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# Corrosion resistance and adhesion strength of a spin-assisted layer-by-layer assembled coating on AZ31 magnesium alloy

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ABSTRACT

A polyvinylpyrrolidone (PVP)/polyacrylic acid (PAA) layer-by-layer (LbL) assembled composite coating with a multilayer structure for the corrosion protection of AZ31 magnesium alloy was prepared by a novel spin-casting method. The microstructure and composition of this coating were investigated by means of SEM, XRD and FT-IR measurements. Moreover, electrochemical, immersion and scratch tests *in vitro* were performed to measure the corrosion performance and the adhesion strength. These results indicated that the $(PVP/PAA)_{10}$ composite coating with defect-free, dense and uniform morphologies could be successfully deposited on the surface of magnesium alloy. The coating had excellent corrosion resistance and adhesion strength.



## 1. Introduction

Owing to their excellent physical and mechanical properties, magnesium (Mg) and its alloys have been widely used in a series of fields such as 3C products (computer, communication and consumer electronics), automobile and aerospace industries [1,2]. Moreover, Mg alloys are attracting more and more attention in the area of biomedical materials as a result of the safe biodegradability and good biocompatibility [3,4]. However, inferior corrosion resistance, as an inevitable obstacle, hinders the extensive application of Mg alloys [5].

Surface modification, which is a common method due to its low cost, easy operation and superior performance, is employed to improve the corrosion resistance of Mg alloys, including hydrotalcite coating [6], micro-arc oxidation (MAO) [7–9], plasma electrolytic oxidation (PEO) [10] and chemical conversion coating [11,12]. Among these surface technologies, the layer-by-layer (LbL) assembly technique is excellent to prepare a hybrid coating by means of incorporating polyelectrolytes into the coating according to the electrostatic attraction between the opposite charges [13,14].

It has been reported that some LbL assembled polyelectrolytes coatings have been prepared by dip-coating (D-C) technology [15,16]. Unfortunately, when completely immersed in polyelectrolytes solutions, the substrate would be corroded due to pin-holes or rough surface [17,18]. So, D-C technology could not endow the substrate with excellent corrosion resistance. In order to diminish these defects, the spin-casting (S-C) technology might be a reliable method to prepare a uniform and smooth coating due to the fact that the air shear force and the centrifugal force caused by a high-speed spinning process could rapidly remove the adsorbed water molecules from the coating suspension [19]. Matsuyama [20] synthesized an ultrathin and ordered film composed of silica nanoparticles on an anodic aluminum oxide membrane via S-C method. Furthermore, the S-C method could provide a rapid deposition of polyelectrolytes on the surface of substrate, which induced an almost complete nanostructure, leaving a well-ordered network of nanoscale domains that reflects the arrangement of the driving agents [21,22]. Zhang [23] prepared a silver embedded poly-

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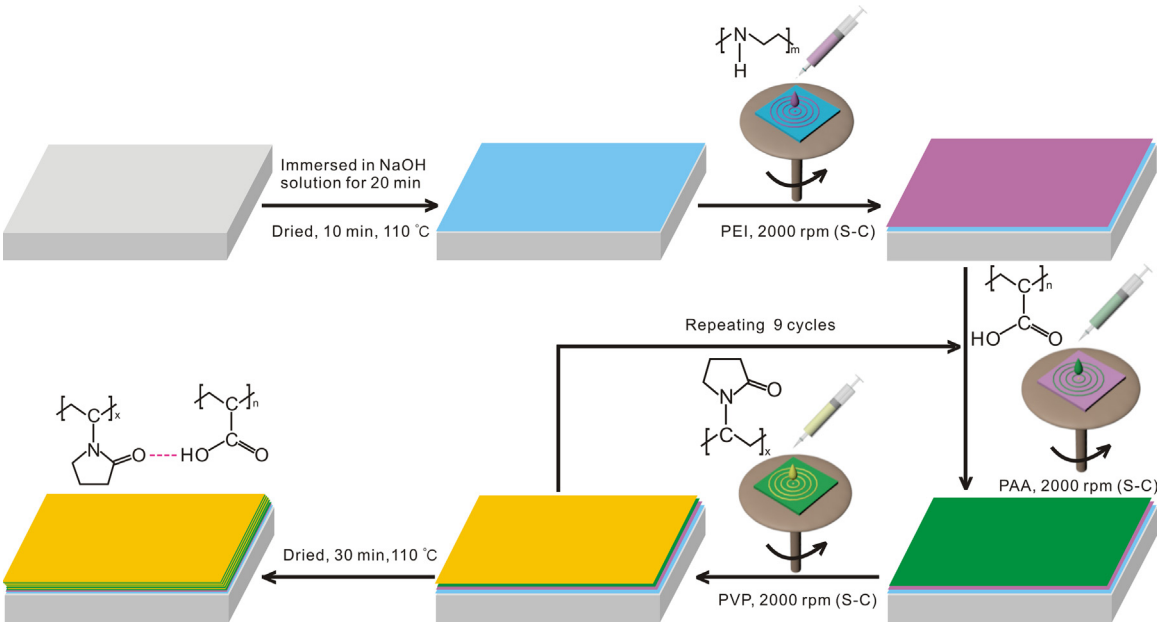


**Fig. 1.** Schematic representation of the S-C technique used for the coating production.

**Table 1**
Composition of AZ31 Mg alloy in wt.%.

| Al | Zn | Mn | Si | Fe | Ni | Cu | Mg |
|---|---|---|---|---|---|---|---|
| 3.1382 | 1.0268 | 0.4395 | 0.0029 | 0.0018 | 0.0007 | 0.0007 | Balance |

electrolyte multilayer on Mg alloy by means of S-C method with enhanced antibacterial property. Thus, it will be especially meaningful to apply the S-C technology to the surface modification of Mg alloy.

As far as we know, there are few reports on applying the co-application of LbL assembling and S-C technique to prepare polyelectrolyte multilayers on Mg alloy. The motivation of this study is to use the spin-assisted LbL assembling technology to fabricate a dense and uniform coating with excellent corrosion resistance and adhesion strength.

## 2. Experimental

### 2.1. Materials

The as-extruded AZ31 Mg alloys were supplied by Shandong Yinguang Yuyuan Light Metal Precise Forming Co., Ltd., China and the chemical composition was listed in Table 1. Polyethylenimine (PEI, Mw = 600), PVP (Mw = 40,000) and PAA (Mw = 800–1000) were all purchased from Qingdao Jingke Chemical Peagent Co., Ltd., China. Here, PEI with easily protonated amino-groups was used as linking agent, which could absorb negatively charged polyelectrolytes.

### 2.2. Substrate surface pre-treatment

These substrates were cut into squares with dimensions of 20 mm × 20 mm × 5 mm, ground with 150/400/800/1500/2500 grit SiC sand papers, cleaned with de-ionized (DI) water and alcohol, and then dried with warm air [24,25]. The polished substrates were immersed into 5 mol/L NaOH solution for 20 min, which could easily etch the Mg alloys (the surface would be negatively chaged). Then the substrates were cleaned with DI water and dried at 110 °C for 10 min.

### 2.3. Fabrication of $(PVP/PAA)_{10}$ LbL coating

In the D-C process, for preparing each layer, the substrate was immmersed into the polyelectrolyte solution for 10 min and then dried in warm air. Solutions A, B and C represent polymers PEI (10 mg/mL, pH = 10.0), PAA (10 mg/mL, pH = 7) and PVP (5 mg/mL, pH = 3.5) respectively. The $(PVP/PAA)_{10}$ LbL assembled coating prepared by D-C method were generated in the following order: $A(BC)_n$, n = 10, where n meant the cycle number. After drying the sample at 110 °C for 30 min, the D-C film was obtained.

In the S-C procedure (Fig. 1), 4 mL PEI was deposited onto the substrate by using S-C technique at a spinning speed of 2000 rpm for 15 s. Then the surface was washed three times with 0.2 mL DI water at the same speed for 15 s. Moreover, the LbL assembled multilayer was generated at the same spinning speed and time under the following order: $(BC)_n$, n = 10, where n meant the cycle number. Finally, the sample was dried at 110 °C for 30 min to obtain the S-C film.

### 2.4. Surface analysis

The surface morphology was observed by Field-emission scanning electron microscopy (FE-SEM, Nova Nano SEM 450, USA). The phase composition of the samples was investigated by X-ray diffraction (XRD, Rigaku D/MAX 2500PC, Japan), with a Cu target at a scanning rate of 8°/min. The diffraction patterns were obtained between 10° and 80°. The possible chemical bonds formed in the samples were analysed by Fourier transform infrared spectroscopy (FT-IR, Nicolet 380, Thermo electron, USA). The water contact angles (CA) were measured using the JC2000C1 contact angle goniometer (Shanghai Zhongchen Digital Technic Apporatus Corporation, Shanghai, China). The volume of water drops was 2 μL.

### 2.5. Corrosion characterization

#### 2.5.1. Electrochemical measurements

Corrosion resistance of the $(PVP/PAA)_{10}$ LbL coating was evaluated by potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) measurements using an electrochemical analyser (PAR Model 2273, Princeton, USA) in a