**In vitro** corrosion resistance of layer-by-layer assembled polyacrylic acid multilayers induced Ca–P coating on magnesium alloy AZ31

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**Abstract**

Biodegradable magnesium (Mg)-based alloys have aroused great concern owing to their promising characteristics as temporary implants for orthopedic application. However, the undesirable rapid corrosion rate under physiological conditions has limited the actual clinical application. This study reports the use of a novel biomimetic polyelectrolyte multilayer template, based on polyvinylpyrrolidone (PVP) and polyacrylic acid (PAA) via layer-by-layer (LbL) assembly, to improve the corrosion resistance of the alloy. Surface characterization techniques (field-emission scanning electron microscopy, Fourier transform infrared (FTIR) spectrophotometer and X-ray diffractometer) confirmed the formation of biomineralized Ca–P coating on AZ31 alloy. Both hydrogen evolution and electrochemical corrosion tests demonstrated that the corrosion protection of the polyelectrolyte-induced Ca–P coating on AZ31 alloy. The formation mechanism of biomineralized Ca–P coating was proposed.

**1. Introduction**

Biodegradable magnesium (Mg)-based alloys with close density and mechanical properties to the natural bone, have received great consideration owing to their promising characteristics as temporary implants for orthopedic application, which have the ability to degrade inside the human body to avoid the second surgery [1–3]. However, the main drawback of employing Mg for orthopedic application is the high degradation rate along with the generation of hydrogen gas and boom in alkalinity of body fluid [4–6]. Surface modification is a viable option to control Mg degradation rate and enhance its bioactivity for accelerating the healing process [2,7–9].

As the main composition of bones, calcium-bearing phosphate (Ca–P) coatings have been paid more attentions due to their superior biocompatibility and corrosion resistance, which can be fabricated through chemical conversion [10–12], cathodic electrodeposition (EDP) [13–15] and sol-gel [16,17], etc. And hydrothermal deposition (HDP) is a more economical and convenient method to prepare crystalline Ca–P coating on metallic materials [18–20]. It is, however, difficult to obtain the coatings of pure calcium orthophosphates on biodegradable Mg and its alloys due to the severe corrosion of Mg substrate in aqueous solutions at elevated temperatures. As a result, the released Mg\(^{2+}\) ions may lead to the formation of a corrosion product layer of Mg(OH)\(_2\) and substitute for Ca\(^{2+}\) ions in the structure of the calcium orthophosphates coatings [21].

In order to improve the purity, compactness and bonding strength of Ca–P coatings, complexing agents, organic and polymer compounds as an inducer or template were used to accelerate the deposition of calcium orthophosphates, based on the molecular recognition. For instance, ethylene diamine tetraacetic acid (EDTA), especially for Na-EDTA [10,22] and Ca-EDTA [23], can coordinate with metallic ions to form stable chelates [22], and thus is often used to construct Ca–P coatings. Ca-EDTA can supply a sufficiently high concentration of Ca\(^{2+}\) ions to cause precipitation, and then achieving a highly crystalline coating [24].

The organic and polymer compounds, used in the coating preparation, include peptide, dopamine, glucose, amino acids and protein. Cui et al. [25] showed that a novel biomimetic peptide with triple repeat of a tri-residue sequence (aspartic acid-serine-serine) can direct Ca–P formation on the AZ31B alloys and result in a very different Ca–P crystal structure. Cao et al. [11] formed an arginine-glycine-aspartic acid-cysteine peptide-induced Ca–P coating using a biomimetic...
method, which presented an improved anticorrosion ability and cellular responses. That is, many peptides can be used as inducers to obtain Ca–P coatings on Mg alloys, but the peptides tend to lose their activity in alkaline or high temperature environments. Ca–P coatings also can be successfully achieved on Mg alloys through a biomimetic strategy in presence of mussel-inspired polydopamine (PDA) [26,27], but the immersion process of the PDA leads to corrosion of the Mg substrate, which goes against the protection improvement of the composite coating. Glucose was selected by Li et al. to induce a Ca–P coating to enhance the corrosion resistance of pure Mg through the changes between glucose and gluconic acid during hydrothermal process [18]. Noticeably, the uniformity of adsorption directly affects the homogeneity of the obtained Ca–P coatings.

Also, silk fibroin is used to obtain Ca–P coating with the addition of Ca, Sr and P sources. The composite films acted as effective barriers to retard substrate corrosion significantly; and the cytocompatibility and ontogenetic performance of the coated samples were improved [28]. Furthermore, Cui et al. [10,29] exhibited a novel SnO2-doped Ca–P coating on degradable Mg alloys. SnO2 nanoparticles, embedded in the coating, enhanced the compactness and crystallization of the coatings and acted as a foreign material to provide homogeneous nucleation sites for the deposition of Mg2+ and Ca2+ with PO43− ions. But the bonding strength of the obtained Ca–P coating is deficient to be used as bone implants.

Layer-by-layer (LbL) films (or “polyelectrolyte multilayers”) are potential templates for the biomimetic deposition of Ca–P coatings for bone tissue engineering by improving the heterogeneous nucleation of Ca–P precipitates and homogeneous deposition of Ca–P coatings [30]. Early on, NgaNam et al. [31] indicated that the poly(ethylenglycoline)–(poly(styrene sulfonate)-poly(allylamine hydrochloride))2 (PEI-PSS-PAH)2 polyelectrolyte multilayers, both negatively or positively charged, led to a decrease of the supersaturating ratio for heterogeneous nucleation of calcium phosphate crystals. Li et al. [32] showed that Ca–P precipitates were successfully deposited on the surface of gelatin/PSS covered polycaprolactone fibers by mineralization, in which gelatin and PSS were immobilized by Lbl assembly. Ji et al. [33] constructed a hydroxyapatite (HA) coating with polymeric multilayers based on ciprofloxacin (CIP) and PAH via LbL assembly, obtained a compact flake morphology and high crystallized apatite structure with the bone-like hydroxyapatite. Li et al. [34] developed a hydroxyapatite coating, an inner (PVP/PAA)5.5 polyelectrolyte multilayer was designed to be used as a template to induce the Ca–P composite coating on AZ31 alloy.

2.2. Coating preparation

The polished substrates were immersed in a 1 M NaOH solution at 60 °C for 1 h, followed by thoroughly cleaning with DI water and drying with warm air. Then, the Lbl assembled templates were generated via a dip-coating method in the following sequence: “ABCBCBCBCBCB”. Solutions A and C were comprised of the cationic polyelectrolytes PEI (pH 10.9) and PVP (pH 3.5) at concentrations of 10 and 5 g L−1 in DI water, respectively. Solution B contained the anionic polyelectrolyte PAA (pH 7.0) at a concentration of 10 g L−1 in DI water. The AZ31 substrates were incubated into solution A for 30 min and solution B and C for 5 min each. Five cycles were performed to obtain (PVP/PAA)5 coated samples [35], and an additional PAA layer was set as the outermost layer.

The Ca–P coatings were prepared by hydrothermal treatment. Ca–P solution was prepared as calcium and phosphate precursors separately, and then mixed with the final concentration of 14 mM calcium nitrate (Ca(NO3)2.4H2O, ≥ 99.0%), 8.4 mM sodium dihydrogen phosphate (NaH2PO4.2H2O, ≥ 99.0%) and 4 mM sodium bicarbonate (NaHCO3, ≥ 99.5%). NaHCO3 was added to the phosphate solution as a buffering agent. The (PVP/PAA)5 modified AZ31 substrate and the prepared Ca–P solution (60 mL) were transferred into 100 mL Teflon-lined 304 stainless steel reactors, which were maintained in an electric oven (DHG-9070 A, China) at 90 °C for 4 h. Finally, the samples were removed, washed thoroughly with DI water at least three times, and dried in electric oven at 80 °C (Called as II coating). A Ca–P solution containing PVP and PAA with the same concentration as Lbl monomer solution (Called as III coating) and a sample without pretreated polyelectrolyte template (Called as I coating) were used as controls. The preparation process is schematically illustrated in Fig. 1.

2.3. Surface analysis

Field-emission scanning electron microscopy (FE-SEM, Nova NanoSEM 450, USA) was used to study the surface morphologies of the coatings. The possible chemical bonding formed in the coatings was confirmed by virtue of a Fourier transform infrared (FTIR) spectrophotometer (Nicolet 380, Thermo Electron Corporation, USA). X-ray diffractometer (XRD, Rigaku D/MAX 2500 PC, Japan) was employed to determine the crystal structures of the samples.

2.4. Corrosion characterization

2.4.1. Electrochemical test

An electrochemical analyzer (PAR Model 2273, Princeton, USA) was used to obtain the potentiodynamic polarization curves and electrochemical impedance spectra (EIS). A three-electrode cell set-up was selected in which the prepared sample with an exposed area of 1 cm2 was the working electrode; and a saturated calomel electrode and a platinum sheet were acted as the reference and counter electrodes, respectively. A stable open circuit potential (OCP) was established with 600 s prior to the EIS testing. EIS studies were conducted at OCP for a...
10-mV sinusoidal amplitude over a frequency range of 0.01 Hz–100 kHz. The acquired EIS plots were analyzed using ZSimpWin software (Version 3.10, USA) and best-fitted to the appropriate equivalent circuit (EC) models. After that, polarization of the samples started from approximately −2 V to −1 V with a scan rate of 1 mV s⁻¹. The obtained electrochemical parameters (corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$) and Tafel slopes ($\beta_a$ and $\beta_c$)) were fitted using the Tafel extrapolation method. The experiment was performed in a corrosive environment of Hank’s solution (8.0 g L⁻¹ NaCl, 0.4 g L⁻¹ KCl, 0.14 g L⁻¹ CaCl₂, 0.35 g L⁻¹ NaHCO₃, 1.0 g L⁻¹ glucose (C₆H₁₂O₆), 0.1 g L⁻¹ MgCl₂·6H₂O, 0.06 g L⁻¹ MgSO₄·7H₂O, 0.06 g L⁻¹ KH₂PO₄, and 0.06 g L⁻¹ Na₂HPO₄·12H₂O). The polarization resistance ($R_p$) and

**Fig. 1.** Schematic construction of the Ca–P coatings via hydrothermal treatment.

**Fig. 2.** SEM images of the (a and b) I, (c and d) II and (e and f) III coatings; (A) Element contents and corresponding Ca/P ratios, (B) FTIR spectra and (C) XRD patterns of the obtained coatings.
corrosion protection efficiency ($\eta$) were calculated using Equations (1) and (2) [39–41]. All the electrochemical tests were repeated in triplicate to maintain the reproducibility.

$$R_p = \frac{\beta_i \beta_i}{2.303 \eta_i \eta_i (\eta_i + \beta_i)}$$  \hspace{1cm} (1)

$$\eta = (i_{corr \ (bare)} - i_{corr \ (coated)})/ i_{corr \ (bare)} \times 100\%$$  \hspace{1cm} (2)

where $i_{corr \ (bare)}$ and $i_{corr \ (coated)}$ represent the corrosion current density of bare AZ31 alloy and coated samples.

### 2.4.2. Hydrogen evolution test

Hydrogen evolution process was monitored by placing the substrates in Hank’s solution at 37 °C under an inverted funnel connected to a graduated burette and testing the water level in the burette intermittently for 250 h with full surface exposure. Four samples for each condition were conducted to ensure the repeatability.

### 2.5. Scratch measurement

Scratch measurements were implemented to represent the adhesion force of the coating (critical load) via MML Nanotest system (Micro Materials, Ltd). Scratches of 2 mm length were made by a diamond Rockwell indenter with a spherical tip radius of 25 μm sliding at a constant speed of 2 mm min$^{-1}$ under increasing loads from 0 to 20 N. Scratch images were captured using an in-situ optical microscope system in order to locate initial failure of the coating. The tests were repeated for three times.

### 3. Results

#### 3.1. Surface analysis

Fig. 2 shows the SEM morphologies of the obtained three coatings under different conditions. For the I coating, it exhibits a stereoscopic blade morphology with some clusters (Fig. 2a and b). When the (PVP/PAA)$_{3.5}$ template is used, the coating becomes more compact than I coating (Fig. 2c and d). While for the III coating, it is obvious that the same concentration of free PVP and PAA in the Ca–P solution leads to many micro-cracks with a width of ~1 μm on the surface of the coating, and the coating displays an amorphous state (Fig. 2e and f).

The element contents and corresponding Ca/P ratios of the obtained coatings are displayed in Fig. 2A. The obtained three coatings are mainly composed of Ca, P, C and O elements. While for the III coating, some Mg, Al and Zn elements are found, which can be ascribed to the corrosion of the samples. The corresponding Ca/P ratios for the I, II, and III coatings are 1.08, 1.10 and 0.80. Fig. 2B and C shows the FTIR spectra and XRD patterns of the obtained three coatings, respectively. The peaks observed at 1113, 1071, 1032 cm$^{-1}$ can be correlated to the $\nu_3$ phosphate (PO$_4^{3-}$) region of HA. The doublet peaks at 601 and 562 cm$^{-1}$ result from the $\nu_4$ bending vibration of PO$_4^{3-}$ [25,42]. The results are further confirmed in the XRD patterns (Fig. 2C). As expected, all the samples exhibit some high intense peaks corresponding to α-Mg$_2$, which may be ascribed to that the porous nature of the coatings [43].

The main composition of the obtained I and II coatings is HA and (Ca, Mg)$_3$(PO$_4$)$_2$, and the peaks intensity of II coating is much higher than the I coating. Only (Ca, Mg)$_3$(PO$_4$)$_2$ can be found on the surface of the III coating, which may be ascribed to the PVP and PAA in the Ca–P solution is not conducive to nucleation and growth of Ca–P crystals (Fig. 2) [37].

The cross-sectional images of I and II coatings are shown in Fig. 3. Both coatings display a similar morphology with different thickness, and the coatings can be divided into three layers. The whole thickness of I and II coatings is 6.91 and 12.69 μm, respectively. It is obvious that the inner two layers are more compact than the outer layer. From the EDS mapping images, the O content in the inner layer is higher than the outer layer, while the Ca and P contents in the inner layer is slightly lower than the outer layer, demonstrating that Mg may react with the Ca–P solution in the initial of the film formation.

The comparison between the scratched I and II coated samples is depicted in Fig. 4. Scratch damage starts with cracks emerged at the coating surface. The I and II coatings exhibit cracking and chipping at 9.94 and 10.69 N, respectively. The better adhesion of the II coating may be ascribed to the LbL assembled polyelectrolyte template, which can be coordinated with Ca$^{2+}$ and PO$_4^{3-}$ ions during the film formation. Yang et al. [44] showed that the critical load of micro arc oxidation ceramic coating on AZ31 substrates was about 13 N, which is higher than the obtained II coating. But the critical load of 10.69 N for the II coating is much higher than the CaHPO$_4$·2H$_2$O coating of 1.35 N on ZnAM50 sample [45] and the (CIP/PAH)$_{10}$/CIP induced HA coating of 2.70 N on AZ31 substrate [33].

#### 3.2. Formation process

SEM morphologies (Fig. 5) with different hydrothermal times disclose the formation process of the II coating. In the initial of 10 min, some pores and cracks appear on the surface of the sample (Fig. 5a and b). After hydrothermal treatment with 30 min, a thin Ca–P coating with small flower-like crystals is preferentially deposited on the scratches (Fig. 5c and d), then the crystals grow up and cover the entire surface. After a 2-h hydrothermal treatment, the Ca–P coating is overlaid on the surface of the AZ31 alloy homogeneously (Fig. 5g and h). Then, the Ca–P coating becomes more and more compact after hydrothermal treatment of 3 h (Fig. 5i and j). The changes of compositions will be analyzed in Fig. 6.

Fig. 6 displays the (A) element contents and corresponding Ca/P ratios, (B) FTIR spectra and (C) XRD patterns of the II coating in the process of formation. It can be seen that the contents of Ca and P elements and Ca/P ratios increase with the hydrothermal time, and 2 h for the hydrothermal treatment later, the Ca and P elemental contents achieve a balance between the deposition and degradation of Ca–P crystal. The intensity of the peaks in FTIR spectra and XRD patterns also confirms the results in Fig. 6A. During the hydrothermal treatment, the main composition changes from H$_3$PO$_4$ at 1132, 1062 and 528 cm$^{-1}$ (Mg(H$_2$PO$_4$)$_2$ to PO$_4^{3-}$ at 1102, 1028, 600 and 561 cm$^{-1}$ (HA and (Ca, Mg)$_3$(PO$_4$)$_2$, which also can be confirmed by the lower Ca and higher Mg contents in the inner layer of the cross-sectional images for the II coating (Fig. 3).

#### 3.3. Corrosion behavior

Transient thermodynamic and kinetic information on the electrochemical corrosion of all the samples in Hank’s solution is provided by the potentiodynamic polarization curves in Fig. 7. The corresponding parameters of all the samples are listed in Table 1. All the coated samples show lower $i_{corr}$ values compared with the bare AZ31 samples, and the II coating (8.05 × $10^{-8}$ A cm$^{-2}$) exhibits the lowest $i_{corr}$ values among all the coated samples. This value is nearly three orders of magnitude lower than those of the bare AZ31 (1.96 × $10^{-7}$ A cm$^{-2}$). In addition, the polarization curves of the different samples show differences in both the anodic and cathodic polarization regions. The bare AZ31 displays typical active anodic polarization curves, with a steady increase of the Mg dissolution rate for all the anodic part, indicating that the surface of AZ31 substrate possesses a high active state. In contrast, all coated samples show a noticeable passivation-like section in the anodic polarization, revealing the suppressed anodic dissolution reaction as the rate-determining step. Note that, the cathodic hydrogen evolution reaction is also restrained in all the coated Mg samples, which can be confirmed in Fig. 9. The II coating processes the highest $R_p$ and $\eta$ values, demonstrating the good corrosion resistance of the induced Ca–P coating.
The corrosion mechanisms of the samples are further evaluated by EIS curves, which are shown in Fig. 8 with the corresponding EC models. The diameters of the capacitive loops for all samples can be ranked as follows: II coating > III coating > I coating > AZ31 substrate. Generally speaking, the larger capacitive loop represents the better corrosion resistance, implying that the Ca–P coating, induced by LbL assembled template, has the best protection against corrosive ions in Hank’s solution.

The Nyquist plots (Fig. 8A–C) display that the bare and coated AZ31 are characterized by two and three capacitive loops in the different ranges of frequency, respectively. For the bare AZ31, CPE$_1$ and $R_f$ are used to characterize the corrosion products layer in the high-frequency range. The low-frequency capacitive loop is described by CPE$_2$ and $R_{ct}$ to characterize the interfacial charge transfer reaction. Differently, three capacitive loops are related to the three Ca–P coatings, which have a dense inner layer and a loose outer layer (Fig. 3), represented with $R_{11}$ and $R_{12}$ in collocation with CPE$_1$ and CPE$_2$ [46]. In both ECs, $R_{1}$, $R_f$ and $R_{ct}$ represent the solution resistance, coating resistance and charge transfer resistance. A constant phase element (CPE) is used instead of a pure capacitive, which is defined by admittance ($Y_0$) and power index number ($n$), and can be calculated by the formula of $Y_{CPE} (\omega) = 1/Z_{CPE} = Y_0(j\omega)^n$ [27]. The fitting results of EIS data are listed in Table 2. The highest $R_{ct}$ values of II coating also confirms the good corrosion protection to hinder the permeation of the corrosive ions.

Bode plots of Fig. 8D show that the impedance modulus of Ca–P coated samples are higher than that of the bare AZ31. The II coating has an impedance modulus of $1.7 \times 10^5 \ \Omega \ \text{cm}^2$, which is higher than the III coating of $6.4 \times 10^4 \ \Omega \ \text{cm}^2$ and I coating of $1.2 \times 10^4 \ \Omega \ \text{cm}^2$. The phase angles (Fig. 8E) of II and III coatings with three time constants are higher than the I coating and bare AZ31. The phase angle of I coating is close to 46°, lower than that of the other specimens, which may be caused by the incompactness of the coating. But it has a wider range of frequencies with an additional time constant than the untreated AZ31 [20]. These reveal that the II coating is an effective physical barrier to corrosion in Hank’s solution.

Hydrogen evolution volume (HEV) and rate (HER) for the four samples are used to evaluate the corrosion behavior during a 250-h immersion in Hank’s solution (Fig. 9). It is obvious that the II coating has the lowest HEV and HER over an entire period of immersion time. The HEV and HER for I coating are slightly lower than the bare AZ31, attributing to the corrosion protection of Ca–P coating. For the III coating, the HEV and HER are lower than that of the I coating in stage I, demonstrating that the corrosion resistance of the III coating is better than the I coating in the short term, which is consistent with

Fig. 3. Cross-sectional images and corresponding EDS mapping of the (a–f) I and (g–l) II coatings.

Fig. 4. Scratch track view of the bare AZ31 in comparison to (a) I and (b) II coatings.
After that, the HEV and HER of the III coating increase gradually until they are higher than the I coating (stage II) and AZ31 substrate (stage III), which may be ascribed to a large number of microcracks in the coating acted as the invasion channels for corrosive ions, accelerating galvanic corrosion of the AZ31 substrate (Fig. 2). In the initial 15 h, the HERs for all samples decrease due to the formation of Mg(OH)$_2$ corrosion product. After an immersion of 250 h, the corrosion rates of four samples can be ranked as: III coating ($0.0102 \pm 0.0022$ mL cm$^{-2}$ h$^{-1}$) > AZ31 substrate ($0.0089 \pm 0.0042$ mL cm$^{-2}$ h$^{-1}$) > I coating ($0.0110 \pm 0.0015$ mL cm$^{-2}$ h$^{-1}$) > II coating ($0.0056 \pm 0.0054$ mL cm$^{-2}$ h$^{-1}$). The photographs of the four samples after an immersion of 250 h are shown in Fig. 9C, a complete and dense coating is still presented on the surface of the AZ31 substrate for II coating, agreeing with the results of the hydrogen evolution test. Thus, II coating exhibits the best corrosion protection during immersed in Hank’s solution for 250 h.

SEM images of the AZ31 substrate, I and II coatings after an immersion of 250 h in Hank’s solution are displayed in Fig. 10a-f. Many cracks of corrosion products with a width of ~5 μm appear on the surface of the bare AZ31. While for the I coating, the distribution of the lamellar structure is uneven with some cluster of blocks, due to the precipitation of the corrosion products. It is no obvious changes for the II coating, confirming the good corrosion resistance during immersion.

FTIR spectra and XRD patterns of the samples after an immersion of 250 h in Hank’s solution are shown in Fig. 10A and B. The peaks observed at 1106, 1063 and 1029 cm$^{-1}$ can be correlated to the $v_3$ phosphate (PO$_4^{3-}$) region of HA. The doublet peaks at 600 and 562 cm$^{-1}$ result from the $v_4$ bending vibration of PO$_4^{3-}$ [25,42]. The peaks appeared at 1374 and 868 cm$^{-1}$ are related to the vibration of HPO$_4^{2-}$ [42]. And the peak presented at 1433 cm$^{-1}$ results from $v_3$ vibration of CO$_3^{2-}$ [25]. These results will be further confirmed in the XRD patterns (Fig. 10B). The main composition of the obtained I and II coatings remains to be HA and (Ca, Mg)$_3$(PO$_4$)$_2$, and (Ca, Mg)$_3$(PO$_4$)$_2$.
Table 1
Electrochemical parameters of the polarization curves for the bare and coated AZ31 in Hank's solution.

| Samples   | $E_{corr}$ (V) | $i_{corr}$ (A·cm$^{-2}$) | $\beta_a$ (mV·dec$^{-1}$) | $\beta_c$ (mV·dec$^{-1}$) | $R_p$ (Ω·cm$^2$) | $\eta$ (%) |
|-----------|---------------|--------------------------|---------------------------|---------------------------|------------------|------------|
| AZ31      | $-1.51$       | $1.96 \times 10^{-5}$    | 47.12                     | 170.97                    | $1.60 \times 10^6$ |            |
| I coating | $-1.57$       | $1.77 \times 10^{-6}$    | 147.26                    | 116.74                    | $1.59 \times 10^7$ | 90.97      |
| II coating| $-1.36$       | $8.05 \times 10^{-8}$    | 115.38                    | 168.60                    | $3.69 \times 10^8$ | 99.59      |
| III coating| $-1.40$      | $1.07 \times 10^{-7}$    | 66.88                     | 155.06                    | $1.90 \times 10^8$ | 99.45      |

Fig. 8. (A–C) Nyquist, (D and E) Bode plots and (F) corresponding EC models of the (a) AZ31 substrate, (b) I, (c) II and (d) III coatings in Hank's solution.

Fig. 9. (A) HEV, (B) HER curves and (C) photographs with an immersion of 250 h: (a) AZ31 substrate, (b) I, (c) III and (d) II coatings in Hank's solution.
precipitate is observed on the surface of the AZ31 substrate after 250 h immersion. The stability morphology and composition of the coatings also indicate the good corrosion resistance of the II coating during immersion.

4. Discussion

4.1. Influence of the coating preparation methods and inducers

In general, the preparation method is a primary factor to affect the properties of Ca–P coatings. It is obvious that the Ca–P coating formed by HDP [38] provides best corrosion resistance among all coating methods.
preparation methods, such as radio frequency magnetron sputtering [47], microwave aqueous synthesis (MAS) [48], EDP [49] and mixed electric discharge machining (MEDM) [14]. For the HDP method, the different pH value [19] and Ca/P ratio [50] of the hydrothermal solution, hydrothermal temperature [38] and time [51] and types of alloy lead to the different Ca–P coating with different properties. Thus, the HDP becomes the most commonly used coating preparation method due to its simple operation and easy control of variables.

In order to improve the corrosion resistance of Mg alloys in further, many inducers are selected to construct the Ca–P coatings to improve its integrity and compactness. The \( \delta_0 \) of the Ca–P coatings formed with different inducer is exhibited in Fig. 11a. It can be seen that the Ca–P coatings with the organic inducers, especially for glucose [18], deoxyribonucleic acid (DNA) [52], PDA [26], RGDC [11], have a better improvement in corrosion resistance than the Ca–P coatings with the inorganic inducers [53,54]. Compared with the Na-EDTA [10,29], the Ca-EDTA [20] can be used to form a Ca–P coating with good corrosion resistance. Although the heterogeneous nucleation of SnO2 is helpful for film formation, the enhancement of corrosion resistance is still limited. Otherwise, a LbL assembled (CIP/PAH)\(_{10}\)/CIP multilayer is also used to prepare a HA coating, but the increase of corrosion resistance is lesser than the (PVP/PAA)\(_{5.5}\) induced Ca–P coating on AZ31 substrate [33]. This can be ascribed to the molecular structure of the assembly monomer, which is plenty of –COOH in PAA.

When the pH value of PAA solution is 7.0, the pKa of PAA solution is 6.64, thus the distribution fraction of -COO\(^-\) in PAA can be calculated with:

\[
\delta = 1 - \frac{[H^+]}{K_a + [H^+]} \tag{3}
\]

Where \( \delta_0 \) is the distribution fraction after one step dissociation, \( K_a \) is the acid equilibrium constant. Thus, the distribution fraction of -COO\(^-\) in PAA is 0.6961, indicating most of the –COOH changes to -COO\(^-\), which is beneficial to the adsorption of Ca\(^{2+}\) to develop Ca-PAA complex.

Kaabi Falahieh Asl et al. [55] has formed a Ca–P coating with PAA,
which the PAA is mixed in the phosphate and calcium ion precursors. The obtained Ca–P coating displays a good corrosion protection with good cytocompatibility, and the incorporation of PAA in the coating changes the phase formation route during HDP process. By increasing the PAA concentration, the formation of the tricalcium phosphate phase changes the phase formation route during HDP process. By increasing the PAA concentration, the formation of the tricalcium phosphate phase increases. But the coating shows a globular morphology with some pores, hindering the protection for Mg substrates due to the penetration of the corrosive ions. Therefore, a (PVP/PAA)5.5 template is beneficial to prepare a more compact and homogeneous foliated Ca–P coating (Fig. 2) to protect the bare AZ31 for a long term (Fig. 9). As the similar compositions with natural bone, the obtained II coating good cytocompatibility may be suitable to be applied as orthopedic implants. 4.2. Coating formation mechanism

The coating formation mechanisms of the II coating via HDP with LbL assembled templates are shown in Fig. 12. In the initial stage of HDP, the water molecules are penetrated through the LbL assembled (PVP/PAA)5.5 templates. The electrochemical corrosion of the skin layer for the AZ31 substrate results in some Mg2+ ions (Equations (4)–(6)).

\[
\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad (4)
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{2OH}^- + \text{H}_2 \uparrow \quad (5)
\]

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \uparrow \quad (6)
\]

An inner Mg(H2PO4)2 can be formed by:

\[
\text{Mg}^{2+} + 2\text{H}_2\text{PO}_4^- \rightarrow \text{Mg(H}_2\text{PO}_4)_2 \quad (7)
\]

Stereohiphine blade-shaped Ca-P coating is formed on the surface of the AZ31 substrate, which is a typical result of the strong electrostatic interaction between the -COO group (PAA) or polar lactam bonds (PVP) and Ca2+ ions. A (PVP/PAA)5.5 template is beneficial to the homogeneous adsorption of Ca2+ ions, improving the nucleation and growth of the Ca-P coating.

Then, the dihydrogen phosphate (H2PO4−) ions are transformed into phosphate (PO43−) ions through the following ionic reactions (Equations (8) and (9)):

\[
\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O} \quad (8)
\]

\[
\text{HPO}_4^{2-} + \text{OH}^- \rightarrow \text{PO}_4^{3-} + \text{H}_2\text{O} \quad (9)
\]

Thus, the Ca-P coating composed of Mg(H2PO4)2, (Ca, Mg)3(PO4)2 and HA is obtained by the following reactions:

\[
3\text{Ca}^{2+} + 3\text{Mg}^{2+} + 2\text{PO}_4^{3-} \rightarrow (\text{Ca}, \text{Mg})_3\text{PO}_4_2 \quad (10)
\]

\[
10\text{Ca}^{2+} + 2\text{OH}^- + 6\text{PO}_4^{3-} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \quad (11)
\]

However, the free PAA and PVP mixed in Ca-P solution may go against the nucleation and growth of the Ca-P crystals (Fig. 2) to the disadvantages of the corrosion protection for Mg alloys (Fig. 9).

5. Conclusion

A novel polyelectrolyte multilayer template, based on PAA and PVP via LbL assembly, is used to construct biomimetic Ca-P coating to improve the corrosion resistance of the AZ31 alloy.

(1) The polyelectrolyte multilayer induced Ca-P coating shows a compact stereohiphine blade morphology with the thickness of 12.69 μm.

(2) The (PVP/PAA)5.5 template improves the binding force of the Ca-P coating from 9.94 to 10.69 N.

(3) Both hydrogen evolution and electrochemical corrosion tests demonstrated that the template-induced Ca-P coating exhibits a good corrosion protection for AZ31 alloy.

(4) The free PAA and PVP may go against the nucleation and growth of the Ca-P crystals, but the LbL assembled (PVP/PAA)5.5 template, which the distribution fraction of -COO− in PAA is 0.6961, is beneficial to the formation of the tricalcium Ca-P coating, because most of the −COOH changes to −COO− to adsorb Ca2+ for development of Ca-PAA complex.

CRediT authorship contribution statement

Lan-Yue Cui: Conceptualization, Formal analysis, Writing - original draft. Shen-Cong Cheng: Data curation. Lu-Xian Liang: Data curation. Jing-Chao Zhang: Data curation. Shuo-Qi Li: Funding acquisition. Zhen-Lin Wang: Data curation. Rong-Chang Zeng: Funding acquisition, Writing - review & editing.

Declaration of competing interest

The authors declared that they have no conflicts of interest to this work.

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