \mu\text{m} \times 100 \mu\text{m} \times 5 \mu\text{m}$ PVDF/ SnO_2 block was subjected to uniform sinusoidal compression along its thickness direction at 1 Hz with a displacement amplitude of $0.1 \mu\text{m}$ on the top electrode, while the bottom face remained mechanically fixed and electrically grounded as shown in Fig. 6 (a). This excitation generates a nominal thickness strain amplitude of 2%, which is within the linear piezoelectric regime. The mechanical performance of the PVDF/ SnO_2 -based harvester was evaluated through synchronized temporal analysis of the internal stress states and kinematic strain (Fig. 6 (c)). The device exhibits a highly symmetric harmonic response, reaching a peak axial stress (σ_{zz}) of ± 17.218 MPa. This stress level maximizes the piezoelectric potential without exceeding the plastic yield threshold of the β -phase PVDF crystalline domains, observed around 30 MPa [43,64]. The observed peak-to-peak strain swing ($\Delta\epsilon \approx 4.0\%$) indicates high mechanical compliance. Furthermore, the convergence of the maximum axial stress and the peak Von Mises stress ($\sigma_v = 17.244$ MPa) confirms a state of nearly pure uniaxial compression. This stress state optimization is critical for maximizing the d_{33} piezoelectric coefficient contribution, as it minimizes parasitic shear modes that could lead to reduced energy conversion efficiency.

The electromechanical response was mapped into a power-strain phase-space for both passive standard energy harvester (SEH) and active parallel synchronized-switch harvesting on inductor (P-SSHI) configurations (Figs. 6 (d) and (e)). The passive mode attained an average power output (P_{avg}) of 0.359 nW, utilizing an optimal load resistance of $1.47 \times 10^{10} \Omega$. The phase-space trajectory exhibits a clear orbital pattern in which instantaneous power peaks coincide with the largest strain rates, consistent with the derivative nature of piezoelectric current generation. The clustering of the cycles in the narrow interquartile range (IQR) and the mean cycle trajectory confirms the structural integrity of the PVDF/ SnO_2 film and the absence of mechanical fatigue. This cyclic consistency is important for autonomous sensing applications where predictable power envelopes are required for energy management. The P-SSHI mode, incorporating synchronized voltage inversion at strain extrema with an efficiency factor $\gamma = 0.75$, significantly enhances extraction, yielding $P_{\text{avg}} = 1.251$ nW at $R_{\text{opt}} = 1.47 \times 10^{11} \Omega$. This is a $3.48\times$ improvement over passive. The expanded phase-space loop in Fig. 6 (e) reflects amplified voltage swings and reactive compensation, enabling higher power despite the ultra-low capacitance.

The Table 4 shows the active mode's voltage amplification with power density of 12.51 mW/cm^3 (similar range as reported in [65]), and energy efficiency per cycle (64.94%). The efficiency for average power is 0.52% for SEH and 1.82% for P-SSHI, which falls in the range of reported value [66]. The formulations and the supporting results related to the thickness-mode energy harvester are provided in supplementary Information Sec S4 .

5.2. Constraint and electromechanical response of a PVDF/ SnO_2 piezoelectric actuator

For actuators, PVDF/ SnO_2 composites utilize the converse piezoelectric effect to produce mechanical displacement from electrical input. SnO_2 enhances mechanical compliance, allowing large strains (up to 2% and $\Delta\epsilon = 4\%$ which is within the yield strength from Section 5.1) under applied voltages. SnO_2 enable secondary functions, such as self-cleaning and optical clarity, making them preferable for integrated systems over high- β alternatives that may compromise flexibility. These findings indicate that PVDF/ SnO_2 's role persists in applications such as IoT harvesters and soft actuators, where holistic properties are more important than isolated metrics [67]. The PVDF/ SnO_2 film is

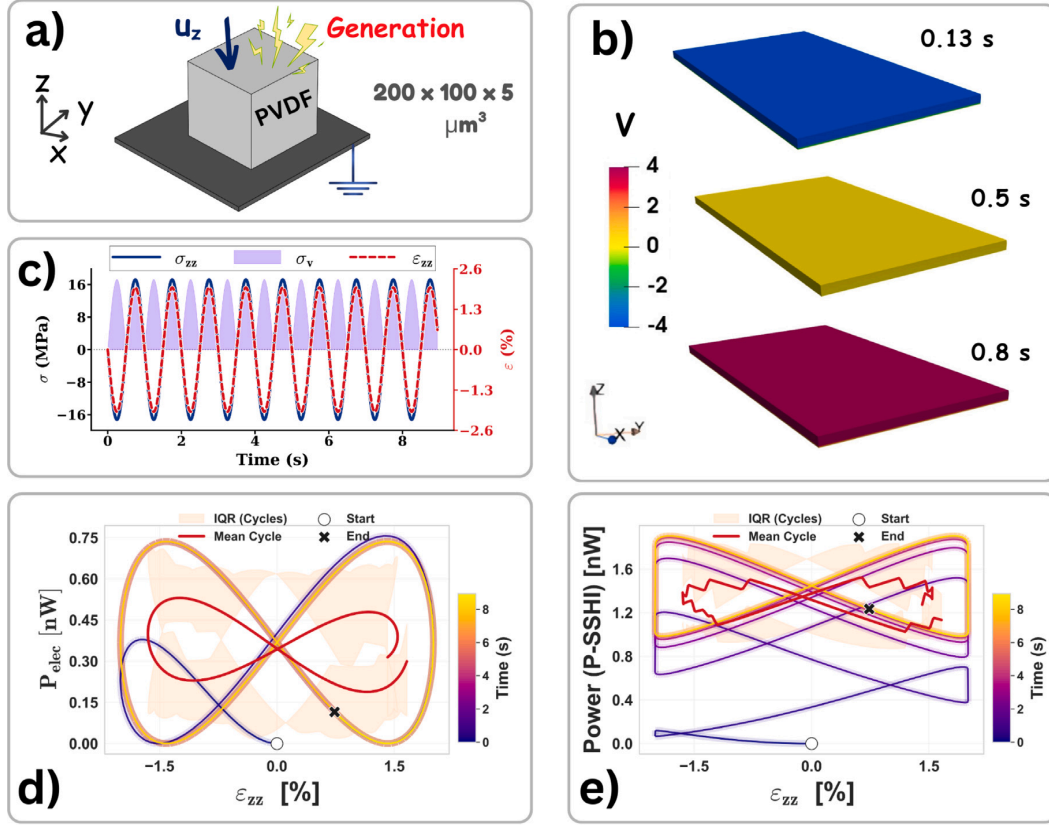


Fig. 6. Dynamic electromechanical characterization of piezoelectric harvester: (a) Setup with $0.1 \mu\text{m}$ uniform sinusoidal compression on the top electrode along its thickness at 1 Hz. The bottom face is mechanically fixed and electrically grounded. (b) The distribution of generated voltage at maximum positive, zero, and negative amplitudes. (c) Evolution of the longitudinal stress (σ_{zz}), equivalent Von Mises stress (σ_v), and longitudinal strain (ϵ_{zz}). The symmetric stress response ($\pm 17.22 \text{ MPa}$) and corresponding 4.0% peak-to-peak strain swing ($\Delta\epsilon$). (d) Instantaneous P_{elec} as a function of ϵ_{zz} for a PVDF harvester operating in passive mode at $R_{\text{opt}} = 1.47 \times 10^{10} \Omega$. The trajectory depicts the evolution of the harvesting cycles over time. An average power output of 0.359 nW is achieved. (e) Phase-space plot for the P-SSHI (active) mode, showing enhanced power extraction with an average power of 1.251 nW under optimal load ($R_{\text{opt}} = 1.47 \times 10^{11} \Omega$).

Table 4

Key Performance Metrics for Passive standard energy harvester (SEH) and parallel synchronized-switch harvesting on inductor (P-SSHI) Harvesting Modes at 1 Hz excitation.

Metric	Passive (SEH)	P-SSHI (Active)
Optimal Resistance (R_{opt})	$1.47 \times 10^{10} \Omega$	$1.47 \times 10^{11} \Omega$
Peak Open Circuit Voltage (V_{oc})	4.70 V	4.70 V
Peak Harvested Voltage (V_{out})	3.33 V	16.72 V
Peak Electrical Power (P_{elec})	0.756 nW	1.905 nW
Average Electrical Power (P_{avg})	0.359 nW	1.251 nW
Total Energy Harvested (E_{total})	3.212 nJ	11.187 nJ
Peak Mechanical Power (P_{mech})	107.713 nW	107.713 nW
Avg Mechanical Power ($P_{\text{mech,avg}}$)	68.767 nW	68.767 nW
Total Available Mech Energy (approx)	17.227 nJ	17.227 nJ
Efficiency per cycle ($\eta_E = E_{\text{elec}}/E_{\text{mech}}$)	18.65%	64.94%
Efficiency per cycle ($\eta_P = P_{\text{elec}}/P_{\text{mech}}$)	0.52%	1.82%

sandwiched between polymer PEDOT:PSS electrodes [68,69] as in the representative figure of Fig. 7 (a). The influence of mechanical boundary conditions on the apparent piezoelectric response of polymer-based actuators was quantified by comparing a free-standing PVDF/SnO₂ laminate with an otherwise identical structure subjected to lateral clamping.

The FEM quantifies the effect of stress redistribution induced by boundary conditions on longitudinal actuation. The transverse contribution enhances axial strain when d_{31} and d_{33} have the same sign, and

reduces it when their signs are opposite [70]. Since PVDF/SnO₂ system has opposite-signed d_{31} and d_{33} , the intrinsic axial response is reduced. However, if fabrication or microstructural design is modified so that the device-level effective response produces same-sign contributions (for example via auxetic or re-entrant architectures, composite layering with oriented fillers, or engineered heterostructures) [71,72], clamped conditions can amplify the effective $|d_{33}|$ beyond the intrinsic value. Here, the sign-aligned configuration is used as a reference case to illustrate the constructive limit of boundary-condition-induced amplification and to highlight the potential to tune axial actuation via mechanical constraints and electromechanical coupling.

As shown in Fig. 7 (b), the free configuration achieves higher peak volumetric energy density ($160.2 \times 10^3 \text{ kJ/m}^3$) compared to the constrained state, as lateral boundary relaxation allows greater total strain accumulation. However, this increased energy capacity comes at the cost of spatial accuracy; Fig. 8 (a) shows the free case has sideways drift, whereas the constrained condition enhances actuation purity (u_z/u_x) and increases axial reach by 56.7%. In Fig. 7 (b), the constrained actuator provides a more stable and higher-magnitude axial stroke throughout the excitation cycle. The Fig. 7 (c) presents the spatial distribution of axial and lateral deflection for the free standing case and Fig. 7 (d) shows the distribution for the axial deflection for constrained case, as the lateral deflection is negligible.

The effective longitudinal piezoelectric coefficient extracted from the finite-element results is $d_{33}^{\text{FEM}} = 45.95 \text{ pm/V}$. For comparison, the

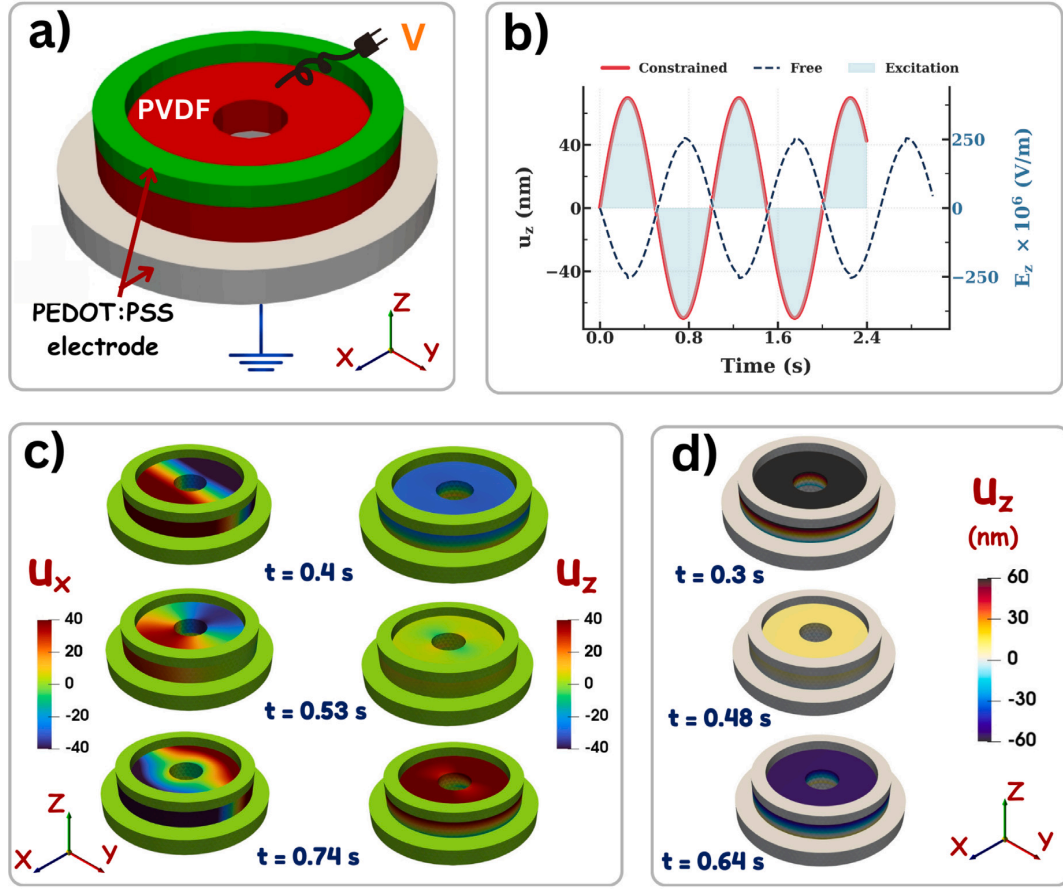


Fig. 7. Electromechanical characterization of the ring-type PVDF/SnO₂ actuator. (a) Schematic of the actuator assembly featuring a ring-shaped PVDF piezoelectric element sandwiched between polymer PEDOT:PSS electrodes. The device operates under a sinusoidal excitation voltage applied to the top electrode while the base remains grounded and fixed. (b) Comparison between **Constrained** and **Free**: lateral boundary conditions reveals that mechanical confinement enhances peak axial deflection to 69.6 nm. The shaded region denotes the temporal profile of the input electric field (E_z). (c) Spatial distribution of parasitic lateral (u_x) and primary axial (u_z) displacement fields for the **Free** condition. (d) Evolution of axial displacement (u_z) under the **Constrained** condition; the rigid lateral boundary suppresses transverse fluctuations, resulting in a highly pure, unidirectional mechanical stroke.

analytical upper bound assuming isotropic in-plane clamping (zero lateral strain with in-plane isotropy) is given by [73]:

$$d_{33}^{\text{iso}} = d_{33} - 2 \frac{s_{13}^E}{s_{11}^E + s_{12}^E} d_{31}, \quad (5)$$

which yields ≈ 62 pC/N using the material parameters of the nanocomposite. This value significantly overestimates the simulated response because the ring-shaped geometry imposes *anisotropic* in-plane mechanical constraints, violating the isotropy assumption underlying Eq. (5). A generalized expression that accounts for arbitrary in-plane anisotropy is

$$d_{33}^{\text{eff}} = d_{33} - s_{13}^T S^{-1} \mathbf{d}_l, \quad (6)$$

where s_{13} and $\mathbf{d}_l$ are the transverse compliance and piezoelectric sub-vectors, and $\mathbf{S}$ is the in-plane stiffness matrix derived from the specific boundary conditions and geometry. Evaluation of Eq. (6) for the constrained ring actuator produces $d_{33}^{\text{eff}} \approx 45$ pC/N, in close agreement with the finite-element value of 45.95 pm/V. This confirmation validates both the computational model and the role of geometric anisotropy in determining the realized electromechanical coupling under lateral confinement, emphasizing the necessity of full tensorial analysis for non-uniform device architectures. The electro-mechanical formulation

of the Eq. (5) and (6) is explained in supplementary information Sec. S6. Lateral clamping suppresses transverse strains ϵ_{xx} and ϵ_{yy} to numerical zero, enforcing a plane-strain-dominated state. As a consequence, the electrical work supplied to the system is preferentially converted into longitudinal deformation ϵ_{zz} rather than parasitic lateral expansion. This constraint-induced redirection of strain exhibits a substantial increase in axial displacement and elastic energy storage, despite a rise in normal stresses associated with reaction forces at the boundaries. Importantly, the von Mises stress decreases under clamped conditions, indicating a shift from distortional to predominantly hydrostatic stress components, which is favorable for polymeric piezoelectrics. A key outcome is the enhancement of the d_{33}^{eff} , extracted from fitting the FEM simulated electric field-strain response. While the intrinsic material coefficient remains unchanged, the apparent d_{33}^{eff} increases from 26.9 pm/V in the free-standing configuration to 45.95 pm/V under lateral clamping. This enhancement arises from electromechanical coupling through constrained transverse modes (via d_{31} and elastic compliance terms). Table 5 summarizes the electromechanical performance metrics for both configurations. The results establish lateral mechanical constraint as a design strategy to achieve large axial stroke, high energy density, and near-uniaxial actuation in PVDF-based systems without altering material composition or poling chemistry. The

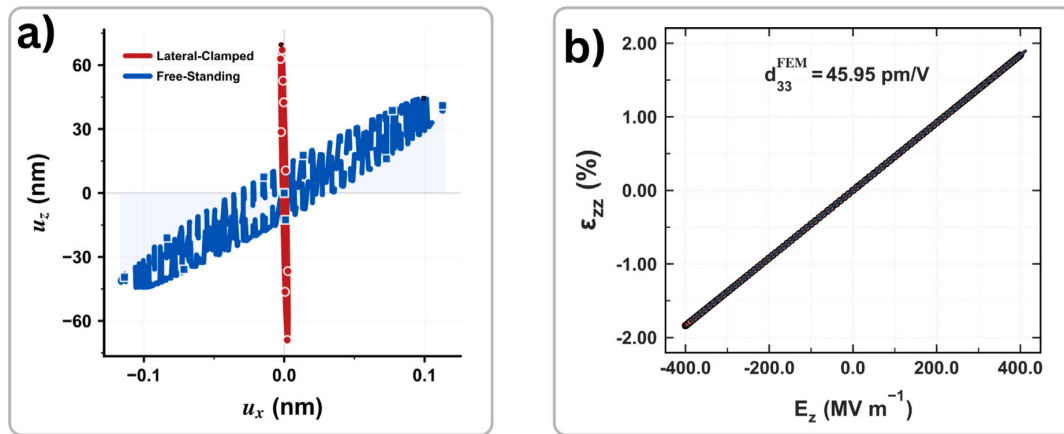


Fig. 8. Analysis comparing axial displacement (u_z) against parasitic lateral motion (u_x) (a) Free condition exhibits a coupled response reaching a maximum $u_z = 44.41$ nm. In contrast, the **Constrained** condition optimizes the trajectory, reaching an enhanced axial stroke of $u_z = 69.60$ nm while parasitic lateral motion is confined within the range of $[-0.1168, 0.1140]$ nm. (b) The linear relationship between axial strain (ϵ_{zz}) and applied electric field (E_z) is plotted based on FEM results. The slope of the linear regression yields ($d_{33}^{FEM} = 45.95$ pm/V) the effective sensitivity, demonstrating high electromechanical linearity and providing a fundamental metric for the actuator's performance.

Table 5

Comparative analysis of mechanical and electromechanical parameters. The effective piezoelectric coefficient is reported as a modulus $|d_{33}^{eff}|$ to facilitate direct comparison of magnitude enhancement.

Parameter	Free-Standing	Lateral-Clamped
Peak electric field (MV/m)	400.0	400.0
Longitudinal strain ϵ_{zz} (%)	1.145	1.838
Transverse strain ϵ_{xx} (%)	0.683	~0
Transverse strain ϵ_{yy} (%)	0.093	~0
Axial displacement u_z (nm)	44.4	69.6
Lateral displacement u_x (nm)	0.117	0.0029
Von Mises stress (MPa)	15.3	4.83
Total elastic energy (J)	4.5×10^{-10}	1.6×10^{-9}
Energy density (kJ/m ³)	45.3	160.2
$ d_{33}^{eff} $ (pm/V)	27.46	45.95

Supplementary Information **Sec. S5** contains details for the boundary conditions and the supporting electro-mechanical response for the actuators' simulations.

6. Conclusions

This study combined literature mining, experimental fabrication, machine learning, and finite-element modeling to investigate PVDF/SnO₂ electrospun nanofibers as a multifunctional piezoelectric material. The NLP screening helped identify SnO₂ as a promising but still underexplored filler for PVDF. Experimental characterization confirmed that electrospinning and SnO₂ incorporation improved the fiber morphology and increased the electroactive β -phase fraction. Under the optimized conditions, the composite showed a reduction in fiber diameter from 680 nm to 290 nm and an increase in β -phase content from 0.3456 in PVDF powder to 0.5725 in the SnO₂-doped composite. The PGMLpiezo model provided an estimate of the piezoelectric response, predicting a longitudinal coefficient of $|d_{33}| = 28.91$ pC/N for the 1.5 wt.% SnO₂-PVDF composite. This value was then used in FEM to evaluate device-level behavior. For the thickness-mode energy harvester, the model predicted an open-circuit voltage of 4.7 V and a power output in the nanowatt range, with improved performance under the active P-SSHI configuration. For the actuator geometry, lateral clamping significantly enhanced the effective axial response, increasing the stroke by 56.7% and raising the effective piezoelectric coefficient to 45.95 pm/V.

The results show that SnO₂ is a viable filler for improving the electromechanical response of electrospun PVDF. Also, combining experiment with machine learning is an effective strategy for linking material design to device performance. At the same time, the study also shows that the observed actuation and harvesting performance depends strongly on geometry, boundary conditions, and the assumptions used in tensor reconstruction and continuum modeling.

CRediT authorship contribution statement

Sachin Poudel: Writing – original draft, Visualization, Validation, Software, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Weronika Smok:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis. **Rubi Thapa:** Writing – review & editing, Validation, Software. **Anna Timofiejczuk:** Writing – review & editing, Validation, Supervision. **Nele Moelans:** Writing – review & editing, Validation, Project administration, Methodology, Funding acquisition, Formal analysis. **Anil Kunwar:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.susmat.2026.e02008>.

Data availability

The data and analytic code for this study are available in https://github.com/Sachinscnpdl/PVDF_Piezoelectric. The graphical user interface of PGMlpiezo can be accessed via: <https://pgmlpiezo.streamlit.app/>.

References

- [1] H. Zhang, X. Ji, Z. Wang, S. Tang, Z. Wang, W. Zhu, Advances in intelligent polyvinylidene fluoride-based piezoelectric composites for self-powered wearable electronics, *Small* 22 (2) (2026) e09387.
- [2] B. Nayak, S. Anwar, S. Anwar, Free-standing PVDF film for piezoelectric energy harvesting and sensing applications, *Mater. Sci. Eng.: B* 323 (2026) 118777.
- [3] Y. Lv, T. Yang, E. Wang, B. Shen, K. Wang, H. Wang, K.-C. Chou, X. Hou, High-sensitivity PZT-OV/Ti3C2Tx/PVDF piezoelectric fiber for self-powered vital signs monitoring, *EScience* (2026) 100530.
- [4] H. Liu, B.-W. Li, J. Chen, Z. Shen, X. Zhang, J. Wang, C.-W. Nan, Concurrent enhancement of breakdown strength and dielectric constant in poly (vinylidene fluoride) film with high energy storage density by ultraviolet irradiation, *ACS Omega* 7 (30) (2022) 25999–26004.
- [5] S. Prasad, H. Chouhan, B.C. Mushahary, R. Chakravarty, B. Parida, R. Parida, Exploring optical, dielectric and transport properties in PVDF films for advanced applications, *Mater. Chem. Phys.* 332 (2025) 130227.
- [6] P. Manchi, S.A. Graham, H. Patnam, M.V. Paranjape, J.S. Yu, High-efficiency poly (vinylidene fluoride-co-hexafluoropropylene) loaded 3D marigold flower-like bismuth tungstate triboelectric films for mechanical energy harvesting and sensing applications, *Small* 18 (20) (2022) 2200822.
- [7] S. Mametja, M. Mabuza, E. Sadiku, R. Mohlamonyane, J. Sefadi, Development of energy-efficient polymers by using conductive nanohybrid fillers: recent progress and future prospects, *Adv. Compos. Hybrid Mater.* 8 (3) (2025) 258.
- [8] G. Kalimuldina, N. Turdakyn, I. Abay, A. Medebayev, A. Nurpeissova, D. Adair, Z. Bakenov, A review of piezoelectric PVDF film by electrospinning and its applications, *Sensors* 20 (18) (2020) 5214.
- [9] Y. Xue, T. Yang, E. Wang, H. Wang, L. Zhu, S. Cao, X. Hou, K.-C. Chou, Unveiling the contribution of piezoelectric and ferroelectric effect to inorganic halide perovskites photodetectors, *Nano Energy* 125 (2024) 109491.
- [10] Y. Zhang, C. Zhu, S. Bai, J. Mao, F. Cheng, Recent advances and future perspectives of PVDF-based composite polymer electrolytes for lithium metal batteries: a review, *Energy & Fuels* 37 (10) (2023) 7014–7041.
- [11] K.H. Khan, A. Haleem, S. Arwisha, A. Shah, H. Hussain, PVDF-based solid polymer electrolytes for lithium-ion batteries: strategies in composites, blends, dielectric engineering, and machine learning approaches, *RSC Adv.* 15 (26) (2025) 20629–20656.
- [12] X. Song, T. Zhang, S. Huang, J. Mi, Y. Zhang, J. Travas-Sejdic, A.P. Turner, W. Gao, P. Cao, Constructing a PVDF-based composite solid-state electrolyte with high ionic conductivity 1i6. 5La3Zr1. 5Ta0. 1Nb0. 4o12 for lithium metal battery, *J. Power Sources* 564 (2023) 232849.
- [13] Q. Wu, M. Fang, S. Jiao, S. Li, S. Zhang, Z. Shen, S. Mao, J. Mao, J. Zhang, Y. Tan, et al., Phase regulation enabling dense polymer-based composite electrolytes for solid-state lithium metal batteries, *Nat. Commun.* 14 (1) (2023) 6296.
- [14] T. Yang, D. Jia, B. Xu, Y. Hao, Y. Hou, K. Wang, E. Wang, Z. Du, S. Cao, K.-C. Chou, et al., Textured CsPbI3 nanorods composite fibers for stable high output piezoelectric energy harvester, *EScience* 4 (5) (2024) 100273.
- [15] Y. Pei, X.C. Zeng, Elastic properties of poly (vinylidene fluoride)(PVDF) crystals: A density functional theory study, *J. Appl. Phys.* 109 (9) (2011).
- [16] X. Hu, M. You, N. Yi, X. Zhang, Y. Xiang, Enhanced piezoelectric coefficient of PVDF-trfe films via in situ polarization, *Front. Energy Res.* 9 (2021) 621540.
- [17] L. Zhou, T. Yang, C. Guo, K. Wang, E. Wang, L. Zhu, H. Wang, S. Cao, K.-C. Chou, X. Hou, PVDF/6H-SiC composite fiber films with enhanced piezoelectric performance by interfacial engineering for diversified applications, *J. Mater. Sci. Technol.* 170 (2024) 238–245.
- [18] G. Han, Z. Zeng, Z. Kong, N. Lu, Y. Feng, Enhancing piezoelectricity of PVDF with organic dopants: From atomic-scale insights to advanced wearable devices, *Nano Energy* (2025) 111383.
- [19] M. Salama, A. Hamed, S. Noman, G. Magdy, N. Shehata, I. Kandas, Boosting piezoelectric properties of PVDF nanofibers via embedded graphene oxide nanosheets, *Sci. Rep.* 14 (1) (2024) 16484.
- [20] B. Amrutha, A.A. Prabhu, M. Pathak, Enhancing piezoelectric effect of PVDF electrospun fiber through nio nanoparticles for wearable applications, *Heliyon* 10 (7) (2024).
- [21] S. Sukumaran, S. Chatbouri, D. Rouxel, E. Tisserand, F. Thiebaud, T. Ben Zineb, Recent advances in flexible PVDF based piezoelectric polymer devices for energy harvesting applications, *J. Intell. Mater. Syst. Struct.* 32 (7) (2021) 746–780.
- [22] S. Shankhdhar, D. Arora, H. Rahman, R. Kumar, B. Ranjan, K. Kaushlendra, D. Kaur, Harnessing the mechanical and magnetic energy with PMN-PT/Ni-Mn-In-based flexible piezoelectric nanogenerator, *Nano Energy* 133 (2025) 110441.
- [23] Z. Chen, H. Yang, H. Yu, T. Yu, L. Liu, Y. Lu, W. Gao, Comprehensive effects of isomeric doping on electrospun PVDF films: Towards smart wiper systems enabled by piezoelectric nanogenerators and machine learning, *Nano Energy* (2025) 111094.
- [24] J. Yuan, Z. Li, Y. Yang, A. Yin, W. Li, D. Sun, Q. Wang, Applications of machine learning method in high-performance materials design: a review, *J. Mater. Informatics* 4 (3) (2024) N-A.
- [25] H.-W. Wang, D.J. Wesolowski, T.E. Proffen, L. Vleck, W. Wang, L.F. Allard, A.I. Kolesnikov, M. Feygenson, L.M. Anovitz, R.L. Paul, Structure and stability of SnO2 nanocrystals and surface-bound water species, *J. Am. Chem. Soc.* 135 (18) (2013) 6885–6895.
- [26] H. Wang, J. Yuan, J. Xi, J. Du, J. Tian, Multiple-function surface engineering of SnO2 nanoparticles to achieve efficient perovskite solar cells, *J. Phys. Chem. Lett.* 12 (37) (2021) 9142–9148.
- [27] E. Kar, N. Bose, B. Dutta, S. Banerjee, N. Mukherjee, S. Mukherjee, 2D SnO2 nanosheet/PVDF composite based flexible, self-cleaning piezoelectric energy harvester, *Energy Convers. Manage.* 184 (2019) 600–608.
- [28] B. Wu, Y. Yang, L. Wang, H. Xu, Y. Huang, J. Kang, Y. Xiong, K. Yin, M. Nie, L. Sun, SnO2 induced electrostatic polarization PVDF composite nanofibers for efficient energy harvesting and self-powered wireless monitoring/motion recognition systems, *Chem. Eng. J.* 495 (2024) 153483.
- [29] A. Tsyganov, M. Vikulova, D. Artyukhov, A. Bainyashev, V. Goffman, A. Gorokhovskiy, E. Boychenko, I. Burmistrov, N. Gorshkov, Permittivity and dielectric loss balance of PVDF/K1. 6fe1. 6ti6. 4o16/MWCNT three-phase composites, *Polymers* 14 (21) (2022) 4609.
- [30] M. Yousaf, M.J.I. Khan, Theoretical and experimental study of electronic, structural and optical properties of PVDF-SnO2:Zr nanocomposites for novel optoelectronic applications, *Phys. Scr.* 99 (9) (2024) 095939, <http://dx.doi.org/10.1088/1402-4896/ad6aa7>, URL <http://dx.doi.org/10.1088/1402-4896/ad6aa7>.
- [31] B. Wu, Y. Yang, L. Wang, H. Xu, Y. Huang, J. Kang, Y. Xiong, K. Yin, M. Nie, L. Sun, SnO2 induced electrostatic polarization PVDF composite nanofibers for efficient energy harvesting and self-powered wireless monitoring /motion recognition systems, *Chem. Eng. J.* 495 (2024) 153483, <http://dx.doi.org/10.1016/j.cej.2024.153483>, URL <https://www.sciencedirect.com/science/article/pii/S1385894724049726>.
- [32] S. Vaidya, M. Joshi, S. Ghosh, N. More, R. Velyutham, S.S. Babu, G. Kapusetti, Bioactive ZnO decorated PVDF-based piezoelectric, osteoconductive nanofibrous coatings for orthopedic implants, *J. Biomed. Mater. Res. Part A* 113 (8) (2025) e37971.
- [33] A. Thakur, M. Jangra, S. Dam, S. Hussain, Enhanced dielectric constant with addition of a low amount of sno2 nanoparticles as fillers in a PVDF matrix with low dielectric loss, *Nano-Structures & Nano-Objects* 34 (2023) 100978.
- [34] M. Stramarkou, I. Tzegiannakis, E. Christoforidi, M. Krokida, Use of electrospinning for sustainable production of nanofibers: A comparative assessment of smart textiles-related applications, *Polymers* 16 (4) (2024) 514.
- [35] R. Abdullhussain, A. Adebisi, B.R. Conway, K. Asare-Addo, Electrospun nanofibers: Exploring process parameters, polymer selection, and recent applications in pharmaceuticals and drug delivery, *J. Drug Deliv. Sci. Technol.* 90 (2023) 105156.
- [36] A. Rubin Pedrazzo, C. Cecone, S. Morandi, M. Manzoli, P. Bracco, M. Zanetti, Nanosized sno2 prepared by electrospinning: Influence of the polymer on both morphology and microstructure, *Polymers* 13 (6) (2021) 977.
- [37] H. Fong, I. Chun, D.H. Reneker, Beaded nanofibers formed during electrospinning, *Polymer* 40 (16) (1999) 4585–4592.
- [38] X. Hu, X. Chen, M. Gagnorio, C. Wu, Y. Luo, C. Hélix-Nielsen, P. Yu, W. Zhang, Beaded electrospun polyvinylidene fluoride (PVDF) membranes for membrane distillation (MD), *J. Membr. Sci.* 661 (2022) 120850.
- [39] E. Ghafari, X. Jiang, N. Lu, Surface morphology and beta-phase formation of single polyvinylidene fluoride (PVDF) composite nanofibers, *Adv. Compos. Hybrid Mater.* 1 (2) (2018) 332–340.
- [40] R. Peng, B. Zhang, G. Dong, Y. Wang, G. Yang, J. Zhang, B. Peng, Y. Zhao, M. Liu, Enhanced piezoelectric energy harvester by employing freestanding single-crystal BaTiO3 films in PVDF-trfe based composites, *Adv. Funct. Mater.* (2024) 2316519.
- [41] A. Huang, Y. Zhu, S. Peng, B. Tan, X. Peng, Improved energy harvesting ability of single-layer binary fiber nanocomposite membrane for multifunctional wearable hybrid piezoelectric and triboelectric nanogenerator and self-powered sensors, *ACS Nano* 18 (1) (2024) 691–702, <http://dx.doi.org/10.1021/acsnano.3c09043>, URL <https://doi.org/10.1021/acsnano.3c09043>.
- [42] P. Sajkiewicz, A. Wasiak, Z. Gocłowski, Phase transitions during stretching of poly (vinylidene fluoride), *Eur. Polym. J.* 35 (3) (1999) 423–429.
- [43] N. Ahbab, S. Naz, T.-B. Xu, S. Zhang, A comprehensive review of piezoelectric PVDF polymer fabrications and characteristics, *Micromachines* 16 (4) (2025) 386.
- [44] S. Poudel, R. Thapa, R. Basnet, A. Timofiejczuk, A. Kunwar, Piezotensornet: crystallography informed multi-scale hierarchical machine learning model for rapid piezoelectric performance finetuning, *Appl. Energy* 361 (2024) 122901.
- [45] M. Yasar, P. Hassett, N. Murphy, A. Ivankovic, β phase optimization of solvent cast PVDF as a function of the processing method and additive content, *ACS Omega* (2024).

- [46] N. Bhadwal, R. Ben Mrad, K. Behdian, Review of piezoelectric properties and power output of PVDF and copolymer-based piezoelectric nanogenerators, *Nanomaterials* 13 (24) (2023) 3170.
- [47] L. Ruan, X. Yao, Y. Chang, L. Zhou, G. Qin, X. Zhang, Properties and applications of the β phase poly (vinylidene fluoride), *Polymers* 10 (3) (2018) 228.
- [48] U. Subedi, A. Kunwar, Y.A. Coutinho, K. Gyanwali, Pympealab toolkit for accelerating phase design in multi-principal element alloys, *Met. Mater. Int.* 28 (1) (2022) 269–281.
- [49] T. Yamada, T. Ueda, T. Kitayama, Piezoelectricity of a high-content lead zirconate titanate/polymer composite, *J. Appl. Phys.* 53 (6) (1982) 4328–4332.
- [50] H. Khanbareh, S. van der Zwaag, W.A. Groen, In-situ poling and structurization of piezoelectric particulate composites, *J. Intell. Mater. Syst. Struct.* 28 (18) (2017) 2467–2472.
- [51] L. Gong, Y. Wang, X. Cheng, R. Zhang, H. Zhang, A novel effective medium theory for modelling the thermal conductivity of porous materials, *Int. J. Heat Mass Transfer* 68 (2014) 295–298.
- [52] J. Wang, J.K. Carson, M.F. North, D.J. Cleland, A new approach to modelling the effective thermal conductivity of heterogeneous materials, *Int. J. Heat Mass Transfer* 49 (17–18) (2006) 3075–3083.
- [53] J.C. Halpin, S. Tsai, Effects of environmental factors on composite materials, 1969.
- [54] E.C.B. Câmara, R.C.S. Freire Jr., Using neural networks to modeling the transverse elasticity modulus of unidirectional composites, *Compos. Part B: Eng.* 42 (7) (2011) 2024–2029.
- [55] Z.-H. Shen, J.-J. Wang, J.-Y. Jiang, S.X. Huang, Y.-H. Lin, C.-W. Nan, L.-Q. Chen, Y. Shen, Phase-field modeling and machine learning of electric-thermal-mechanical breakdown of polymer-based dielectrics, *Nat. Commun.* 10 (1) (2019) 1843.
- [56] R. Newnham, D. Skinner, L. Cross, Connectivity and piezoelectric-pyroelectric composites, *Mater. Res. Bull.* 13 (5) (1978) 525–536.
- [57] J. Mangeri, et al., A parallel finite-element code for evaluating ferroic nanostructures and electronic properties at mesoscale, 2025, <https://mangerij.github.io/ferret/>, Accessed: 2026-04-13.
- [58] J. Mangeri, Y. Espinal, A. Jokisaari, S.P. Alpay, S. Nakhmanson, O. Heinonen, Topological phase transformations and intrinsic size effects in ferroelectric nanoparticles, *Nanoscale* 9 (4) (2017) 1616–1624.
- [59] D. Gaston, C. Newman, G. Hansen, D. Lebrun-Grandie, MOOSE: A parallel computational framework for coupled systems of nonlinear equations, *Nucl. Eng. Des.* 239 (10) (2009) 1768–1778.
- [60] G. Giudicelli, A. Lindsay, L. Harbour, C. Icenhour, M. Li, J.E. Hansel, P. German, P. Behne, O. Marin, R.H. Stogner, et al., 3.0-MOOSE: Enabling massively parallel multiphysics simulations, *SoftwareX* 26 (2024) 101690.
- [61] C.M. Frostenson, P.A. Olsson, P. Hyldgaard, Polyvinyl fluoride: Predicting polarization in a complex soft matter system, *Phys. Rev. Mater.* 8 (11) (2024) 115603.
- [62] J. Zhou, M. Liu, S. Gao, X. Gao, C. Li, W. Yang, R. Zhuo, F. Li, Design strategies for high-performance piezoelectric energy harvesting devices, *Adv. Mater.* (2025) e12672.
- [63] S. Khan, A. Kumrawat, B. Mukherjee, Performance improvement of a self-powered P-SSHI based piezoelectric energy harvester by tuning the switching delay and inversion factor, *Sustain. Energy Technol. Assessments* 75 (2025) 104240.
- [64] Y. Ibrahim, V. Naddeo, F. Banat, S.W. Hasan, Preparation of novel polyvinylidene fluoride (PVDF)-tin (IV) oxide (SnO₂) ion exchange mixed matrix membranes for the removal of heavy metals from aqueous solutions, *Sep. Purif. Technol.* 250 (2020) 117250.
- [65] X. Yuan, Z. Mai, H. Li, X. Gao, A. Yan, D. Jiang, X. Wei, H. Jiang, S. Dong, Enhanced energy density in piezoelectric PVDF-polymer nanocomposite via multiple mechanism synergetic action, *Nano Energy* 127 (2024) 109734.
- [66] A.M. Chandran, S. Varun, P.K.S. Mural, Flexible electroactive PVDF/ZnO nanocomposite with high output power and current density, *Polym. Eng. Sci.* 61 (6) (2021) 1829–1841.
- [67] C.M. Costa, V.F. Cardoso, P. Martins, D.M. Correia, R. Goncalves, P. Costa, V. Correia, C. Ribeiro, M.M. Fernandes, P.M. Martins, et al., Smart and multifunctional materials based on electroactive poly (vinylidene fluoride): recent advances and opportunities in sensors, actuators, energy, environmental, and biomedical applications, *Chem. Rev.* 123 (19) (2023) 11392–11487.
- [68] Y. Lee, V.K. Bandari, V.P. Paliakkara, S. Monteiro Augusto, R. Ehrler, O. Hellwig, S. Amann, K. Stöwe, R. Thalheim, O.G. Schmidt, Monolithic integration of printable PVDF-trfe piezoelectric multifunctional devices: From sensing to actuation, *Adv. Funct. Mater.* 35 (3) (2025) 2413500.
- [69] G.J. Adekoya, O.C. Adekoya, E.R. Sadiku, Y. Hamam, S.S. Ray, Effect of borophene and graphene on the elastic modulus of PEDOT: Pss film—A finite element study, *Condens. Matter* 7 (1) (2022) 22.
- [70] C. Revenant, S. Toinet, E. Lawrence Bright, M. Benwadih, The longitudinal and transverse piezoelectric effects of the ferroelectric polymer p (VDF-trfe), *Macromol. Mater. Eng.* 310 (5) (2025) 2400420.
- [71] M.-M. Yang, T.-Y. Zhu, A.B. Renz, H.-M. Sun, S. Liu, P.M. Gammon, M. Alexe, Auxetic piezoelectric effect in heterostructures, *Nat. Mater.* 23 (1) (2024) 95–100.
- [72] X. Zhou, K. Parida, J. Chen, J. Xiong, Z. Zhou, F. Jiang, Y. Xin, S. Magdassi, P.S. Lee, 3D printed auxetic structure-assisted piezoelectric energy harvesting and sensing, *Adv. Energy Mater.* 13 (34) (2023) 2301159.
- [73] K. Lefki, G. Dormans, Measurement of piezoelectric coefficients of ferroelectric thin films, *J. Appl. Phys.* 76 (3) (1994) 1764–1767.

A.6 Publication VI [\[P-VI\]](#): Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures



Integrating Experiments and Phase Field Method Through Informatics for Tailored Corrosion Performance of Additively Manufactured Steel Microstructures

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Abstract Additively manufactured super duplex stainless steel (SDSS 2507) is used in marine hardware, but its microstructure and passive-film stability depend strongly on post-processing. We present an integrated framework that combines experiments, physics-based modeling, and machine learning to predict corrosion performance in laser powder bed fusion (LPBF) of 2507. Coupons were printed and subjected to heat treatments: as-printed, stress-relieved at 400 – 550°C for 1h, and solution-annealed at 1100°C for 15 min. XRD was used to quantify the microstructure, and corrosion behavior was evaluated in 3.5 wt.% NaCl using CPP and EIS. The austenite fraction correlated with improved passivity and repassivation. Stress relieving at 500°C/1h provided the most favorable balance between polarization resistance and repassivation stability, whereas 550°C/1h showed weaker passive-film recovery despite high apparent resistance. A neural-network model trained on electrochemical data was used to screen process–structure–property pathways for LPBF SDSS 2507.

Keywords Apparent polarization resistance · Additive manufacturing · Machine learning · Phase field method

1 Introduction

Corrosion-induced material degradation remains a major engineering problem because it reduces structural integrity, shortens service life, and increases safety risks in transportation, infrastructure, energy, utilities, and manufacturing [1]. In stainless steels, degradation is mainly associated with pitting corrosion [2], galvanic corrosion at material interfaces [3], and stress corrosion cracking (SCC) driven by coupled mechanical and chemical effects [4]. These mechanisms are controlled by alloy chemistry and are further affected by temperature, pH, chloride concentration [5, 6], humidity [7, 8], stray currents [9], oxygen level [10], and impurities [11]. Their effect is particularly severe in marine and petrochemical environments [12], where chloride attack, microbial activity, and sustained mechanical loading promote localized corrosion and SCC [13, 14]. Super duplex stainless steels (SDSS), including UNS S32750 and S32760, are designed for such aggressive environments. Their high strength and corrosion resistance arise from a two-phase ferrite–austenite microstructure enriched with Cr, Mo, and N. This chemistry provides a pitting resistance

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equivalent number (PREN) above 40, exceeding that of 316 L stainless steel and standard duplex 2205 [15, 16]. SDSS therefore shows strong resistance to pitting, crevice corrosion, and chloride-induced SCC [17, 18], with reported low corrosion rates during seawater exposure and reliable performance in aggressive in-situ studies [17, 18]. These properties make SDSS suitable for offshore cooling systems, subsea equipment, pump shafts, and desalination piping [19]. Laser powder bed fusion (LPBF) can extend the use of SDSS to complex marine components, but it also introduces rapid solidification, residual stress, porosity, and chemical heterogeneity.

The relation between heat-treatment path, phase evolution, and electrochemical response is not straightforward, especially when several corrosion indicators must be interpreted together. Conventional corrosion assessment methods, including cyclic potentiodynamic polarization (CPP), electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR), and mass-loss analysis, are reliable but time- and equipment-intensive [20, 21]. Pilot-scale inhibitor studies can require months of monitoring [22], and empirical models often fail to capture coupled composition–process interactions [23]. Computational approaches such as multiscale modeling, density functional theory, molecular dynamics, and computational fluid dynamics are also expensive or difficult to apply across broad alloy and processing spaces [24, 25]. These constraints motivate faster predictive tools that retain physical meaning.

Measurement-driven optimization studies have shown that process variables can be linked to multiple performance responses through structured experimental design and statistical ranking methods [26]. Machine learning (ML) has shown strong potential for corrosion prediction using elemental, environmental, image, and sensor data [27–32]. However, corrosion models for LPBF stainless steels still require better coupling between experimentally measured electrochemical behavior, process-sensitive descriptors, and physics-based interpretation. This work addresses that gap by integrating LPBF experiments, heat treatment, XRD/SEM characterization, CPP and EIS measurements, phase-field modeling, and ML-based prediction. The objective is to establish a process–structure–property framework that links heat-treatment-controlled phase evolution to corrosion performance in LPBF SDSS 2507.

2 Materials and Methods

2.1 Characterization and Electrochemical Evaluation

The chemical composition of the super duplex stainless steel (SDSS) powder, grade UNS S32750 (EN 1.4410)/Osprey[®] 2507 VIGA produced by Sandvik Osprey Ltd., is presented in Table 1. The 2507 powder is a gas-atomized powder characterized by spherical particles with particle sizes ranging from 15 to 53 μm . The powder was used to fabricate square samples (1.0 cm $\times$ 1.0 cm) by laser powder bed fusion (LPBF), as shown in Fig. 1a. Specimens were fabricated using a Renishaw AM125 metal 3D printer (Wotton-under-Edge, UK) with a 180 W ytterbium fiber laser ($\lambda = 1.074 \mu\text{m}$) and a scan speed of 300 mm s^{-1} . Processing was carried out in an argon atmosphere. A gas recirculation system (10 Hz, $\sim 200 \text{ L/min}$) kept the oxygen concentration below 10 ppm during building, decreasing it from an initial value of 400 ppm (0.04 wt.%).

A meander-scanning approach was employed, with a rotation of 67° after completing each layer. Printing parameters were optimized based on the minimum porosity observed in the cross-sectional faces of the samples. The printing parameters were laser power $P = 180 \text{ W}$, hatch distance $h = 120 \mu\text{m}$, layer thickness $t = 30 \mu\text{m}$, and scan speed $V = 300 \text{ mm/s}$ as portrayed in Fig. 1b. The volumetric energy density (VED) is a critical parameter in laser powder bed fusion, and the specified parameters were computed using the following equation [33].

$$\text{VED} = \frac{P}{V \cdot h \cdot t} = 166 \text{ J/mm}^3 \quad (1)$$

Because VED depends on the assigned layer thickness, the areal energy density, $\text{AED} = \frac{P}{V \cdot h}$, was also used to describe the laser input. The AED was 5.0 J/mm². The specimens underwent post-processing heat treatment as shown in Fig. 1d, and the following conditions were analyzed: (i) As printed, without any post-processing heat treatment (AS); (ii) Stress-relieving of as-printed samples at 400°C (SR400), 450°C (SR450), 500°C (SR500), and 550°C (SR550) for 1 h, with slow cooling in the furnace, and (iii) Solution annealing of as-printed samples at 1100°C (SA 1100) for 15 min, rapid cooling in water. Metallographic samples for analysis were prepared using an automated grinding and polishing machine. The samples were ground with SiC papers, polished with diamond suspension, and finished with 0.04 μm colloidal silica. For metallographic examination, a LEICA MEF4A light optical microscope (LOM) (Leica Microsystems, Wetzlar, Germany) and a scanning electron microscope (SEM) Supra 35 from Zeiss Company (Jena, Germany) were used.

Table 1 Chemical composition of AISI 2507 powder (wt.%), showing major and trace alloying elements relevant to duplex stainless steel

Element	Fe	Cr	Ni	Mo	Mn	Si	N	Cu	C	P	S	O
wt. %	Bal.	24.44	9.11	3.68	0.38	0.29	0.30	0.14	0.01552	0.02328	0.00097	0.01649

X-ray diffraction (XRD) analysis was conducted with the Panalytical X'Pert Pro diffraction system manufactured by Panalytical B.V. A cobalt anode lamp ($K\alpha_{Co}$, $\lambda = 0.179$ nm) was employed, operated at 40 kV with a filament current of 30 mA. Measurements were performed in the Bragg-Brentano configuration, spanning an angular range of 30 – $100^\circ 2\theta$, with a step increment of 0.05° and a counting duration of 100 s. The diffractograms were subsequently examined using X'Pert High Score Plus, in conjunction with the specific Joint Committee on Powder Diffraction Standards (JCPDS) and the Inorganic Crystal Structure Database (ICSD), as shown in Fig. 6a. The printed samples were subjected to electrolytic etching with a 10% oxalic acid solution as the electrolyte for the corrosion test. An electric voltage ranging from 3 to 6 volts was applied for a duration of 5 to 60 s on the sample dimensions in Fig. 1d.

Corrosion resistance was analyzed using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Corrosion tests were conducted using an Atlas 0531EU & IA potentiostat station in a 3.5% NaCl solution at room temperature, in accordance with PN-EN ISO 17475 [34]. The sample cross-section was exposed to the electrolyte. Electrochemical tests were conducted in a three-electrode configuration: the test sample served as the working electrode, an Ag/AgCl reference electrode (at 207 mV at 25°C) was employed, and a platinum wire served as the auxiliary electrode. The exposed geometry is shown in Fig. 1e. The open-circuit potential E_{OCP} was recorded for one hour. Anodic polarization was started from $E_{OCP} - 100$ mV and scanned at 1 mV/s until the current density reached 1 mA/cm^2 . The scan was then reversed to the initial potential, and Tafel extrapolation was performed using AtlasLab. The extracted electrochemical parameters were: corrosion current density (J_{corr}), corrosion potential (E_{corr}), and polarization resistance (R_p), which were calculated using the Stern–Geary Eq. (2) [35], where β_a and β_c are the constants for the anodic and cathodic Tafel slopes, respectively.

$$R_p = \frac{\beta_a + \beta_c}{2.3 \cdot I_{corr} \cdot (\beta_a + \beta_c)} \quad (2)$$

The breakdown potential (E_{br}) was identified from the depassivation point and the inflection of the anodic curve, whereas the repassivation potential (E_{rp}) was determined from the intersection between the reverse and forward scans. EIS measurements were performed using the same test rig under open-circuit potential (OCP), over a frequency range of 10^4 – 10^{-3} Hz with a sinusoidal amplitude of 10 mV. The impedance spectra were represented as Nyquist plots (Z_{real} vs. $-Z_{imag}$) and Bode plots ($|Z|$ and phase angle θ vs. frequency f). Data were fitted to an equivalent electrical circuit

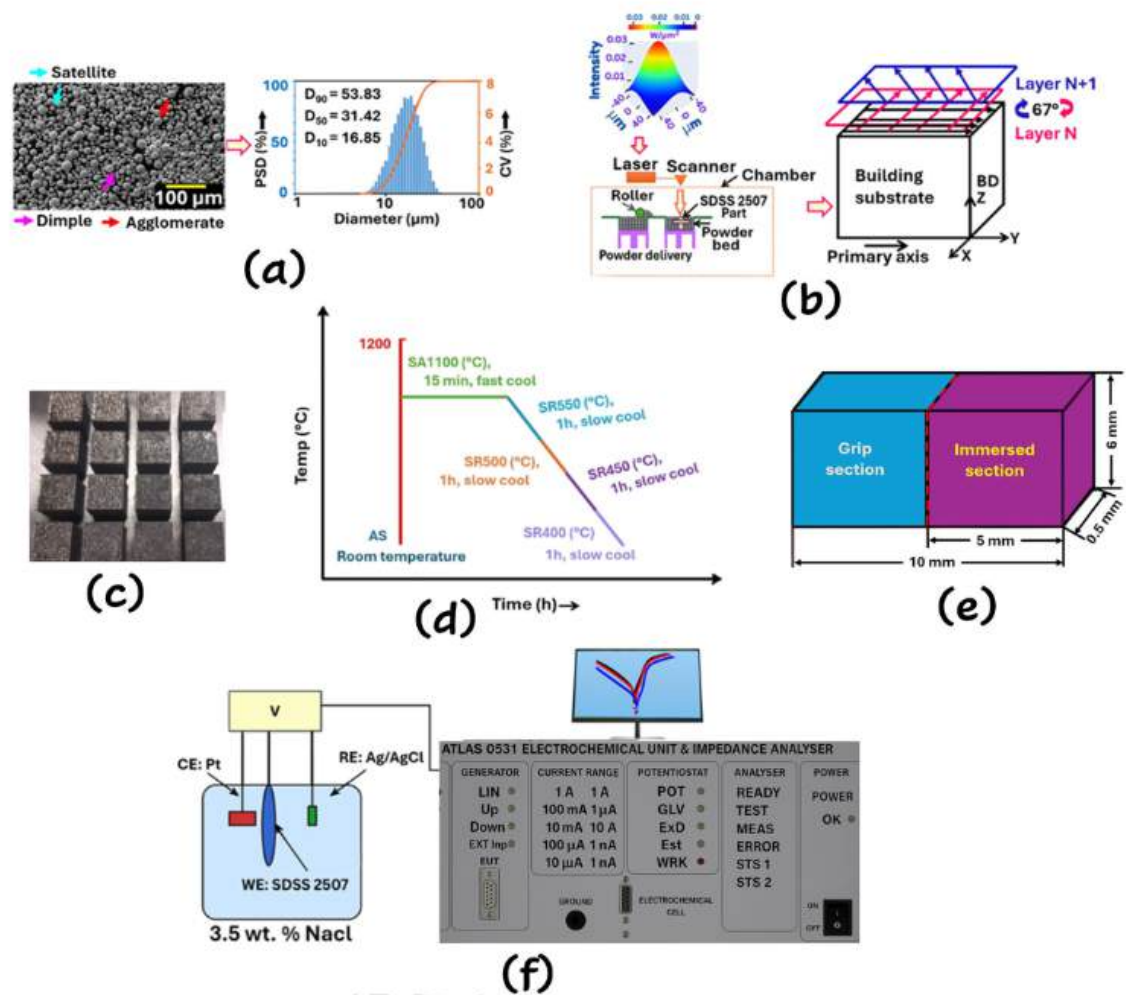


Fig. 1 **a** SEM micrographs of SDSS 2507 powder with particle size distribution curves and its cumulative frequency curves. **b** Illustrative diagram of the Laser Powder Bed Fusion (L-PBF) process, emphasizing the controlled bidirectional scanning strategy to optimize microstructure and mechanical properties. **c** As-printed L-PBF samples

before post-processing. **d** Heat-treatment schedule for LPBF-processed SDSS 2507 specimens. **e** Geometric dimensions of the corrosion specimens prepared for electrochemical testing. **f** Configuration of the corrosion testing apparatus, detailing electrode placement and solution environment

(EEC) using AtlasLab and EC-Lab. For each heat-treatment condition, three independently prepared specimens were tested, and the CPP and EIS traces reported in the main figures were selected using predefined resistance-based criteria: R_p for CPP and R_{ct} for EIS. All tabulated CPP (Table 4) and EIS (Table 5) parameters were extracted from the same selected traces to maintain consistency between the curves and the reported electrochemical values.

2.2 Process-Window-Agnostic Determinants of Corrosion Resistance

To extend the process–structure–property analysis beyond the experimentally tested heat treatments, a descriptor space was constructed to connect composition and processing variables with the apparent polarization resistance R_p . Physics-informed phase-stability constraints were embedded in the feature design, and the resulting microstructural trends were examined through phase-field simulations in Section 2.3.

2.2.1 Descriptor Construction and Model Architecture

The dataset consists of 287 literature-derived entries extracted from reported potentiodynamic polarization data, with composition, processing route, heat-treatment condition, cooling medium, electrolyte condition, and apparent polarization resistance used as model variables. Six datasets with the same nominal composition and different processing conditions were used to train the machine-learning model, as described in Section 2.1. The details on data extraction are provided in Appendix A. The radial composition–corrosion map summarizes elemental and combined composition descriptors for each sample. The sectors represent Cr, Mo, N, Ni, Ni+N, and Cr+Mo; bar length denotes normalized concentration, and angular position is ordered by measured R_{rp} . The empirical relations for the ferrite and austenite fractions are derived from elemental compositions. The pro-ferrite panel (C_{eq}) stabilizes ferrite while the pro-primary austenite panel (N_{eq}) is an austenite stabilizer [36]. Outer rings show the estimated ferrite and austenite fractions, with ring height proportional to phase fraction and

color indicating $\mathcal{R}$, as shown in Fig. 2 extbf(a). Details are provided in Appendix A2.

Figure 3a schematically presents the neural network used to predict $\mathcal{R}$. The model fuses four complementary feature blocks: elemental composition X_{El} ; process parameters X_{Pr} (both categorical and numerical); atomic/bulk descriptors $X_{Atomic-Bulk}$ generated by Matminer/Magpie featurizers (e.g., Stoichiometry, ElementProperty, Miedema) that produce electrochemical and thermodynamic descriptors from composition input as implemented in the featurization pipeline; and interaction/process parameters X_{Intr} . Training used a physics-constrained bias through the Structural Panelized Element Representation (SPER) to guide the model toward known composition–phase trends. The X_{Intr} block was engineered to represent corrosion-relevant composition–process interactions. It contains composition-based descriptors (e.g., PREN, C_{eq} , N_{eq} including nitrogen, phase class, Ni^2 , logNi, Ni–Cr interaction), numerical processing variables, categorical metadata (manufacturing route, cooling, post-processing), and interaction terms that couple composition with processing conditions (e.g.,

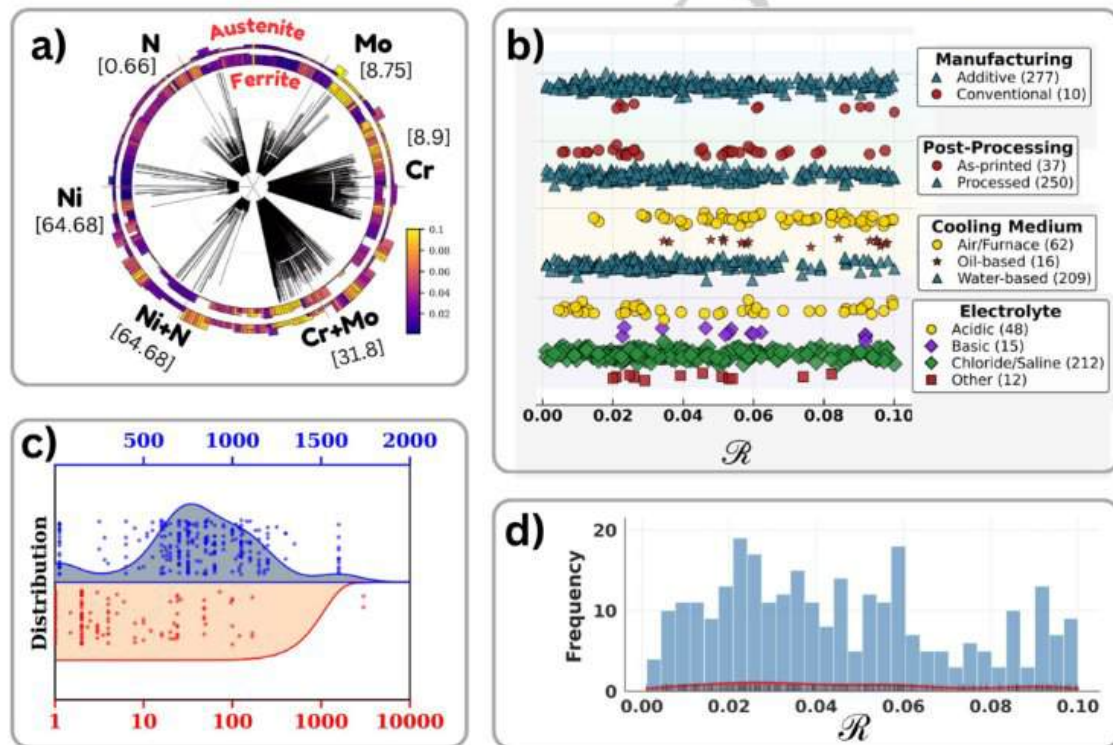


Fig. 2 **a** Composition-based structure awareness map showing that higher Ni and Mo contents correlate with improved corrosion resistance $\mathcal{R}$ (Vcm^2/A); outer phase-ring estimates (C_{eq}/N_{eq}) highlight composition–phase balance patterns linked to passivity and pitting susceptibility. **b** The categorical X_{Pr} : manufacturing route, cooling

technique, post-processing, electrolyte environment, along with the number of datasets in each sub-category. **c** The distribution of numerical X_{Pr} (heat-treatment temperature T in $^{\circ}C$, cooling duration t in h). **d** The frequency distribution of the target $\mathcal{R}$, (Vcm^2/A)

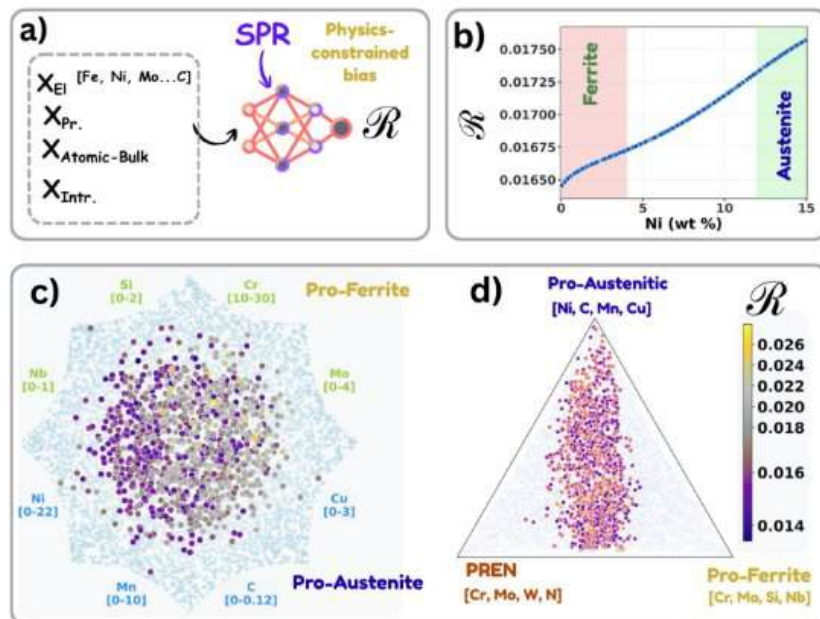


Fig. 3 **a** Input features for training: X_{EI} , X_{Pr} , $X_{Atomic-Bulk}$, and X_{Intr} . The NN processes these inputs to predict $\mathcal{R}$. The model is enhanced with a "physics-constrained bias" through a Structurally Panelized Element Representation (SPER). **b** Correlation between Ni (wt %) and predicted $\mathcal{R}$ under *Ceteris Paribus* conditions. Higher Ni content corresponds to increased predicted $\mathcal{R}$. Shaded regions denote distinct predicted $\mathcal{R}$ ranges: pink for ferrite phase (<4 wt%) and green for austenite phase (>12 wt%). **c** Representations of the eight alloying elements: Pro-ferrite [Mo, Cr, Si, Nb] and pro-austenite [Ni, Mn, C,

Cu] with their respective compositional ranges annotated. Predicted value positions are determined by normalized compositional weighting, and their shading is based on the predicted $\mathcal{R}$ value. **d** Triangular plot of candidate stainless steel compositions projected in PREN-SPER. Each marker corresponds to a generated alloy composition, positioned using barycentric normalization with auto-scaling of axes to ensure balanced representation. The same color scale applies to both (c) and (d)

PREN- T , T - t). The complete list of engineered features and interaction terms is provided in Tables 6, 7.

Feature importance was evaluated using a histogram-based gradient boosting regressor and permutation scores. These analyses ranked Ni, Cr, and Mo among the key predictors while retaining categorical processing variables. To improve sampling near compositionally sparse regions, Ni-focused perturbation and controlled augmentation of scarce experimental cases were applied only within the measured compositional range. The predictive pipeline is model-agnostic but implemented using a Tabular ResNet [37] with residual blocks, Ni-boosted attention.

2.2.2 Predictive Performance

In the 10-fold ensemble, all fold-wise R^2 values remained above 0.95. The ensemble model presented the measured R_{rp} values with $R^2 = 0.9786$, MAE = 0.0025, and RMSE = 0.0040, as shown in Fig. 10.

The conditional Ni- $\mathcal{R}$ response in Fig. 3b shows a non-linear increase in predicted $\mathcal{R}$ with Ni content, consistent

with the role of Ni as an austenite stabilizer. The shaded regions mark ferritic (Ni < 4%) and austenitic (Ni > 12%) ranges. Figure 3c projects Mo, Cr, Si, Nb, Ni, Mn, C, and Cu on a pro-ferrite/pro-austenite axis, while Fig. 3d maps candidate compositions in a PREN-SPER triangle with marker color and size representing $\mathcal{R}$. The web app is cited in the Data Availability section.

2.3 Computational Modeling of LPBF for Programmed Chemical Behavior

The LPBF phase-field formulation used a pseudo-binary alloy, $Mx_c-Ni_{(1-c)}$, where Mx represents Fe, Mo, Cr, and Cu with total composition c , and the remaining fraction is Ni. In the set (Fe, Mo, Cr, Cu) in "Mx" and Ni element, "Mo" and "Cr" are chosen from pro-ferrite panel, "Ni" and "Cu" are selected from the pro-austenite panel, and Fe is chosen as the "principal element" in the multicomponent duplex stainless steel. The 2D simulation domain of $500 \mu m \times 90 \mu m$ is constructed in MOOSE Framework [38]. The top layer of the domain ($30 \mu m$) represents the powder,

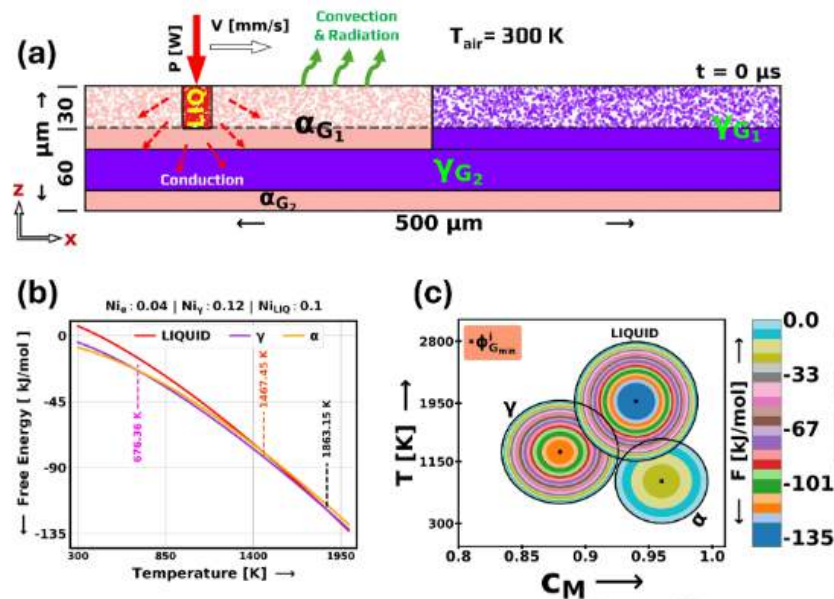


Fig. 4 **a** Schematic diagram for the phase-field laser processing simulation. The top layer ($30\mu\text{m}$) represents the powder, which sits above the film layer of $60\mu\text{m}$ within a domain length of $500\mu\text{m}$. For computational ease, the powder layer is modeled by assigning material properties different from those of the film layer. The computational system comprises three phases: Liquid (red-colored block below the laser arrow), austenite (purple), and ferrite (pink). In addition, the austenite and ferrite phases each consist of two microstructure grains, denoted as γ_{G1} , γ_{G2} , α_{G1} , and α_{G2} . **b** Free-energy versus temperature curves

are plotted for the three phases: LIQUID, austenite (γ), and ferrite (α), at Ni compositions of 0.1, 0.12, and 0.04, respectively. The free-energy curves are generated from the mathematical expressions derived from the thermodynamic database file [39]. **c** Temperature-composition dependent free-energy function plotted in 2D, obtained by fitting the free-energy data from the thermodynamic database file to a paraboloid function. The paraboloid depth, representing the free energies of the three phases, is illustrated by colors as the third dimension

Table 2 Area of the LIQUID phase and the two grains of austenite and ferrite, tabulated for two AED conditions at three simulation times: beginning (t_i), mid-simulation (t_m), and end of simulation (t_e)

Grains / Phase	Size in μm^2 (AED = 5 J/mm^2)			Size in μm^2 (AED = 1.25 J/mm^2)		
	t_i	t_m	t_e	t_i	t_m	t_e
LIQUID	400	4461	7524	400	0	0
austenite (γ_{G1})	7500	6668	2609	7500	7006	7274
austenite (γ_{G2})	20000	22268	24848	20000	19560	19960
ferrite (α_{G1})	7100	2020	1202	7100	8818	8521
ferrite (α_{G2})	10000	9581	8815	1000	9614	9244

below which lies the film layer ($60\mu\text{m}$) as shown in Fig. 4a. In the finite-element model, powder-layer properties were assigned as a fraction of the film-layer properties.

The computational domain initially consists of five grains belonging to three different phases: two austenite grains (γ_{G1} and γ_{G2}), two ferrite grains (α_{G1} and α_{G2}), and the LIQUID phase. The LIQUID phase was initialized to maintain thermodynamic consistency because nucleation was not explicitly modeled. The grain areas at different stages of simulations (initial, intermediate, and final) for the two AED values: 5 J/mm^2 and 1.25 J/mm^2 are presented in the Table 2.

In this pseudo-binary system, the composition of combined metals defines the conserved variable in the phase-field model, with the mole fraction of Mx and Ni summing to unity. The equivalent molar fraction of Mx is denoted by ' c_M ' or ' c ' with its phase-specific values represented as c_γ , c_α , and c_{LIQ} for austenite, ferrite, and LIQUID, respectively. For the non-conserved phase-field variables that distinguish LIQUID, austenite, and ferrite grains, a system of five order parameters is defined. These order parameters, denoted by η_i , are assigned a value of 1 inside their corresponding phase and zero outside, with a diffused interface in between. In the context of the LPBF process, the heat transfer kinetics of the powdered layer (discontinuous phase

in the top portion of Fig. 4a) is different than that of the continuous film layer at the bottom. To distinguish the thermophysical behavior of these layers, the concept of porosity (ψ) is utilized in this work. The film layer has zero porosity, whereas the $0 < \psi < 1$ in the powdered layer. To simplify the numerical formulation, the top layer is also modeled as an **equivalent continuous medium**, with porosity incorporated into the thermophysical properties of density, thermal conductivity, mobilities, and specific heat capacities. To accurately assign material properties to the respective phases and grains in a multi-phase system, a thermodynamically consistent interpolation function is required. In this work, with three phases (no. of phases = 3) and a five-order-parameter ($N = 5$) system, we adopt the interpolation function proposed by Moelans [40], the interpolation expression is presented in Appendix C Eq. 12.

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Laser heating changes the microstructure through the free-energy landscape. The total free energy, F_{tot} , includes bulk and interfacial free-energy densities, as given in Equation 3.

$$F_{tot} = \int_V (f_{bulk} + f_{int}) dV = \int_V \left(\sum_i \frac{G_i^m(c, T)}{V_m} + m f_{barrier} + \frac{\kappa}{2} \sum_i (\nabla \eta_i)^2 \right) dV \quad (3)$$

The bulk free energy density, consists of the temperature-dependent free energies of each phase G_i , interpolated between the respective phases (i) with an interpolation function. The term V_m in Eq. 3 is the molar volume, assumed to be the same for all the phases, with a value of $7.0923 \times 10^{-6} \text{ m}^3/\text{mol}$ (molar volume of Iron [41]). $G_i^m(c, T)$ represents the molar Gibbs free energy of phase ' i ', which is the function of temperature and composition. The temperature-composition dependent Gibbs free energy of the system is given by Eq. 13 in Appendix C with a visual representation of the Gibbs free energy is shown in Fig. 4b, c.

Table 3 Density, specific heat, and thermal conductivity of FCC austenite and BCC ferrite in the pseudo-binary alloy system at $T = 300 \text{ K}$. The ρ and C_p values are obtained from Desai et al., [43], whereas the k_{th} is obtained from Ho et al., [47]

properties	Film		Powder		T range (K)
	γ (FCC)	α (BCC)	γ (FCC)	α (BCC)	
$\rho \text{ (kg/m}^3\text{)}$	7984.8	7901.6	4391.64	4345.88	298.0 – 3200
$C_p \text{ (J/Kg K)}$	449.30	449.766	247.115	247.37	298.0 – 3200
$k_{th} \text{ (W/m K)}$	81.32	80.44	44.726	44.242	298.0 – 1600

Film values are compositionally averaged in accordance with the rule of mixtures. The phases in the powdered layer (with $\psi > 0$) are considered to have these thermophysical properties equal to 55% of the corresponding film values

The melt pool (liquid phase) dynamics and phase transformation phenomenon (between ferrite and austenite phase microstructures) during the LPBF procedure can be mathematically described by the evolution of the conserved and non-conserved phase-field variables, c and η . For the conserved variable, the evolution of the composition field is governed by Eq. 4.

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(\sum_i h_i M_i \right) \nabla \left(\frac{\partial f_{bulk}}{\partial c_i} \right) \quad (4)$$

Here, M_i is the temperature dependent mobility of i th phase, which depends on the bulk diffusion coefficient D_i , thermodynamic factor A_i and the grain boundary mobility M_{gb} as: $M_i = D_i/A_i + \sum_{j \neq i} h_j M_{gb}$. In the pseudo-binary $M - Ni$ system, the two elements are assumed to have the same diffusion coefficient for a given phase. The thermodynamic factor is calculated as the second-order partial derivative of bulk free energy density with respect to the composition, $A_i = \frac{\partial^2 f_{bulk}(T)}{\partial (c_i)^2}$. In this study, the value of grain boundary mobility M_{gb} is taken as one hundred times the phase mobility [42].

Similarly, the evolution of the non-conserved phase-field variable is given by Eq. 5.

$$\frac{\partial \eta_i}{\partial t} = -L(\eta_1, \dots, \eta_N, T) \left(\frac{\partial f_{bulk}}{\partial \eta_i} - \nabla \cdot \frac{\partial f_{int}}{\partial \nabla \eta_i} \right) \quad (5)$$

The heat transfer in bilayered and tri-phase multigrain microstructures during the LPBF process is described by the following Energy Equation (Eq. 6), where T denotes the temperature field.

$$\rho^j(\eta_1, \dots, \eta_n) C_p^j(\eta_1, \dots, \eta_n) \left(\frac{\partial T}{\partial t} + \vec{u} \cdot \nabla T \right) = k_{th}^j(\eta_1, \dots, \eta_n) \nabla^2 T + Q_{laser} \quad (6)$$

In Eq. 6, Q_{laser} is the heat deposited by the Gaussian laser

beam. The heat-source intensity is $I = \frac{2P}{\pi r_0^2} e^{-2(\frac{r}{r_0})^2}$, with $r_0 = 30 \mu\text{m}$. The terms ρ^j , C_p^j , and k_{th}^j are the density, specific heat capacity, and thermal conductivity of each phase in layer j , where j denotes either the powder layer or the film layer. The thermophysical properties used for the powder and film layers are listed in Table 3. The FCC lattice of γ -Fe has higher atomic packing efficiency than the BCC lattice of α -Fe; therefore, austenite is denser than ferrite at lower temperatures (300–1050 K). Because the thermal expansivity of γ -Fe is higher than that of α -Fe, austenite may become less dense above 1100 K [43]. In the present simulations, most of the material outside the melt

pool remains below 1100 K; therefore, thermal-expansivity-driven density reversal was neglected and austenite was treated as denser than ferrite.

The velocity field $\vec{u}$ represents melt-pool convection and is obtained from the incompressible Navier–Stokes equation under the Boussinesq approximation. The simulations focus on the growth and dissolution of the austenite phase under two areal energy densities (AEDs), 5 J/mm² and 1.25 J/mm², while keeping the remaining computational parameters fixed. Boundary conditions include convective and radiative heat transfer, with an air convection coefficient of 15 W/m²K and an emissivity of 0.3 [44]. Marangoni convection was included through the temperature dependence of the surface-tension coefficient at the LIQUID/AIR interface, with $(d\sigma/dT)_{LIQ/AIR} = -4.3 \times 10^{-4}$ N/(m K) [45,

46]. Under the Boussinesq hypothesis, this temperature dependence was applied only to the tangential surface stress.

2.3.1 Tailored Design of Corrosion-Resistant Phase

Phase evolution was compared at two areal energy densities (AEDs), 5 J/mm² and 1.25 J/mm², while all other computational parameters were kept constant. The simulations focused on the transformation between primary austenite and ferrite.

Snapshots of the two simulations, taken when the laser reached the top-horizontal midpoint of the computational domain, are presented in Fig. 5a and b. At higher AED (laser power 180 W), both primary austenite grains (γ_{G1} and γ_{G2}) grow, while the ferrite phase (α) shrinks, as shown in Figure 5a. The LIQUID phase develops along the laser path

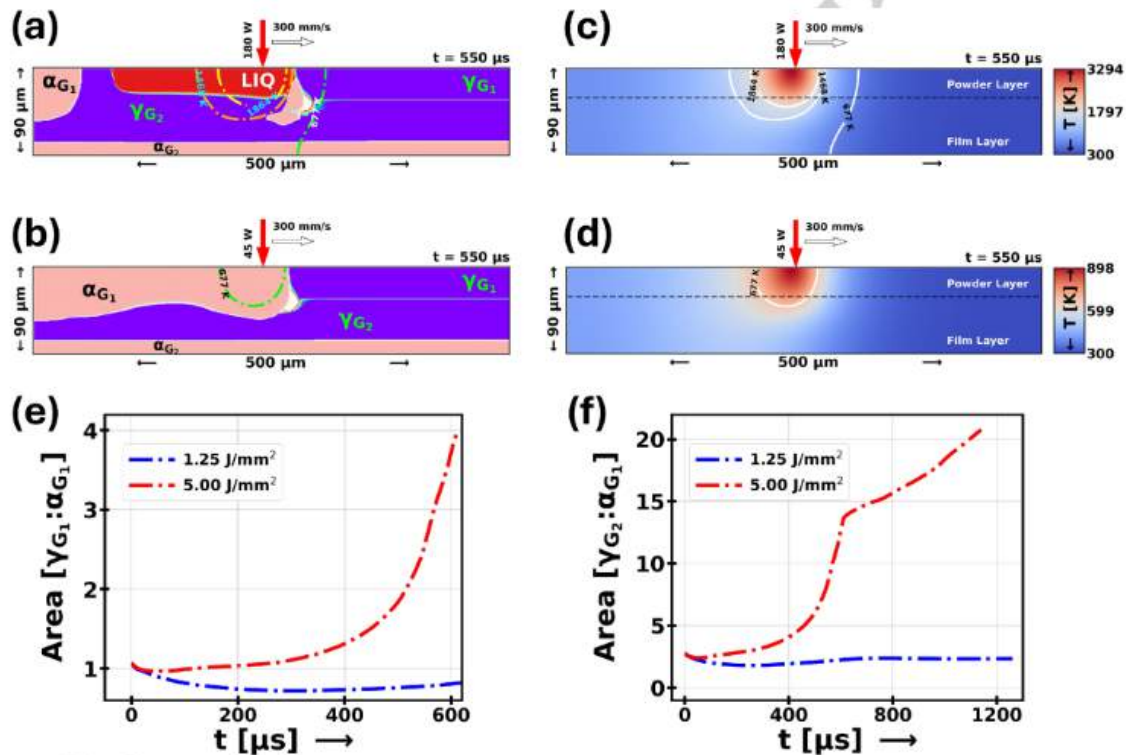


Fig. 5 Visualization of phase growth and temperature distribution at mid-simulation time $t = 550 \mu s$. In **a**, the grain growth of austenite phases γ_{G1} and γ_{G2} (purple) is shown for the higher AED condition of 5 J/mm² (laser power 180 W). The LIQUID phase follows the laser beam as it traverses the top of the domain. A clear shrinkage of the ferrite phase (pink) is observed under the higher-heat condition. The contour lines represent the three transformation temperatures of 667 K, 1468 K, and 1864 K, corresponding to the ferrite-austenite, ferrite-LIQUID, and austenite-Liquid phase transitions, respectively. In **b**, the phase evolution is shown for the lower AED condition of 1.25 J/mm² (laser power 45 W), where the thermodynamically favorable ferrite

phase (α_{G1}) below 667 K grows in a higher proportion compared to the higher AED case. The thermal distribution across the domain at the same simulation time is presented in **c** and **d** for AED conditions of 5 J/mm² and 1.25 J/mm², respectively. The plot in **e** and **f** shows the area proportion of austenite grains to ferrite grains for two AED conditions during the phase-field simulations. In **e**, the ratio of austenite grain γ_{G1} to ferrite grain α_{G1} is presented, while in **f**, the ratio of austenite grain γ_{G2} to ferrite grain α_{G1} is shown. In both plots, it can be observed that under higher AED, the austenite-to-ferrite area ratio increases. Under lower AED, the ratio remains low, indicating preferential ferrite growth

because it is thermodynamically stable at the simulated high temperatures, consistent with the free-energy curves in Figure 4b and c.

In contrast, at lower AED (laser power 45 W), the ferrite phase evolves more rapidly, transforming austenite to ferrite under cooler conditions, as shown in Fig. 5b. For accurate comparison, snapshots for both AED conditions were taken at the same simulation time, 550 μ s. The exact areas of all phases and grains at initial ($t_i = 0 \mu$ s), midpoint (t_m , laser at domain center), and end (t_e , laser turned off) are reported in Table 2.

Temperature snapshots at mid-simulation are shown in Figure 5c, d for AEDs of 5 J/mm² and 1.25 J/mm², respectively. The peak temperature measured under high AED reaches about 3294 K, whereas for low AED it is only about 900 K. Figure 5c also shows contour lines at 677 K, 1468 K and 1864 K, corresponding to the transformation temperatures of ferrite to austenite, ferrite to LIQUID and austenite to LIQUID respectively. These transition temperatures are calculated at Ni compositions of 0.04, 0.12, and 0.1 for ferrite, austenite, and LIQUID, respectively, using the thermodynamic database. From these contours, the growth of the austenite phase above 677 K is consistent with the phase evolution observed in Fig. 5a, while the austenite-to-ferrite transformation at lower temperature (Fig. 5b) corresponds well to the temperature distribution in Fig. 5d and the stability of the ferrite phase below 676 K as shown in Fig. 4b. The Supplementary Material includes animations of phase evolution and thermal history for both AED conditions. The simulations indicate that higher AED promotes primary austenite growth by increasing the thermal field above the ferrite-to-austenite transformation range.

2.3.2 Phase Growth Proportion Influenced by AED Values: Austenite versus Ferrite

To quantify the phase-evolution trend, the simulated area ratios of austenite grains to ferrite grains were compared for the two AED conditions. Figure 5e and f show the ratios $\gamma_{G_1}/\alpha_{G_1}$ and $\gamma_{G_2}/\alpha_{G_1}$, respectively. The austenite-to-ferrite area ratio increases under the higher AED condition, indicating preferential austenite growth. In contrast, the lower AED condition maintains a low austenite-to-ferrite ratio throughout the simulation. These trends show that LPBF thermal conditions can shift the simulated phase balance toward primary austenite while reducing ferrite growth.

3 Microstructure and Corrosion Response Under Heat Treatments

3.1 Heat Treatment Effects on Microstructural Analysis

The LPBF of super duplex stainless steel (SDSS) results in a microstructure that is primarily ferritic in the as-printed condition, driven by rapid cooling rates of 10^6 °C/s - 10^8 °C/s. These high cooling rates suppress austenite formation due to limited diffusion time, favoring a ferrite-dominated microstructure, as confirmed by X-ray diffraction (XRD) analysis, as illustrated in Fig. 6b. The diffractogram for the as-printed (AS) sample shows strong ferrite phase peaks at Fe- α (011), (002), and (112), with a weaker austenite peak at Fe- γ (111), indicating an austenite content of approximately 7%. Rapid solidification also induces fine, columnar grains, microsegregation of alloying elements (e.g., Cr, Ni, Mo), and residual stresses [48]. When stress-relieving heat treatments are applied at various temperatures (e.g., 400 °C/1 h, 450 °C/1 h, 500 °C/1 h, 550 °C/1 h), the overall phase composition remains essentially unchanged, but the XRD patterns reveal a slight increase in austenite peak intensities at Fe- γ (111) and (002), particularly noticeable in the SR500/1 h and SR550/1 h conditions. This enhancement reflects partial austenite stabilization [49]. After solution annealing at 1100 °C/15 min (SA1100/15 min), the microstructure becomes more balanced, with ferrite and austenite phases present in nearly equal amounts of 60% austenite, as evidenced by the prominent austenite peaks at Fe- γ (111), (002), and (022) in the XRD pattern [50].

The effect of heat treatment on the microstructural evolution of LPBF-printed SDSS is illustrated in Fig. 6c–h. During LPBF printing, the rapid cooling of SDSS kinetically inhibits the expected phase formation. Consequently, the as-printed material is predominantly a ferritic structure, supersaturated with non-equilibrium concentrations of nickel and nitrogen. This structure is characterized by an ultra-fine sub-grain morphology, high residual stress, solute segregation along grain boundaries, and a mix of fine round 5–20 μ m and elongated 50–70 μ m ferritic grains. The phase imbalance disrupts the beneficial synergy between phases, while solute segregation creates localized, nano-sized regions that are lean in Cr and Mo [51–53].

Stress relieving at 550 °C for 1 h may promote early secondary-phase formation and local Cr, Mo, and N partitioning within the ferritic matrix. The observed SEM contrast is consistent with localized microstructural changes, while nitrogen supersaturation and high dislocation density may provide favorable sites for early precipitation or solute redistribution. Possible nanoscale products may include Cr-rich nitrides or ferrite decomposition products; however,

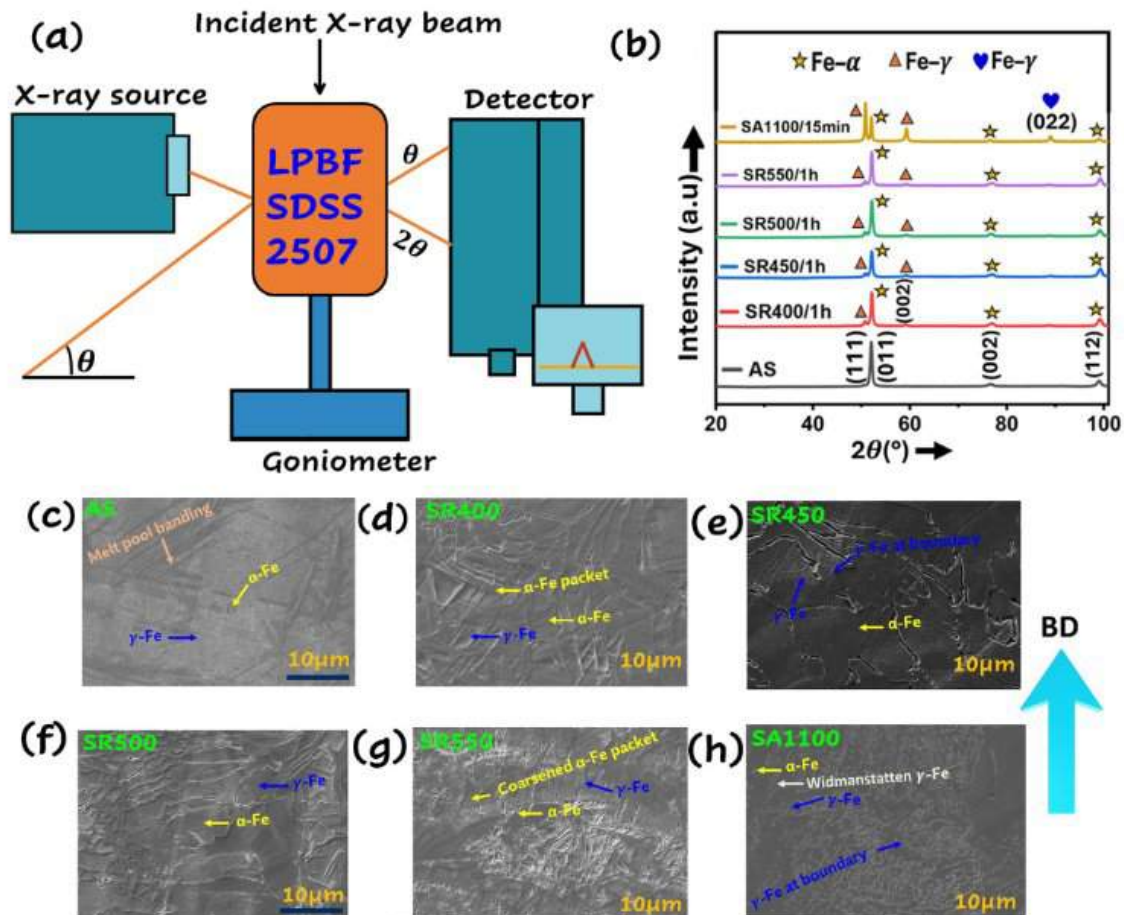


Fig. 6 **a** Bragg-Brentano θ - 2θ XRD geometry. **b** XRD patterns of LPBF SDSS, AED = 5.0 J mm^{-2} , showing ferrite (Fe- α) and austenite (Fe- γ) peaks. Panels **c-h** are SEM XZ cross-sections transverse to the build direction (BD): **c** as-printed, with melt-pool bands and a predominantly α matrix containing sparse γ ; **d-g** stress-relieved at

400, 450, 500 and 550°C for 1 h, showing progressive γ precipitation at ferrite boundaries and within α packets and coarsening at 550°C; **h** solution-annealed at 1100°C for 15 min, exhibiting a near-equilibrium duplex morphology with Widmanstätten γ plates and intergranular γ

their direct identification requires higher-resolution characterization beyond the present XRD and SEM analysis. [54]. The elongated features observed in the ferritic regions suggest localized phase instability or solute partitioning, which can locally disturb passive-film stability [55]. In contrast to the lower-temperature treatments, solution annealing at 1100°C for 15 min followed by water quenching produces a homogenized, near-balanced γ/δ duplex microstructure. The process dissolves all detrimental phases (e.g., α' phase, nitrides/carbides, and precursors to $G/\chi/\sigma$ phases) and eliminates microsegregation. Subsequent rapid cooling reconstructs the microstructure, forming fine, evenly distributed austenite both at grain boundaries and as Widmanstätten

side plates, and allowing Mo and N to repopulate their preferred phases.

3.2 Corrosion Performance Influenced by Heat-Treatment Paths

The microstructural characteristics of LPBF-processed SDSS, as revealed by XRD, have a significant impact on corrosion kinetics. The ferrite-rich as-printed microstructure, with its intense Fe- α peaks, exhibits a higher exchange current density due to a weaker passive film, promoting anodic dissolution in the 3.5% NaCl electrolyte. The fine grains and microsegregation increase local concentration gradients, enhancing localized pitting, while residual

stresses elevate the overpotential, amplifying corrosion rates. The XRD data show that stress-relieving treatments slightly enhance the austenite content, mitigating these effects; however, the most significant improvement occurs after solution annealing, where the balanced phase distribution strengthens the passive film. Surface roughness and porosity from LPBF, along with microsegregation and inclusions, further increase the effective corrosion area and lower the breakdown potential, as these defects are more pronounced in the as-printed and stress-relieved states compared to the annealed condition. During potentiodynamic polarization (starting at $E_{OCP} - 100$ mV, 1 mV/s, up to 1 mA/cm²), the as-printed sample's ferrite dominance and defects lead to higher corrosion current density, while the annealed sample's balanced microstructure improves resistance, aligning with the observed XRD peak evolution.

The absence of a balanced duplex structure in the as-printed condition is fundamentally detrimental to corrosion performance. These regions exhibit a lower pitting resistance equivalent number (PREN) and a reduced repassivation potential, making subsequent post-processing essential to achieve optimal properties. For stress-relieving at 400°C/1h, although this treatment partially relieves residual stresses, the overall corrosion resistance is degraded due to spinodal decomposition facilitating pit nucleation and hindering repassivation [56, 57]. For 450°C/1h, this progression further degrades pitting resistance, typically depressing the repassivation potential compared to the 400°C condition. The root cause remains the same: chromium is sequestered within α' phases, creating nanoscale compositional fluctuations that deplete Cr in the surrounding ferrite and lower its effective PREN [56, 57].

For 500°C/1h, the corrosion response indicates an improved balance between polarization resistance and repassivation stability [56, 57]. For 550°C/1h, possible early secondary-phase formation or local Cr, Mo, and N redistribution may reduce passive-film stability and weaken repassivation [58–60]. Solution annealing optimizes the localized-corrosion performance by shifting corrosion behavior toward that of the bulk alloy chemistry. The result is a pitting resistance comparable to wrought DSS in 0.6 Molar NaCl, evidenced by higher pitting potentials and reduced pit formation, as the high-PREN austenite films mitigate the influence of LPBF-induced defects [53, 61, 62]. The results of the potentiodynamic polarization testing are shown in Fig. 7, and summarized in Table 4. The as-printed (AS) condition exhibited the highest corrosion susceptibility, as indicated by a corrosion current density of 2.37 $\mu\text{A}/\text{cm}^2$ and the most negative corrosion potential of -347 mV. This reduced corrosion resistance is attributed to residual stresses and phase heterogeneities within the as-printed LPBF microstructure. The lowest E_{OCP} indicates

accelerated dissolution kinetics and consequently reduced corrosion resistance [63]. Following 60 min of immersion, all conditions exhibited a positive shift in E_{OCP} , as shown in Fig. 7a–f. Heat treatment significantly increased the E_{OCP} , with values ranging from -347 mV for the as-printed sample to a maximum of -74.3 mV for the stress-relieved at 500°C/1h condition.

All anodic polarization curves show active, pseudo-passive, and transpassive regions in Figure 7g–l. The corrosion potential (E_{corr}) serves as a key indicator of a material's thermodynamic stability, with a lower E_{corr} increasing corrosion susceptibility. The as-printed SDSS had the lowest E_{corr} and showed the earliest corrosion onset. The detectability of the passivation region is controlled by the concentration of chloride ions (Cl^-), with high levels typically suppressing it and obscuring the pitting potential. Under the present conditions, the pseudo-passive range remained stable until the breakdown potential (E_{br}) was reached. The reverse polarization curves exhibited a repassivation effect, with the repassivation potentials (E_{rp}) indicating the conditions under which actively corroding pits cease to propagate.

Reverse-polarization analysis showed repassivation in all specimens. Notably, the kinetics were fastest for the as-printed and SR 400°C/1h specimens, as evidenced by higher E_{rp} and steeper reverse scan slopes as demonstrated in Fig. 7h. The average E_{br} and E_{rp} were 1129 mV and 969 mV, respectively. The narrow reverse-scan hysteresis loop indicated efficient repassivation. The average passive range ($E_{rp} - E_{corr}$) was approximately 1365 mV for most conditions, but decreased to 1070 mV for the SR 400°C/1h specimen. Potentials above E_{br} promote pit nucleation, while potentials near E_{rp} indicate pit closure during the reverse scan. In contrast, exposure to 450°C for 1h resulted in a high E_{br} and an extended passive range, confirming stable passivation with no indications of early breakdown.

The repassivation kinetics identify variations across different thermal treatment conditions. SR 400°C/1h specimens demonstrated accelerated repassivation of $E_{rp} = 992$ mV with minimal hysteresis. SA 1100°C/15 min specimens showed beneficial repassivation but with slightly lower E_{rp} . Conversely, as-printed and intermediate-temperature specimens exhibited marginally wider hysteresis loops, attributed to residual stresses and dislocation density that impede passive film reformation. In sharp contrast, the SR550°C/1h condition exhibited weaker repassivation stability, which may be associated with early secondary-phase formation and/or local Cr, Mo, and N redistribution. The SR450°C/1h and SR500°C/1h conditions showed moderate hysteresis and lower E_{rp} values compared with the highest repassivation cases. Most conditions showed pit closure during the reverse scan, with narrow hysteresis loops and E_{rp} values approaching E_{br} .

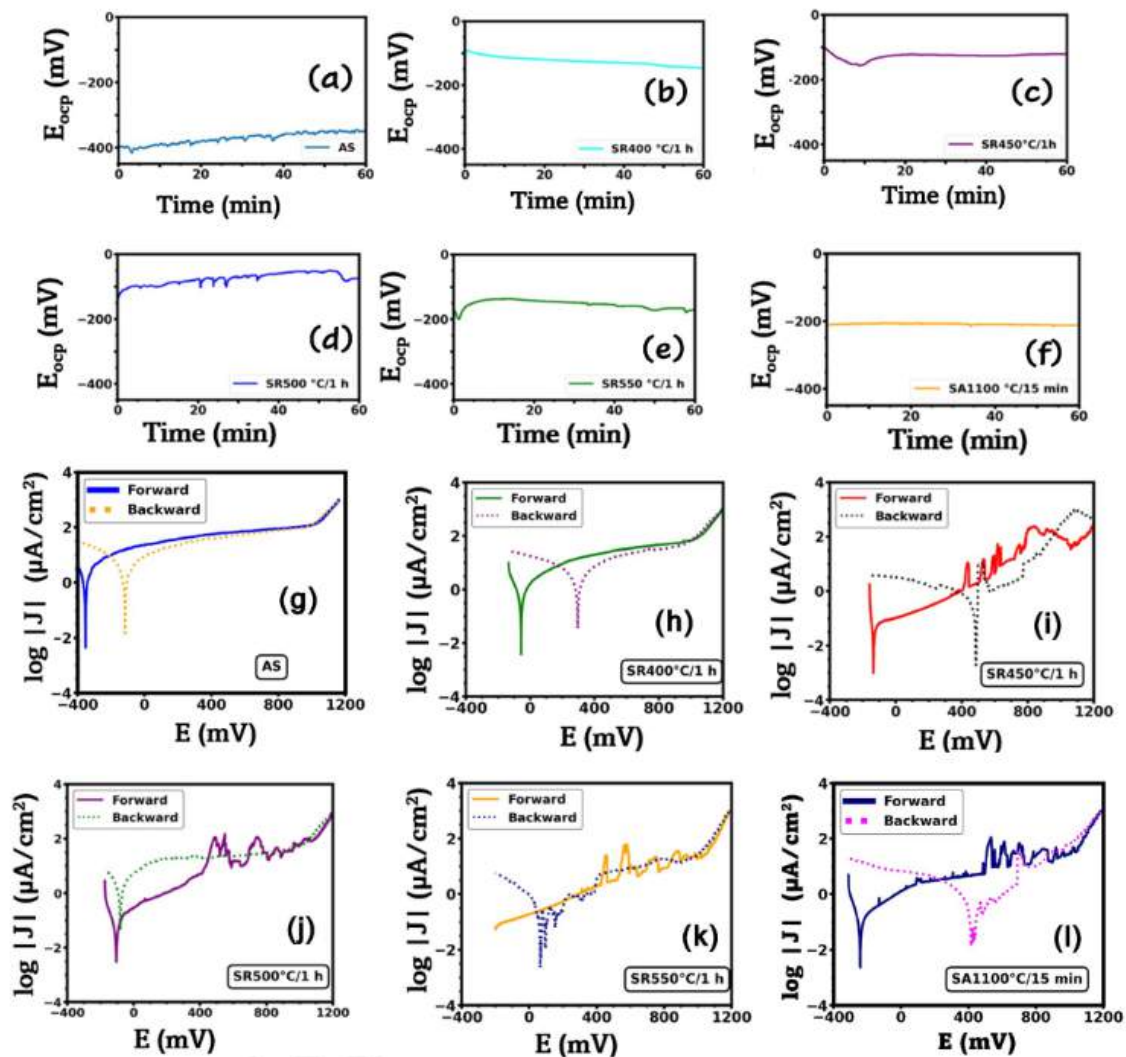


Fig. 7 Potentiodynamic polarization results of LPBF-printed SDSS samples (area-normalized) under various heat treatments: a–f Open circuit potential (OCP) behavior. g–l Cyclic potentiodynamic polarization curves (CPP) behavior

The heat treatments changed the corrosion response, as shown in Table 4. The as-printed condition had the lowest R_p . Stress-relieving treatments progressively increased R_p from 28.80 kΩcm² (SR 400°C/1h) to 201.80kΩcm² (SR 500°C/1h). Despite its high numerical value, SR 550°C/1h had the highest R_p (216.84kΩcm²) but showed severe passive instability. The solution-annealed sample showed high resistance (R_p = 165.45 kΩ cm²). Stress relieving at 500°C for 1h provided the most favorable balance between high polarization resistance and passive-film stability among the tested conditions.

3.3 EIS Response of Heat-Treated Samples

EIS measurements were performed on LPBF-printed 2507 SDSS in 3.5% NaCl. The Nyquist plots in Figure 8a show depressed capacitive arcs whose radii increase after heat treatment. The SR500°C condition shows the highest impedance, followed by SR550°C, while the as-printed condition shows the lowest values. This pattern indicates improved charge-transfer resistance and stronger barrier behavior after heat treatment. The Bode plots in Figure 8b, d support the same trend. The impedance modulus ($|Z|$) remains high across a broad frequency range for the 500°C and 550°C

Table 4 Electrochemical parameters obtained from Tafel analysis of potentiodynamic polarization curves for LPBF-printed SDSS under different heat treatment conditions

Sample	E_{ocp}	E_{br}	E_{rp}	$E_{rp} - E_{corr}$	J_{corr}	$J_{corr,app}$	β_a	β_c	E_{corr}	R_p	$R_{p,app}$
Condition	(mV)	(mV)	(mV)	(mV)	($\mu A/cm^2$)	($\mu A/cm^2$)	(mV)	(mV)	(mV)	($k\Omega \cdot cm^2$)	($k\Omega \cdot cm^2$)
AS	-347	1095	1000	1378	2.37	121	289.22	83.72	-378.62	11.88	8.30
SR 400°C/1 h	-146	1127	992	1070	0.83	64.57	232.75	72.64	-78.36	28.80	15.40
SR 450°C/1h	-121	1153	960	1351	0.36	147.19	263.70	39.89	-126.10	41.99	6.50
SR 500°C/1h	-74.3	1152	962	1088	0.10	47.86	259.17	55.18	-127.00	201.80	20.10
SR 550°C/1h	-170	1141	841	1078	0.06	16.98	508.07	34.57	-237.79	216.84	49.50
SA 1100°C/15 min	-212	1123	874	1124	0.11	28.18	213.73	54.63	-250.68	165.45	31.00

As-printed (AS); stress-relieved at 400°C/1h (SR400/1h), 450°C/1h (SR450/1h), 500°C/1h (SR500/1h), 550°C/1h (SR550/1 h); and solution-annealed at 1100°C/15 min (SA1100/15 min). Parameters include open circuit potential (E_{ocp}), breakdown potential (E_{br}), repassivation potential (E_{rp}), the difference $E_{rp} - E_{corr}$, corrosion current density (J_{corr}), apparent corrosion density $J_{corr,app}|_{E=E_{rp}}$, anodic and cathodic Tafel slopes (β_a , β_c), corrosion potential (E_{corr}), polarization resistance (R_p), and apparent polarization resistance at repassivation potential ($R_{p,app}$)

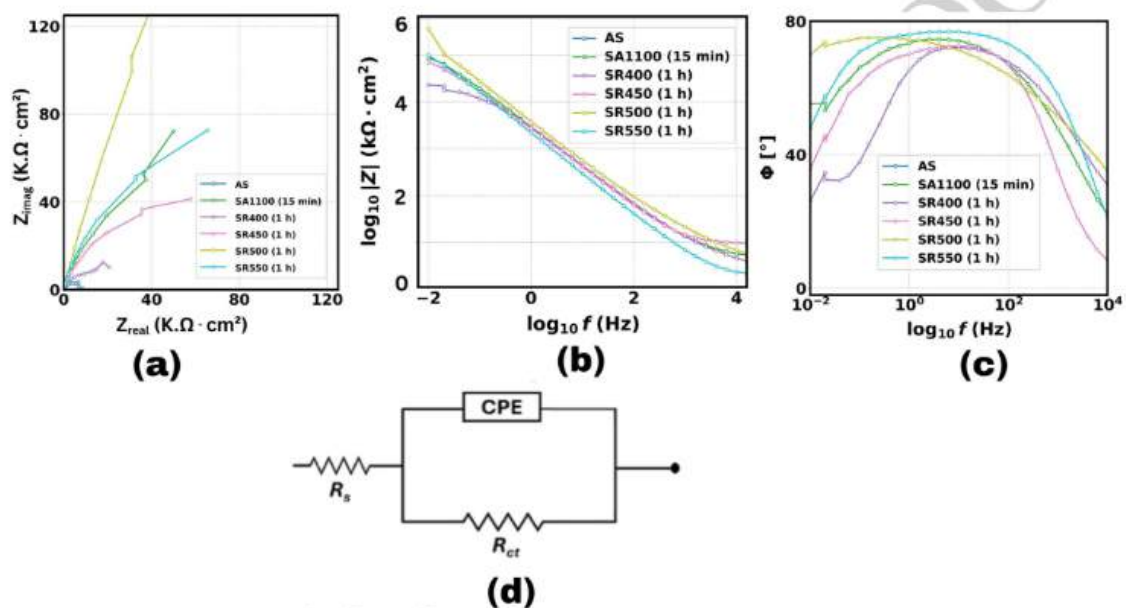


Fig. 8 Electrochemical impedance spectroscopy (EIS) of LPBF-fabricated 2507 SDSS (area-normalized): **a** Nyquist plots; **b** Bode magnitude $|Z|$; **c** Bode phase Φ measured over 10^{-2} Hz– 10^4 Hz; and **d** equivalent electrical circuit (EEC) used for fitting, $R_s = (CPE \parallel R_{ct})$. Here R_s is the solution resistance, R_{ct} the charge-transfer resistance (proportional to the low-frequency semicircle diameter), and the con-

stant-phase element ($\overline{Y}_0, n$) accounts for non-ideal interfacial capacitance due to surface roughness/heterogeneity. Heat treatments-AS, SR400/1 h, SR450/1 h, SR500/1 h, SR550/1 h, and SA1100/15 min shift the low-frequency $|Z|$ and raise the phase-angle maximum relative to AS, indicating an increase in interfacial polarization resistance consistent with larger R_{ct} .

C samples, indicating stable barrier properties. Conversely, the as-printed and 400°C samples exhibit a gradual modulus loss. The phase-angle response shows a broad peak for the heat-treated samples, with the SR500°C condition giving the highest phase shift, consistent with capacitive passive-film behavior [64].

Given the singular capacitive loop observed across all samples, the data were fitted to a one-time-constant EEC (Fig. 8d), consistent with models applied to other

stress-relieved AM stainless steels [65]. The model consists of the solution resistance (R_s) in series with a parallel combination of the charge-transfer resistance (R_{ct}) and a constant-phase element (CPE, Q_{dl}). A CPE was used to account for surface heterogeneity and non-ideal capacitance [66]. The double-layer capacitance (C_{dl}) was calculated from the CPE parameters using established methods [67]. The parameters in Table 5 are consistent with the Tafel trends. For a one-time-constant system, the charge-transfer

Table 5 Electrochemical impedance parameters for LPBF-printed 2507 SDSS under different heat treatments

Sample Condition	R_s ($\Omega \cdot \text{cm}^2$)	Y_{dl} ($\mu\text{F} \cdot \text{s}^{(n-1)} \cdot \text{cm}^{-2}$)	n (-)	C_{dl} ($\mu\text{F} \cdot \text{cm}^{-2}$)	R_{ct} ($\text{K}\Omega \cdot \text{cm}^2$)
AS	3.67	177.20	0.81	194.10	8.32
SR 400° C/1 h	3.81	52.40	0.77	163.60	31.48
SR 450° C/1 h	5.82	60.30	0.67	104.80	113.32
SR 500° C/1 h	4.57	79.00	0.77	229.00	285.61
SR 550° C/1 h	1.29	81.57	0.81	152.30	207.88
SA 1100° C/15 min	9.24	81.90	0.82	128.40	116.91

As-printed (AS); stress-relieved at 400°C/1h (SR400/1 h); 450°C/1h (SR450/1 h); 500°C/1h (SR500/1 h); 550°C/1h (SR550/1 h); and solution-annealed at 1100°C/15 min (SA1100/15 min). Parameters include solution resistance (R_s), constant phase element parameters (Y_{dl} , n), double-layer capacitance (C_{dl}), and charge transfer resistance (R_{ct})

resistance (R_{ct}) is equivalent to the polarization resistance (R_p), which is inversely related to the corrosion rate. The R_{ct} ($\approx R_p$) values show the effect of heat treatment. Similar to the Tafel analysis of the anodic polarization curves, the as-printed samples exhibited nearly comparable R_{ct} values. The highest R_{ct} was obtained after treatment at 500°C, followed by 550°C and SA1100°C. The increase in R_{ct} indicates improved passive-film resistance compared with the as-printed condition, consistent with previous reports [65].

The CPE exponent n of Table 5 deviates from ideal behavior ($n = 1$) for all samples (0.67–0.82), reflecting their inherent surface heterogeneity. The relation between C_{dl} and protectiveness is not direct [68, 69]. The SR500°C sample has high C_{dl} , suggesting that its corrosion response is governed by passive-film chemistry and homogeneity rather than thickness alone. This enhancement is primarily attributed to stress-relief treatments (samples undergoing step in Fig. 1d) that mitigate the non-uniform residual stress distribution from the as-printed state, thereby reducing susceptibility to localized corrosion. Local nitride formation or solute partitioning can reduce repassivation stability, while its effect on the area-averaged EIS response may remain limited.

4 Conclusions

LPBF-printed SDSS 2507 showed a predominantly ferritic as-printed microstructure with limited austenite formation. Post-processing heat treatment is therefore necessary to restore the duplex phase balance and improve passive-film

stability in chloride-containing environments. XRD and SEM confirmed that stress-relieving treatments produced gradual austenite precipitation, whereas solution annealing at 1100°C for 15 min followed by quenching generated a more balanced duplex morphology.

The electrochemical results show that corrosion resistance is not governed by polarization resistance alone. Repassivation behavior and passive-film stability must also be considered. Stress relieving at 500°C for 1h provided the most favorable balance between high polarization resistance and stable repassivation. Although the 550°C treatment produced high apparent resistance, its passive response was less stable, consistent with possible secondary-phase formation or local solute redistribution. Solution annealing increased the austenite fraction and improved passive-film stability, making it a conservative route for seawater-relevant applications.

The experimental, phase-field, and machine-learning results connect processing, phase evolution, and corrosion response in LPBF SDSS 2507. The main design principle is to promote austenite formation while avoiding heat-treatment conditions that trigger secondary precipitation or passive-film instability. The approach supports screening of process–structure–property pathways for corrosion-resistant additively manufactured marine components.

Appendix A: Quantifying Corrosion Behavior

A1. Theory of Ion Transport

To model ion transport and electrochemical reactions during corrosion in a 3.5% NaCl electrolyte, the Nernst-Planck framework was applied, considering diffusion and electromigration as advection terms. The flux of ionic species i (e.g., Fe^{2+} , Cl^-) is governed by:

$$J_i = -D_i \nabla c_i + c_i v_{\text{elec},i} \quad (7)$$

where J_i is the flux ($\text{mol}/\text{m}^2 \cdot \text{s}$), D_i is the diffusion coefficient (m^2/s), c_i is the concentration (mol/m^3), and $v_{\text{elec},i} = -\frac{z_i F D_i}{RT} \nabla \phi$ is the electromigration velocity (m/s), with z_i as the charge number, $F = 96485 \text{ C/mol}$ (Faraday's constant), $R = 8.314 \text{ J/mol} \cdot \text{K}$ (gas constant), $T = 298 \text{ K}$ (temperature), and $\nabla \phi$ as the electric field (V/m). The continuity equation incorporates a source term for corrosion reactions:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot J_i = R_i \quad (8)$$

The source term R_i ($\text{mol}/\text{m}^3\cdot\text{s}$) models ion production (e.g., Fe^{2+} from anodic dissolution) at the electrode surface using Butler-Volmer kinetics, expressed as $R_i = \frac{j_0}{zF\delta} \left[\exp\left(\frac{(1-\alpha)zF\eta}{RT}\right) - \exp\left(-\frac{\alpha zF\eta}{RT}\right) \right]$, where j_0 is the exchange current density, α is the charge transfer coefficient, $\eta = E - E_{\text{eq}}$ is the overpotential, and δ is the boundary layer thickness. During anodic polarization, the applied potential starts at $E_{\text{OCP}} - 100$ mV and increases at 1 mV/s until the current density reaches 1 mA/cm², driving the overpotential η and thus the anodic term in R_i , which dominates ion production (e.g., Fe^{2+}). The Tafel slopes (β_a, β_c) in Eq. 2, derived from Butler-Volmer kinetics, link the measured corrosion parameters (J_{corr} , E_{corr} , R_p) to the electrochemical processes observed in the experiments.

A2. Apparent Polarization Resistance and Corrosion Behavior

Electrochemical corrosion is governed by electrode potential E (V) and current density J (A/cm^2). A more negative E favors oxidation. A more positive E favors reduction. The corrosion potential E_{corr} is the equilibrium where anodic and cathodic rates balance and net current is zero. The polarization resistance $R_p = \left(\frac{dE}{dJ}\right)_{E_{\text{corr}}}$ is the slope of the E - J curve near E_{corr} . Larger R_p means the material resists changes in current and generally corrodes more slowly. R_p is used in the Stern-Geary relation to estimate J_{corr} and the metal loss rate.

Cyclic potentiodynamic polarization (CPP) uses forward and reverse potential sweeps to probe localized corrosion. A hysteresis loop indicates a tendency for sustained localized attack. The repassivation potential E_{rp} is found where the reverse scan intersects the forward scan. Below E_{rp} pits tend to repassivate. If E_{rp} is much lower than the pitting potential, the material is more susceptible to stable pit growth. The apparent polarization resistance at E_{rp} is estimated as $R_{p,\text{app}}|_{E=E_{\text{rp}}} = E_{\text{rp}}/J_{\text{rp}}$ [$\text{V cm}^2/\text{A}$] and it characterizes the system's ability to return to a passive state [70–72].

Predicting the full E - J relation $\mathcal{R}$ is central to corrosion assessment. The shape of this polarization curve determines corrosion rates and device performance. Near open-circuit potential, $\mathcal{R}$ gives R_p and thus J_{corr} . In electrochemical devices, $\mathcal{R}$ also shows how overpotential affects kinetics and transport. Machine learning models have recently predicted E/J behavior in battery electrodes. Those results suggest similar data-driven approaches can aid corrosion prediction and accelerate alloy screening [27, 73–75].

Appendix B: Data Preprocessing and Feature Engineering

See Tables 6, 7, 8

Table 6 Matminer feature extractors and their relevance to corrosion physics. Each descriptor captures aspects of chemical bonding, electronic structure, microstructural stability, or phase energetics that influence corrosion, passivation, and dissolution behavior

Extractor	Relevance to corrosion mechanisms
Stoichiometry	Elemental ratios (e.g., Cr, Mo, Ni fractions) predict passive film stability and pitting resistance
Elementproperty (Maggpie)	Statistical measures of atomic properties (electronegativity, atomic radius, valence counts) govern interfacial stability, passive film formation, and galvanic effects
Atomicorbitals	HOMO/LUMO energy descriptors provide insight into electron donation/acceptance during redox reactions at the metal-electrolyte interface
Miedema	Formation enthalpies and miscibility tendencies indicate phase stability, segregation, and microgalvanic coupling susceptibility
Yangsolutionsolution	Atomic size and modulus mismatch parameters relate to solid solution strengthening and dislocation-mediated dissolution pathways
Valenceorbital	Orbital occupancies reflect bond reactivity, metal-oxygen bonding character, and vulnerability to oxidative attack
Electronegativitydiff	Polarity differences between constituent elements drive galvanic corrosion, selective dissolution, and passive film breakdown

See Figs. 9 and 10

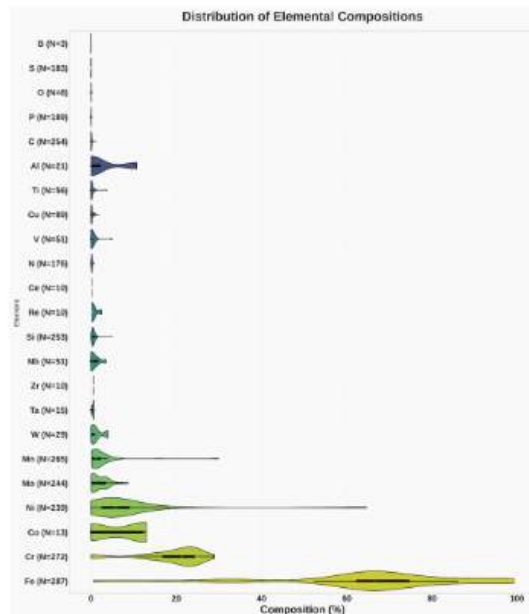


Fig. 9 The range of compositions present in the ML model training database, along with the number of datasets where particular elements are present

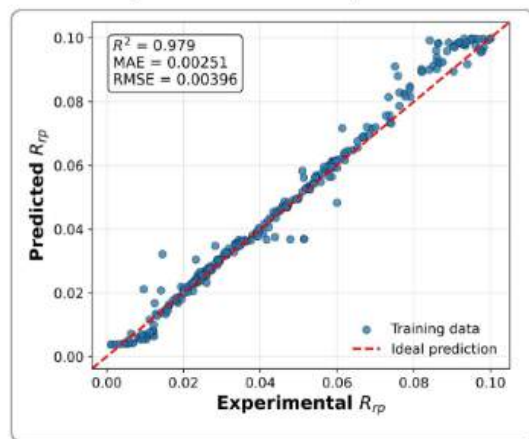


Fig. 10 Parity plot of loaded-model predictions for the training model. Experimental R_{rp} values are compared with the predicted R_{rp} values obtained from the saved 10-fold neural-network ensemble

The conventional pitting resistance equivalent number (PREN) is a useful but structure-agnostic scalar that collapses bulk composition into a single sum and therefore cannot represent phase-specific or element-level structural effects. The standard form is:

$$\text{PREN} = \%Cr + 3.3 \times (\%Mo + 0.5 \times \%W) + 16 \times \%N. \quad (9)$$

To recover phase sensitivity, we split alloying chemistry into a pro-ferrite panel [Cr-Mo-Si-Nb] and a pro-austenite panel [Ni-C-Mn-Cu] and represent each panel by a small linear rule [36]:

$$\begin{aligned} C_{eq} &= 1.0(\%Cr) + 1.0(\%Mo) + 1.5(\%Si) + 0.5(\%Nb), \\ N_{eq} &= 1.0(\%Ni) + 30.0(\%C) + 0.5(\%Mn) + 0.3(\%Cu), \end{aligned} \quad (10)$$

From which the austenite and ferrite fractions are estimated as:

$$f_{\gamma} = \frac{N_{eq}}{N_{eq} + C_{eq}}, \quad f_{\alpha} = 1 - f_{\gamma}. \quad (11)$$

Mo, Si, and Nb are not included in the pro-austenite panel. Molybdenum (Mo), Silicon (Si), and Niobium (Nb) enhance stress corrosion cracking (SCC) resistance by improving passivation and microstructure stability, with Mo increasing the pitting resistance equivalent number. Similarly, in the rule expression for austenite, the Ni, having a moderately smaller structural correlation score, i.e., $w_{Ni}^{\gamma} = 1$, compared to C, indicates that Ni can be present in both phases but is more favorable for austenite. C, along with Mn and Cu, is absent in the pro-ferrite panel. Mn and Ni stabilize the austenitic phase, while Cu strengthens the passive oxide layer, reducing the corrosion current density (J_{corr}) in chloride environments. These rules provide a physics-based bias to the PREN expression and retain element-level structural information.

Table 7 Derived Interaction terms and their physical interpretations

Term	Physical interpretation
$T \times t, T/t, T/\log t$	Combined thermal exposure effects influencing phase transformation rates and oxide growth kinetics
T^2, t^2	Nonlinear acceleration of degradation once critical thermal or temporal thresholds are exceeded
$Ni^2, \log(Ni), Ni \times Cr$	Complex, non-monotonic effects of Ni on austenite stability and its coupled role with Cr in transpassive dissolution
$\text{PREN} \times T, \text{PREN} \times (T/t)$	Interaction between alloy passivation capacity and thermally induced stresses governing film breakdown susceptibility

These terms represent nonlinear composition–processing–corrosion interactions.

Appendix C: Computational Engineering of Laser-Steel Interface

This appendix describes the phase-field framework used to model the laser–steel interface. A pseudo-binary representation is first used to reduce the multicomponent steel

chemistry to a binary form for numerical modeling. The governing thermodynamic and kinetic equations are then presented.

C1. Pseudo-Binary Thermodynamic Representation of Multicomponent Steel System

Primary austenite (γ) is more resistant to pitting and crevice corrosion than ferrite (α), and Ni stabilizes the austenite phase. The phase-field simulations use a pseudo-binary formulation to link LPBF process conditions with ferrite–austenite evolution. Laser power and scan speed change the thermal field and therefore the growth kinetics of the γ and α phases. At AED = 5 J/mm², the simulated γ phase grows more than at AED = 1.25 J/mm².

C2. Mathematical Formulation of the Phase-Field Model

The interpolation function used to assign material properties between the liquid, austenite, and ferrite phases is expressed in Eq. 12. Here, G_1 and G_2 denote two grains belonging to the same phase.

$$h_i = \begin{cases} \frac{\eta_i^2}{N} & ; \text{LIQUID} \\ \frac{\sum_{k=1}^N \eta_k^2}{\eta_{c,\alpha}^2 + \eta_{c,\gamma}^2} & ; \text{AUSTENITE (Primary); FERRITE} \end{cases} \quad (12)$$

The paraboloid-fitted free energy of individual phases is given by Eq. 13:

$$G_i^m = F_i [A_i(c - c_{eq}^i)^2 + B_i(T - T_{eq}^i)^2 + C_i] \quad (13)$$

where c and T denote the composition and temperature, respectively. The coefficients F_i , A_i , B_i , and C_i are determined by fitting the thermodynamic free energy data from databases [39] to a paraboloid function [76]. The fitted coefficients are listed in Table 8.

Table 8 Coefficients of the composition–temperature–dependent free-energy paraboloid for the three phases in Eq. 13

Phase	Austenite (γ)	Ferrite (α)	LIQUID
Coefficient			
F_i	7932.8	2397.7	6983.4
A_i (J/mol)	7125	7560	8545
B_i (J/mol·K ²)	3×10^{-5}	3×10^{-5}	3×10^{-5}
C_i (J/mol)	15	10	20

Table 8 Coefficients of the composition–temperature–dependent free-energy paraboloid for the three phases in Eq. 13

Phase	Austenite (γ)	Ferrite (α)	LIQUID
Coefficient			
c_{eq}^i	0.88	0.96	0.94
T_{eq}^i (K)	1280.5	881	1975

The chemical driving force for a given phase is assumed identical in both the powdered and film layers; porosity is assumed only to influence kinetics and not the magnitude of the driving force

In Eq. 3, m and κ are model parameters related to the diffuse interface width (δ) and interfacial energy σ [J/m²], expressed as $m = 6\sigma/\delta$ and $\kappa = 0.75\delta\sigma$. In this study, the value of δ and σ is taken to be 10 μ m and 0.5 J/m² respectively. The term f_{barrier} represents the fourth-order Landau polynomial of the phase-field variable, as defined in Eq. 14, with $\beta = 1.5$.

$$f_{\text{barrier}} = \sum_i \left(\frac{(\eta_i)^4}{4} - \frac{(\eta_i)^2}{2} \right) + \beta \sum_i \sum_{j \neq i} \eta_i^2 \eta_j^2 + \frac{1}{4} \quad (14)$$

The interfacial mobility function $L(\eta_1, \dots, \eta_N, T) = L_i$ in Eq. 5 is defined as:

$$L_i = \frac{\sum_{i=1}^N \sum_{j>1}^N L_{ij} \eta_i^2 \eta_j^2}{\sum_{i=1}^N \sum_{j>1}^N \eta_i^2 \eta_j^2} \quad (15)$$

where L_{ij} denotes the interfacial mobility, approximated as:

$$L_{ij} = \frac{4m}{3\kappa} \times \frac{M_i + M_j}{\tau} \quad (16)$$

Here, M_i and M_j represent the diffusion mobilities of the i^{th} and j^{th} phases within the film layer, while $\tau = 0.15$ [77]. The mobilities within the powder layer are assumed to be 0.55 times those of the corresponding film layer.

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Data Availability The experimental data related to the experimental processing, characterization, testing, and analysis are available at https://github.com/anilkunwar/laser_processed_steel_microstructure_experimental_data. The code and data for phase-field simulations are available at https://github.com/subediupadesh/PhaseField_CRAMS.

Finally, the codes and datasets for machine learning techniques are available at https://github.com/Sachinscnpdl/ss_corrosion_ML.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

- Y. Ji, N. Li, Z. Cheng, F. Xiaoqian, M. Ao, M. Li, X. Sun, T. Chowwanonthapunya, D. Zhang, K. Xiao et al., Random forest incorporating ab-initio calculations for corrosion rate prediction with small sample alloys data. *Npj Materials Degradation* **6**(1), 83 (2022)
- G.S. Frankel, Pitting corrosion of metals: a review of the critical factors. *J. Electrochem. Soc.* **145**(6), 2186 (1998)
- G.-L. Song, Potential and current distributions of one-dimensional galvanic corrosion systems. *Corros. Sci.* **52**(2), 455–480 (2010)
- A. King, G. Johnson, D. Engelberg, W. Ludwig, J. Marrow, Observations of intergranular stress corrosion cracking in a grain-mapped polycrystal. *Science* **321**(5887), 382–385 (2008)
- A.A. Dastgerdi, A. Brenna, M. Ormellese, M. Pedferri, F. Bolzoni, Experimental design to study the influence of temperature, pH, and chloride concentration on the pitting and crevice corrosion of uns s30403 stainless steel. *Corros. Sci.* **159**, 108160 (2019)
- Z. Wang, L. Zhang, Z. Zhang, L. Minxu, Combined effect of pH and h₂s on the structure of passive film formed on type 316l stainless steel. *Appl. Surf. Sci.* **458**, 686–699 (2018)
- X. Minghe, Q. Zhang, X.X. Yang, Z. Wang, J. Liu, Z. Li, Impact of surface roughness and humidity on x70 steel corrosion in supercritical co₂ mixture with so₂, h₂o, and o₂. *The Journal of Supercritical Fluids* **107**, 286–297 (2016)
- S. Patel, A. Rogalsky, M. Vlasea, Towards understanding side-skin surface characteristics in laser powder bed fusion. *J. Mater. Res.* **35**(15), 2055–2064 (2020)
- X. Wenqiang, Yu. Li, H. Li, K. Wang, C. Zhang, Y. Jiang, S. Qiang, Corrosion mechanism and damage characteristic of steel fiber concrete under the effect of stray current and salt solution. *Constr. Build. Mater.* **314**, 125618 (2022)
- Z. Pei, D. Zhang, Y. Zhi, T. Yang, L. Jin, D. Fu, X. Cheng, H.A. Terry, J.M.C. Mol, X. Li, Towards understanding and prediction of atmospheric corrosion of an fe/cu corrosion sensor via machine learning. *Corros. Sci.* **170**, 108697 (2020)
- J. Sun, H. Tang, C. Wang, Z. Han, S. Li, Effects of alloying elements and microstructure on stainless steel corrosion: A review. *Steel Res. Int.* **93**(5), 2100450 (2022)
- G. Vukelić, B. Mihaljević, Š. Ivošević, Marine environment effect on welded additively manufactured stainless steel aisi 316l. *Journal of Marine Science and Engineering* **13**(3), 459 (2025)
- Y. Yang, C. Chen, Y. Zhuang, Z. Suo, Reviewing the progress of corrosion fatigue research on marine structures. *Frontiers in Materials* **11**, 1399292 (2024)
- X. Li, Y. Liu, Z. Han, G. Chen, A risk-based maintenance decision model for subsea pipeline considering pitting corrosion growth. *Process Saf. Environ. Prot.* **184**, 1306–1317 (2024)
- C. Sung, K. Kim, W. Chung, B.-H. Shin, Electrochemical properties of uns s 32750 and uns s 32760 annealed super duplex stainless steels. *Int. J. Electrochem. Sci.* **17**(5), 220526 (2022)
- AV. Yarovchuk, AS. Dikov, KV. Tsay, Peculiarities of stress corrosion fracture of sensitized and neutron irradiated chromium-nickel austenitic steel. In *Journal of Physics: Conference Series*, volume 2155, page 012011. IOP Publishing, 2022
- J. Zhu, D. Li, W. Chang, Z. Wang, H. Lihua, Y. Zhang, M. Wang, Z. Yang, J. Song, S. Chen et al., In situ marine exposure study on corrosion behaviors of five alloys in coastal waters of western pacific ocean. *J. Market. Res.* **9**(4), 8104–8116 (2020)
- R. Francis, G. Byrne, Duplex stainless steels-alloys for the 21st century. *Metals* **11**(5), 836 (2021)
- A. Shokri, M.S. Fard, Corrosion in seawater desalination industry: A critical analysis of impacts and mitigation strategies. *Chemosphere* **307**, 135640 (2022)
- A.M. Memon, I.H. Imran, L.M. Alhems, Neural network based corrosion modeling of stainless steel 316l elbow using electric field mapping data. *Sci. Rep.* **13**(1), 13088 (2023)
- S. Hägg Mameng, S. Wegrelius, L. Hosseinpour, Stainless steel selection tool for water application: pitting engineering diagrams. *Frontiers in Materials* **11**, 1353907 (2024)
- H.-J. Ge, Y.-H. Bai, H. Zhang, H.-R. Yuan, Z.-J. Zhu, P. Liu, Y.-X. Zeng, J.-Y. Wang, Role of crevice size induced microenvironment variation within the gap in initiating crevice corrosion of 201 stainless steel. *Frontiers in Materials* **11**, 1543536 (2025)
- Y. Zhao, K. Xi, P. Yue, B. He, S. Zhang, H. Li, T. Zhang, F. Wang, Impact of multi-factor coupling on the corrosion behavior of 254smo stainless steel in an aggressive oilfield environment containing co₂ and h₂s. *Corros. Sci.* **235**, 112215 (2024)
- Z. Yang, C. Ma, Y. Zhang, D. Zhuoyang, P. Zhou, Y. Zhao, T. Zhang, F. Wang, Corrosion-life prediction model for 316l stainless steel under electronic special gases containing trace moisture employed in semiconductor manufacturing industry. *Corros. Sci.* **241**, 112510 (2024)
- Y. Zhao, Y. Liu, W. Qi, T. Zhang, F. Wang, A multi-factor coupling prediction model for crack growth of hp-13cr stainless steel under extreme oilfield environments. *SSRN* (2024). <https://doi.org/10.2139/ssrn.4905267>
- R. Viswanathan, S. Ramesh, S. Maniraj, V. Subburam, Measurement and multi-response optimization of turning parameters for magnesium alloy using hybrid combination of taguchi-gra-pca technique. *Measurement* **159**, 107800 (2020)
- J. Newman, NP. Balsara. *Electrochemical systems*. John Wiley & Sons, 2021
- P. Wang, W. Huanchun, X. Liu, X. Chaoliang, Machine learning-assisted prediction of stress corrosion crack growth rate in stainless steel. *Crystals* **14**(10), 846 (2024)
- A. Hussein Khalaf, Y. Xiao, N. Xu, B. Wu, H. Li, B. Lin, Z. Nie, J. Tang, Emerging ai technologies for corrosion monitoring in oil and gas industry: A comprehensive review. *Eng. Fail. Anal.* **155**, 107735 (2023). <https://doi.org/10.1016/j.engfailanal.2023.107735>
- P. Patel, V. Aryai, E. Arzaghi, H. Kafian, R. Abbassi, V. Ganiya, Classification of pitting corrosion damage in process facilities using supervised machine learning. *The Canadian Journal of Chemical Engineering* **103**(1), 153–169 (2025)
- D. Ruiz, A. Casas, C.A. Escobar, A. Perez, V. Gonzalez, Advanced machine learning techniques for corrosion rate estimation and prediction in industrial cooling water pipelines. *Sensors* **24**(11), 3564 (2024)
- C. Mathew, E. Adu-Gyamfi, A review on ai-driven environmental-assisted stress corrosion cracking properties of conventional and advanced manufactured alloys. *Corros. Eng., Sci. Technol.* **60**(2), 145–158 (2025)
- H. Sun, X. Chu, Z. Liu, A. Gisele, Yu. Zou, Selective laser melting of maraging steels using recycled powders: A comprehensive microstructural and mechanical investigation. *Metall. and Mater. Trans. A* **52**, 1714–1722 (2021)

34. Corrosion of metals and alloys—electrochemical test methods—guidelines for conducting potentiostatic and potentiodynamic polarization measurements, 2010
35. D. Mareci, G.H. Nemtoi, N. Aelenei, C. Bocanu, The electrochemical behaviour of various non-precious ni and co based alloys in artificial saliva. *Eur. Cell. Mater.* **10**(8), 1–7 (2005)
36. K. Ogawa, Effects of nickel and nitrogen on austenite phase growth in rapid cooled microstructure from high temperature in duplex stainless steel. *ISIJ Int.* **62**(4), 726–732 (2022)
37. Y. Gorishniy, I. Rubachev, V. Khrulkov, A. Babenko, Revisiting deep learning models for tabular data. *Adv. Neural. Inf. Process. Syst.* **34**, 18932–18943 (2021)
38. M.R. Tonks, D. Gaston, P.C. Millett, D. Andrs, P. Talbot, An object-oriented finite element framework for multiphysics phase field simulations. *Comput. Mater. Sci.* **51**, 20–29 (2012). <https://doi.org/10.1016/j.commatsci.2011.07.028>
39. W.-M. Choi, Y.H. Jo, D.G. Kim, S.S. Sohn, S. Lee, B.-J. Lee, A thermodynamic description of the co-cr-fe-ni-v system for high-entropy alloy design. *Calphad*, 66:101624, 2019. <https://doi.org/10.1016/j.calphad.2019.05.001>. URL <https://www.sciencedirect.com/science/article/abs/pii/S0364591618302165>
40. N. Moelans, A quantitative and thermodynamically consistent phase-field interpolation function for multi-phase systems. *Acta Materialia*, 59:1077–1086, 2011. ISSN 13596454. <https://doi.org/10.1016/j.actamat.2010.10.038>. URL <https://linkinghub.elsevier.com/retrieve/pii/S1359645410007019>
41. S.P. Ong, W.D. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V.L. Chevrier, K.A. Persson, G. Ceder, Python materials genomics (pymatgen): A robust, open-source python library for materials analysis. *Computational Materials Science*, 68:314–319, 2013. <https://doi.org/10.1016/j.commatsci.2012.10.028>. URL <https://www.sciencedirect.com/science/article/pii/S0927025612006295>
42. J. Hektor, M. Ristinmaa, H. Hallberg, S.A. Hall, S. Iyengar, Coupled diffusion-deformation multiphase field model for elastoplastic materials applied to the growth of Cu₆Sn₅. *Acta Materialia*, 108:98–109, apr 2016. ISSN 13596454. <https://doi.org/10.1016/j.actamat.2016.02.016>. URL <https://linkinghub.elsevier.com/retrieve/pii/S1359645416300933>
43. P. D. Desai, Thermodynamic properties of iron and silicon. *Journal of Physical and Chemical Reference Data*, 15 (3):967–983, 1986. ISSN 1529-7845. <https://doi.org/10.1063/1.555761>
44. N. Zhao, Y. Zhong, M.L. Huang, H.T. Ma, W. Dong, Growth kinetics of Cu₆Sn₅ intermetallic compound at liquid-solid interfaces in Cu/Sn/Cu interconnects under temperature gradient. *Scientific Reports*, 5:13491, 8 2015. ISSN 2045-2322. <https://doi.org/10.1038/srep13491>. URL <https://www.nature.com/articles/srep13491>
45. A. Kasama, A. McLean, W.A. Miller, Z. Morita, M.J. Ward, Surface tension of liquid iron and iron-oxygen alloys. *Can. Metall. Q.* **22**(1), 9–17 (1983). <https://doi.org/10.1179/cmq.1983.22.1.9>
46. V. Klapczynski, D. Le Maux, M. Courtois, E. Bertrand, P. Pailard, Surface tension measurements of liquid pure iron and 304l stainless steel under different gas mixtures. *Journal of Molecular Liquids*, 350:118558, 2022. ISSN 0167-7322. <https://doi.org/10.1016/j.molliq.2022.118558>. URL <https://www.sciencedirect.com/science/article/pii/S0167732222000939>
47. C. Y. Ho, R. W. Powell, P. E. Liley, Thermal conductivity of the elements. *Journal of Physical and Chemical Reference Data*, 1 (2):279–421, 1972. ISSN 1529-7845. <https://doi.org/10.1063/1.3253100>
48. Y. Zhou, W. Wang, L. Li, S. Wang, Z. Huang, Z. Zhang, D. Kong, F. Shang, B. Zhang, X. Li, et al. Microstructure and corrosion performance of laser powder bed fusion produced duplex stainless steel using ni over-alloyed mixed powder. *Corrosion Science*, page 113025, 2025
49. Y. Xiong, W. Shi, T. Zhao, E. Akiyama, U. Ramamurty, Corrosion and stress corrosion cracking resistances of laser powder bed fused and binder jetted 316l austenitic stainless steel. *Corrosion Science*, page 112968, 2025
50. C. Zhao, Y. Bai, Q. Yan, B. Li, Enhanced corrosion resistance of laser powder bed fusion 316l stainless steel by modifying the microstructure through heat treatment. *J. Market. Res.*, (2025)
51. L. Gargalis, L. Karavias, J.S. Graff, S. Diplas, E.P. Koumoulos, E.K. Karaxi, A comparative investigation of duplex and super duplex stainless steels processed through laser powder bed fusion. *Metals* **13**(11), 1897 (2023)
52. Z. Brytan, M. Dagnaw, J. Bidulská, R. Bidulský, M.R. Muhamad, Post-processing effect on the corrosion resistance of super duplex stainless steel produced by laser powder bed fusion. *Materials* **17**(12), 2807 (2024)
53. A. Mulhi, S. Dehgahi, P. Waghmare, A.J. Qureshi, Process parameter optimization of 2507 super duplex stainless steel additively manufactured by the laser powder bed fusion technique. *Metals* **13**(4), 725 (2023)
54. M. Knyazeva, M. Pohl, Duplex steels: part i: genesis, formation, structure. *Metallography, Microstructure, and Analysis* **2**, 113–121 (2013)
55. M. Knyazeva, M. Pohl, Duplex steels. part ii: carbides and nitrides. *Metallography, microstructure, and analysis*, 2 (5):343–351, 2013
56. R. Iva, G.S. acchi, C.L. Kugelmeier, IGR. Santos, A.A. endes Filho, DCC. Magalhães, CRM. Afonso, V.L. Sordi, CAD. Rovere, New insights into the hardening and pitting corrosion mechanisms of thermally aged duplex stainless steel at 475° c: a comparative study between 2205 and 2101 steels. *Journal of Materials Science & Technology*, 98: 123–135, 2022
57. K.W. Chan, S.C. Tjong, Effect of secondary phase precipitation on the corrosion behavior of duplex stainless steels. *Materials* **7**(7), 5268–5304 (2014)
58. N. Sathirachinda, R. Pettersson, S. Wessman, J. Pan, Study of nobility of chromium nitrides in isothermally aged duplex stainless steels by using skpfm and sem/eds. *Corros. Sci.* **52**(1), 179–186 (2010)
59. P.-C. Lin, Y.-T. Tsai, N.-H. Gan, J.-R. Yang, S.-H. Wang, H.-Y. Chang, T.-R. Lin, P.-K. Chiu, Characteristics of flakes stacked cr₂n with many domains in super duplex stainless steel. *Crystals* **10**(11), 965 (2020)
60. N. Pettersson, R.F.A. Pettersson, S. Wessman, Precipitation of chromium nitrides in the super duplex stainless steel 2507. *Metall. and Mater. Trans. A*. **46**(3), 1062–1072 (2015)
61. M.L. Gatto, A. Santoni, E. Santeccchia, S. Spigarelli, F. Fiori, P. Mengucci, M. Cabibbo, The potential of duplex stainless steel processed by laser powder bed fusion for biomedical applications: A review. *Metals* **13**(5), 949 (2023)
62. M.B. Mampuya, M.C. Umba, K. Mutombo, P.A. Olubambi, Effect of heat treatment on the microstructure of duplex stainless steel 2205. *Materials Today: Proceedings* **38**, 1107–1112 (2021)
63. V. Mahey, Processing duplex stainless steel via laser-and electric arc-based directed energy deposition to explore microstructure-property relationships (Iowa State University, 2025), (Master's thesis)
64. L. Reimann, Z. Brytan, G. Jania, Influence of filler metal on electrochemical characteristics of a laser-welded coermow alloy used in prosthodontics. *Materials* **15**(16), 5721 (2022)
65. A. Sangoi, F. Müller, M. Becker, Heat-treatment effects on corrosion of additively manufactured 316l stainless steel via eis. *Journal of Electrochemical Corrosion Science* **12**(1), 45–58 (2025)
66. D. Vladimir, Jović, Calculation of a pure double layer capacitance from a constant phase element in the impedance measurements. *Journal of Materials Protection* **63**(1), 50–57 (2022)

67. Bio-Logic Science Instruments. Application note #20. Application Note 20, Bio-Logic Science Instruments, Knoxville, TN, USA, 2019. URL www.biologic.net. Available online: www.biologic.net (accessed on 14 September 2025)
68. Y. Okazaki, Characterization of oxide film of implantable metals by electrochemical impedance spectroscopy. *Materials* **12**(21), 3466 (2019)
69. Y. Wang, W. Taibin, L. Che, G. Huang, Microstructure and recrystallization behavior of heating rate-controlled electrolytic capacitor aluminum foil under cold forming and annealing. *Materials* **16**(11), 4128 (2023)
70. Y. Gong, Q. Liu, H. Zhang, Cyclic polarization and localized corrosion behavior of lpbf-manufactured 316l stainless steel in chloride media. *Corros. Sci.* **243**, 112381 (2024). <https://doi.org/10.1016/j.corsci.2024.112381>
71. S. T. Ali, A. Riis, R. M. Larsen. (2024) Comparison of test methods for crevice corrosion propagation and repassivation potential of stainless steel AISI 316. *Mater. Sci. Eng. Int. J.* **8**(1), 9–13, <https://doi.org/10.15406/mseij.2024.08.009>
72. L. Zhang, Y. Chen, J. Li, Double effects of O_2 on passive film of super 13Cr stainless steel in CO_2 saturated environment. *Sci. Rep.* **15**, 1208 (2025). <https://doi.org/10.1038/s41598-025-01208-7>
73. J. Ibada et al., Data-driven prediction of overpotential and current density behavior in battery electrode systems. *Electrochim. Acta* **451**, 141016 (2023). <https://doi.org/10.1016/j.electacta.2023.141016>
- 74" GrobidStyleApplied="Changed. S. Pourrahimi, S. Hakimian, A.-H. Bouzid, L.A., Hof, On the use of machine learning algorithms to predict the corrosion behavior of stainless steels in lactic acid. *Metals* **13**(8), 1459 (2023)
75. F. Hou, H.-H. Wu, D. Zhu, J. Zhang, L. Hou, S. Wang, G. Wu, J. Gao, J. Ma, X. Mao, Interpretable material descriptors for critical pitting temperature in austenitic stainless steel via machine learning. *Npj Materials Degradation* **9**(1), 16 (2025)
76. S. Poudel, N. Moelans, R. Thapa, A. Timofiejczuk, D. Panthi, A. Kunwar, Unraveling elastochemical effects in microstructural evolution of Al-Cu-Ni system through DFT-informed multi-phase field simulations. *Int. J. Solids Struct.* **300**(112894), 8 (2024). <https://doi.org/10.1016/j.ijsolstr.2024.112894>
77. A. Kunwar, J. Hektor, S. Nomoto, Y.A. Coutinho, N. Moelans, Combining multi-phase field simulation with neural network analysis to unravel thermomigration accelerated growth behavior of Cu₆Sn₅ IMC at cold side Cu-Sn interface. *Int. J. Mech. Sci.* **184**, 105843 (2020). <https://doi.org/10.1016/j.ijmecsci.2020.105843>

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A.7 Publication VII [\[P-VII\]](#): Post-process heat treatment design for tunable strength and toughness in L-PBF 2507 super duplex stainless steel



Full length article

Post-process heat treatment design for tunable strength and toughness in L-PBF 2507 super duplex stainless steel

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Elastoplastic modeling

ABSTRACT

Laser powder bed fusion (LPBF) of 2507 super duplex stainless steel (SDSS) commonly produces ferrite-rich microstructures with high strength but limited plastic accommodation. This study defines a volumetric energy-density (VED)-based process window for LPBF 2507 and compares as-printed (AS), stress-relieved (SR), and solution-annealed (SA) conditions using microstructural characterization, mechanical testing, and finite-strain elastoplastic simulation. Near-full-density builds were obtained above approximately 160 J mm^{-3} . X-ray diffraction (XRD) confirmed ferrite-dominated AS and SR states and supported ferrite peak-broadening analysis, while electron backscatter diffraction (EBSD) quantified phase balance. AS and SR remained strongly ferritic, whereas, among the tested post-processing conditions, SA at $1100^\circ\text{C}/15 \text{ min}$ produced an approximately balanced ferrite–austenite phase constitution, with about 51% ferrite and 49% austenite. This transition reduced tensile strength from 1393 MPa in AS to 861 MPa in SA, but increased elongation from 1.15% to 12.57%. Finite-strain J_2 plasticity simulations showed that post-processing mainly modifies yield-stress level, strain localization, and plastic strain accumulation before instability.

1. Introduction

Laser powder bed fusion (LPBF) is increasingly used to fabricate metallic components that require geometric complexity together with reliable performance under thermo-mechanical and corrosive service conditions [1,2]. Super duplex stainless steel (SDSS) 2507 is a particularly relevant alloy for this context because its performance depends strongly on the ferrite–austenite phase balance. Under near-equilibrium conditions, SDSS combines a body-centered cubic (BCC) ferrite matrix, which contributes high strength and stress-corrosion resistance, with face-centered cubic (FCC) austenite, which improves ductility and fracture toughness [3,4]. This duplex synergy also supports the pitting and stress-corrosion resistance that distinguishes SDSS from conventional austenitic stainless steels such as 316L. The LPBF thermal cycle disrupts this equilibrium phase balance. High cooling rates and steep thermal gradients kinetically stabilize δ -ferrite and suppress the diffusional $\delta \rightarrow \gamma$ transformation [5,6]. Consequently, LPBF 2507 is usually ferrite-dominated in the as-built state, with only limited austenite at grain boundaries or as sparse intragranular Widmanstatten-like features [7,8]. This phase imbalance reduces the ductility and toughness normally expected from duplex design, even though strength remains

high [9,10]. The key challenge is therefore not to reproduce wrought duplex behavior directly after printing, but to determine whether post-processing can recover a useful balance between strength, ductility, and toughness.

Post-process heat treatment provides the main route for correcting the ferrite-rich LPBF microstructure. Low-temperature stress relief, typically near 300°C to 500°C , mainly reduces residual stress and partially recovers the dislocated ferritic substructure, with limited influence on phase balance [11,12]. High-temperature solution annealing, typically near 1040°C to 1100°C , promotes ferrite-to-austenite rebalancing and can dissolve deleterious secondary phases, although it also reduces strength [10,13]. The final response depends on the as-built defect state, the retained ferrite fraction, and the kinetics of austenite reformation during thermal exposure [14,15]. Despite the growing literature on LPBF duplex and super duplex stainless steels, three issues remain insufficiently connected. First, many studies optimize printing parameters without linking volumetric energy density (VED), porosity, and phase constitution in a single process map [4,16]. Second, mechanical characterization is often limited to hardness or tensile strength, with

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Table 1
Alloy chemistry of AISI 2507 powder, showing major and trace elements relevant to LPBF.

Element	Fe	Cr	Ni	Mo	Mn	Si	N	Cu	C	P	S	O
wt.%	Bal.	25	6.3	3.8	0.4	0.35	0.30	0.15	0.016	0.024	0.001	0.017

less emphasis on how heat treatment changes ductility and impact behavior. Third, computational models are commonly used to reproduce nominal stress–strain curves, but less often to compare strain localization and plastic accommodation across ferrite-rich and duplex-restored states [17–19]. A combined experimental–computational comparison is therefore needed to connect processing, phase constitution, and mechanical response in LPBF SDSS 2507.

This study addresses this gap by defining a VED-based process window for high-density LPBF 2507 and by comparing the microstructural and mechanical effects of three conditions: as-printed (AS), low-temperature stress-relieved (SR), and solution-annealed (SA). Finite-strain J_2 elastoplastic simulations are used to interpret the measured tensile response, strain localization, and necking behavior. The analysis is framed as a quantitatively anchored comparison of ferrite-rich AS/SR states and a duplex-rebalanced SA state produced from the same selected LPBF parameter set, with porosity screening, electron backscatter diffraction (EBSD) phase quantification, mechanical testing, and calibrated strain-localization analysis treated as one processing, structure, property chain.

2. Materials, processing, and characterization

2.1. Fabrication and testing

Gas-atomized super duplex stainless steel powder (UNS S32750/EN 1.4410, Osprey[®] AISI 2507 VIGA, Sandvik Osprey Ltd.) with the chemical composition listed in Table 1 was used in this study.

The powder exhibited a predominantly spherical morphology with a particle size distribution ranging from 15 to 53 μm (Fig. 1a, b). Laser powder bed fusion was carried out using an AM125 system (Renishaw, UK) equipped with a Yb-fiber laser ($\lambda = 1.074\mu\text{m}$, $P_{\text{max}} = 200\text{ W}$). Square specimens measuring $1.0\text{ cm} \times 1.0\text{ cm}$ were fabricated in an argon atmosphere with the oxygen level maintained below 10 ppm using a gas recirculation system. A commercially pure mild-steel substrate was used to promote initial bonding. A meander scanning strategy with 67° interlayer rotation was adopted to reduce systematic texture accumulation (Fig. 1c, d). Process parameters were varied over a broad volumetric energy density (VED) range, and base-plate preheating to 150°C was applied only to parameter sets P1–P6 (Fig. 3). The parameter matrix intentionally combines a broad VED range with explicitly identified preheated and non-preheated builds; therefore, the porosity results are discussed as a process-window map, with the preheating state retained as a separate processing descriptor.

Three thermal conditions were investigated: as-printed (AS), stress-relieved at 300°C for 5 h (SR) with furnace cooling, and solution-annealed at 1100°C for 15 min (SA) followed by water quenching. The SA condition was selected within the high-temperature solution-annealing range for duplex stainless steels to promote ferrite-to-austenite rebalancing while limiting unnecessary thermal exposure. The present comparison, therefore, evaluates one representative solution-treatment condition rather than a full heat-treatment optimization matrix.

Metallographic preparation consisted of sequential grinding with SiC abrasive papers (500–2000 grit), followed by polishing with diamond suspensions of 9, 3, and $1\mu\text{m}$ and final polishing with $0.04\mu\text{m}$ colloidal silica suspension. Microstructural characterization was first performed using light optical microscopy (LEICA MEF4 A) and scanning electron microscopy (Zeiss Supra 35) with energy-dispersive X-ray spectroscopy (EDS) capability to examine defect morphology and ferrite–austenite phase morphology. Electron backscatter diffraction (EBSD)

was then used to quantify phase balance and crystallographic-domain features. EBSD maps were acquired at 20 kV using a hexagonal grid with a step size of $0.4\mu\text{m}$. The corresponding row spacing was $0.346\mu\text{m}$, and the mapped field was approximately $220.0 \times 220.0\mu\text{m}^2$, giving an analyzed area of approximately $4.84 \times 10^4\mu\text{m}^2$. Quantitative ferrite–austenite phase fractions were therefore taken from the EBSD phase maps.

X-ray diffraction (XRD) was used as a complementary method for phase identification, peak-position comparison, and ferrite line-broadening analysis. XRD was performed with a step size of 0.05° and a counting time of 100 s per step, corresponding to an effective scan rate of $0.0005^\circ\text{ s}^{-1}$ ($0.03^\circ\text{ min}^{-1}$). Phase identification was performed using X'Pert HighScore Plus with Joint Committee on Powder Diffraction Standards (JCPDS) and Inorganic Crystal Structure Database (ICSD) reference databases. The weak austenite reflections in AS and SR were used as supporting qualitative diffraction evidence and interpreted together with EBSD phase mapping. For ferrite line-broadening analysis, full width at half maximum values were converted from degrees to radians before calculation, a Scherrer shape factor of $\kappa = 0.9$ was used, and the same peak-fitting protocol was applied to all conditions. The apparent ferrite crystallite size was estimated using $D = \kappa\lambda/(\beta \cos \theta)$, followed by $\delta = 1/D^2$ and $\epsilon = \beta/(4 \tan \theta)$ for the corresponding line-broadening-derived dislocation-density and microstrain indicators.

Mechanical testing was performed on horizontally oriented specimens (perpendicular to the build direction) using standardized procedures. Tensile properties were measured using flat dog-bone specimens (ISO 2740) on a Zwick Z100 universal testing machine at room temperature, in accordance with PN-EN-ISO 6892-1. Tensile testing followed PN-EN-ISO 6892-1 Method A at an initial strain rate of $2.5 \times 10^{-4}\text{ s}^{-1}$, corresponding to 0.45 mm min^{-1} for $L_0 = 30\text{ mm}$. The reported elongation values correspond to the specimen geometry shown in Fig. 9. Hardness was assessed using both Rockwell A measurements (Zwick ZHR 4150TK, ISO 6508, 60 kgf) and Vickers microhardness profiles ($\text{HV}_{0.1}$, ASTM E384, 100 gf). The Rockwell A measurements correspond to macrohardness on the top surface and polished cross-section, whereas $\text{HV}_{0.1}$ refers to cross-sectional microhardness. Impact testing used full-size unnotched Charpy-type bars ($55 \times 10 \times 10\text{ mm}^3$) on a machine verified according to PN-EN ISO 148-2. The specimens had the geometry shown in Fig. 1(f) and were tested using the same support span and impact configuration for all conditions. Because the specimens were full-sized and unnotched, the absorbed energies are reported as geometry-specific values for direct comparison among AS, SR, and SA and are not converted to V-notched Charpy energy. Complementary analysis included fractographic examination using a Phenom G2 XL scanning electron microscope and quantitative porosity analysis on metallographically prepared horizontal sections.

Porosity was determined by computer image analysis (Image Pro Plus 7.0) using 10 optical micrographs per condition. For each parameter set, porosity was evaluated from repeated fields of view and reported as mean values; the revised VED–porosity plot includes error bars and sample labels to show scatter and parameter identity. The solution-annealed specimens underwent ductile bending during impact testing, so SEM fractography was focused on the AS and SR specimens that produced analyzable fracture surfaces.

2.2. Feedstock crystallography and initial LPBF response

The super duplex stainless steel powder, grade 2507, exhibits a particle size distribution ranging from $16.85\mu\text{m}$ (D_{10}) to $53.83\mu\text{m}$ (D_{90}) with an average volume diameter of $31.42\mu\text{m}$ (Fig. 1b), where D_{10} ,

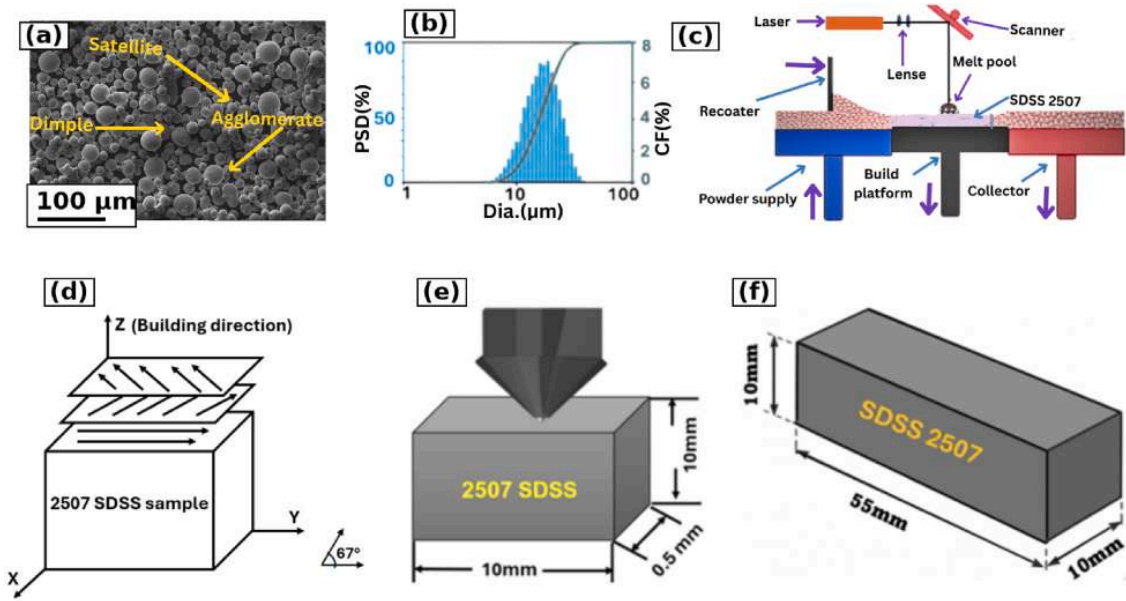


Fig. 1. Overview of feedstock characteristics, LPBF processing, and specimen geometries for SDSS 2507: (a) gas-atomized SDSS 2507 powder morphology; (b) particle size distribution ($D_{10} = 16.85 \mu\text{m}$, $D_{50} = 31.42 \mu\text{m}$, $D_{90} = 53.83 \mu\text{m}$); (c, d) LPBF process schematic with bidirectional scan strategy and 67° interlayer rotation along XY plane; (e) Vickers hardness specimen geometry; (f) unnotched Charpy specimen geometry.

D_{50} , and D_{90} represent the maximum particle diameters below which 10%, 50%, and 90% of the sample volume exists, respectively. Microstructural characterization shows that the gas-atomized powder is predominantly ferritic at room temperature, with thin austenite (γ) films along cellular/dendritic boundaries (Fig. 2). This microstructure results from primary δ/α solidification and rapid cooling during atomization, which suppresses ferrite $\rightarrow$ austenite transformation while allowing limited γ nucleation at chemically segregated boundaries [19].

EBSD analysis reveals predominantly equiaxed ferrite grains with a weak texture. Abundant low-angle boundaries (2° to 15°) are observed within the ferritic matrix, consistent with subgrain/dislocation-wall structures associated with rapid solidification and thermal contraction during LPBF. A continuous high-angle boundary network ($> 15^\circ$) defines the crystallographic grain boundaries. This behavior is consistent with LPBF-processed duplex stainless steels, where rapid solidification promotes ferrite-rich microstructures [5,20]. The solidified microstructure reflects the cooling rate-controlled $\delta \rightarrow \gamma$ transformation in duplex stainless steels [21]; ferrite forms first during cooling from the melt, while subsequent austenite nucleation is constrained by the high cooling rate, with morphology evolving from allotriomorphic to Widmanstätten/acicular forms as undercooling increases. The volumetric energy density (VED) was calculated as

$$V_{ED} = \frac{P}{vht}, \quad (1)$$

where P is the laser power in W, v is the scan speed in mm s^{-1} , h is the hatch spacing in mm, and t is the layer thickness in mm. With these units, V_{ED} is obtained in J mm^{-3} . Hatch spacing and layer thickness values expressed in micrometers were converted to millimeters before calculation.

The calculated values in Table 2 were verified by direct substitution into Eq. (1). Scan speeds are reported to two decimal places where needed to preserve consistency between the displayed process parameters and the corresponding rounded VED values.

Pore morphology was strongly dependent on the applied process window. At low energy density, porosity was dominated by large irregular lack-of-fusion defects and partially fused regions, as illustrated

Table 2

LPBF process-parameter matrix and calculated volumetric energy density for SDSS 2507.

Sample	P (W)	v (mm s^{-1})	h (mm)	t (mm)	V_{ED} (J mm^{-3})
P1	200	300.00	0.100	0.030	222.22
P2	190	300.00	0.100	0.030	211.11
P3	180	300.00	0.100	0.030	200.00
P4	170	300.00	0.100	0.030	188.89
P5	160	300.00	0.100	0.030	177.78
P6	150	300.00	0.100	0.030	166.67
A1	180	250.00	0.120	0.030	200.00
A2	180	300.00	0.120	0.030	166.67
A3	180	375.00	0.120	0.030	133.33
A4	180	500.00	0.120	0.030	100.00
B1	180	391.67	0.120	0.030	127.66
B2	180	470.00	0.120	0.030	106.38
B3	180	587.50	0.120	0.030	85.11
B4	180	783.33	0.120	0.030	63.83
C1	180	525.00	0.120	0.030	95.24
C2	180	630.00	0.120	0.030	79.37
C3	180	787.50	0.120	0.030	63.49
C4	180	1050.00	0.120	0.030	47.62
D1	180	666.67	0.120	0.030	75.00
D2	180	800.00	0.120	0.030	62.50
D3	180	1000.00	0.120	0.030	50.00
D4	180	1333.33	0.120	0.030	37.50

for the lower-VED parameter combinations in Fig. 3b. With increasing VED, incomplete-melting-induced porosity decreased, consistent with improved melt-pool overlap and consolidation [12]. A smaller population of nearly spherical pores, attributed to gas entrapment during melting or gas inherited from feedstock particles, remained morphologically distinct from the irregular lack-of-fusion defects [12, 19].

Because the present parameter matrix was designed to identify a practical low-porosity processing window, Fig. 4 is interpreted as a process-window screening map. The preheated P1–P6 series and

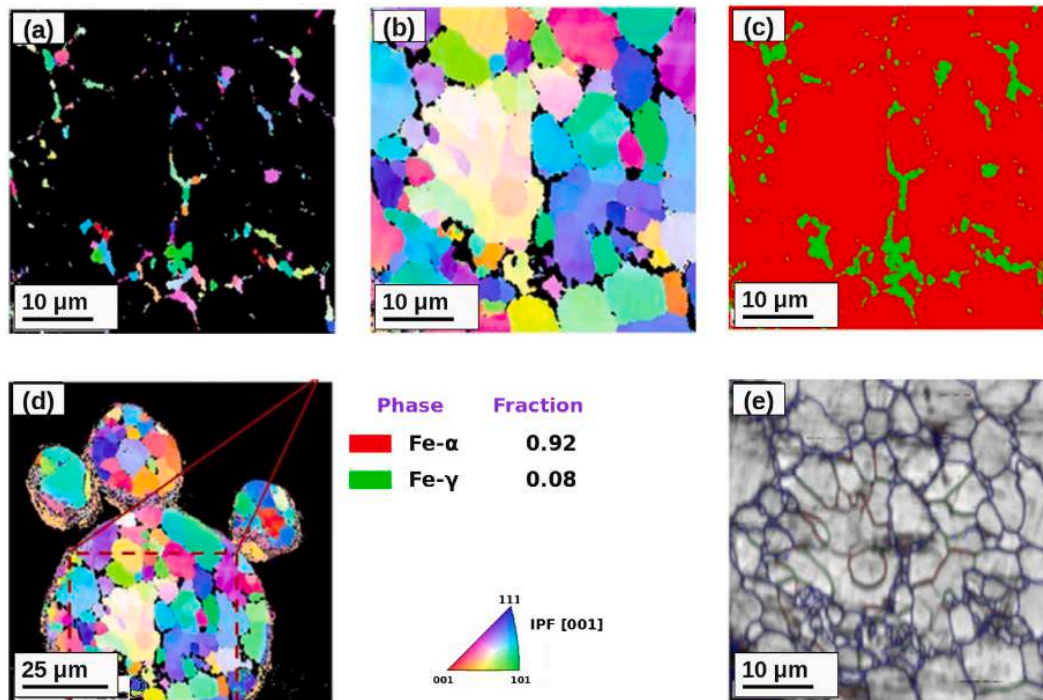


Fig. 2. EBSD crystallographic characterization of SDSS 2507 powder feedstock: (a) austenite phase IPF map, (b) ferrite phase IPF map, and (c) phase distribution map (ferrite: red; austenite: green). (d) Combined IPF map showing microstructural morphology with crystallographic orientation key, and (e) grain-boundary map with misorientation classification: 2° to 5° (red), 5° to 15° (green), and 15° to 180° (blue). Total boundaries analyzed: 15044 with cumulative boundary length of 1.56 mm for misorientations above 2°.

the non-preheated A–D series are plotted as distinct subsets in Fig. 4. The fitted curve is used as a descriptive guide to summarize the observed densification trend across the explored parameter space. Near-full densification was defined operationally as a mean porosity of ≤ 1.0 area%, measured by optical image analysis on repeated metallographic fields. The 0.5 area% line in Fig. 4 is used as a stricter low-porosity guide. These thresholds provide practical criteria for selecting a robust LPBF parameter set for subsequent microstructural and mechanical evaluation.

The processing condition selected for subsequent study, shown within the low-porosity region in Fig. 4, used laser power $P = 180$ W, hatch spacing $h = 120 \mu\text{m}$ (0.120 mm), layer thickness $t = 30 \mu\text{m}$ (0.030 mm), and scan speed $v = 300 \text{ mm s}^{-1}$. Direct substitution into Eq. (1) gives

$$V_{\text{ED}} = \frac{180}{300 \times 0.120 \times 0.030} = 166.67 \text{ J mm}^{-3}.$$

2.3. Phase evolution from XRD and SEM

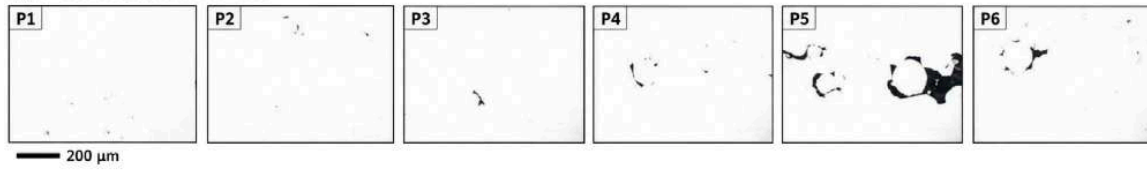
X-ray diffraction shows a strong dependence of phase constitution on post-process thermal history in LPBF-processed SDSS 2507 (Fig. 5). In the as-printed condition, the diffraction pattern is dominated by ferritic reflections, with strong Fe-α (110), (200), and (211) peaks, whereas the austenite contribution is weak. This response is consistent with rapid solidification during LPBF, which suppresses diffusion-controlled austenite formation and stabilizes a ferrite-rich metastable microstructure [10]. Heat treatment changes the diffraction response. Stress relief at 300 °C for 5 h preserves the ferrite-dominated phase constitution while promoting partial recovery of the as-built defect structure. Only weak austenite-related diffraction features are detected in the ferrite-rich AS and SR states. For this reason, the AS/SR austenite

contents are quantified from EBSD phase maps, while XRD is used primarily for qualitative phase identification, peak-position comparison, and ferrite peak-broadening analysis. In contrast, solution annealing at 1100 °C for 15 min produces substantially stronger γ reflections, including (111), (200), (220), (311), and (222), together with reduced relative ferrite peak intensity, consistent with marked phase rebalancing toward a duplex microstructure [16].

Quantitative analysis of the ferrite reflections (Table 3) shows progressive peak sharpening from the AS/SR conditions to the SA condition, as indicated by lower mean full width at half maximum values. The present diffraction analysis evolution supports reduced ferrite line broadening after high-temperature treatment and is consistent with recovery of microstrain, reduction in stored defect density, and an increase in apparent ferritic crystallite size [22–24]. The derived crystallite size, dislocation-density, and microstrain values are therefore reported as ferrite line-broadening metrics that complement the EBSD-based phase and microstructural analysis. The austenite response is evaluated through the EBSD phase maps and the stronger SA austenite reflections, providing a consistent two-phase comparison across the AS, SR, and SA conditions. Phase-fraction assessment is reported from EBSD, while XRD is used to support phase identification, peak-position comparison, and ferrite line-broadening analysis.

Scanning electron microscopy further clarifies the morphological consequences of this phase evolution (Fig. 6). The as-printed microstructure (Fig. 6(a, b)) consists primarily of irregular ferritic grains aligned preferentially along the build direction, with a bimodal morphology comprising finer equiaxed regions (5 μm to 20 μm) and elongated grains extending to approximately 50 μm to 70 μm. Columnar growth is evident near melt-pool boundaries, while the fine-scale architecture is dominated by cellular or dendritic substructure. Austenite is limited and appears mainly at prior ferrite grain boundaries and triple junctions as grain-boundary allotriomorphic constituents [5,

(a) P-series parameter set



(b) A–D parameter series

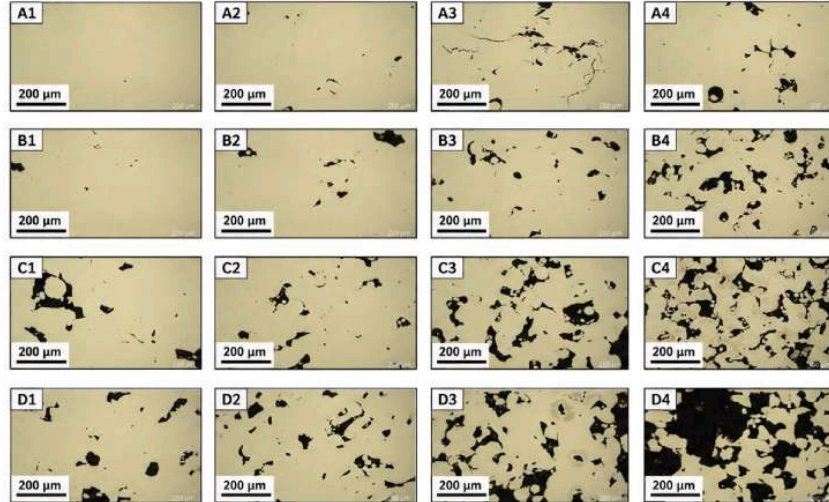


Fig. 3. Optical micrographs of LPBF-fabricated SDSS 2507 obtained under different printing parameters: (a) specimens fabricated using the P1–P6 parameter set, corresponding to the preheated screening subset; and (b) specimens fabricated using the A1–A4, B1–B4, C1–C4, and D1–D4 parameter sets. The micrographs show the evolution of defect population and morphology across the explored process window. Low-energy-density conditions contain more irregular lack-of-fusion and partially fused regions, whereas higher-energy-density conditions show reduced defect severity and transition toward a low-porosity regime.

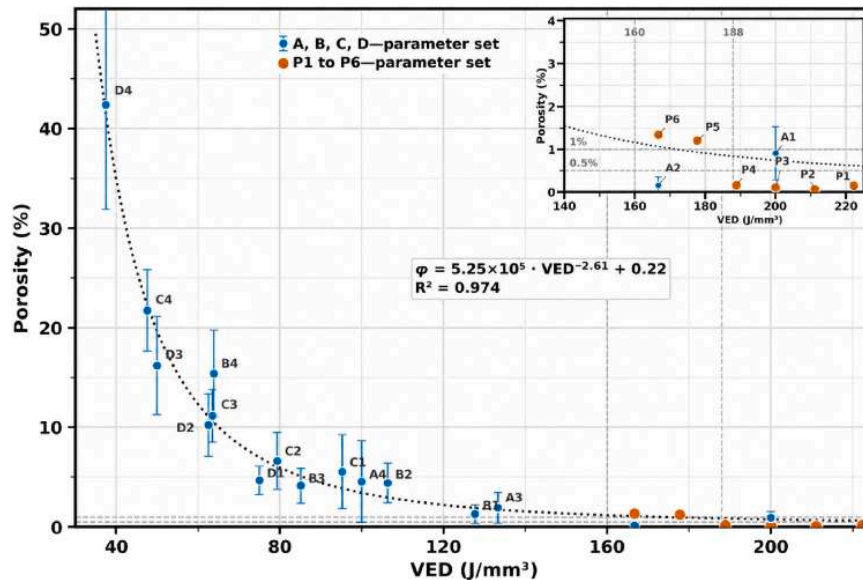


Fig. 4. VED–porosity map for LPBF SDSS 2507. Error bars are shown where repeated image-analysis fields were available in the plotted dataset; P1–P6 are retained as the preheated screening subset, while A–D represent the non-preheated parameter sets. The dotted line is a descriptive empirical inverse power-law fit, $\phi = 5.25 \times 10^5 V_{ED}^{-2.61} + 0.22$, with $R^2 = 0.974$, where ϕ is porosity in area percent. The horizontal lines at 1.0 percent and 0.5 percent mark near-full-density and low-porosity guides; vertical lines at approximately 160 and 188 $J\ mm^{-3}$ mark the corresponding high-VED regime. The fit summarizes the densification trend across the screened parameter space and is used as a practical guide for process-window selection.

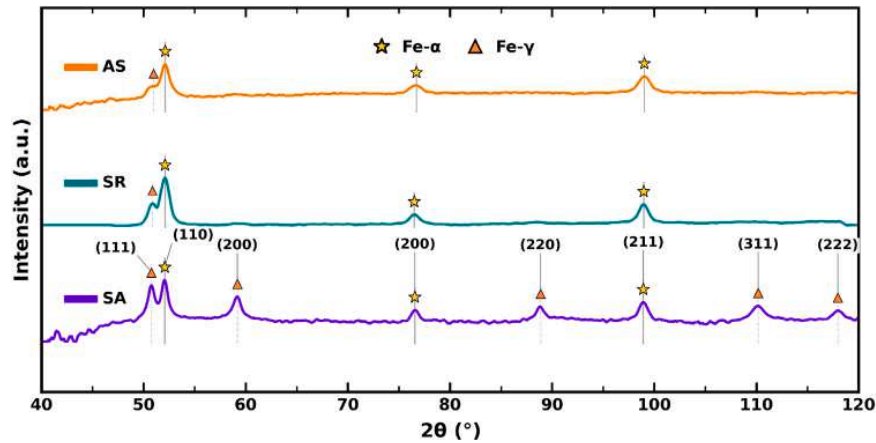


Fig. 5. XRD patterns of LPBF SDSS 2507 in the AS, SR, and SA heat-treated conditions, used for qualitative phase identification and peak-position comparison. AS and SR show dominant Fe- α reflections, whereas SA exhibits clearly resolved Fe- γ reflections in addition to Fe- α , indicating phase rebalancing toward a duplex ferrite-austenite constitution.

Table 3

Ferrite-phase XRD peak-position and line-broadening parameters for LPBF-processed SDSS 2507. The 2θ peak positions and full width at half maximum (FWHM) values, β , were extracted from the Fe- α (110), (200), and (211) reflections. The arithmetic mean FWHM, $\bar{\beta}$, was used as the line-broadening input to estimate the apparent crystallite size (D), dislocation density (δ), and microstrain (ϵ).

Condition	2θ (°)			FWHM, β (°)			$\bar{\beta}$ (°)	D (nm)	δ (10^{-3} nm^{-2})	ϵ (10^{-3})
	110	200	211	110	200	211				
AS	52.10	76.64	99.02	0.50	1.24	0.95	0.90	12.16	7.85	5.21
SR	52.05	76.51	98.95	0.50	1.27	0.87	0.85	13.06	7.07	4.94
SA	52.05	76.58	98.92	0.37	0.75	0.76	0.63	20.44	2.78	3.46

9]. Phase labels in the SEM micrographs are assigned using correlative EBSD phase mapping and XRD phase identification, while etched SEM contrast provides the morphological context for interpreting phase distribution. Solution annealing (Fig. 6(c, d)) produces a marked microstructural reconfiguration. The ferrite fraction is reduced, and austenite is distributed more extensively throughout the microstructure as intergranular and intragranular Widmanstätten-like morphologies. The resulting structure is more spatially balanced than in the as-built condition and is consistent with the stronger Fe- γ reflections observed by XRD in Fig. 5. At the present evidence level, the effect of solution treatment is most appropriately interpreted as phase rebalancing accompanied by recovery of the highly constrained ferritic cellular structure [25].

2.4. EBSD-based phase balance and boundary analysis

EBSD analysis confirms that the microstructure of LPBF-processed SDSS 2507 is strongly dependent on post-process thermal history, as shown in Fig. 7. The phase maps resolve the ferrite-austenite balance in each analyzed field, while the inverse pole figure (IPF) maps and boundary statistics capture the corresponding evolution in reconstructed crystallographic domains and boundary character. Reported size values are EBSD-reconstructed crystallographic domain sizes obtained using a grain tolerance angle of two degrees. They describe crystallographic domains or subgrains resolved by EBSD and can therefore differ from the larger morphological features visible in SEM. Throughout this analysis, these values are referred to as reconstructed crystallographic domain size or EBSD-reconstructed grain/domain size, rather than direct SEM grain size. The EBSD analysis was performed on

selected representative fields with a defined scan area, step size, and reconstruction protocol. The resulting phase fractions, reconstructed crystallographic domain sizes, and boundary fractions provide field-level quantitative estimates for direct comparison among the AS, SR, and SA conditions.

In the as-printed condition, the analyzed field is strongly ferritic (Fe- $\alpha \approx 96.4\%$, Fe- $\gamma \approx 3.6\%$) and predominantly consists of primary δ -ferrite with a fine reconstructed crystallographic domain structure. The average EBSD-reconstructed grain/domain size is approximately $1.6 \mu\text{m}$. As shown in Fig. 7(d), the IPF map reveals elongated ferritic domains together with a dense population of low-angle grain boundaries (LAGBs; 2° – 15°), whereas high-angle grain boundaries (HAGBs; $>15^\circ$) form a comparatively lower-fraction network. The phase-specific reconstructed crystallographic domain sizes indicate a bimodal distribution, with average reconstructed sizes of approximately $0.8 \mu\text{m}$ for γ -Fe and $2.3 \mu\text{m}$ for α -Fe. After stress relief at 300°C for 5 h, the analyzed field remains ferrite-dominated (Fe- $\alpha \approx 99.5\%$, Fe- $\gamma \approx 0.5\%$). Because the γ fraction is very small in both AS and SR, the AS–SR comparison is reported as a field-level EBSD trend and interpreted within the context of field selection, indexing quality, and phase-cleanup parameters. The average EBSD-reconstructed grain/domain size increases to approximately $4.0 \mu\text{m}$, with reconstructed α -Fe and γ -Fe sizes of about $7.7 \mu\text{m}$ and $0.8 \mu\text{m}$, respectively. This increase is consistent with recovery processes, including dislocation rearrangement, subgrain coalescence, and refinement of the low-angle boundary network under the adopted reconstruction criterion.

Substantial microstructural rebalancing occurs after solution annealing at 1100°C for 15 min, where the analyzed field shows a near-balanced duplex structure (Fe- $\alpha \approx 50.98\%$, Fe- $\gamma \approx 49.07\%$). In this

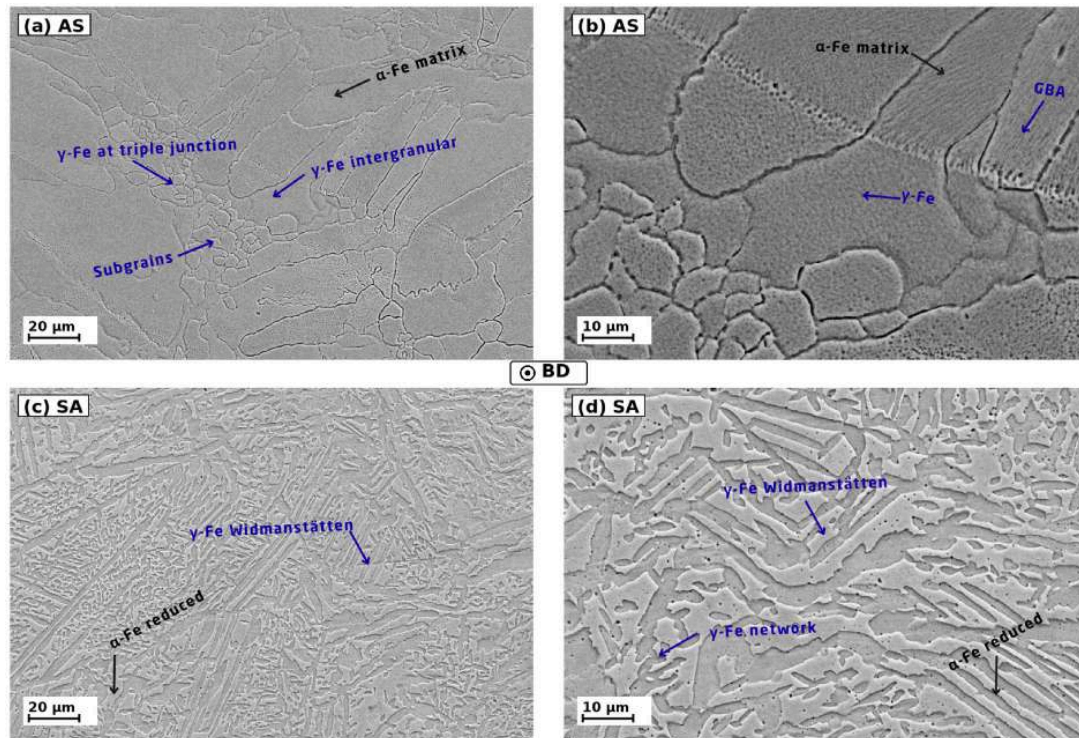


Fig. 6. SEM micrographs of LPBF-built 2507 SDSS acquired on horizontal sections, i.e., the XY plane perpendicular to the build direction (BD ⊙, out of the image plane): (a, b) AS and (c, d) SA. The micrographs show the ferrite-dominated cellular/dendritic morphology in the AS condition and the more spatially balanced ferrite–austenite morphology after solution annealing. Phase interpretation combines EBSD phase mapping, XRD phase identification, and etched SEM morphology.

condition, austenite is distributed more extensively within the ferritic matrix, including Widmanstätten-like morphologies visible in Fig. 7(f). The reconstructed phase-specific crystallographic domain sizes are approximately 3.5 μm for $\alpha\text{-Fe}$ and 2.1 μm for $\gamma\text{-Fe}$, with an overall EBSD-reconstructed grain/domain size of about 2.3 μm . Relative to AS and SR, the SA condition exhibits a larger HAGB fraction and a substantially more balanced ferrite–austenite phase constitution. The higher HAGB fraction and more continuous austenite distribution provide a microstructural basis for more distributed plastic accommodation, consistent with the improved elongation, reduction in area, and impact-energy absorption. Quantitative comparison of Figs. 7(a)–(c) and 7(g) shows that the analyzed AS and SR regions are ferrite-dominated and rich in LAGBs, whereas the analyzed SA region shows an approximately balanced duplex phase constitution with a more extensive HAGB network. Within the examined AS, SR, and SA conditions, the EBSD results show that low-temperature stress relief promotes recovery of the ferritic as-built structure, whereas solution annealing produces an approximately balanced duplex microstructure in the analyzed field [26].

3. Mechanical response and elastoplastic interpretation

3.1. Hardness, tensile response, and impact behavior

The hardness response was first evaluated to establish how post-processing changed the near-surface and cross-sectional mechanical state of LPBF-manufactured SDSS 2507. Rockwell A hardness was measured on both the top surface and polished cross-section, whereas $\text{HV}_{0.1}$

was measured on the polished cross-section. The numerical values are summarized in Table 4, and the corresponding trends are shown in Fig. 8(a, b).

The as-printed (AS) condition exhibited the highest hardness response, with Rockwell A hardness values of 70.60 ± 2.30 HRA on the surface and 72.22 ± 1.21 HRA on the cross-section. The corresponding cross-sectional microhardness was 511.31 ± 29.74 $\text{HV}_{0.1}$. After stress relief (SR), the hardness decreased only slightly, giving 69.16 ± 2.30 HRA on the surface, 69.92 ± 1.53 HRA on the cross-section, and 496.19 ± 45.85 $\text{HV}_{0.1}$. In contrast, solution annealing (SA) produced the dominant hardness reduction, lowering the Rockwell hardness to 63.58 ± 1.27 HRA on the surface and 60.48 ± 2.49 HRA on the cross-section, with a cross-sectional microhardness of 358.35 ± 53.07 $\text{HV}_{0.1}$. The AS–SR difference is small relative to the measured scatter and indentation scale, indicating that low-temperature stress relief preserves much of the ferrite-dominated high-hardness state. The clearest trend is the pronounced softening after SA. This response is consistent with the transition from a ferrite-dominated LPBF microstructure containing fine cellular/subgrain features to a more balanced duplex structure after solution annealing [15,16,27].

The tensile and impact response was then evaluated to determine whether the hardness trends translated into broader changes in strength, ductility, and absorbed-energy capacity. Fig. 9(b–d) shows the engineering stress–strain curves for the AS, SA, and SR conditions, together with the calibrated finite-element-model (FEM) responses up to the onset of necking. The corresponding tensile and impact properties are summarized in Table 5.

The as-printed (AS) condition showed the highest tensile strength, with a yield strength of 1211 ± 108 MPa and an ultimate tensile strength

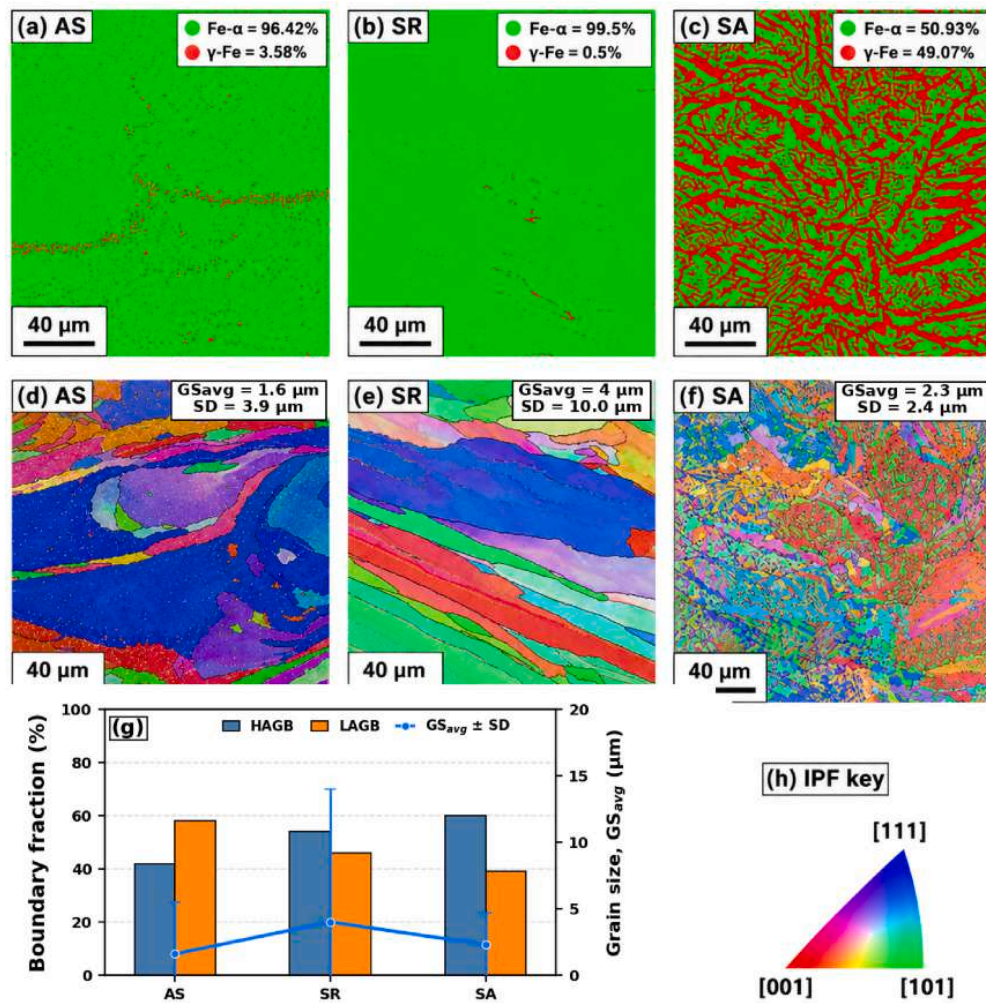


Fig. 7. EBSD maps of LPBF 2507 SDSS on horizontal sections (XY plane, perpendicular to the build direction): (a–c) phase maps for AS, SR, and SA; (d–f) corresponding IPF maps; (g) HAGB fraction, LAGB fraction, EBSD-reconstructed grain/domain size, and orientation concentration relative to the build direction. The EBSD values provide field-level quantitative estimates from selected representative maps and enable consistent comparison of the analyzed AS, SR, and SA regions.

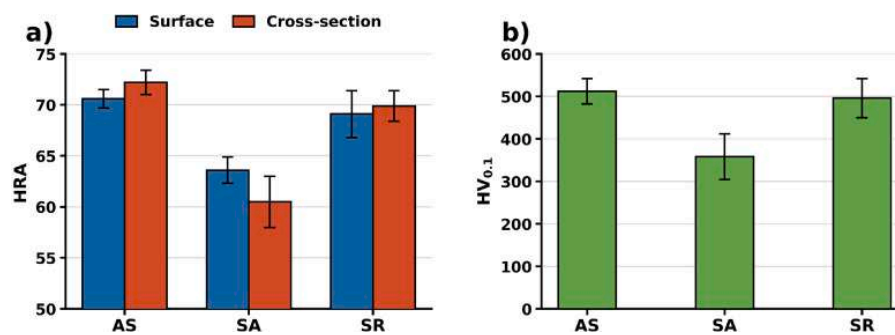


Fig. 8. Hardness response of LPBF-manufactured SDSS 2507 measured along the XY plane under different post-processing conditions: (a) Rockwell A hardness measured on the top surface and polished cross-section of AS, SR, and SA specimens; and (b) cross-sectional Vickers microhardness, $HV_{0.1}$. Solution annealing produces the strongest hardness reduction, whereas the AS and SR conditions retain comparatively high hardness.

Table 4

Hardness of LPBF-processed SDSS 2507 under different post-processing conditions. Rockwell A hardness was measured on both the top surface and polished cross-section, while Vickers microhardness was measured on the polished cross-section using an $HV_{0.1}$ load. Values are reported as mean $\pm$ standard deviation.

Condition	Rockwell A hardness (HRA)		Vickers microhardness
	Surface	Cross-section	$HV_{0.1}$, cross-section
AS	70.60 $\pm$ 2.30	72.22 $\pm$ 1.21	511.31 $\pm$ 29.74
SR	69.16 $\pm$ 2.30	69.92 $\pm$ 1.53	496.19 $\pm$ 45.85
SA	63.58 $\pm$ 1.27	60.48 $\pm$ 2.49	358.35 $\pm$ 53.07

Table 5

Tensile and impact properties of LPBF SDSS 2507 in the AS, SR, and SA conditions. Values are mean $\pm$ standard deviation where applicable. EL, A, denotes total elongation after fracture. E_{app} denotes the apparent tensile modulus extracted from the initial linear region of the engineering stress-strain curves and used for model calibration.

Sample	YS (0.2%) [MPa]	UTS [MPa]	E_{app} [GPa]	EL, A [%]	RA [%]	Impact energy [J]
AS	1211 $\pm$ 108	1393 $\pm$ 5	172	1.15 $\pm$ 0.07	2.35 $\pm$ 0.52	103 $\pm$ 26.67
SR	1082 $\pm$ 162	1350 $\pm$ 8	188	1.50 $\pm$ 0.31	3.18 $\pm$ 0.73	122.5 $\pm$ 38.89
SA	506 $\pm$ 75	861 $\pm$ 3	150	12.57 $\pm$ 0.34	27.25 $\pm$ 0.96	$\geq$ 450

of 1393 $\pm$ 5 MPa, but the deformation capacity was limited, with total elongation of only 1.15 $\pm$ 0.07% and reduction in area of 2.35 $\pm$ 0.52%. Stress relief (SR) preserved a broadly similar high-strength response, with 1082 $\pm$ 162 MPa yield strength and 1350 $\pm$ 8 MPa ultimate tensile strength, while producing only a modest increase in elongation and reduction in area. Thus, SR remains mechanically close to AS and is best interpreted as a recovery-dominated reference state rather than as a treatment that restores a balanced duplex mechanical response [16,28].

In contrast, solution annealing (SA) produced the dominant mechanical transition in the present study. The yield strength decreased to 506 $\pm$ 75 MPa and the ultimate tensile strength to 861 $\pm$ 3 MPa, while the total elongation increased to 12.57 $\pm$ 0.34% and the reduction in area increased to 27.25 $\pm$ 0.96%. The reduction in area therefore follows the same hierarchy as elongation, increasing from AS to SR and then markedly after SA. This response is consistent with the microstructural transition from a strongly ferritic, defect-rich as-built state to a more spatially balanced duplex structure after solution annealing.

The impact response follows the same hierarchy. AS and SR absorbed 103 $\pm$ 26.67 J and 122.5 $\pm$ 38.89 J, respectively, whereas the SA specimens exceeded the fracture capacity available under the full-size unnotched Charpy configuration used here. The absorbed energy is therefore reported as $\geq$ 450 J and treated as a geometry-specific impact response for this test configuration.

3.2. Finite-strain elastoplastic model

The mechanical response of SDSS 2507 was modeled using a finite-strain, total-Lagrangian framework. Mechanical equilibrium was enforced as

$$\nabla_0 \cdot \mathbf{P} + \mathbf{b}_0 = \mathbf{0}, \quad (2)$$

where $\mathbf{P}$ is the first Piola–Kirchhoff stress and body forces ($\mathbf{b}_0$) are neglected. The deformation gradient is $\mathbf{F} = \nabla \chi$, and the multiplicative split $\mathbf{F} = \mathbf{F}_e \mathbf{F}_p$ separates elastic and plastic deformation. Plastic flow is assumed to be isochoric ($\det \mathbf{F}_p = 1$). The elastic response was assumed isotropic, using the calibrated apparent tensile modulus E_{app} and Poisson's ratio ν . Plastic yielding followed a J_2 von Mises criterion expressed in terms of the Kirchhoff stress $\boldsymbol{\tau}$ [29]. Stress updates and internal-variable evolution were computed using a fully implicit return-mapping algorithm in the Simo–Hughes formulation. The flow stress was represented by the following saturation-type hardening law [30]:

$$\sigma_y(\bar{\epsilon}_p) = \sigma_p + (\sigma_u - \sigma_p) [1 - \exp(-c_1 \bar{\epsilon}_p)] (1 + c_2 \bar{\epsilon}_p), \quad (3)$$

where $\bar{\epsilon}_p$ is the equivalent plastic strain, σ_p is the initial yield stress, σ_u is the saturation stress, and c_1 and c_2 are fitted hardening coefficients.

For the three sample conditions (AS, SA, SR), the fitted values are $c_1 = \{640, 120, 640\}$ and $c_2 = \{7, 5.6, 5\}$, respectively. These coefficients are phenomenological calibration parameters. They describe the fitted hardening-curve shape and should not be interpreted as unique microstructural constants. This hardening law captures the rapid initial strengthening followed by the gradual approach to saturation that is characteristic of the calibrated experimental curves. For further details on the computational framework for finite-strain elastoplasticity, refer to Neupane et al. [31].

The model was implemented in the MOOSE finite-element framework under plane-stress assumptions to represent the thin tensile specimens [32]. The displacement components u_x and u_y were used as primary variables. The left boundary was fixed in both directions, and tensile loading was applied on the right boundary as a traction calculated from a time-ramped total force:

$$F(t) = \begin{cases} F_{\max} t/t_{\text{end}}, & t < t_{\text{end}}, \\ F_{\max}, & t \geq t_{\text{end}}, \end{cases} \quad t_x(t) = \frac{F(t)}{A_0}, \quad (4)$$

with $F_{\max} = 24$ kN, $t_{\text{end}} = 200$ s, and $A_0 = 18$ mm² the initial gauge area. Transient simulations used a Newton–Raphson solver with hypr BoomerAMG preconditioning. Key solver and time-stepping settings were a relative nonlinear tolerance of 10^{-6} , an absolute nonlinear tolerance of 10^{-8} , and adaptive time stepping with an initial $\Delta t = 0.5$ s. Element-average and extreme-value postprocessors monitored stress, strain, and equivalent plastic strain in the gauge region; reaction forces were obtained by nodal summation on the fixed boundary. Within this calibrated plane-stress framework, the simulated fields are used to interpret localization and plastic accommodation up to instability.

3.3. Strain localization and plastic accommodation

The finite-strain J_2 plasticity simulations connect the experimental stress–strain response (Fig. 9) with the simulated stress and strain-partitioning fields (Fig. 10). Consistent with the elastoplastic framework in Section 3.2, the calibrated FEM comparison resolves the evolution of von Mises stress, equivalent plastic strain, and the decomposition of macroscopic strain into elastic (ϵ_e) and plastic (ϵ_p) components during uniaxial loading. This comparison clarifies how the AS, SR, and SA conditions differ not only in strength level, but also in the spatial distribution and magnitude of plastic deformation before instability.

In the AS condition (Fig. 10(a)), the calibrated FEM comparison indicates rapid strain localization after yielding. Plastic strain begins to concentrate at approximately $t = 82$ s, and the specimen reaches instability by about $t = 120$ s. At this stage, only a small amount

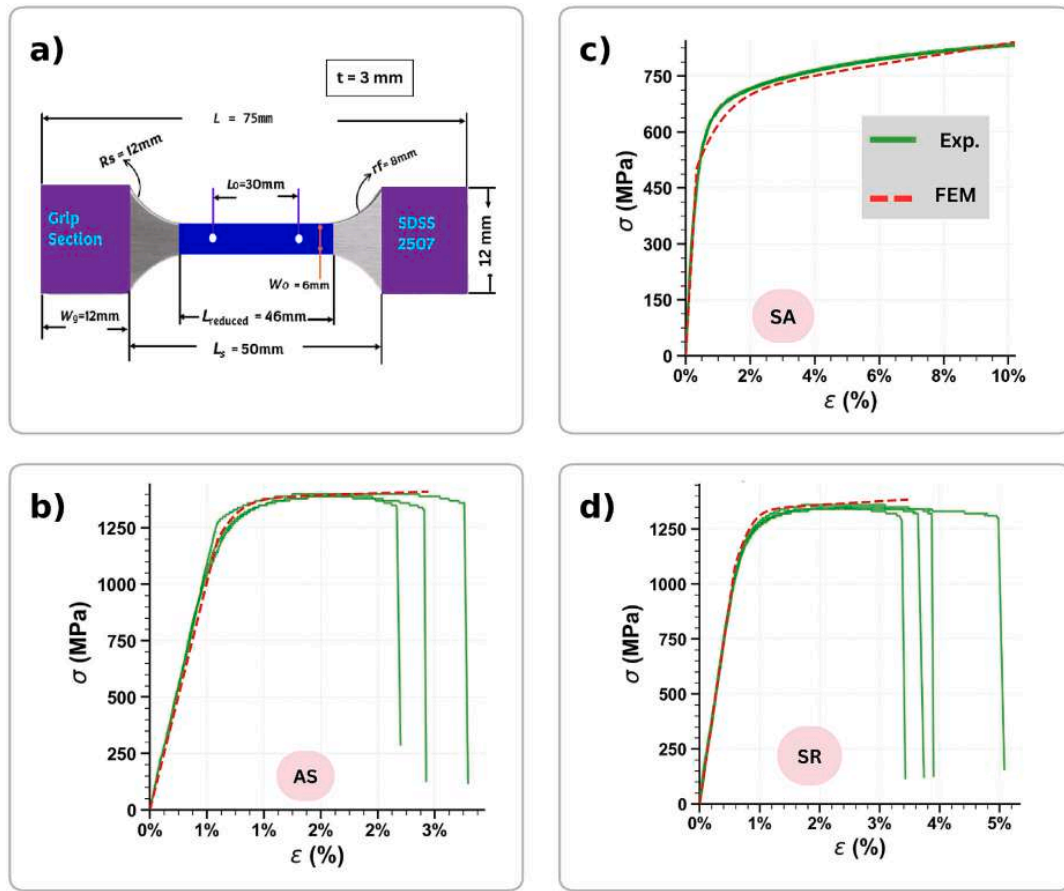


Fig. 9. Geometry and tensile response along the XY plane in different post-processing conditions: (a) schematic of the flat dog-bone tensile specimen with thickness $t = 3$ mm; (b–d) engineering stress–strain curves for the AS, SA, and SR conditions, comparing experimental measurements (Exp.) with calibrated finite-element-model (FEM) simulations up to the onset of necking.

of plastic strain is accumulated ($\epsilon_p \approx 3.4 \times 10^{-3}$), while the elastic component remains comparable in magnitude ($\epsilon_e \approx 8.1 \times 10^{-3}$). This limited plastic accommodation is consistent with the low elongation and reduction in area reported in Table 5. The simulated localization pattern is also consistent with the ferrite-rich microstructure, where plastic flow is comparatively confined.

The SA condition shows a distinctly different deformation mode (Fig. 10(b)). Plasticity starts at a lower stress level, but it spreads over a broader region of the gauge section instead of concentrating rapidly into a narrow localization band. At the final simulated stage, the plastic strain component reaches approximately $\epsilon_p \approx 0.120$, whereas the elastic contribution remains small ($\epsilon_e \approx 5.7 \times 10^{-3}$). The calibrated FEM comparison indicates that the improved tensile ductility and impact-energy absorption of SA are consistent with sustained plastic deformation rather than elastic stretching. The more balanced ferrite–austenite structure and the wider plastic zone therefore provide a coherent explanation for the higher elongation, reduction in area, and absorbed energy.

The SR condition remains closer to AS than to SA, but the calibrated FEM comparison indicates a modest improvement in plastic accommodation (Fig. 10(c)). Plastic strain develops later than in SA and remains more localized, yet the plastic zone is slightly more extended than in the AS specimen. At the final simulated stage, the plastic component

reaches approximately $\epsilon_p \approx 7.8 \times 10^{-3}$, which is higher than in AS but far below that of SA. This behavior is consistent with stress relief acting mainly through recovery of the ferritic as-built substructure rather than through restoration of a balanced duplex phase constitution. The higher effective initial slope used for SR is treated as a calibration value obtained from the measured tensile response.

Overall, the calibrated FEM comparison indicates that heat treatment modifies three linked features of the response: the yield-stress scale, the spatial distribution of plastic strain, and the amount of plastic strain accumulated before instability. AS and SR retain high stress-bearing capacity with comparatively concentrated plasticity, whereas SA enables broader and more sustained plastic flow, providing a coherent explanation for the improved ductility and geometry-specific impact-energy response. These simulated fields are therefore interpreted as calibrated localization and plastic-accommodation comparisons up to instability.

3.4. Fractography of ferrite-rich states

Fractographic analysis focused on the as-printed (AS) and stress-relieved (SR) conditions, which produced fracture surfaces suitable for SEM observation after Charpy impact testing. The solution-annealed (SA) specimens showed extensive ductile bending under the full-size

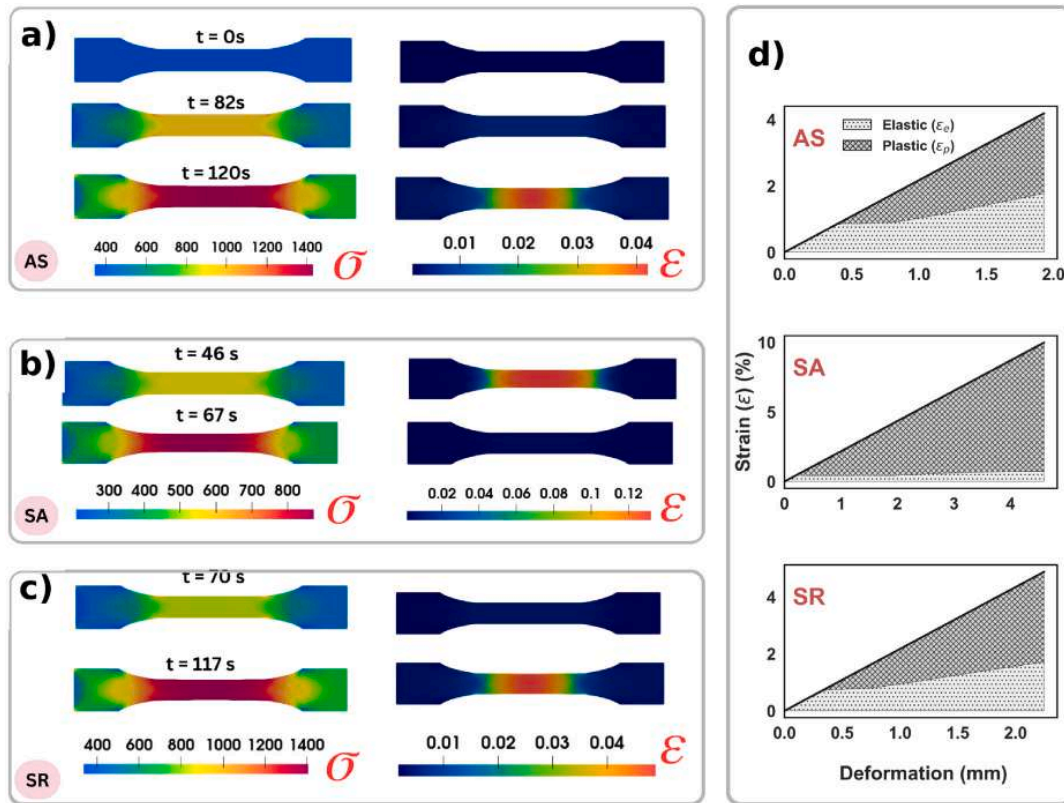


Fig. 10. (a) Evolution of von Mises stress, σ , and equivalent plastic strain, ϵ , in the AS specimen at selected loading times, highlighting early strain localization and rapid neck formation. (b) Corresponding fields for the SA condition, indicating reduced stress levels and a broader plastic zone consistent with enhanced ductility. (c) Stress and plastic-strain distributions in the SR specimen, where high stress-bearing capacity is preserved while strain localization is delayed relative to the AS state. (d) Decomposition of total strain into elastic (ϵ_e) and plastic (ϵ_p) components.

unnotched Charpy configuration. The SA response is therefore evaluated through complementary evidence from phase balance, tensile ductility, geometry-specific absorbed energy, and simulated plastic-strain distribution.

The AS fracture surface (Fig. 11(a, b)) is coarse and irregular, with pores, lack-of-fusion (LOF) defects, and crack-like features. The dominant defects are irregular LOF cavities and partially fused regions, with smaller rounded gas pores distributed locally. These features are consistent with preferential fracture-initiation sites and suggest local crack deflection or coalescence along the ferrite-rich matrix, supporting the view that defect morphology and connectivity can influence fracture response strongly [33–36]. The present fractography is therefore used as qualitative morphological evidence. At higher magnification, terraced facets and river-like patterns support a predominantly quasi-cleavage fracture morphology in the ferrite-dominated AS microstructure. This morphology is consistent with the measured AS strength–ductility response and absorbed impact energy.

The SR fracture surface (Fig. 11(c, d)) shows a similar overall fracture character, with terraced lamellae, microcracks, and defect-associated crack-initiation regions. These features suggest that SR retains a predominantly quasi-cleavage morphology while showing improved plastic accommodation relative to AS. This interpretation is consistent with the mechanical results, where stress relief increases elongation, reduction in area, and absorbed impact energy while preserving a high-strength ferrite-rich state. Low-temperature stress relief therefore acts primarily as a recovery treatment for the ferritic as-built

structure, whereas the larger ductility and impact-energy improvement is associated with the SA-induced duplex phase rebalancing discussed in Section 3.2 and Fig. 9.

4. Conclusions

This study established a volumetric energy density (VED)-based process window for laser powder bed fusion (LPBF) 2507 super duplex stainless steel (SDSS), linking densification, microstructure, and mechanical response. Porosity decreased with increasing VED, and the near-full-density criterion of less than 1% porosity was reached above approximately 160 J mm^{-3} . Separating the preheated and non-preheated parameter sets presents the VED–porosity relation as a practical process-window map.

The as-built (AS) and stress-relieved (SR) conditions retained ferrite-dominated phase constitutions, whereas, within the tested matrix, the solution-annealed (SA) condition at 1100°C for 15 min produced an approximately balanced ferrite-austenite structure. SR mainly promoted recovery within the ferritic matrix, while SA enabled phase rebalancing and increased the high-angle boundary fraction. This microstructural transition explains the shift from high strength with localized plasticity in AS/SR to lower strength but markedly improved ductility and impact-energy absorption after SA.

The calibrated finite element method (FEM) comparison shows that post-processing modifies the yield-stress scale and plastic-flow distribution before instability. AS and SR retained high stress-bearing

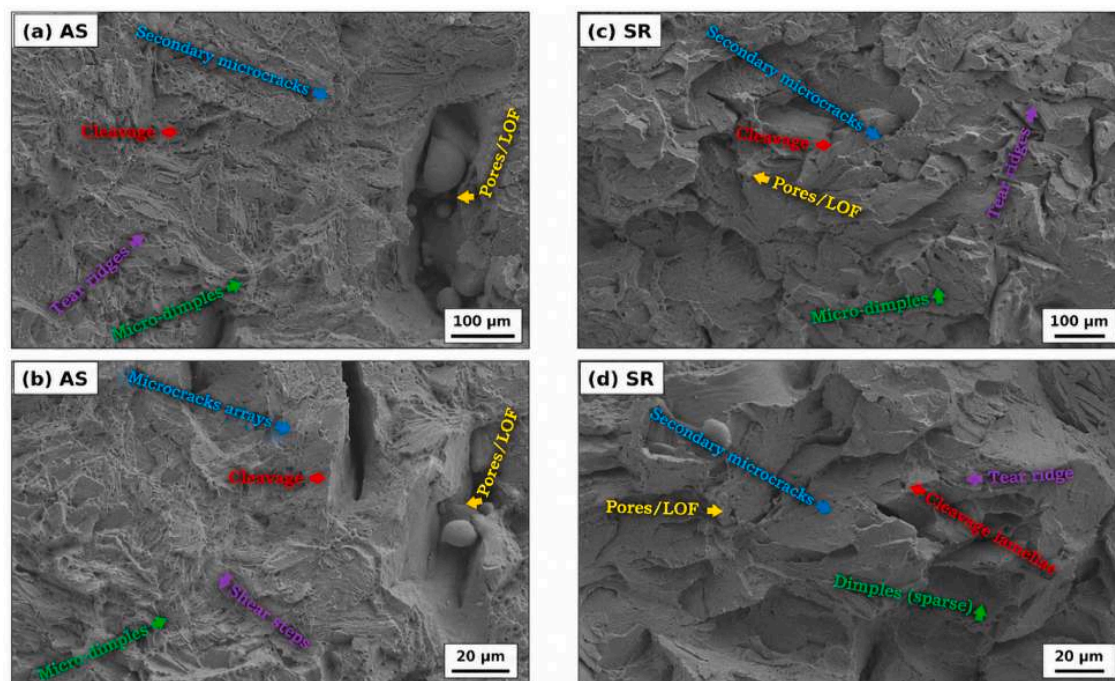


Fig. 11. SEM fractographs of LPBF SDSS 2507 after Charpy impact testing: (a, b) AS and (c, d) SR. The first and second rows show lower- and higher-magnification views, respectively. AS and SR show defect-associated crack initiation with predominantly quasi-cleavage fracture features. The SA condition showed extensive ductile bending, and its enhanced impact response is assessed through phase balance, tensile ductility, absorbed energy, and simulated plastic-strain distribution.

capacity with localized deformation, whereas SA supported broader plastic accommodation through the rebalanced duplex morphology. Fractography of AS and SR supports defect-assisted quasi-cleavage features, while the improved SA response is supported by phase constitution, tensile ductility, absorbed impact energy, and simulated strain distribution.

CRediT authorship contribution statement

Mengistu Dagnaw: Writing – original draft, Visualization, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sachin Poudel:** Writing – review & editing, Visualization, Software, Formal analysis, Data curation, Conceptualization. **Mariusz Król:** Writing – review & editing, Validation, Resources, Investigation, Formal analysis. **Zbigniew Brytan:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The experimental data and analysis files related to LPBF processing, microstructural characterization, hardness, and tensile testing are available at <https://github.com/mengedagnaw/lpbf-sdss-2507-hardness-tensile>. The finite-element-model data and code are available at https://github.com/Sachinscnpdl/SDSS_steel_FEM.

References

- [1] W.E. Frazier, Metal additive manufacturing: a review, *J. Mater. Eng. Perform.* 23 (6) (2014) 1917–1928.
- [2] L.E. Murr, Strategies for creating living, additively manufactured, open-cellular metal and alloy implants by promoting osseointegration, osteoinduction and vascularization: An overview, *J. Mater. Sci. Technol.* 35 (2) (2019) 231–241.
- [3] C. Xie, B. Li, G. Liu, J. Liu, H. Ying, D. Li, S. Wang, L. Wang, Study on the effect of solution treatment on mechanical and corrosion properties of SAF 2507DSS produced by LPBF, *J. Mater. Res. Technol.* 26 (2023) 2070–2081.
- [4] L. Karavias, L. Gargalis, J.S. Graff, M. Johansen, S. Diplas, E.K. Karaxi, Tensile properties and fracture analysis of duplex (2205) and super duplex (2507) stainless steels, produced via laser powder bed fusion additive manufacturing, *Met.* (2075-4701) 14 (7) (2024).
- [5] S.R. Narasimharaju, W. Zeng, T.L. See, Z. Zhu, P. Scott, X. Jiang, S. Lou, A comprehensive review on laser powder bed fusion of steels: Processing, microstructure, defects and control methods, mechanical properties, current challenges and future trends, *J. Manuf. Process.* 75 (2022) 375–414.
- [6] X. Li, F. Shen, W. Du, L. Cao, L. Pan, T. Ma, X. Fang, The deterministic effect of laser energy density on the microstructures of novel duplex stainless steel fabricated via in-situ alloying in laser powder bed fusion, *Mater. Sci. Eng.: A* 891 (2024) 145908.
- [7] T. DebRoy, H.L. Wei, J.S. Zuback, T. Mukherjee, J.W. Elmer, J.O. Milewski, A.M. Beese, A.D. Wilson-Heid, A. De, W. Zhang, Additive manufacturing of metallic components—process, structure and properties, *Prog. Mater. Sci.* 92 (2018) 112–224.
- [8] T. Niendorf, S. Leuders, A. Riemer, H.A. Richard, T. Tröster, D. Schwarze, Highly anisotropic steel processed by selective laser melting, *Met. Mater. Trans. B* 44 (4) (2013) 794–796.

- [9] A. Mulhi, S. Dehgahi, P. Waghmare, A.J. Qureshi, Process parameter optimization of 2507 super duplex stainless steel additively manufactured by the laser powder bed fusion technique, *Metals* 13 (4) (2023) 725.
- [10] X.-x. Zhu, L. Dong, G. Li, X.-g. Li, Laser powder bed fusion of 2507 duplex stainless steel: microstructure, mechanical properties, and corrosion performance, *Mater. Sci. Eng.: A* 913 (2024) 147084.
- [11] B. Vrancken, Study of Residual Stresses in Selective Laser Melting (Ph.D. thesis), Arenberg Doctoral School, Faculty of Engineering Science, KU Leuven, Heverlee, Belgium, 2016, URL https://lirias.kuleuven.be/bitstream/123456789/542751/1/thesis+Bey+Vrancken+v01-06-2016+FINAL_compressed.pdf, Ph.D. Thesis.
- [12] A. Sola, A. Nouri, Microstructural porosity in additive manufacturing: The formation and detection of pores in metal parts fabricated by powder bed fusion, *J. Adv. Manuf. Process.* 1 (3) (2019) e10021.
- [13] O.M. Akselsen, R. Bjørge, H.W. Ånes, X. Ren, B. Nyhus, Effect of sigma phase in wire arc additive manufacturing of superduplex stainless steel, *Metals* 11 (12) (2021) 2045.
- [14] M. Piras, A. Hor, E. Charkaluk, Microstructure mastering and fatigue behavior of duplex stainless steel obtained with laser powder bed fusion, in: *Material Forming*, 2024, pp. 290–299.
- [15] M.L. Gatto, A. Santoni, E. Santicchia, S. Spigarelli, F. Fiori, P. Mengucci, M. Cabibbo, The potential of duplex stainless steel processed by laser powder bed fusion for biomedical applications: A review, *Metals* 13 (5) (2023) 949.
- [16] K.P. Davidson, R. Liu, C. Zhu, M. Cagici, L.P. Tan, A. Alagesan, S. Singamneni, Effect of build orientation and heat treatment on the microstructure, mechanical and corrosion performance of super duplex stainless steels fabricated via laser powder bed fusion, *Mater. Adv.* 5 (20) (2024) 8177–8198.
- [17] C. Cui, L. Becker, E. Gärtner, J. Boes, J. Lentz, V. Uhlenwinkel, M. Steinbacher, S. Weber, R. Fichte-Heinen, Laser additive manufacturing of duplex stainless steel via powder mixture, *J. Manuf. Mater. Process.* 6 (4) (2022) 72.
- [18] M. Ghoncheh, A. Shahriari, N. Biribilis, M. Mohammadi, Process-microstructure-corrosion of additively manufactured steels: a review, *Crit. Rev. Solid State Mater. Sci.* 49 (4) (2024) 607–717.
- [19] C. Cui, F. Stern, N. Ellendt, V. Uhlenwinkel, M. Steinbacher, J. Tenkamp, F. Walther, R. Fichte-Heinen, Gas atomization of duplex stainless steel powder for laser powder bed fusion, *Materials* 16 (1) (2023) 435.
- [20] L. Gargalis, L. Karavias, J.S. Graff, S. Diplas, E.P. Koumoulos, E.K. Karaxi, A comparative investigation of duplex and super duplex stainless steels processed through laser powder bed fusion, *Metals* 13 (11) (2023) 1897.
- [21] L. Luengas, E.v. Morales, L. de Souza, A. Bott, Austenite transformation in duplex stainless steels under fast cooling rates, *Contrib. Pap. MS&T19* (2019).
- [22] T. Tański, Z. Brytan, K. Labisz, Fatigue behaviour of sintered duplex stainless steel, *Procedia Eng.* 74 (2014) 421–428.
- [23] Z. Brytan, Comparison of vacuum sintered and selective laser melted steel aisi 316L, *Arch. Met. Mater.* (2017).
- [24] S. Rai, B. Choudhary, T. Jayakumar, K.B.S. Rao, B. Raj, Characterization of low cycle fatigue damage in 9cr–1mo ferritic steel using X-ray diffraction technique, *Int. J. Press. Vessels Pip.* 76 (5) (1999) 275–281.
- [25] P. Salvetr, A. Školáková, D. Melzer, M. Brázda, J. Duchoň, J. Drahokoupil, P. Svora, Š. Msallamová, P. Novák, Characterization of super duplex stainless steel SAF2507 deposited by directed energy deposition, *Mater. Sci. Eng.: A* 857 (2022) 144084.
- [26] L. Becker, J. Boes, J. Lentz, C. Cui, M. Steinbacher, Y. Li, R. Fichte-Heinen, W. Theisen, S. Weber, Influence of annealing time on the microstructure and properties of additively manufactured X2CrNiMoN25–7–4 duplex stainless steel: Experiment and simulation, *Materialia* 28 (2023) 101720.
- [27] S. Papula, M. Song, A. Pateras, X.-B. Chen, M. Brandt, M. Easton, Y. Yagodzinskyy, I. Virkkunen, H. Hänninen, Selective laser melting of duplex stainless steel 2205: effect of post-processing heat treatment on microstructure, mechanical properties, and corrosion resistance, *Materials* 12 (15) (2019) 2468.
- [28] N. Haghdadi, M. Laleh, H. Chen, Z. Chen, C. Ledermueller, X. Liao, S. Ringer, S. Primig, On the pitting corrosion of 2205 duplex stainless steel produced by laser powder bed fusion additive manufacturing in the as-built and post-processed conditions, *Mater. Des.* 212 (2021) 110260.
- [29] J.C. Simo, T.J. Hughes, *Computational Inelasticity*, Springer, 1998.
- [30] J. Byun, C. Jee, I. Seo, M. Joun, Characterization of double strain-hardening behavior using a new flow of extremum curvature strain of voce strain-hardening model, *J. Mech. Sci. Technol.* 36 (8) (2022) 4115–4126.
- [31] S. Neupane, S. Poudel, A. Ghimire, S. Shakya, Enhanced mechanical performance and biodegradability in filler-reinforced potato biopolymers for sustainable packaging, *Mater. Today Commun.* (2025) 114081.
- [32] D. Gaston, C. Newman, G. Hansen, D. Lebrun-Grandie, MOOSE: A parallel computational framework for coupled systems of nonlinear equations, *Nucl. Eng. Des.* 239 (10) (2009) 1768–1778.
- [33] A.D. Anto, S. Dey, R. Kiran, Deciphering the fracture initiation mechanism in additive-manufactured 17-4 steel, *J. Mater. Civ. Eng.* 36 (6) (2024) 04024122.
- [34] D.S. Watring, J.T. Benzing, O.L. Kafka, L.-A. Liew, N.H. Moser, J. Erickson, N. Hrabe, A.D. Spear, Evaluation of a modified void descriptor function to uniquely characterize pore networks and predict fracture-related properties in additively manufactured metals, *Acta Mater.* 223 (2022) 117464.
- [35] O.V. Eliseeva, Utilizing the Structure-Property Relationship of Porosity and Composition in Additively Manufactured Metallic Systems (Ph.D. thesis), Graduate and Professional School, Texas A&M University, 2021, URL <https://hdl.handle.net/123456789/example123>, Available via OAKTrust Digital Repository at Texas A&M University.
- [36] W. Hahne, Optimization of laser powder bed fusion process parameters for 316L stainless steel (Master's thesis), Uppsala University, Department of Chemistry - Ångström, Inorganic Chemistry, 2021, p. 52, URL <http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-448263>, Independent thesis Advanced level (professional degree), 20 credits/30 HE credits.

Appendix B

Signed Declarations of Co-Authors

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Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. S. Poudel, U. Subedi, M. O. Hamid, K. Gyanwali, N. Moelans, A. Timofiejczuk, and A. Kunwar, *AlloyManufacturingNet for discovery and design of hardness-elongation synergy in multi-principal element alloys*, Engineering Applications of Artificial Intelligence, vol. 132, p. 107902, 2024.
DOI: <https://doi.org/10.1016/j.engappai.2024.107902> - 5 %
CRedit author contribution: Validation, Supervision, Data curation, Visualization, Resources, Writing – review & editing.
2. S. Poudel, R. Thapa, R. Basnet, A. Timofiejczuk, and A. Kunwar, *PiezoTensorNet: Crystallography informed multi-scale hierarchical machine learning model for rapid piezoelectric performance finetuning*, Applied Energy, vol. 361, p. 122901, 2024.
DOI: <https://doi.org/10.1016/j.apenergy.2024.122901> - 5 %
CRedit author contribution: Writing – review & editing, Validation, Supervision, Methodology.
3. S. Poudel, N. Moelans, R. Thapa, A. Timofiejczuk, D. Panthi, and A. Kunwar, *Unraveling elastochemical effects in microstructural evolution of Al–Cu–Ni system through DFT-informed multi-phase field simulations*, International Journal of Solids and Structures, vol. 300, p. 112894, 2024.
DOI: <https://doi.org/10.1016/j.ijsolstr.2024.112894> - 4 %
CRedit author contribution: Writing – review & editing, Validation, Supervision, Methodology.
4. S. Poudel, W. Smok, R. Thapa, A. Timofiejczuk, N. Moelans, and A. Kunwar, *Physics-guided machine learning for enhanced piezoelectric performance in electrospun PVDF/SnO₂ nanofibers*, Sustainable Materials and Technologies, p. e02008, 2026.
DOI: <https://doi.org/10.1016/j.susmat.2026.e02008> - 3 %
CRedit author contribution: Writing – review & editing, Validation, Supervision.

My primary contributions to the respective publications were as follows:

- *Paper [1]*: Validation of the model's result and visualization of data.
- *Paper [2]*: Validation, supervision and methodology development of the work.
- *Paper [3]*: Validation, supervision and methodology development.
- *Paper [4]*: Supervision and validation of results.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Anna Timofiejczuk, Ph.D., DSc., Eng.

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. S. Poudel, U. Subedi, M. O. Hamid, K. Gyanwali, N. Moelans, A. Timofiejczuk, and A. Kunwar, *AlloyManufacturingNet for discovery and design of hardness-elongation synergy in multi-principal element alloys*, Engineering Applications of Artificial Intelligence, vol. 132, p. 107902, 2024.
DOI: <https://doi.org/10.1016/j.engappai.2024.107902> - 25 %
CRedit author contribution: Conceptualization, Investigation, Methodology, Software, Validation, Visualization, Data curation, Formal analysis, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing.
2. S. Poudel, R. Thapa, R. Basnet, A. Timofiejczuk, and A. Kunwar, *PiezoTensorNet: Crystallography informed multi-scale hierarchical machine learning model for rapid piezoelectric performance finetuning*, Applied Energy, vol. 361, p. 122901, 2024.
DOI: <https://doi.org/10.1016/j.apenergy.2024.122901> - 20 %
CRedit author contribution: Writing – review & editing, Validation, Supervision, Software, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.
3. S. Poudel, N. Moelans, R. Thapa, A. Timofiejczuk, D. Panthi, and A. Kunwar, *Unraveling elastochemical effects in microstructural evolution of Al–Cu–Ni system through DFT-informed multi-phase field simulations*, International Journal of Solids and Structures, vol. 300, p. 112894, 2024.
DOI: <https://doi.org/10.1016/j.ijsolstr.2024.112894> - 15 %
CRedit author contribution: Writing – review & editing, Validation, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.
4. L. Yi, S. Poudel, S. Kumari, E. Azqadan, A. Kunwar, and N. Moelans, *Roadmaps for dendrite suppression in next generation lithium-ion batteries: Toward sustainable energy solutions*, Energy Storage Materials, vol. 86, p. 105000, 2026.
DOI: <https://doi.org/10.1016/j.ensm.2026.105000> - 15 %
CRedit author contribution: Writing – review & editing, Visualization, Validation, Methodology, Data curation, Conceptualization, Formal analysis, Investigation, Software.
5. S. Poudel, W. Smok, R. Thapa, A. Timofiejczuk, N. Moelans, and A. Kunwar, *Physics-guided machine learning for enhanced piezoelectric performance in electrospun PVDF/SnO₂ nanofibers*, Sustainable Materials and Technologies, p. e02008, 2026.
DOI: <https://doi.org/10.1016/j.susmat.2026.e02008> - 16 %
CRedit author contribution: Writing – review & editing, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.
6. M. Dagnaw, S. Poudel, U. Subedi, R. Thapa, Łukasz Reimann, A. N. S. Appiah, Paweł M. Nuckowski, Mariusz Król, Z. Brytan, N. Moelans, and A. Kunwar, *Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures*, Metals and Materials International, 2026.
DOI: <https://doi.org/10.1007/s12540-026-02369-4> - 9 %

CRedit author contribution: Conceptualization, Methodology, Supervision, Project administration, Funding acquisition, Writing – review & editing.

My primary contributions to the respective publications were as follows:

- *Paper [1]*: Validation of model, conceptualization of hardness-elongation behavior at molecular level, analysis of results.
- *Paper [2]*: Conceptualization, methodology development, software validation, and FEM modeling of electromechanical behavior.
- *Paper [3]*: Conceptualization, methodology development, supervision, and project administration.
- *Paper [4]*: Conceptualization, methodology, and software implementation.
- *Paper [5]*: Conceptualization, methodology, supervision, and development of materials informatics model and analysis of results.
- *Paper [6]*: Conceptualization, methodology development, and supervision of phase-field modeling and machine learning development.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Anil Kunwar, Ph.D., Eng.

Nele Moelans, Ph.D.
KU Leuven
Department of Materials Engineering
Kasteelpark Arenberg 44, 3001 Leuven, Belgium

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. S. Poudel, U. Subedi, M. O. Hamid, K. Gyanwali, N. Moelans, A. Timofiejczuk, and A. Kunwar, *AlloyManufacturingNet for discovery and design of hardness-elongation synergy in multi-principal element alloys*, Engineering Applications of Artificial Intelligence, vol. 132, p. 107902, 2024.

DOI: <https://doi.org/10.1016/j.engappai.2024.107902> - 5 %

CRedit author contribution: Methodology, Validation, Supervision, Funding acquisition, Writing – review & editing.

2. S. Poudel, N. Moelans, R. Thapa, A. Timofiejczuk, D. Panthi, and A. Kunwar, *Unraveling elastochemical effects in microstructural evolution of Al–Cu–Ni system through DFT-informed multi-phase field simulations*, International Journal of Solids and Structures, vol. 300, p. 112894, 2024.

DOI: <https://doi.org/10.1016/j.ijsolstr.2024.112894> - 7 %

CRedit author contribution: Writing – review & editing, Validation, Methodology, Formal analysis.

3. L. Yi, S. Poudel, S. Kumari, E. Azqadan, A. Kunwar, and N. Moelans, *Roadmaps for dendrite suppression in next generation lithium-ion batteries: Toward sustainable energy solutions*, Energy Storage Materials, vol. 86, p. 105000, 2026.

DOI: <https://doi.org/10.1016/j.ensm.2026.105000> - 10 %

CRedit author contribution: Writing – review & editing, Visualization, Validation, Methodology, Data curation, Conceptualization, Formal analysis.

4. S. Poudel, W. Smok, R. Thapa, A. Timofiejczuk, N. Moelans, and A. Kunwar, *Physics-guided machine learning for enhanced piezoelectric performance in electrospun PVDF/SnO₂ nanofibers*, Sustainable Materials and Technologies, p. e02008, 2026.

DOI: <https://doi.org/10.1016/j.susmat.2026.e02008> - 10 %

CRedit author contribution: Writing – review & editing, Validation, Project administration, Methodology, Funding acquisition, Formal analysis.

5. M. Dagnaw, S. Poudel, U. Subedi, R. Thapa, Łukasz Reimann, A. N. S. Appiah, Paweł M. Nuckowski, Mariusz Król, Z. Brytan, N. Moelans, and A. Kunwar, *Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures*, Metals and Materials International, 2026.

DOI: <https://doi.org/10.1007/s12540-026-02369-4> - 7 %

CRedit author contribution: Methodology, Validation.

My primary contributions to the respective publications were as follows:

- *Paper [1]*: Methodology development and validation of the results for multi-principal element alloys.
- *Paper [2]*: Methodology development, validation, and formal analysis.
- *Paper [3]*: Conceptualization, methodology development, and data validation.
- *Paper [4]*: Methodology development, validation, and formal analysis.
- *Paper [5]*: Methodology development, validation, and phase-field modeling.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Nele Moelans, Ph.D.

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. S. Poudel, R. Thapa, R. Basnet, A. Timofiejczuk, and A. Kunwar, *PiezoTensorNet: Crystallography informed multi-scale hierarchical machine learning model for rapid piezoelectric performance finetuning*, Applied Energy, vol. 361, p. 122901, 2024.

DOI: <https://doi.org/10.1016/j.apenergy.2024.122901> - 11 %

CRedit author contribution: Writing – review & editing, Visualization, Validation, Investigation, Formal analysis.

2. S. Poudel, N. Moelans, R. Thapa, A. Timofiejczuk, D. Panthi, and A. Kunwar, *Unraveling elastochemical effects in microstructural evolution of Al–Cu–Ni system through DFT-informed multi-phase field simulations*, International Journal of Solids and Structures, vol. 300, p. 112894, 2024.

DOI: <https://doi.org/10.1016/j.ijsolstr.2024.112894> - 5 %

CRedit author contribution: Writing – review & editing, Visualization, Validation, Software, Formal analysis.

3. S. Poudel, W. Smok, R. Thapa, A. Timofiejczuk, N. Moelans, and A. Kunwar, *Physics-guided machine learning for enhanced piezoelectric performance in electrospun PVDF/SnO₂ nanofibers*, Sustainable Materials and Technologies, p. e02008, 2026.

DOI: <https://doi.org/10.1016/j.susmat.2026.e02008> - 3 %

CRedit author contribution: Writing – review & editing, Validation, Software.

4. M. Dagnaw, S. Poudel, U. Subedi, R. Thapa, Łukasz Reimann, A. N. S. Appiah, Paweł M. Nuckowski, Mariusz Król, Z. Brytan, N. Moelans, and A. Kunwar, *Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures*, Metals and Materials International, 2026.

DOI: <https://doi.org/10.1007/s12540-026-02369-4> - 5 %

CRedit author contribution: Data curation, Methodology, Software, Visualization, Writing-review & editing

My primary contributions to the respective publications were as follows:

- *Paper [1]*: Assisting in formal analysis, visualization and validation.
- *Paper [2]*: Assisting in formal analysis, software implementation, visualization and validation.
- *Paper [3]*: Assisting in materials informatics model development, software implementation, validation, and analysis of results.
- *Paper [4]*: EIS data analysis and interpretation.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Rubi Thapa

Mariusz Król, Ph.D., Eng.
Silesian University of Technology
Faculty of Mechanical Engineering
Department of Engineering Materials and Biomaterials - RMT1

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. M. Dagnaw, S. Poudel, U. Subedi, R. Thapa, Łukasz Reimann, A. N. S. Appiah, Paweł M. Nuckowski, Mariusz Król, Z. Brytan, N. Moelans, and A. Kunwar, *Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures*, Metals and Materials International, 2026.

DOI: <https://doi.org/10.1007/s12540-026-02369-4> - 7 %

CRedit author contribution: Investigation, Resources

2. M. Dagnaw, S. Poudel, M. Król, and Z. Brytan, *Post-process heat treatment design for tunable strength and toughness in L-PBF 2507 super duplex stainless steel*, Materialia, p. 102799, 2026.

DOI: <https://doi.org/10.1016/j.mtla.2026.102799> - 10 %

CRedit author contribution: Writing – review & editing, Validation, Resources, Investigation, Formal analysis.

My primary contributions to the respective publications were as follows:

- *Paper [1]*: Experimental investigation.
- *Paper [2]*: Experimental characterization, data validation, investigation, and formal analysis.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Mariusz Król, Ph.D., Eng.

Mengistu Dagnaw, MSc., Eng.
Silesian University of Technology
Faculty of Mechanical Engineering
Department of Engineering Materials and Biomaterials - RMT1

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. M. Dagnaw, S. Poudel, U. Subedi, R. Thapa, Łukasz Reimann, A. N. S. Appiah, Paweł M. Nuckowski, Mariusz Król, Z. Brytan, N. Moelans, and A. Kunwar, *Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures*, Metals and Materials International, 2026.

DOI: <https://doi.org/10.1007/s12540-026-02369-4> - **19 %**

CRedit author contribution: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing-original draft

2. M. Dagnaw, S. Poudel, M. Król, and Z. Brytan, *Post-process heat treatment design for tunable strength and toughness in L-PBF 2507 super duplex stainless steel*, Materialia, p. 102799, 2026.

DOI: <https://doi.org/10.1016/j.mtla.2026.102799> - **55 %**

CRedit author contribution: Writing – original draft, Visualization, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

My primary contributions to the respective publications were as follows:

- *Paper [1]*: Experimental characterization, conceptualization, methodology development, and writing the original draft.
- *Paper [2]*: Experimental characterization, use of software for visualization and analysis of experimental data, project administration, and writing the original draft.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Mengistu Dagnaw, MSc., Eng.

Upadesh Subedi, MSc, Eng.
Silesian University of Technology
Faculty of Mechanical Engineering
Department of Fundamentals of Machinery Design - RMT6

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. S. Poudel, U. Subedi, M. O. Hamid, K. Gyanwali, N. Moelans, A. Timofiejczuk, and A. Kunwar, *AlloyManufacturingNet for discovery and design of hardness-elongation synergy in multi-principal element alloys*, Engineering Applications of Artificial Intelligence, vol. 132, p. 107902, 2024.

DOI: <https://doi.org/10.1016/j.engappai.2024.107902> - 5 %

CRedit author contribution: Methodology, Validation, Visualization, Formal analysis, Writing – review & editing.

2. M. Dagnaw, S. Poudel, U. Subedi, R. Thapa, Łukasz Reimann, A. N. S. Appiah, Paweł M. Nuckowski, Mariusz Król, Z. Brytan, N. Moelans, and A. Kunwar, *Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures*, Metals and Materials International, 2026.

DOI: <https://doi.org/10.1007/s12540-026-02369-4> - 12 %

CRedit author contribution: Methodology, Software, Validation.

My primary contributions to the respective publications were as follows:

- *Paper [1]*: Methodology development, validation, and visualization of the results.
- *Paper [2]*: Methodology development, validation, and phase-field modeling.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Upadesh Subedi, MSc, Eng.

Zbigniew Brytan, Ph.D., DSc., Eng.
Silesian University of Technology
Faculty of Mechanical Engineering
Department of Engineering Materials and Biomaterials - RMT1

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. M. Dagnaw, S. Poudel, U. Subedi, R. Thapa, Łukasz Reimann, A. N. S. Appiah, Paweł M. Nuckowski, Mariusz Król, Z. Brytan, N. Moelans, and A. Kunwar, *Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures*, Metals and Materials International, 2026.

DOI: <https://doi.org/10.1007/s12540-026-02369-4> - 7 %

CRedit author contribution: Funding acquisition, Project administration, Supervision, Validation, Writing-review & editing

2. M. Dagnaw, S. Poudel, M. Król, and Z. Brytan, *Post-process heat treatment design for tunable strength and toughness in L-PBF 2507 super duplex stainless steel*, Materialia, p. 102799, 2026.

DOI: <https://doi.org/10.1016/j.mtla.2026.102799> - 10 %

CRedit author contribution: Writing – review & editing, Validation, Supervision, Resources, Funding acquisition, Conceptualization.

My primary contributions to the respective publications were as follows:

- *Paper [1]*: Supervision, project administration, funding acquisition, and validation of results.
- *Paper [2]*: Supervision, funding acquisition, and validation of results.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Zbigniew Brytan, Ph.D., DSc., Eng.

Augustine Nana Sekyi Appiah, Ph.D., Eng.
Silesian University of Technology
Faculty of Mechanical Engineering
Materials Research Laboratory
44-100 Gliwice, Poland

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. M. Dagnaw, S. Poudel, U. Subedi, R. Thapa, Łukasz Reimann, A. N. S. Appiah, Paweł M. Nuckowski, Mariusz Król, Z. Brytan, N. Moelans, and A. Kunwar, *Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures*, Metals and Materials International, 2026.

DOI: <https://doi.org/10.1007/s12540-026-02369-4> - 5 %

CRedit author contribution: Investigation.

My primary contribution to the publication was:

- *Paper [1]*: Experimental investigation.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Augustine Nana Sekyi Appiah, Ph.D., Eng.

Dhruba Panthi, Ph.D.
Kent State University at Tuscarawas
Department of Engineering Technology
New Philadelphia, OH 44663, USA

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. S. Poudel, N. Moelans, R. Thapa, A. Timofiejczuk, D. Panthi, and A. Kunwar, *Unraveling elastochemical effects in microstructural evolution of Al–Cu–Ni system through DFT-informed multi-phase field simulations*, International Journal of Solids and Structures, vol. 300, p. 112894, 2024.

DOI: <https://doi.org/10.1016/j.ijsolstr.2024.112894> - 4 %

CRedit author contribution: Writing – review & editing, Validation, Formal analysis.

My primary contribution to the publication was:

- *Paper [1]*: Formal analysis and validation.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Dhruba Panthi, Ph.D.

Erfan Azqadan, PhD
University of Waterloo
Department of Mechanical and Mechatronics Engineering
200 University Ave W, Waterloo, ON N2L 3G1, Canada

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. L. Yi, S. Poudel, S. Kumari, E. Azqadan, A. Kunwar, and N. Moelans, *Roadmaps for dendrite suppression in next generation lithium-ion batteries: Toward sustainable energy solutions*, Energy Storage Materials, vol. 86, p. 105000, 2026.

DOI: <https://doi.org/10.1016/j.ensm.2026.105000> - 2 %

CRedit author contribution: Writing – review & editing, Validation, Methodology.

My primary contribution to the publication was:

- *Paper [1]*: Methodology development and validation.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Erfan Azqadan, PhD

Khem Gyanwali, D.Eng.
Tribhuvan University
Institute of Engineering, Thapathali Campus
Department of Automobile and Mechanical Engineering

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. S. Poudel, U. Subedi, M. O. Hamid, K. Gyanwali, N. Moelans, A. Timofiejczuk, and A. Kunwar, *AlloyManufacturingNet for discovery and design of hardness-elongation synergy in multi-principal element alloys*, Engineering Applications of Artificial Intelligence, vol. 132, p. 107902, 2024.

DOI: <https://doi.org/10.1016/j.engappai.2024.107902> - **5 %**

CRedit author contribution: Supervision, Validation, Resources, Writing – review & editing.

My primary contribution to the publication was:

- *Paper [1]*: Validation of the model's result and supervision.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Khem Gyanwali, D.Eng.

Li Yi, MSc, Eng.
KU Leuven
Department of Materials Engineering
Kasteelpark Arenberg 44, 3001 Leuven, Belgium

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. L. Yi, S. Poudel, S. Kumari, E. Azqadan, A. Kunwar, and N. Moelans, *Roadmaps for dendrite suppression in next generation lithium-ion batteries: Toward sustainable energy solutions*, Energy Storage Materials, vol. 86, p. 105000, 2026.

DOI: <https://doi.org/10.1016/j.ensm.2026.105000> - 36 %

CRedit author contribution: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Software.

My primary contribution to the publication was:

- *Paper [1]*: Investigation, software implementation on data analysis, visualization, and writing the original draft.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Li Yi, MSc, Eng.

Łukasz Reimann, Ph.D., Eng.
Silesian University of Technology
Faculty of Mechanical Engineering
Department of Materials Research Laboratory – RMT L1

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. M. Dagnaw, S. Poudel, U. Subedi, R. Thapa, Łukasz Reimann, A. N. S. Appiah, Paweł M. Nuckowski, Mariusz Król, Z. Brytan, N. Moelans, and A. Kunwar, *Integrating experiments and phase field method through informatics for tailored corrosion performance of additively manufactured steel microstructures*, Metals and Materials International, 2026.

DOI: <https://doi.org/10.1007/s12540-026-02369-4> - 10 %

CRedit author contribution: Data curation, Investigation, Resources

My primary contribution to the publication was:

- *Paper [1]*: Experimental characterization, including sample investigation and data curation.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Łukasz Reimann, Ph.D., Eng.

Mohammed O.A. Hamid, Ph.D., Eng.
University of Khartoum
Mechanical Engineering Department
Thermal Energy Systems Division

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. S. Poudel, U. Subedi, M. O. Hamid, K. Gyanwali, N. Moelans, A. Timofiejczuk, and A. Kunwar, *AlloyManufacturingNet for discovery and design of hardness-elongation synergy in multi-principal element alloys*, Engineering Applications of Artificial Intelligence, vol. 132, p. 107902, 2024.

DOI: <https://doi.org/10.1016/j.engappai.2024.107902> - 4 %

CRedit author contribution: Validation, Formal analysis, Writing – review & editing

My primary contribution to the publication was:

- *Paper [1]*: Validation of model's data and analysis of experimental results.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Mohammed O.A. Hamid, Ph.D., Eng.

Paweł M. Nuckowski, Ph.D., Eng.
Silesian University of Technology
Faculty of Mechanical Engineering
Materials Research Laboratory
44-100 Gliwice, Poland

Declaration

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DOI: <https://doi.org/10.1007/s12540-026-02369-4> - 5 %

CRedit author contribution: Investigation.

My primary contribution to the publication was:

- *Paper [1]*: Experimental investigation.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Paweł M. Nuckowski, Ph.D., Eng.

Rabin Basnet, PhD
The Australian National University
School of Engineering
2601, Canberra, Australia

Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. S. Poudel, R. Thapa, R. Basnet, A. Timofiejczuk, and A. Kunwar, *PiezoTensorNet: Crystallography informed multi-scale hierarchical machine learning model for rapid piezoelectric performance finetuning*, Applied Energy, vol. 361, p. 122901, 2024.

DOI: <https://doi.org/10.1016/j.apenergy.2024.122901> - 3 %

CRedit author contribution: Writing – review & editing, Validation, Methodology.

My primary contribution to the publication was:

- *Paper [1]*: Methodology development and validation.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

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Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. L. Yi, S. Poudel, S. Kumari, E. Azqadan, A. Kunwar, and N. Moelans, *Roadmaps for dendrite suppression in next generation lithium-ion batteries: Toward sustainable energy solutions*, Energy Storage Materials, vol. 86, p. 105000, 2026.

DOI: <https://doi.org/10.1016/j.ensm.2026.105000> - 2 %

CRedit author contribution: Writing – review & editing, Validation, Methodology.

My primary contribution to the publication was:

- *Paper [1]*: Methodology development and validation.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

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Declaration

I hereby declare that my contribution percentages in the following publications were as follows:

1. S. Poudel, W. Smok, R. Thapa, A. Timofiejczuk, N. Moelans, and A. Kunwar, *Physics-guided machine learning for enhanced piezoelectric performance in electrospun PVDF/SnO₂ nanofibers*, Sustainable Materials and Technologies, p. e02008, 2026.

DOI: <https://doi.org/10.1016/j.susmat.2026.e02008> - 18 %

CRedit author contribution: Writing – review & editing, Validation, Methodology, Investigation, Formal analysis.

My primary contribution to the publication was:

- *Paper [1]*: Experimental characterization of the PVDF and PVDF/SnO₂ nanopolymers.

Furthermore, I declare that I have been informed that the use of the above-mentioned publications in the doctoral dissertation of **Sachin Poudel**, MSc, Eng., entitled:

“Scale Bridging Computational and Data-Driven Design of Microstructures in Multicomponent Alloys for Advanced Functional Materials”

Weronika Smok, Ph.D., Eng.