

Preparation and Corrosion Resistance of Biodegradable PDLLA-Mg-1.0Ca-ZnP Composite Material

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Abstract. Objective: Preparation of the novel material for bone repair. Methods: PDLLA coating method was used. Results: The PDLLA-Mg-1.0Ca-ZnP composite material was prepared by using both PDLLA coating and the phosphate coating (recorded ZnP), and the corrosion resistance of PDLLA-Mg-1.0Ca-ZnP were tested. Conclusion: Electrochemical tests showed that PDLLA-AZ31 had higher free corrosion potentials (Ecorr) and lower corrosion currents (Icorr), high impedance in the simulated body fluid (SBF) at 37°C.

Introduction

Various studies showed that magnesium had nice degradation and mechanical properties, density analogous to natural bones [1]. Currently, there are many studies, which mainly focus on commercial alloys, such as AZ31 and Mg-RE alloys [2-4]. However, it is reported that Al element can cause nerve toxicity and restraining growth to the human body [5]. Moreover, the RE may cause the severe hepatotoxicity [5]. Calcium is one of the most attractive elements due to the fact that it is a major component of human bones and essential in chemical signaling with cells. Moreover, magnesium is necessary for the calcium incorporation into the bone, which might be expected to be beneficial to the bone healing with the co-releasing of Mg and Ca ions [6].

However, the introduction of Ca can decrease the corrosion resistance. Recently, many surface modification techniques such as electrodeposition[7], polymer coating [8], phosphating treatment [9], and microarc oxidation [10], which are used to increase the corrosion resistance of alloy, have been studied. PDLLA was chosen to use as the coating polymer because it was biodegradable and biocompatible, and had been approved to apply in clinical operations by FDA [11].

Materials and Methods

Preparation of PDLLA-Mg-1.0Ca-ZnP Composite Materials. Firstly, Mg-1.0Ca alloy (1wt. % Ca) was prepared from pure Mg (99.98%) and Mg-Ca alloy (30wt.% Ca) in a crucible under a mixed gas atmosphere of SF₆ and CO₂. And then Mg-1.0Ca alloy was cut to round plates (Φ12mm×2.5mm). All the specimens were mechanically polished up to 1000 grit and then were electropolished and dried at room temperature.

Secondly, ZnP coating is formed on Mg-1.0Ca alloy by zinc phosphating in phosphating bath. The optimal contents of chemical compositions of the zinc phosphating and experimental conditions are listed in Table 1[12]. The zinc phosphating Mg-1.0Ca was named Mg-1.0Ca-ZnP.

Thirdly, PDLLA (-CHCH₃COO)_n) with an average molecular weight of about 50, 000 was bought from Shandong Province. The PDLLA was dissolved in dichloromethane as the

concentration 3wt%. PDLLA coating was carried out by soaking Mg-1.0Ca into PDLLA solution at room temperature. And then all samples were dried at 40°C for 72h. Surface morphologies of magnesium substrate and magnesium compound were observed with SEM.

Table 1 Compositions of the phosphating bath and experimental conditions

	Degreasing	Ultrasonic derusting	Surface conditioning	Phosphating/L
Compositions	NaOH 1.5wt%	$H_3PO_4 : HNO_3 = 300:1$	200-250ml/L HF	H_3PO_4 (85wt. %) 30ml
				ZnO 6.8g
				NaF 1.8
				NaNO ₃ 2.8
				NaNO ₂ 1.2
				Citric acid 2.8
				MEA 1.2
				SDS 0.15
Conditions	1min 50-60°C	3-5s 25°C	15min 25°C	10min 45°C

Electrochemical test. Electrochemical test was performed to evaluate the corrosion resistance of Mg-1.0Ca and PDLLA-Mg-1.0Ca-ZnP. The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were tested. The electrochemical test was conducted with a three-electrode system in 150ml SBF at 37°C. A saturated calomel electrode and platinum mesh were used as the reference and counter electrode, respectively. The polarization curves were measured at a scan rate of 1mVs⁻¹. The free corrosion potential (E_{corr}) and current (I_{corr}) for each specimen were also tested. In the potentiodynamic polarization test, a scanning rate of 2mVs⁻¹ was applied.

Results and Discussion

Electrochemical behavior. Representative polarization curves of Mg-1.0Ca and PDLLA-Mg-1.0Ca-ZnP are depicted in Fig. 1. The untreated Mg-1.0Ca alloy has a negative corrosion potential in SBF of about -1806mV. The corrosion potential (E_{corr}) of PDLLA-Mg-1.0Ca-ZnP is much more positive, shifting to about 1538mV. The corrosion current density (I_{corr}) of PDLLA-Mg-1.0Ca-ZnP (1.068e-008Acm⁻²) is about four orders of magnitude lower than that of the untreated sample (3.103 e-004Acm⁻²), indicating much lower corrosion rates for the PDLLA coated sample in SBF compared to the Mg-1.0Ca alloy.

The corrosion potential (E_{corr}) reflected the combined outcome of all the electrochemical reactions taking place at the electrode /solution interface. The variation in the corrosion potential with immersion time can be employed to study what goes on at the electrode/solution interface. The typical E_{corr} -t curves determined from the Mg-1.0Ca and PDLLA-Mg-1.0Ca-ZnP are shown in Fig.1. It can be seen that the E_{corr} of the PDLLA-Mg-1.0Ca-ZnP sample is -1583, which is much more positive than that of Mg-1.0Ca. Therefore, comparing the curves of Mg-1.0Ca and PDLLA-Mg-1.0Ca-ZnP, we can find that, at the beginning of test, the potential of them all have an increase quickly, however, the curve of PDLLA-Mg-1.0Ca-ZnP moves to smooth and steady state quickly, while the curve of Mg-1.0Ca increases continually till the last. The results can be attributed to the chemical dissolution. As it is well-known that when the magnesium-based alloy is put into water medium, magnesium reacts with water to product the main byproduct Mg(OH)₂, which leads to the precipitation of the corrosion products as magnesium hydroxide, magnesium phosphate, and magnesium carbonates[13]. However, when magnesium alloy was coated, the coating PDLLA protected the magnesium alloy from corrosion potential increasing gradually with immersion time.

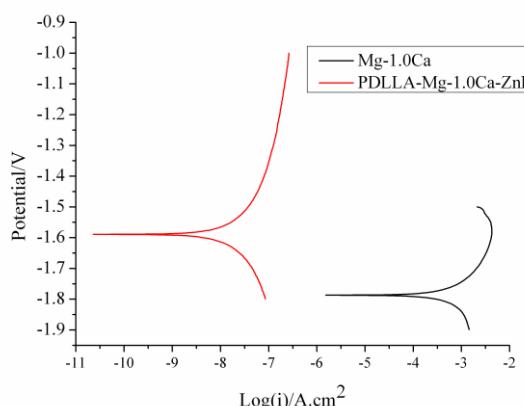


Figure 1. Potentiodynamic polarization curves of the PDLLA-Mg-1.0Ca-ZnP in SBF

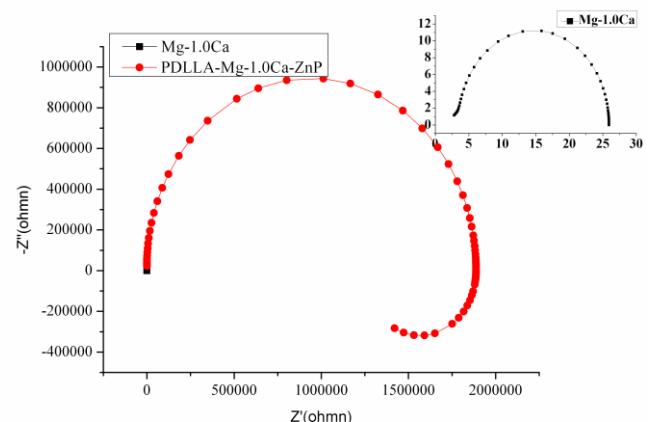


Figure 2. Representative EIS spectra of the Mg-1.0Ca and PDLLA-Mg-1.0Ca-ZnP and Mg-1.0Ca in SBF

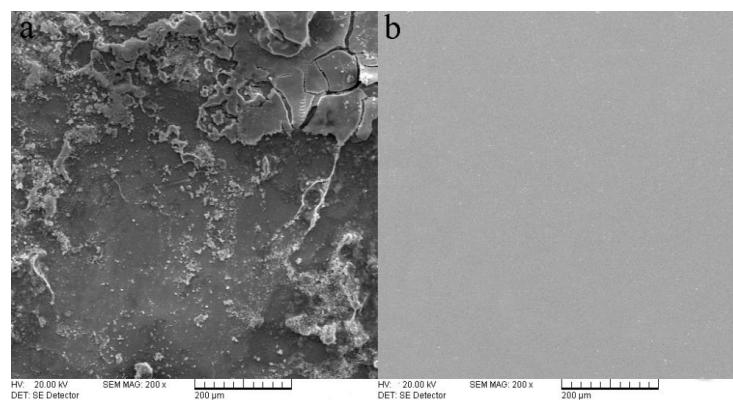


Figure 3. The SEM of Mg-1.0Ca (a) and PDLLA-Mg-1.0Ca-ZnP (b) after EIS test ($\times 200$)

EIS is a powerful technique to study the corrosion of uncoated magnesium alloy and coated magnesium alloy. It can evaluate the corrosion properties of all samples quantitatively, which is difficult to evaluate by conventional corrosion evaluation method. By appropriate interpretation of EIS data in conjunction with an EC, the detailed information on the corrosion process at the electrolyte/electrode interface can be provided. This technique is more effective to study the localized corrosion via small pores [14]. The representative EIS curves obtained from Mg-1.0Ca alloy and PDLLA-Mg-1.0Ca-ZnP alloy as function of immersion time in SBF are shown in Fig. 2. The EIS curve can be divided into three stages: low frequencies, medium frequencies and high frequencies. Right from the beginning of immersion, a capacitive loop at medium frequencies, and a Warburg loop at low frequencies, this is aroused by ionic migration impedance. The high frequency behavior of EIS is associated with electrolyte impedance including water and salt. The medium-high frequency of EIS is associated with the interface, which shows passivation coating impedance and charge transfer impedance in interface, therefore the properties of the coatings and their changes can be determined at the medium-high frequencies [14]. Comparing the EIS of Mg-1.0Ca with EIS of PDLLA-Mg-1.0Ca-ZnP in Fig. 2, we can find that the impedance increased from 30 to 1.5e6. Moreover, from the results of Fig. 3, we can find that the PDLLA-Mg-1.0Ca-ZnP shows the smooth intact surface morphology, while Mg-1.0Ca shows severe corrosion. All results showed that PDLLA coating played an obvious role in improving the corrosion resistance of Mg-1.0Ca alloy.

Considering the nice corrosion resistance of PDLLA-Mg-1.0Ca-ZnP, it was used directly for the following cell experiments.

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