ABSTRACT

The development of implant coatings with enhanced surface chemical properties for bone and dental defect treatment is a central challenge in biomaterials science. Combining calcium carbonate (CC) and hydroxyapatite (HA) integrates the high bioresorbability and calcium ion release of CC with the structural stability and bone-like chemistry of HA, enhancing bioactivity and promoting osteointegration along a biomimetic pathway. This doctoral dissertation presents a comprehensive investigation of the anodization-derived plasma electrolytic oxidation (PEO) process for the fabrication of implant coatings, considering it as one of the most promising surface modification techniques due to the high mechanical performance of the resulting layers and the limited influence of thermal effects, yet still insufficiently explored in the context of carbonate additives. The aim of this work was to develop PEO coatings on titanium implants incorporating CC and HA, overcoming the existing challenges associated with their incorporation, and ultimately obtaining bioactive, corrosion-resistant, and functionally robust layers with a well-defined phase composition. A further objective was to clarify particle-incorporation mechanisms in PEO, with particular emphasis on the role of particle crystallinity.

A literature overview covered fundamentals of biomedical implants; the roles, properties, and synthesis of CC; coating methods and characterization; and PEO principles, capabilities, and limitations. This review enabled the identification of the most suitable strategy for creating working PEO bath, which was based on the synthesis of CC particles via carbonation followed by their partial reaction with a dibasic phosphate electrolyte. The experimental work was divided into three stages: (1) Preliminary experiments aimed at establishing relationships between PEO parameters in phosphate-carbonate baths and resulting coating properties, focusing on morphology and elemental composition; (2) The influence of particle crystallinity—addressed here as an independent factor not previously examined—was evaluated with respect to coating phase composition, bioactivity, thickness and internal structure, wettability, and surface roughness; (3) Final optimization procedures were carried out, leading to the fabrication of the optimized CC–HA coatings including a detailed description of their fabrication protocol, as well as comprehensive physicochemical, biological and other functional characterization, and elucidation of the coating formation mechanism.

Key analytical methods for coating characterization included SEM for surface and cross-sectional morphology; EDX, XPS, XRD, and Raman spectroscopy for composition and phase analysis; and SBF tests, cell culture assays, and antibacterial tests for biological performance. Coating functional assessments comprised water contact angle (determination of wettability), immersion-based ion release, streaming potential (surface charge), scratch testing (adhesion strength), and corrosion studies using EIS and potentiodynamic polarization (PDP). Electrolyte bath characterization included pH and conductivity measurements, chromatographic monitoring of dissolved phosphate and carbonate contents, electron microscopy for particle size and morphology, elemental analysis and FTIR for particle chemistry, and XRD for particle crystallinity.

Results obtained within experiments in stage (1) showed that electrolyte concentration and conductivity directly correlate with coating pore size, with consistent trends across pH values. pH exerted a secondary yet notable effect on pore shape and surface elemental composition. Importantly, soluble carbonate salts did not yield incorporation of phases other than anatase; at higher concentrations they suppressed micro-discharges, reduced pore size, and rendered PEO inoperative above ~90–95%. Stage (2) demonstrated that suspended particle crystallinity markedly affects coating bioactivity—especially the kinetics of HA-like layer formation—as well as surface topography (pore shape, size distribution uniformity, total porosity, and pore density). Amorphous particles resulted in higher calcium content in outer layers, plausibly due to rougher particle surfaces enhancing retention within the porous oxide.

Stage (3) confirmed that the literature-derived electrolyte-preparation strategy, combined with optimization of component concentrations, ratios, and process voltage, enables simultaneous incorporation of CC and HA. Monitoring of bath preparation indicated that reaction of CC nanoparticles with phosphate ions produces 1–2 μm CC–HA agglomerates that are optimal for PEO treatment. The resulting coatings displayed typical PEO morphology, ~25 μm thickness, moderate porosity, and elevated Ca and P contents. Raman spectroscopy identified CC, HA, anatase, and amorphous TiO_2; XRD additionally detected rutile, perovskite, and brushite. Incorporation of CC–HA particles improved corrosion resistance and adhesion; the coatings were highly biocompatible, bacteriostatic, hydrophilic, moderately negatively charged, and released calcium ions continuously for one month in PBS.

Overall, the PEO method—and specifically the proposed electrolyte-preparation route—demonstrates the capacity for concurrent CC and HA incorporation and efficiently yields coatings that satisfy criteria relevant to *in vivo* use. To the best of our knowledge, this study constitutes the first successful direct incorporation of a carbonate phase as solid particles into a PEO coating and the first application of a carbonation-based particle synthesis tailored to PEO. The carbonation approach offers a neutral, ready-to-use suspension free of conductive impurities, avoiding purification or redispersion steps, which are common in suspension-assisted PEO. From a practical perspective, the developed coatings show promise for the fabrication of implants with enhanced osteointegration and improved long-term durability. Furthermore, the obtained results lay the groundwork for further optimization of carbonate-based systems for biomedical and broader applications. Future work should refine electrolyte composition, evaluate performance under clinically relevant conditions, deepen insight into carbonate behavior during PEO, and design alternative particle systems for standalone or combined CC incorporation.