In Vitro Corrosion and Cytocompatibility of a Microarc Oxidation Coating and Poly(L-lactic acid) Composite Coating on Mg–1Li–1Ca Alloy for Orthopedic Implants

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ABSTRACT: Manipulating the degradation rate of biomedical magnesium alloys poses a challenge. The characteristics of a microarc oxidation (MAO), prepared in phytic acid, and poly(L-lactic acid) (PLLA) composite coating, fabricated on a novel Mg–1Li–1Ca alloy, were studied through field emission scanning electron microscopy (FE-SEM), electron probe X-ray microanalysis (EPMA), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The corrosion behaviors of the samples were evaluated via hydrogen evolution, potentiodynamic polarization and electrochemical impedance spectroscopy in Hanks’ solution. The results indicated that the MAO/PLLA composite coatings significantly enhanced the corrosion resistance of the Mg–1Li–1Ca alloy. MTT and ALP assays using MC3T3 osteoblasts indicated that the MAO/PLLA coatings greatly improved the cytocompatibility, and the morphology of the cells cultured on different samples exhibited good adhesion. Hemolysis tests showed that the composite coatings endowed the Mg–1Li–1Ca alloys with a low hemolysis ratio. The increased solution pH resulting from the corrosion of magnesium could be tailored by the degradation of PLLA. The degradation mechanism of the composite coatings was discussed. The MAO/PLLA composite coating may be appropriate for applications on degradable Mg-based orthopedic implants.

KEYWORDS: magnesium alloy, degradation, microarc oxidation, poly(L-lactic acid), biomaterial

1. INTRODUCTION

The regeneration of bone defects using biomedical materials such as bioceramics, stainless steel, titanium, polymers and composites has been extensively studied in recent years.1–4 In comparison with these materials, magnesium (Mg) alloys show great potential in clinical applications because their good biocompatibility, degradability and mechanical properties are similar to those of human bone.5–7 However, the poor corrosion resistance of Mg alloys leads to a rapid increase in the pH value and hydrogen collection in the microenvironment surrounding the implant.8–10 Therefore, it is of importance to control the degradation of Mg alloys to an appropriate rate. Usually, the corrosion resistance of Mg alloys can be improved by means of purifying and alloying,11–13 refinement of microstructure by postprocessing14,15 and surface modification, such as phosphate conversion coatings,16,17 microarc oxidation (MAO) coatings,18,19 polymeric coatings,19 silane-modified coatings,20 layer-by-layer assembly21–25 and layered double hydroxide.26,27

Numerous studies have been conducted on biomedical Mg alloys, such as Mg–Al (AZ31), Mg–Zn (Mg–6Zn, Mg–Zn–
Nd), Mg–Mn, Mg–RE (WE43), Mg–Ca (Mg–0.8Ca) and Mg–Li (LAE442) alloys.\textsuperscript{11–15} Ca-bearing Mg alloys (Mg–Ca) have attracted particular attention because Ca is a major element of human bone and can refine the microstructure of Mg alloys.\textsuperscript{11} However, Mg–Ca alloys exhibit poor corrosion resistance.\textsuperscript{11,13}

Additionally, Mg–Li alloys are remarkably malleable and ultratough due to the alloying element Li. Li is the only element that can change the microstructure of Mg alloys from HCP crystalline into α (-Mg), α + β (-Li) and β phases with increasing Li concentration.\textsuperscript{10,11,14} Usually, β (-Li) phase has a body-centered cubic structure and better ductility than α (-Mg) phase. Higher Li content leads to an enhancement in deformability of binary Mg–Li alloys. The introduction of Ca into Mg–Li alloys gives rise to an increase in tensile strength. In addition, Li possesses higher activity than Mg, and exerts a pronounced influence on the corrosion resistance. Li concentration below 9 wt % in Mg is beneficial for the corrosion resistance; however, increasing Li concentration significantly accelerates the corrosion of Mg alloys.\textsuperscript{28}

Trace of Li element has a necessary and beneficial function for human body. Mg–Li–Al–RE alloy (LAE442) demonstrates superior in vivo corrosion resistance and good biocompatibility.\textsuperscript{10} The Li concentration in bone slightly increased after implantation. The contents of Li in liver and bone of rabbit are 1.4 μg·kg\textsuperscript{-1} and 0.08 mg·kg\textsuperscript{-1}, respectively; far below any physiological risk level.\textsuperscript{29} However, the alloy has higher contents of Al and RE elements. The Al element is reported to be predominantly accumulated in the nervous system and has been implicated in the pathogenesis of Alzheimer’s disease, and the RE elements including Ce, Pr and Y exhibit hepatotoxicity.\textsuperscript{15} Thus, Al- and RE-free Mg–Li–Ca alloys may be more suitable for degradable biomaterials.

The earlier research of our group shows that the Mg–Li–Ca alloy exhibits a higher in vitro corrosion resistance than Mg–Ca alloys due to the formation of a compact corrosion product layer.\textsuperscript{11,14} The microstructure of the dual phase Mg–9Li–1Ca alloy is characterized by α (-Mg) and β (-Li) phases and intermetallic compound Mg–Li–Ca particles, and the oxide films, composed of Mg- and Li-bearing compounds acting as barrier layers, greatly improve the corrosion performance of the alloy.\textsuperscript{14}

Among the various surface modifications, i.e., the MAO coating, also known as plasma electrolytic oxidation (PEO) coatings, have been widely employed on Mg alloys. MAO/PEO refers to a high-voltage plasma-assisted anodic oxidation process in which plasma discharges cause the partial short-term melting of the oxide layer and promote the formation of a highly adherent ceramic oxide coating. This coating possesses advantages such as high hardness, good wear resistance and moderate corrosion resistance.\textsuperscript{30}

MAO coatings prepared in different solutions, e.g., silicate, phosphate and fluoride electrolytes, exhibit different morphological characteristics, porosities, thicknesses and corrosion rates.\textsuperscript{31,32} MAO coatings prepared in phytic acid (C\textsubscript{6}H\textsubscript{18}O\textsubscript{24}P\textsubscript{6}) solution exhibit a better pore uniformity and corrosion resistance than those produced in silicate solution.\textsuperscript{33,34} Despite the remarkably advantageous properties of the MAO coating, the presence of micropores and cracks generated during the microarc discharges provides paths for aggressive ions to penetrate into and react with the substrate, thereby accelerating corrosion. Fischerauer et al.\textsuperscript{35} studied the degradation rates of uncoated and MAO-coated ZX50 Mg alloy implants in rat femurs and found that in the first 4 weeks, the degradation rate for the uncoated Mg alloys is higher than for the MAO-coated ones. However, the reverse trend happens in the subsequent 4 weeks. The result reveals that porous MAO coatings only improve corrosion performance for a limited period.\textsuperscript{36–38} In other words, it is necessary to seal the pores of the MAO coatings to enhance the corrosion resistance and provide a longer protection.

Poly(lactic acid) (PLA), as a biodegradable and biocompatible polymer, has been approved for human clinical uses including small load-bearing bone implants and cardiovascular scaffolds.\textsuperscript{39–41} It undergoes a degradation process by the simple hydrolysis of an ester bond, and the final products are water and carbon dioxide. A significant drawback of PLA is that its degradation generates acidic products that lower the local solution pH, accelerating further degradation and triggering inflammatory and foreign body reactions in vivo.\textsuperscript{42–44} Substantial investigations, involving those on the corrosion performance of PLA coatings on Mg and its alloys, have been carried out.

Taking the degradation features of Mg alloys and PLA into consideration, PLA polymeric coatings on Mg alloys have become a potential option to maintain the pH values at a normal level as well as to control the corrosion rate. Abdal-hay et al.\textsuperscript{45,46} found that polymeric membranes of pristine and hydroxyapatite-doped PLA strongly enhance the corrosion resistance and bending strength of the Mg substrate and ameliorates cell growth. Xu et al.\textsuperscript{46,47} prepared poly(L-lactic acid) (PLLA) and poly(ε-caprolactone) (PCL) coatings of both high molecular weight and low molecular weight on pure Mg, revealing that both films significantly improve cytocompatibility and suppress the pH increase of the medium during Mg degradation. Chen et al.\textsuperscript{48} reported that PLA and PCL coatings on high-purity Mg (HP-Mg) improve the corrosion resistance. In addition, some attempts have been made to apply organic coatings for sealing the micropores and cracks of MAO coatings on Mg alloys. MAO/PLLA composite coatings on WE42, AZ31 and Mg–Li–Ca–Y alloys present excellent cytocompatibility and corrosion resistance.\textsuperscript{39–52} Nevertheless, the degradation mechanism of the MAO/PLLA film on Mg alloys remains unclear.

The purpose of this investigation is to fabricate a porous MAO/PLLA composite coating on the novel Mg alloy Mg–1Li–1Ca and to obtain insight into the degradation mechanism and cytocompatibility of the Mg–1Li–1Ca alloy with and without the MAO/PLLA coating.

2. MATERIALS AND METHODS

2.1. Samples and Coating Preparation Procedures. An as-extruded Mg–Li–1Ca (1.26 wt % Li, 0.95 wt % Ca, and balanced Mg) alloy was chosen as the substrate. The material was cut into square specimens with dimensions of 20 mm × 20 mm × 4 mm for in vitro degradation in Hanks’ balanced salt solution (HBSS, 8 g·L\textsuperscript{-1} NaCl, 0.4 g·L\textsuperscript{-1} KCl, 0.14 g·L\textsuperscript{-1} CaCl\textsubscript{2}, 0.35 g·L\textsuperscript{-1} NaHCO\textsubscript{3}, 1 g·L\textsuperscript{-1} glucose, 0.1 g·L\textsuperscript{-1} MgCl\textsubscript{2}·6H\textsubscript{2}O, 0.1 g·L\textsuperscript{-1} MgSO\textsubscript{4}·7H\textsubscript{2}O, 0.06 g·L\textsuperscript{-1} KH\textsubscript{2}PO\textsubscript{4} and 0.126 g·L\textsuperscript{-1} Na\textsubscript{2}HPO\textsubscript{4}·12H\textsubscript{2}O) with pH = 7.4 and 10 mm × 10 mm × 4 mm for cytocompatibility tests. Prior to the coating preparation, the samples were mechanically ground with 400–2500 grit SiC paper and then ultrasonically cleaned in acetone for 2 min, washed with deionized (DI) water and dried in a dry chamber.

The pretreated specimens were anodized by self-made MAO equipment, consisting of a power supply, a stainless steel barrel, and a stirring and cooling system. The MAO treatment was carried out for 800 s using the stainless steel barrel as the cathode at a frequency of 100 Hz alternating current with a bridge-rectifier waveform, a
breakdown voltage of 170–180 V, and a duty cycle of 50%. The electrolyte, comprising 10 g L\(^{-1}\) NaOH and 8 g L\(^{-1}\) phytic acid, was continuously stirred during the anodization process. After the preparation of the coating, the samples were rinsed with DI water and dried by warm air.

PLLA (MW = 200,000, Shandong Institute of Medical Instruments, China) was dissolved in dichloromethane with continuously stirring for a 5 wt % solution. The MAO-treated substrates were then immersed into the polymeric solution for 60 s, withdrawn and dried in a self-made freeze-drying device. The prepared samples were hung in a precooled airtight container using dry ice. The air was then evacuated, and the container was put in a dry chamber at 55 °C for 12 h to allow solvent evaporation as well as to achieve a porous film. Prior to the dipping process, all of the specimens were placed in a dry chamber at 120 °C for 10 min to remove the moisture from the porous MAO coating.

2.2. Characterization of Coatings and in Vitro Degradation.

2.2.1. Surface Analysis. The surface and cross-sectional morphologies of the MAO/PLA coating were investigated using a field-emission scanning electron microscope (FE-SEM, Nova NanoSEM 450, USA). All samples for the SEM observation were sputtered with gold. Both the coated and bare samples before and after the in vitro degradation tests were examined by a X-ray diffraction meter (XRD, Rigaku D/Max 2500PC, Japan) with a Cu target (\(\lambda = 0.154 \text{ nm}\)) at a scanning rate of 0.02 s\(^{-1}\) in the 2θ range of \(10^\circ–90^\circ\). The chemical composition of the coating was inspected through energy-dispersive X-ray spectroscopy (EDS, Oxford Isis) affiliated with electron probe X-ray microanalysis (EPMA, JXA-8230, Japan).

2.2.2. Electrochemical Corrosion Test. The potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were performed on a potentiostat (PARSTAT 2273) in HBSS. All of the electrochemical tests were conducted in a classical three-electrode system that consists of the sample as the working electrode (1 cm\(^2\)), a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The PDP curves were recorded with a sweep rate of 2 mV s\(^{-1}\), and EIS measurements were acquired from \(10^3\) to \(10^{-2}\) Hz using a 5 mV amplitude perturbation.

2.2.3. In Vitro Immersion Tests. The substrate, MAO and MAO/PLLA-coated substrates were prepared in triplicate and immersed in 300 mL of HBSS. The ratio of the sample surface area to solution exposed area (cm\(^2\)) and immersion time (h), respectively. Immersion time can be related through Figure 1. The hydrogen evolution rate (HER) as a function of immersion time was recorded every hour during the immersion. PDP curves were recorded with a sweep rate of 2 mV s\(^{-1}\) using a 5 mV amplitude perturbation.

\[ \text{HER} = \frac{V_{\text{H2}}}{s \cdot t} \]  

(1)

where \(V_{\text{H2}}\) is the hydrogen evolution volume (mL), \(s\) and \(t\) are the exposed area (cm\(^2\)) and immersion time (h), respectively.

The pH value of the solution was measured by a pH meter (PH-400). Immersion period of 140 h was predetermined upon the possible observation on the failure of the MAO/PLA coating, and for the insight into the corrosion mechanism of the MAO/PLA coating.

2.3. Cytocompatibility and Hemolysis Tests.

2.3.1. Cell Culture and Preparation of Extracts. Murine MC3T3-E1 osteoblast-like cells (Cells Resource Centre of Shanghai Institute for Biological Science, Shanghai, China) were utilized for cell culture studies. Cells were cultured in minimum essential medium alpha (\(\alpha\)-MEM, Hyclone) containing 1% penicillin/streptomycin antibiotics and 10% fetal bovine serum (Gibco, Australia) at 37 °C in a humidified atmosphere of 5% CO\(_2\). At 78–80% confluence, the cells were enzymatically detached with a minimum amount of trypsin–EDTA (Sigma-Aldrich, USA) and resuspended in culture medium. The cells were then recultured until the third passage, which was used for the experiments. The specimens were sterilized by ethylene oxide and then placed in clean centrifuge tubes with added \(\alpha\)-MEM at a ratio of 3 mL·cm\(^{-2}\). After 24 h of incubation at 37 °C, the samples were removed, and the media containing the extracts of different samples were collected for the following tests.

2.3.2. MTT Assay. The 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) assay was used to determine the proliferation and viability based on the reductive cleavage of MTT (a yellow salt) to formazan (a dark blue/purple compound) by the mitochondrial dehydrogenase of living cells. The cell suspension was adjusted to a cell density of 1 × 10\(^4\) mL\(^{-1}\), and then 200 \(\mu\)L was added into each well of 96-well plates, which were sealed by phosphate buffered solution (pH 7.4, FBS, Solibo) in the outer 40 wells. The wells with the cell suspension were divided into 4 groups: the Mg–1L1–1Ca substrate group, MAO group, MAO/PLLA group, control group (culture media containing cell suspension) and blank group (culture media alone), each with 5 wells. After 24 h of incubation, the culture media were removed, together with the leaching liquor of the substrates. The bare substrate, MAO and MAO/PLLA-coated samples were added into the wells of the corresponding groups in volumes of 100 \(\mu\)L, whereas equivalent volumes of culture media were supplied to the control group and blank group. The culture medium of each well was changed every other day during the testing period, and 20 \(\mu\)L MTT solution was injected on each of days 1, 3 and 5. The 96-well plates were kept in the incubator for 4 h. After incubation, the medium was removed, and the formazan crystals were solubilized in DMSO. The absorbance (A) was measured by a universal microplate spectrophotometer (722, Shanghai Precision Science Instrument, China) at a wavelength of 490 nm, and the relative growth rate (RGB %) of the cells was calculated by the relation below

\[ \text{RGB} = \frac{A_{\text{fi}}}{A_{\text{fl}} \times 100\%} \]

(2)

where \(A_{\text{fi}}\) is the absorbance of the testing specimen and \(A_{\text{fl}}\) is the absorbance of the control groups. The results are expressed as the mean ± standard deviation of five samples per group and were compared using Student’s t-test, with a significance level of \(P < 0.05\).

2.3.3. Alkaline Phosphatase (ALP) Assay. An alkaline phosphatase colorimetric assay kit (Nanjing Jiancheng, China) was used to evaluate the osteoblast differentiation. The cell suspension was adjusted to a
cell density of $1 \times 10^4$ mL$^{-1}$, and 2 mL of the suspension was added into the first four wells of a 6-well plate. After being seeded for 24 h, the culture media were removed and rinsed twice by PBS. Then, α-MEM and the extracts of the bare substrates, the MAO-coated samples, and the PLLA coating and MAO coating interlocked. Different chemicals used in the prepared solutions.

### 2.3.4. Cellular Adhesion and Morphology Imaging

A 1.5 mL suspension was seeded onto the substrates, the MAO and PLLA-coated samples after sterilization by ethylene oxide at a cell density of $5 \times 10^4$ cells per well in 24-well plates. After 24 h of culturing in a cell incubator, the specimens were taken out and immobilized by 4% glutaraldehyde for 12 h and then dehydrated with ethanol step by step. Lyophilization was applied in the dehydration to prevent the samples from shrinking and to maintain the structure and morphology of the cells. Following the drying process, the samples were coated with platinum, and the SEM micrographs were observed using FE-SEM.

### 2.3.5. Hemolysis Test

The hemolysis test in vitro was conducted as follows: 10 mL fresh rabbit arterial blood from a healthy New Zealand white rabbit, containing 0.5 mL potassium oxalate (20 g·L$^{-1}$) anticoagulant was added into the culture media with different extracts prepared in the previous step, kept at 37 °C for 60 min, and then centrifuged at 3000 rpm for 5 min. Three sets of parallel tests were settled, and the A of the supernatant solution was measured using a universal microplate spectrophotometer at a wavelength of 520 nm and converted into the amount of ALP (U·L$^{-1}$).

### 3. RESULTS AND DISCUSSION

#### 3.1. Microstructure of the Alloy and Morphologies of the Coatings

The microstructure of the Mg–1Li–1Ca alloy after etching was characterized by the α-Mg phase and the intermetallic compounds Mg$_2$Ca dispersed in the grain interiors and at the grain boundaries (Figure 2), in which the Li atoms are solid-soluted. The Mg$_2$Ca phase, with a higher corrosion potential than the α-Mg matrix, may lead to microgalvanic corrosion between the Mg$_2$Ca phase and its neighboring α-Mg matrix. The typical morphology of the MAO coating in Figure 3a demonstrates the presence of microcracks and micropores. Interestingly, a porous PLA film was also prepared on the MAO-coated substrates, as depicted in Figure 3b. The EDS result of the MAO coating, as shown in the inset of Figure 3a, demonstrates that the MAO coating is mainly composed of Mg, O, and traces of Ca and P, indicating the presence of MgO and calcium phosphates. It is likely that the Ca and P of the MAO coating are from the substrate and electrolytes used in the formation of the coating, respectively, while the presence of C and O designates the MAO/PLLA coating, as shown in the inset of Figure 3b.

Figure 4 shows the cross-sectional SEM micrographs and elemental mapping of the substrates with MAO/PLLA films. The MAO and the PLLA coatings have thicknesses of approximately 3 and 10 μm, respectively. As illustrated in Figure 4b, the intensity of C decreased when the EDS scan line approached the PLLA/MAO interface, confirming the existence of the PLLA/MAO interlock. Nevertheless, it can be recognized that C diffused into the MAO layer, indicating that the PLLA sealed the porous film and the PLLA coating and MAO coating interlocked.

#### 3.2. Hydrogen Evolution Rates and pH Measurements

The hydrogen evolution rate (HER) vs immersion time curves of the coated and uncoated samples are shown in Figure 5. In the initial stage of immersion, the HER of the substrates is much higher than that of the coated samples, and some bubbles can be seen on the surfaces of the substrates, whereas no bubbles were observed on the coated ones. However, the HER of the MAO-coated specimens began to increase rapidly at an immersion of 50 h and finally became slightly higher than that of the substrates after 85 h of immersion, compared with the constant HER of the MAO/PLLA-coated samples. It is noted that similar degradation behavior occurs on the MAO coating on Mg–1Li–1Ca–1.0Y alloy based on our previous study. Namely, the HERs of the MAO coating on Mg–1Li–1Ca–1.0Y alloy (0.142 mL·cm$^{-2}$·h$^{-1}$) surpasses that of the substrate after an immersion time of 9 h. Interestingly, the HERs of the MAO coating on the Mg–1Li–1Ca alloy (0.004 mL·cm$^{-2}$·h$^{-1}$) is much lower than that on the Mg–1Li–1.12Ca–1.0Y alloy, and it is until 85 h that the HERs of the MAO coating surpasses that of the substrate, although the MAO thickness (about 3 μm) on the Mg–1Li–1Ca alloy is much lower than that (approximately 10 μm) on the former alloy. The result designates that the MAO coating on the Mg–1Li–1Ca alloy possesses superior corrosion resistance to that on the Mg–1Li–1.12Ca–1.0Y alloy, that is, the thickness of MAO is not a critical factor influencing the corrosion resistance. This abnormal scenario may be attributable to the different chemicals used in the prepared solutions. The MAO coatings were prepared in a silicate electrolyte containing 20 g·L$^{-1}$ NaOH, 20 g·L$^{-1}$ Na$_2$SO$_4$, 15g·L$^{-1}$ NaB$_4$O$_7$, and 1.5% Triton X-100 solution was added into each well, and the plate was placed into a refrigerator for 10 h at 4 °C. The four groups of the Mg–1Li–1Ca substrates, the MAO and PLLA-coated samples, and the control were settled with 5 wells. The corresponding supernatants were supplemented by the volume of 50 μL per well in a 96-well plate. The addition of reagents was following the instructions of the ALP kit, and the absorbance was measured using a universal microplate spectrophotometer at a wavelength of 520 nm and converted into the amount of ALP (U·L$^{-1}$).

$$HR(\%) = \frac{A_{pe} - A_{nc}}{A_{pe} - A_{ac}} \times 100\%$$

where $A_t$ is the A of the testing specimen, $A_{nc}$ is the A of the negative control group (10 mL of culture medium with 0.2 mL of diluted blood) and $A_{ac}$ is the A of the positive control group (10 mL distilled water with 0.2 mL diluted blood).
and 10 g·L⁻¹ \( \text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \) together with 7.5 g·L⁻¹ phytic acid for the \( \text{Mg}_{1.21}\text{Li}_{1.12}\text{Ca}_{1.0}\text{Y} \) alloy, and in an electrolyte comprising 10 g·L⁻¹ \( \text{NaOH} \) and 8 g·L⁻¹ phytic acid for the \( \text{Mg}_{1}\text{Li}_{1}\text{Ca}_{1} \) alloy. As a result, a thinner and more compact MAO coating formed on the \( \text{Mg}_{1}\text{Li}_{1}\text{Ca}_{1} \) alloy (Figure 4a,c).

After 140 h of immersion, the average HER of the substrate, the MAO and MAO/PLLA-coated samples were 2.12, 1.58 and 0.56 \( \text{mL} \cdot \text{cm}^{-2} \cdot \text{h}^{-1} \), respectively. The HER indicate that the MAO/PLLA coating greatly enhanced the corrosion resistance of the \( \text{Mg}_{1}\text{Li}_{1}\text{Ca}_{1} \) alloy and also reveal that the disadvantage of the MAO coatings in the corrosion process that could be improved by PLLA modification are consistent with Fischerauer’s research.35

Figure 6 designates the changes in the pH value of the solutions with the immersion time. The process can be divided into four stages. In stage one, there was a significant increase in the solution pH for each sample, resulting from the corrosion of the Mg alloys. For the bare substrate and the MAO-coated samples, this was followed by a decrease that led to a period of stable pH values, which can be defined as stage two. During this stage, stable oxide films have been formed, so the reaction slowed down after the initial 10 h of immersion. However, it is noteworthy that \( \text{H}_2\text{O} \) and \( \text{Cl}^- \) can diffuse into the PLLA coating and react with the MAO coating and substrate before the hydrolysis degradation of the polymer films in the first 10 h of immersion, which can explain the slight increased state of the
immersion time for the PLLA coating on the PTFE plate. The acidity of PLLA coating; a linear decrease in solution pH over time. The free corrosion potential (Ecorr) and properties of the surfaces changed during the immersion. The structures of the coated and uncoated samples in HBSS with and without immersion are shown in Figure 7, showing that the structures of the coated and uncoated samples in HBSS with and without immersion are shown in Figure 7, showing that the structures of the coated and uncoated samples. 

3.3. Electrochemical Behavior. PDP curves obtained for the coated and uncoated samples in HBSS with and without immersion are shown in Figure 7, showing that the structures of the coated and uncoated samples. The free corrosion potential (Ecorr) and corrosion current density (Icorr) were derived from these data by the Tafel extrapolation method and are summarized in Table 1. It can be seen that the Ecorr of the samples without the immersion follows this consequence: MAO/PLLA > MAO > bare substrate. This indicates that the coated samples exhibited a lower thermodynamic tendency toward electrochemical corrosion, the MAO/PLLA coating showed the lowest tendency to participate in the anodic reaction, and the Icorr of the MAO/PLLA-coated sample is about 2 orders of magnitude lower than that of the bare substrate, which indicates that the corrosion resistance is effectively improved. After immersion in HBSS for 140 h, the Ecorr decreases in the order of MAO/PLLA > substrate > MAO, so that the MAO-coated sample exhibits a stabilized thermodynamic stability during the immersion time. Compared with the substrate, an increase in Icorr for the MAO coating is in pronounced agreement with the results from HER (Figure 5) and the reverse change in solution pH (Figure 6), implying that the MAO coating suffered from severe attack from the solution and the delamination of the MAO coating. A similar scenario is also discerned on the degradation of the MAO/PLLA coating on the Mg–Li–Ca–Y alloy. The Ecorr and Icorr of the bare substrate were, however, enhanced and lowered, respectively, which is probably related to the protection of the compact corrosion product layer. The MAO/PLLA-coated sample retains significant corrosion resistance, which is consistent with the HERs. The PDP curve of the MAO/PLLA coating, nevertheless, show no significant difference among the three samples after immersion in HBSS for 140 h, which are ascribed to the peeling-off of the MAO coating and the swelling of the PLLA coating after a long period of immersion.

Figure 7 shows Nyquist plots of the uncoated and coated samples with and without immersion in HBSS for 140 h. All of the Nyquist plots were fitted with the corresponding equivalent circuits, which are also designated in Figure 8b–g. As shown in the Nyquist plots, the MAO/PLLA-coated samples exhibited the best corrosion resistance, and the impedance of the MAO-coated and immersion treated MAO/PLLA-coated samples decreased, while that of the bare substrate increased after being immersed for 140 h. The experimental data were processed using ZSimpWin 3.4, and the χ² values of the fitting results are within a permissible range (Table 2).

Figure 8a shows Nyquist plots of the uncoated and coated samples with and without immersion in HBSS for 140 h. All of the Nyquist plots were fitted with the corresponding equivalent circuits, which are also designated in Figure 8b–g. As shown in the Nyquist plots, the MAO/PLLA-coated samples exhibited the best corrosion resistance, and the impedance of the MAO-coated and immersion treated MAO/PLLA-coated samples decreased, while that of the bare substrate increased after being immersed for 140 h. The experimental data were processed using ZSimpWin 3.4, and the χ² values of the fitting results are within a permissible range (Table 2).

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where \( Y_0 \) is the constant of the CPE, \( j \omega \) is the complex variable for sinusoidal perturbations with \( \omega = 2\pi f \), and \( n \) is the exponent of CPE with values between 0 and 1. The CPE acts as a pure resistor when \( n \) equals 0 and as an ideal capacitor when \( n \) equals 1. The value of \( n \) is associated with the nonuniform distribution of current as a result of both the degree of roughness of the surface as well as the degree of the oxide's heterogeneity. The middle capacitive loop is attributed to the film resistance (\( R_f \)) and the film capacitance (CPEf) of the electrolyte penetrating through the corrosion product layer on the surface of the substrate. The increased \( R_f \) from 908.9 to 6248 and 75490 \( \Omega \cdot \text{cm}^2 \) confirms that the MAO/PLLA-coated sample retains good corrosion resistance. The inductive loop, corresponding to an inductor \( L \) and a resistor \( R_L \) at the low frequency, is ascribed to the absorption and peeling of the corrosion products such as Mg(OH)\(_2\). Figure 8d,f shows similar Nyquist plots, which can be fitted with one equivalent circuit, exhibiting the multilayer structure of both coatings. The circuit contains the \( R_f \), \( C_{dl} \), \( R_0 \) and the polarization resistance (\( R_p \)), the outer porous layer capacitance (\( C_p \)) and the inner barrier layer capacitance (CPE1).

Nyquist plots and equivalent circuits of the bare substrate and coated samples with 140 h of immersion in HBSS are shown in Figure 8c,e,g, respectively. The Nyquist plot of the substrates demonstrates a capacitive loop at a high frequency in Figure 8c, representing the charge transfer process, and an oblique line in a middle low frequency range, corresponding to the corrosion reaction being controlled by the diffusion process. Therefore, as depicted in Figure 8c, the equivalent circuit of the substrate after immersion is similar to that of the substrate without immersion, with replacement of the inductor with a Warburg resistance. The reason for this change is that as the immersion time is prolonged, the produced corrosion products cover the surface of the substrate, leading to the formation of a compact corrosion product layer that isolates the solution from the substrates. Therefore, the diffusion process plays an important role in parallel with the absorption and delamination of the corrosion products without immersion,
Table 2. Electrochemical Data Obtained by Equivalent Circuit Fitting of EIS Curves of Uncoated and Coated Samples with and without Immersion for 140 h

<table>
<thead>
<tr>
<th>Samples</th>
<th>R_Ω (Ω)</th>
<th>R_p (Ω)</th>
<th>R_2 CPE (Ω)</th>
<th>C_1 (F/cm^2)</th>
<th>C_2 (F/cm^2)</th>
<th>CPE (Ω)</th>
</tr>
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<tbody>
<tr>
<td>substrate-0 h</td>
<td>3.2×10^-2</td>
<td>5.8×10^-3</td>
<td>2.0×10^-2</td>
<td>1.7×10^-3</td>
<td>2.6×10^-1</td>
<td>1.5×10^-2</td>
</tr>
<tr>
<td>MAO-0 h</td>
<td>5.8×10^-4</td>
<td>1.3×10^-4</td>
<td>1.5×10^-4</td>
<td>1.1×10^-4</td>
<td>2.6×10^-1</td>
<td>1.5×10^-2</td>
</tr>
<tr>
<td>MAO/PLLA-0 h</td>
<td>3.3×10^-2</td>
<td>1.2×10^-3</td>
<td>1.5×10^-2</td>
<td>1.1×10^-3</td>
<td>2.6×10^-1</td>
<td>1.5×10^-2</td>
</tr>
<tr>
<td>substrate-140 h</td>
<td>3.2×10^-2</td>
<td>5.8×10^-3</td>
<td>2.0×10^-2</td>
<td>1.7×10^-3</td>
<td>2.6×10^-1</td>
<td>1.5×10^-2</td>
</tr>
<tr>
<td>MAO-140 h</td>
<td>5.8×10^-4</td>
<td>1.3×10^-4</td>
<td>1.5×10^-4</td>
<td>1.1×10^-4</td>
<td>2.6×10^-1</td>
<td>1.5×10^-2</td>
</tr>
<tr>
<td>MAO/PLLA-140 h</td>
<td>3.3×10^-2</td>
<td>1.2×10^-3</td>
<td>1.5×10^-2</td>
<td>1.1×10^-3</td>
<td>2.6×10^-1</td>
<td>1.5×10^-2</td>
</tr>
</tbody>
</table>

which can be equivalent to an inductor. As for the Nyquist plots in Figure 8e, an inductor L and a resistor R_s simultaneously appear at the low frequencies due to the formation of corrosion pits on the coatings. However, the MAO/PLLA coating maintained its integrity, whereas serious corrosion occurred on the MAO coatings due to a hydration reaction and the dissolution of Mg, resulting in localized destruction and the loss of the protective layer.

3.4. Cytocompatibility and Hemolysis Tests. Table 3 shows the result of the hemolysis test of the bare substrate, MAO and MAO/PLLA coated samples. Compared with the bare substrate, the HR of the MAO coating was lowered by up to 12.48%, indicating that it may lead to severe hemolysis when contacted with the blood. The MAO/PLLA coating exhibited a HR of 0.17%, which is much lower than 5% (a judging criterion for excellent blood compatibility), indicating the excellent blood compatibility of the composite coatings.

The cytotoxicity of the MAO and MAO/PLLA-coated samples was determined using MC3T3-E1 cells and the MTT assay (Figure 9). The relative growth ratio (RGR) of the three groups is less than 100% after 24 h of culture, whereas the RGR of the MAO/PLLA coating slightly exceeds 100% after a culture of 72 h. MC3T3-E1 cells in the extract media of the MAO/PLLA coating showed an obviously higher proliferation rate and vitality than those on the Mg–1Li–1Ca substrates and the MAO coating. It is noteworthy that the lowest cytotoxicity of the MAO-coated samples may be ascribed to the influence of the electrolytes, which persisted in the micropores after the MAO process. It is also interesting to note that the RGR of the Mg–1Li–1Ca substrates is close to that of the composite coatings due to the protective film generated during the extraction process, which is consistent with the results of the ions released during immersion, such as Mg^{2+}, Ca^{2+} and Li^+, which are of small volume less than the tolerated contents of osteoblasts.28

Table 3. HR (%) of the Mg–Li–Ca Substrate, MAO, and MAO/PLLA (n = 5)

<table>
<thead>
<tr>
<th>samples</th>
<th>HR, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate</td>
<td>61.35 ± 0.36</td>
</tr>
<tr>
<td>MAO</td>
<td>12.48 ± 0.18</td>
</tr>
<tr>
<td>MAO/PLLA</td>
<td>0.17 ± 0.04</td>
</tr>
</tbody>
</table>

Figure 9. RGR of MC3T3-E1 cells cultured for different times in extract media from the substrates, MAO and MAO/PLLA coated samples compared to in α-MEM culture medium. Error bars represent ± S for n = 5 and P < 0.05, as indicated by the asterisk (*).
ALP activity is one of the most widely used markers for early osteoblastic differentiation.\textsuperscript{56,57} ALP is a ubiquitous enzyme that catalyzes the hydrolysis of phosphate esters at alkaline pH. The differentiation of MC3T3 cells on differently treated samples was evaluated in up to 7 days of culture using ALP as an early phase marker. Figure 10 shows the ALP activity of the osteoblast culture in the extract media of the Mg−1Li−1Ca substrates, MAO and MAO/PLLA-coated samples, as well as pure culture media as a control. The osteoblasts cultured in the extracts of the MAO/PLLA coatings displayed a highest ALP expression among the samples, which indicates a stronger ability for cell differentiation.\textsuperscript{56,57} The ALP expression of the substrates and the MAO coatings shows a parallel trend to the MTT assay.

The morphologies of MC3T3-E1 cells cultured on the coated and uncoated samples for 24 h are presented in Figure 11. After 24 h of the culture, it is clear that the cells cultured on the MAO/PLLA coatings exhibited good adhesion, which can be identified by the number of spreading cells as well as the spreading shape and areas. Additionally, the cells displayed numerous filopodia extensions (Figure 11e,f). It is especially noteworthy that the edges of the pores on the MAO/PLLA coatings can be easily attached to by the filopodia, which strongly enhances the cell adhesion. Although the cells cultured on the substrates and the MAO coatings also adhered to the surface and filopodia protrusions were also observed in Figure 11a−d, their growth seemed to be inhibited.

4. DISCUSSION

The surface appearances of the coated and uncoated samples after immersion in HBSS for 140 h are shown in Figure 12. A compact corrosion layer with micro cracks is formed on the surface of the substrate (Figure 12a). Corrosion pits on the MAO coating destroyed its integrity (Figure 12b). However, the surface of the MAO/PLLA coating showed no obvious variation on most of its surface (Figure 12c) with few corrosion pits covered by white corrosion products. With the integrity and mechanical property of the duplex coating being undermined during the immersion by the diffusion of H₂O, solution ions and the release of H₂, the corrosion products centralized under the polymeric PLLA film. Then, the delamination and collapse of the PLLA coating occurred, which was demonstrated by the distinct shearing boundary on the MAO/PLLA surface (Figure 12d). The EDS spectra of each sample after immersion in HBSS for 140 h is also demonstrated by the insets in Figure 12, revealing that the MAO/PLLA coating had similar elemental compositions on the substrate and the MAO coating, mainly containing O, Mg, P and Ca (Figures 12a,b).

Interestingly, the centralization of corrosion products around the corrosion pit in Figure 12d was destroyed by the stream of electrons released during the immersion, exposing the corrosion pit to the microscope. An opening pore can be clearly observed in Figure 13, and C, O, Mg, Ca and P appear to be uniformly distributed in the corrosion products. It is noteworthy that around the corrosion pit, the concentrations of Mg and O are much higher than those of Ca and P, and the distribution of Ca corresponds to that of P. The elemental distribution resulted from the formation of different corrosion products, including Mg(OH)₂, which centralized around the corrosion pit, and hydroxyapatite (HA).\textsuperscript{16}

Figure 14 shows the cross-sectional SEM morphology and EDS elemental mapping of the MAO/PLLA coating after immersion. The composite film remained integrated and compact after immersed in HBSS for 140 h, with a small quantity of corrosion pits beneath the polymeric coating, that were produced by the diffusion of H₂O and Cl⁻ through the PLLA and MAO coating into the substrate and the dissolution of Mg, thus resulting in the blistering of the PLLA coating due to the hydrogen evolution. As shown in the EDS elemental mapping, C, O and Mg can be detected on the cross-section of the corrosion pit, suggesting the formation of the hydrolysates of the PLLA coating and the Mg(OH)₂ corrosion products of the alloy.

Figure 15 shows the XRD patterns of the coated and uncoated samples with and without immersion for 140 h. The presence of MgO indicates that the ceramic coatings are formed during MAO treatment in electrolytes containing phytic and NaOH, which is different from the coatings formed in silicate electrolytes.\textsuperscript{27} Interestingly, the presence of calcium lactate ((C₃H₅O₃)₂Ca) can be detected on the MAO/PLLA coating samples after immersion in HBSS, demonstrating the reactions between chemical species such as Ca²⁺ from the corrosion medium and the dissolution of the Mg−1Li−1Ca alloy, and oligomers or monomers such as lactide and lactic acid released by the degradation of the PLLA film.

The cytotoxicity and biocompatibility of clinical materials are also greatly influenced by the corrosion. During the corrosion process, local alkalization and enrichment in Mg²⁺ exert a significant impact on the physiological balance. It is postulated that Mg-based materials degrade too fast, and the high concentration of Mg²⁺ in the solution is responsible for the high hemolysis rate.\textsuperscript{16} Although the MAO coatings reduced the HR to 12.85%, which is much lower than that of the Mg−1Li−1Ca substrates (61.35%), it is not suitable for utilization as blood-contacting materials for the potential danger to erythrocytes. After being sealed with PLLA, MAO/PLLA coatings, with a HR of 0.17%, would have little influence on the blood.

It is well-known that cells are very sensitive to changes in the microsurrounding environment, such as the sharp changes in the pH value and Mg²⁺ concentration. The sharp increase in the pH value and concentration of Mg²⁺ released by the degradation of the substrates and the MAO coatings may hinder cell growth (Figures 9−11). As a biodegradable material, PLLA not only works as a physical barrier layer but also
provides a suitable condition for cell adhesion and proliferation on the Mg−Li−Ca alloys (Figure 11e,f). Combining MAO with PLLA can take advantage of the superiority of the two coatings on biodegradable Mg alloys.

As is well-known, PLA-based materials belong to the family of aliphatic polyesters, so their ester groups are hydrolytically degraded in the presence of water according to the following reaction:

\[ -COO^- + H_2O \rightarrow -COOH + OH^- \]  

Thus, PLA-based materials degrade via a hydrolytic autocatalytic degradation process at the chain end and in the middle of the chain, which are called exo-chain cleavage and endo-cleavage, respectively. However, the cleavage mechanism of PLA dissolved in solution depends on the media pH such that the hydrolytic degradation proceeds with a chain-end scission mechanism in lactyl monomer unit, forming lactic acid in acidic solution, whereas in alkaline solution, hydrolytic degradation takes place via backbiting to form a lactide unit, which is further hydrolyzed to give lactic acid. Degradation of the PLA coating in HBSS at 37 °C and pH 7.4 is similar to in vivo degradation. The degradation in neutral solution seems to be selective and often occurs in amorphous regions, producing hydrophilic groups (−OH and −COOH). The catalytic group (−COOH) is subsequently condensed in the amorphous region between crystalline regions, resulting in the acceleration of the hydrolytic degradation in a restricted area.

The degradation mechanism of PLA-based materials include three models: a surface corrosion mechanism, bulk corrosion mechanism and core-accelerated bulk corrosion mechanism, with a critical thickness \( L_{\text{critical}} \) of polymeric films that can be used as a criterion index to evaluate which corrosion takes place. With the decrease of the thickness of the polymer films, the hydrolytic degradation rate of the material surface slows down, compared with the diffusion rate of water molecules or catalytic substances within the material, and the mechanism model turns from surface corrosion to bulk corrosion. The PLLA coating in this experiment has a thickness (approximately 10 μm) that is lower than \( L_{\text{critical}} \) of 0.5−2 mm. Therefore, the bulk corrosion occurred during the immersion test, which can be divided into three stages: (1) initial water diffusion, absorption and hydration of the PLLA coatings, (2) gradual decrease in molecular weight and (3) formation and dissolution of water-soluble oligomers and monomers. Accompanied with a decrease in the molecular weight and crystallinity, the thickness of the films decreased, causing a release of formed oligomers.

Figure 11. SEM morphologies of MC3T3-E1 cells cultured on (a,b) the Mg−Li−Ca alloys, (c,d) the MAO coating and (e,f) the MAO/PLLA coating for 24 h.
and monomers to the solution, resulting in a reduced autocatalytic effect and a lower degradation rate. Furthermore, the MAO film can significantly influence the degradation behavior of the polymer film. As is well-known, Mg is highly susceptible to galvanic corrosion, leading to the formation of Mg(OH)$_2$ during the chemical reactions, and the presence of Cl$^-$ can dissolve Mg(OH)$_2$, leading to the release of OH$^-$ to the corrosion media. These reactions follow as:

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad (6)$$
$$2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \uparrow \quad (7)$$
$$\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \uparrow \quad (8)$$
$$\text{Mg(OH)}_2 + 2\text{Cl}^- \rightarrow \text{MgCl}_2 + 2\text{OH}^- \quad (9)$$

Figure 12. SEM morphologies and EDS element analysis of surface of the samples after 140 h of immersion: (a) the substrate; (b) the MAO coatings; (c, d) the MAO/PLLA coatings.

Figure 13. SEM morphology of a corrosion pit on the MAO/PLLA surface after 140 h of immersion: (a) SEM micrographs; the elemental mappings of EDS: (b) C, (c) O, (d) Mg, (e) Ca and (f) P.
Therefore, the degradation of Mg eventually results in a locally alkaline environment, which can result in the consumption of the acidic products released by the degradation of the PLLA coatings, accelerating and promoting the hydrolytic degradation of the polymers as well as the loss of the Mg(OH)₂ layers. Our earlier study demonstrates that the microstructure of Mg−1Li−1Ca is composed of an α-Mg phase and intermetallic compound Mg₂Ca particles, which result in an initial corrosion around the Mg₂Ca particles, generating hydrogen bubbles and Mg(OH)₂. The corrosion products gradually concentrate on the interface of the MAO coatings and substrate during the reaction and destroy the MgO layer as

\[ \text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \]  

(10)

Simultaneously, the H₂ liberated also increases the internal stress under the MAO coatings and PLLA coatings and undermines the mechanical properties of the coatings, leading to the generation of peeled off pores and cracks on the PLLA films and finally disintegration into fragments (Figure 12). The detachment of the PLLA coating may be detrimental to

Figure 14. Cross-sectional morphology of MAO/PLLA coating after 140 h of immersion in HBSS: (a, b) cross-sectional morphologies; EMPA image of cross section of blister: (c) elemental mappings of EDS: (d) C, (e) O and (f) Mg.

Figure 15. XRD patterns of the substrate, MAO coatings and MAO/PLLA coatings before and after immersion for 140 h.
application as stent materials, but the composite coating still shows great potential in bone regeneration applications. Above all, the MAO/PLLA composite coating degraded primarily at the inner layer and exhibited features of localized corrosion and pitting corrosion, resulting in the concentration of corrosion products inside and on the surface of coatings, finally leading to localized destruction and collapse. Thus, a degradation mechanism is schematically illustrated in Figure 16a,b, indicating that the degradation of PLLA on the Mg–1Li–1Ca alloy experienced four steps: (1) water diffusing through the PLLA film onto the MAO coating and the substrate due to the diffusion rate of water being faster than the degradation of the PLLA film, (2) chemical corrosion of the MAO coating (eq 10), (3) electrochemical corrosion of the substrate (eq 6) and (4) the swelling, hydrolysis (eq 5) and rupture of the PLLA film.

5. CONCLUSIONS

Porous MAO/PLLA composite coatings were fabricated by dip-coating and freeze-drying to improve the corrosion resistance of Mg–1Li–1Ca alloys, and the corrosion behaviors of the coatings in HBSS were investigated by SEM, EPMA, XRD and corrosion measurements. The conclusions are as follows: (1) The MAO/PLLA coatings significantly enhanced the corrosion resistance, increasing the $E_{corr}$ from $-1.66$ to $-1.44$ V and decreasing the $I_{corr}$ by approximately 2 orders of magnitude. (2) The corrosion predominantly occurred at the interface of the MAO coating and the substrate, and the accumulation of corrosion products as well as hydrogen bubbles caused swelling and blistering of the PLLA coating due to the faster penetration rate of water into the PLLA coating than its degradation rate. (3) The acidic and alkaline products, respectively resulting from the degradation of PLLA and the corrosion of Mg, neutralized each other to maintain a stable and appropriate pH value in HBSS. (4) The MAO/PLLA coating on Mg alloys greatly enhances its cytocompatibility and blood compatibility, and provides an appropriate solution pH and porous microstructure, which is helpful for the attachment of cells. The MAO/PLLA coating may be a promising approach for bone tissue regeneration engineering.

Figure 16. Schematic illustrations of degradation mechanism of the porous MAO/PLLA composite coatings on the Mg–1Li–1Ca alloys in HBSS: (a) the swelling of PLLA and corrosion of the substrate at the initial stage, (b) the blistering and final peeling-off of PLLA under the pressure of hydrogen gas and corrosion products.

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Notes

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