

Self-healing hybrid coating of phytic acid/silane for improving the corrosion resistance of magnesium alloy

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Abstract In order to improve the corrosion resistance of a biodegradable magnesium alloy, a series of phytic acid/3-aminopropyltrimethoxysilane (γ -APS) hybrid coatings was prepared on AZ31 magnesium alloys by dipping the magnesium alloy into the mixing solution of phytic acid and γ -APS. During the preparation of hybrid coatings, the pH values of the mixing solutions greatly affected the uniformity of the coatings and subsequently influenced their corrosion resistance. Electrochemical tests indicated that the hybrid coating prepared in the solution of pH = 8.0 could highly improve corrosion resistance of AZ31 magnesium alloys. Meanwhile, corrosion current density of the hybrid coating coated sample was significantly decreased from the uncoated sample of 138.1 ± 11.9 to $8.5 \pm 0.8 \mu\text{A cm}^{-2}$. Immersion test in simulated body fluid revealed that the cracks on the surface of the hybrid coating gradually healed up during the lengthy immersion.

Keywords Hybrid coating, Self-healing, Magnesium alloy, Corrosion resistance, Biomedical materials

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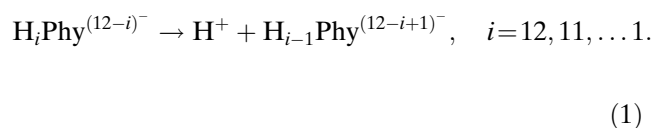
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Introduction

Over the past decades, magnesium (Mg) and its alloys have been regarded as promising implant materials due to their high specific strength, excellent biodegradability, suitable density, and low Young's modulus similar to natural human bone. However, the fast corrosion rate and related side effects, such as an inhomogeneous localized degradation and a quick decline of their mechanical strength, hinder their applications in biomedical applications.^{1–7} Surface treatments developed using appropriate coatings, such as organic coatings, inorganic coatings, and composite coatings, have been proven to effectively retard the corrosion process of magnesium alloys.^{1,8–12} However, the traditional coatings could only provide corrosion protection of magnesium alloys for a certain time, and they would quickly lose their physical barrier property when defects appear on the surface of coatings during the long-term immersion test. Nowadays, hybrid coatings with “self-healing” ability have been confirmed to be a very promising application for improving corrosion resistance of magnesium alloys.^{13–15} Compared to traditional coatings, self-healing hybrid coatings intelligently respond to damages caused by the external environment and to rebuild their original structures to gain long-term corrosion resistance. When faced with physical and chemical damages in the service environment, the existence of silane components in the coating allow for a self-healing ability.^{16–18} Moreover, some researchers have already proven that the combination of phosphate/silanes and phosphonic acid/silanes in composite or hybrid coating will greatly improve the corrosion resistance of the alloy substrate.^{19,20}

Phytic acid ($\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$) is a kind of natural macromolecular compound, and it can be considered an acid containing 12 protons, which can be successively dissociated according to the following process:



The different protonated forms of phytic acid are denoted by $H_{12}\text{Phy}$, $H_{11}\text{Phy}^-$, ..., Phy_{12}^{12-} , which have unique capabilities of chelating with many cations, such as magnesium, copper, and zinc. They would react with metal atoms or cations of alloys to form chelate compounds and thus create a strong bond between alloy substrate and chelating compound layer.^{21–23} Moreover, many researchers have revealed that phytic acid (also abbreviated as InsPi_6) is beneficial to cell differentiation and anticancer applications.^{24–26} The lower phosphorylated forms (InsPi_{1-5}) derived from phytic acid are also useful for regulating vital cellular functions.^{27,28} Previous studies showed that magnesium phytic acid coating had good bioactivity and biocompatibility; however, it easily lost corrosion protection in the long-term immersion process.^{29,30} Silanes are a group of silicon-based organic–inorganic materials with the general formula $\text{R}_0(\text{CH}_2)_n\text{Si}(\text{OR})_3$, where R_0 is an organofunctional group and R is a hydrolysable alkoxy group. Nowadays, it has been reported that the existence of 3-aminopropyltrimethoxysilane ($\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, known as γ -APS) in the coating can effectively improve corrosion resistance of magnesium alloys by undergoing self-crosslinking via siloxane bonds ($\text{Si}-\text{O}-\text{Si}$).^{31–33} Liu and co-workers have confirmed that although the coating with a single component of silane could highly improve the corrosion resistance of magnesium alloy substrate, their bioactivity and biocompatibility may not meet the demand in clinic.³² Meanwhile, Mistry and co-workers found that silanes could be used to prepare self-healing hybrid coating by reacting with phytic acid.^{14,29,32} In order to improve the corrosion resistance and biological properties of magnesium alloy, a series of phytic acid/ γ -APS hybrid coatings was prepared on magnesium alloys in this work; moreover, their corrosion resistance and “self-healing” ability were systematically investigated.

Experimental methods and materials

Materials and reagents

Sodium hydroxide (NaOH ; Kermel, China; minimum 99.0 wt%), phytic acid ($\text{C}_6\text{H}_6(\text{H}_2\text{PO}_4)_6$; Aladdin, China; minimum 70.0 wt%), 3-aminopropyltrimethoxysilane ($\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$; Aladdin, China; minimum 97.0 wt%), and triethylamine ($(\text{C}_2\text{H}_5)_3\text{N}$; Aladdin, China; minimum 99.0 wt%) were selected in this study. All reagents were used as received without further purification. In addition,

AZ31 magnesium alloy substrates (Al 3.0 wt%, Zn 1.0 wt%, Mn 0.2 wt%, and balanced Mg) were purchased from Henan Yuhang Material Co.

Synthesis of hybrid coatings on AZ31 magnesium alloy substrates

Commercial AZ31 magnesium alloys with an approximate size of 10.0 mm × 10.0 mm × 2.0 mm were used as substrates, polished with SiC papers up to 2000 grit, and cleaned ultrasonically in distilled water, ethanol, and acetone successively for 0.25 h, respectively, followed by drying at 25°C for use. Then, the substrates were immersed in 3 M NaOH solution at 80°C for 1 h. The alkaline-treated magnesium alloy substrates were rinsed thoroughly with distilled water and dried at 25°C. 0.8 g Phytic acid and 0.3 g γ -APS were added to 50 mL distilled water/ethanol mixed solution under continuous magnetic stirring at 20°C for 0.5 h to obtain homogeneous solutions; meanwhile, pH values of the solutions were adjusted to 5.0, 6.5, and 8.0 using triethylamine, respectively.

Then, phytic acid/3-aminopropyltrimethoxysilane hybrid coatings were prepared on AZ31 magnesium alloys by dipping the magnesium alloy into the mixing solution. The alkali-treated substrates were immersed in different solutions (pH value ~5.0, 6.5, and 8.0) for 0.5 h while maintaining a constant reaction temperature of 35°C, followed by rinsing thoroughly with distilled water and drying at 30°C for 24 h in an electric vacuum drying oven. Finally, the coated samples were heat-treated in the oven under 100°C for 1 h. The corresponding samples prepared in different solutions (pH value ~5.0, 6.5, and 8.0) were denoted as PAS1, PAS2, and PAS3; furthermore, the uncoated AZ31 magnesium alloy substrate was used as control group (named as AZ31).

Coating characterization

The surface morphologies of hybrid coatings were characterized via field-emission scanning electron microscope (SEM, Hitachi S-4800, Japan). Meanwhile, chemical compositions of all the samples (AZ31, PAS1, PAS2, and PAS3) were analyzed by energy-dispersive spectrum (EDS, 7401 Oxford) attached to SEM mentioned above.

Immersion test

During the whole immersion test, all the samples were immersed in simulated body fluid (SBF) (pH = 7.4) at $37 \pm 0.5^\circ\text{C}$ by using an immersion oscillator (WE-3, China). And, the concentration of ions in the SBF

formulation was prepared according to Kokubo's work (142.0 Na⁺, 5.0 K⁺, 1.5 Mg²⁺, 2.5 Ca²⁺, 147.8 Cl⁻, 4.2 HCO₃⁻, 1.0 HPO₄²⁻, 0.5 SO₄²⁻, all in mM).³⁴ According to ASTM G31-72,³⁵ the volume of solution was calculated based on a volume-to-sample area of 20 mL cm⁻², and the SBF solution was refreshed every 3 days.^{29,36} Then, the samples (AZ31, PAS1, PAS2, and PAS3) were taken out from SBF solution after 1, 4, 7, and 14 days, and pH values of residual solutions were measured by a pH meter (Leici PHS-25, China). The samples used to measure mass loss were cleaned by chromic acid to remove degradation products, rinsed with distilled water, cleaned ultrasonically in ethanol, and dried in air.^{2,35,36} The mass loss was calculated as follows:

$$\text{Mass Loss} = (1 - m_t/m_0) \times 100\%, \quad (2)$$

where m_0 is the weight of the sample before immersion test and m_t is the weight of the sample after immersion for a certain time. Five tests were conducted for each data point, and the results were averaged and presented as means \pm deviation. Besides, the samples immersed in SBF for 4 and 7 days were also picked up, rinsed with distilled water, dried in air, and characterized by SEM.

Electrochemical test

The electrochemical measurements were taken in SBF at $37 \pm 0.5^\circ\text{C}$ by using an electrochemical workstation (CHI600C, China). A three-electrode cell, i.e., a sample (working electrode), a platinum mesh (counter electrode), and a saturated Ag/AgCl reference electrode, was used for the measurements. The exposed area of the working electrode (the coated samples) in the SBF solution was 10.0 mm \times 10.0 mm. In order to reach a stable open-circuit potential (OCP), the working electrode was allowed to equilibrate in SBF solution for 0.2 h before commencing the potentiodynamic polarization and electrochemical impedance spectra (EIS) tests. The potentiodynamic polarization tests were carried out at a scan rate of 1.0 mV s⁻¹. The electrochemical impedance spectra were obtained over a frequency range from 0.01 Hz to 100,000 Hz. At least five parallel samples were tested to ensure repeatability.^{37,38}

Results and discussion

Coating characterization and formation kinetics of hybrid coatings

Figure 1 shows the surface morphologies of the uncoated AZ31 magnesium alloy and the hybrid

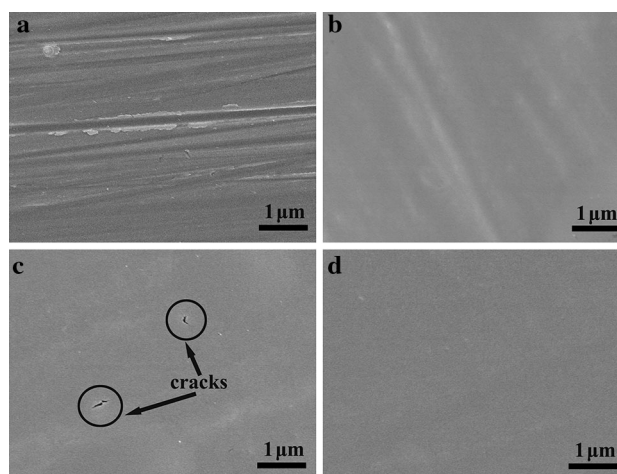


Fig. 1: Surface morphologies of (a) uncoated AZ31 magnesium alloy, (b) PAS1, (c) PAS2, and (d) PAS3 hybrid coating coated magnesium alloys

coatings coated magnesium alloys. Compared with the uncoated sample AZ31 (Fig. 1a) which showed obvious polishing scratches on the surface, the surface morphologies of the coated samples (PAS1, PAS2, and PAS3) had significant differences. Sample PAS1 prepared in acidic solution of pH value ~ 5.0 was inhomogeneous and undulating, while sample PAS2 prepared in approximately neutral solution of pH value ~ 6.5 had obvious cracks on the surface. Sample PAS3 prepared in alkaline solution of pH value ~ 8.0 was homogeneous and crack-free. In comparison with chemical composition of AZ31, all the hybrid coatings (PAS1, PAS2, and PAS3) had relatively high contents of characteristic elements Si and P derived from γ -APS and phytic acid (shown in Table 1), suggesting that the hybrid coatings had synthesized in situ on the surfaces of AZ31 magnesium alloy substrates. Some research reported that phytic acid and γ -APS were pH-sensitive substances and their related reactions were highly influenced by pH values of the solutions.^{14,30,39} During the synthesis process of hybrid coatings, the phytic acid chelate reaction, hydrolysis, and condensation reactions between silane molecules were dominant reactions, which determined the composition and morphology of the hybrid coating. According to the results of SEM and EDS, it can be speculated that pH values greatly influenced the dominant reactions. The possible equations are illustrated as follows:

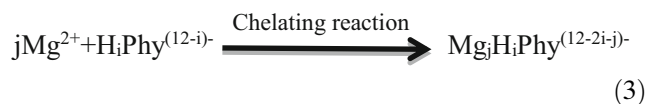
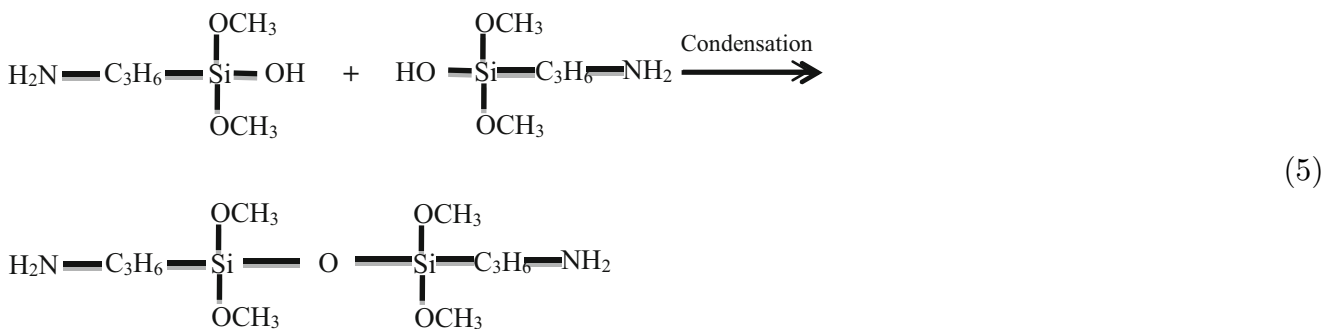
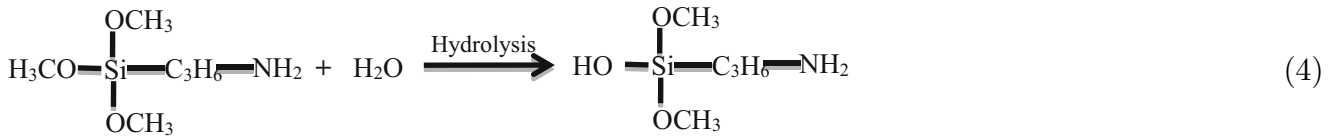


Table 1: Element compositions (wt%) found by EDS from the surfaces of AZ31, PAS1, PAS2, and PAS3

Sample	C	N	O	Mg	Si	P
AZ31	3.7	0.7	3.9	90.9	0.3	0.5
PAS1	20.6	4.4	24.7	40.3	5.5	4.5
PAS2	23.7	6.6	26.6	35.1	4.1	3.9
PAS3	25.4	6.4	33.2	23.9	5.7	5.4



where j is the content of magnesium ions in each magnesium phytic acid molecule. According to the species distribution diagrams for the Mg–InsP₆ system reported by Torres and co-workers, Mg₅H₂Phy was the most stable and insoluble component among all stoichiometries of magnesium phytic acid chelates, which would form under the pH value of 5.0 and higher. More importantly, under the alkaline condition (pH ~8.0 and higher), magnesium phytic acid chelating in hybrid coating would only produce a single component of Mg₅H₂Phy,^{39–41} which would enhance the stability and strength of sample PAS3. Meanwhile, the hydrolysis and condensation reactions of γ -APS were also affected by pH values of the solutions, as shown in equations (4) and (5). It has been reported that most silane molecules would undergo self-crosslinking via siloxane bonds (Si–O–Si) in the alkaline solution (pH ~8.0)³²; therefore, almost no defect was formed in sample PAS3 during the preparation process, as shown in Fig. 1d.

In vitro degradation behavior

The immersion tests can provide additional information with respect to the long-term corrosion resistance of the uncoated AZ31 and hybrid coatings coated magnesium alloys.^{38,42–44} Figure 2a shows the amount of mass loss of the samples after immersion in SBF for different times. Compared with the uncoated AZ31 magnesium alloy which almost disappeared after immersion in SBF for 14 days, the mass loss of samples PAS1, PAS2, and PAS3 after 14-day immersion in SBF was merely 11.2 ± 0.6, 15.6 ± 0.8, and 8.3 ± 0.4 wt%, respectively, demonstrating that sample PAS3 could provide the most effective protection for magnesium alloy substrates among all the hybrid coatings. Meanwhile, it can be observed that pH values of uncoated samples (shown in Fig. 2b) increased rapidly during the whole immersion period, reaching 11.1 ± 0.1 after a 14-day immersion, while the pH values of the immersing medium containing hybrid coating coated magnesium

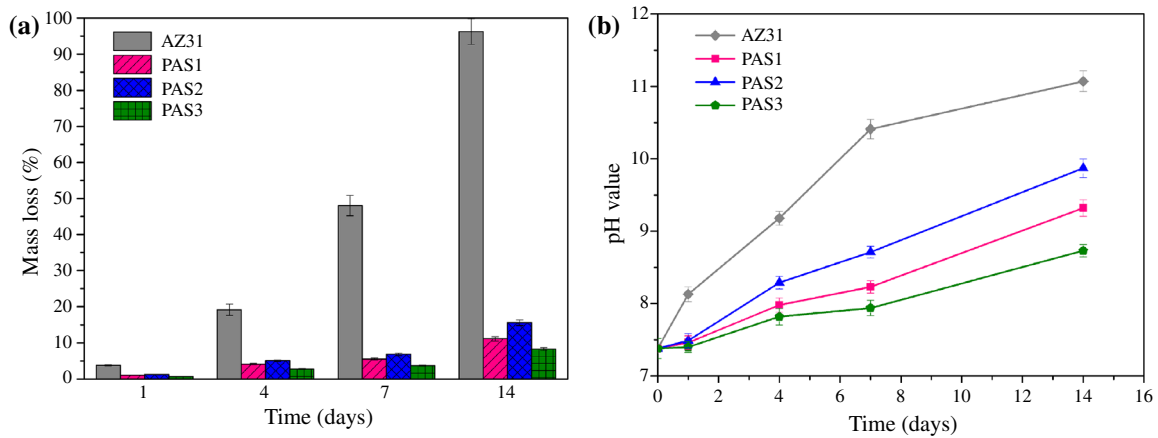


Fig. 2: (a) The mass loss (wt%) and (b) pH variations of different samples (AZ31, PAS1, PAS2, and PAS3) after immersion in SBF for 1, 4, 7, and 14 days

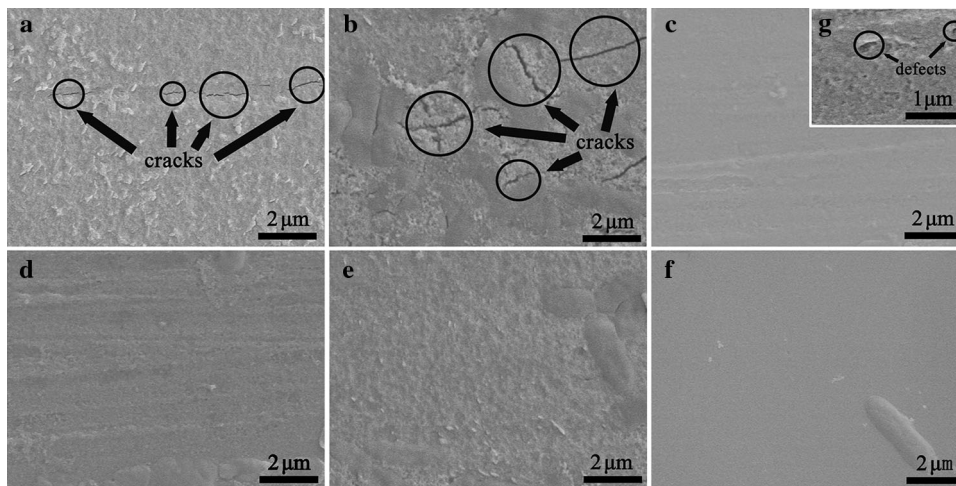


Fig. 3: Surface morphologies of PAS1, PAS2, and PAS3 after immersion in SBF for 4 days (a, b, c) and 7 days (d, e, f), respectively, and (g) the enlarged view of (c)

Table 2: Element compositions (wt%) found by EDS from the surfaces of PAS1, PAS2, and PAS3 after immersion for 7 days

Sample	C	N	O	Mg	Si	P
PAS1	16.7	5.9	23.6	35.2	10.1	8.5
PAS2	21.0	4.7	26.2	32.9	8.4	6.9
PAS3	25.2	5.8	25.3	23.7	11.4	8.7

alloy samples exhibited different variation trends: After a 4-day immersion, pH values of samples PAS1, PAS2, and PAS3 were 8.0 ± 0.1 , 8.3 ± 0.1 , and 7.8 ± 0.1 , respectively. However, during the 4–7 days, the increase in pH values relatively slowed down, and after immersion in SBF for 14 days, pH values of samples PAS1, PAS2, and PAS3 were merely 9.3 ± 0.1 , 9.9 ± 0.1 , and 8.7 ± 0.1 respectively, much lower than that of the uncoated AZ31 magnesium alloys. As shown in Fig. 2b, the corrosion process of the hybrid coatings

coated magnesium alloys may be summarized as three stages. During the initial 4 days (stage I), the hybrid coatings acted as physical barriers to retard the contact between SBF solution and magnesium alloy substrate; thus, no rapid mass loss and pH variation of hybrid coatings coated magnesium alloy substrates can be seen during this period. However, small cracks were observed on the surface of the hybrid coatings, which resulted from the partial dissolution of the hybrid coatings due to the existing water molecules and

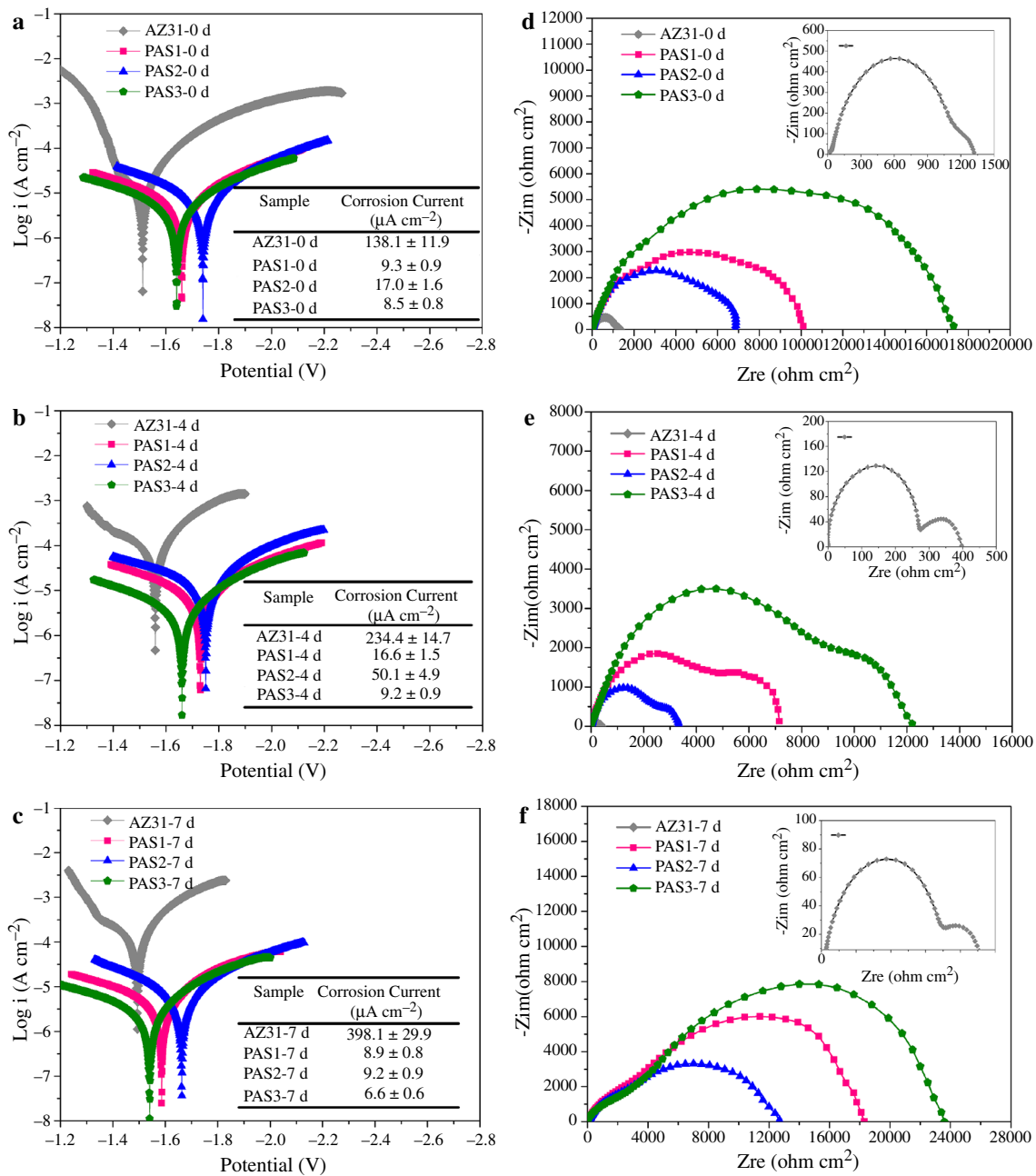


Fig. 4: Polarization curves (a, b, c) and Nyquist plots (d, e, f) of different samples (AZ31, PAS1, PAS2, and PAS3) after immersion in SBF for 0, 4, and 7 days. The inserted figures were uncoated AZ31 magnesium alloys immersed for the same periods

chloride ions in SBF (shown in Figs. 3a–3c). In the later immersion period (4–7 days, stage II), the growth rate of mass loss and pH value showed a decline trend than last stage. Surface morphologies of the samples after immersion for 4 and 7 days in SBF showed that fewer defects or cracks could be observed on the coating surfaces after 7-day immersion than 4-day immersion (shown in Fig. 3); meanwhile, no new component was detected by EDS results (shown in Table 2), suggesting that some defects or cracks on the surfaces of hybrid

coatings may heal up during the stage II. Further increasing the immersion time to 14 days (stage III), the mass loss of all the samples showed slight degradation, and the increase in pH values became slightly faster than stage II. In order to meet the demands of bone repair, a suitable biodegradable implanted material should have low degradation rate and desired mechanical support in the initial stage and then achieve complete dissolution of the implant after bone repairing. The current results revealed that phytic acid/ γ -APS

hybrid coating could increase the corrosion resistance of magnesium alloy in the initial stage, and the protection became less effective as the immersion time was prolonged; thus, it was believed to have potential application for biodegradable magnesium alloys.

Electrochemical behaviors

In order to discuss the influence of pH value during preparation of samples PAS1, PAS2, and PAS3, polarization curves and Nyquist plots (shown in Fig. 4) were made on hybrid coatings coated and uncoated AZ31 magnesium alloys during the immersion test in SBF. The corrosion current (i_{corr}) deduced from the polarization curve, which was commonly used to measure the corrosion resistance of all the samples, is listed in Figs. 4a–4c.^{1,6,44–51} The initial corrosion currents of samples AZ31, PAS1, PAS2, and PAS3 were 138.1 ± 11.9 , 9.3 ± 0.9 , 17.0 ± 1.6 , and $8.5 \pm 0.8 \mu\text{A cm}^{-2}$, respectively, which indicated that hybrid coatings could act as physical barriers to retard the corrosion on magnesium alloy substrate during the long-term immersion test in SBF. However, it was noted that all the corrosion currents of the hybrid coatings coated magnesium alloys increased after a 4-day immersion, reaching 16.6 ± 1.5 , 50.1 ± 4.9 , and $9.2 \pm 0.9 \mu\text{A cm}^{-2}$, respectively, while the corrosion currents had a significant decline during stage II (4–7 days) and the corresponding results were 8.9 ± 0.8 , 9.2 ± 0.9 , and $6.6 \pm 0.6 \mu\text{A cm}^{-2}$ (shown in Fig. 4c), suggesting that the phytic acid/ γ -APS hybrid coatings may exhibit excellent “self-healing” ability.^{16,51–56} It was also reported that the inhibition efficiency was also an important parameter to evaluate the corrosion resistance of a coating.^{47–52} According to the work of Bockris and Khans,⁵² the inhibition efficiency (η) was defined by

$$\eta = (1 - i_{\text{corr}/i}) \times 100\%, \quad (6)$$

where i and i_{corr} represent the corrosion current of the samples without/with hybrid coatings, respectively. The corresponding inhibition efficiencies of hybrid coatings (PAS1, PAS2, and PAS3) were 93.2%, 87.8%, and 93.8%, which indicated that hybrid coatings could

provide effective protection of magnesium alloy in SBF solution. In particular, the inhibition efficiency of the hybrid coating seemed to be intensely influenced by the pH value of preparing solution, and these results were consistent with those obtained from immersion test and corrosion current.

“Self-healing” ability of hybrid coatings

To further prove the “self-healing” ability of phytic acid/ γ -APS hybrid coatings, the impedance data were analyzed by fitting with an equivalent electrical circuit (shown in Fig. 5).^{49–53} The results were all moderately fitted, and the related parameters are listed in Table 3. The proper selection of equivalent electrical circuits was based on the fitting results of the impedance spectra at different immersion stages, where R_s , R_c , and R_{ct} represent solution resistance, coating resistance, and charge transfer resistance, respectively; meanwhile, CPE1 and CPE2 represent coating capacitance and double-layer capacitance, respectively. Among all the five electrical parameters, R_c and R_{ct} were more representative to measure the protection behaviors of a coating.^{53–56} It was apparently concluded that the R_c values of the hybrid coatings (PAS1, PAS2, and PAS3) were 7142 ± 269.4 , 3821 ± 130.8 , and $10,591 \pm 426.1 \text{ ohm cm}^2$, respectively, indicating that sample PAS3 had better resistance against water permeation than PAS1 and PAS2. When the immersion time extended to 4 days, R_c of all the samples declined, and this behavior was typically associated with the loss of hybrid coatings’ barrier properties and increase in water diffusion through the hybrid coating with immersion time prolonged. Besides, when water permeated through the hybrid coating, corrosive ions in SBF solution may reach the coating/magnesium alloy substrate interface causing the release of magnesium ions. After a 7-day immersion, R_c gradually increased among all the samples. This may be due to water permeation into the coating and an increase in the occurrence of water-involved reactions in the hybrid coating, and then, the barrier property of hybrid coating could be enhanced and provide effective protection of magnesium alloy substrate. Meanwhile, R_{ct} showed a similar variation trend with R_c . In the beginning of the EIS experiment, R_{ct} values of the hybrid coatings (PAS1, PAS2, and PAS3) were 3885 ± 183.4 , 2939 ± 112.7 , and $6455 \pm 239.7 \text{ ohm cm}^2$, respectively. With the immersion time extended, the corresponding R_{ct} of sample PAS1 changed from 1942 ± 23.9 to $9887 \pm 353.3 \text{ ohm cm}^2$, PAS2 increased from 677 ± 10.6 to $5865 \pm 212.7 \text{ ohm cm}^2$, and PAS3 changed from 3502 ± 126.7 to $14,314 \pm 608.9 \text{ ohm cm}^2$ after 7-day immersion. The surface morphologies of samples PAS1, PAS2, and PAS3 (shown in Figs. 1 and 3) before and after immersion test indicated that the phytic acid/silane hybrid coatings intelligently responded to damages caused by SBF solution and could rebuild their original structures to gain long-term

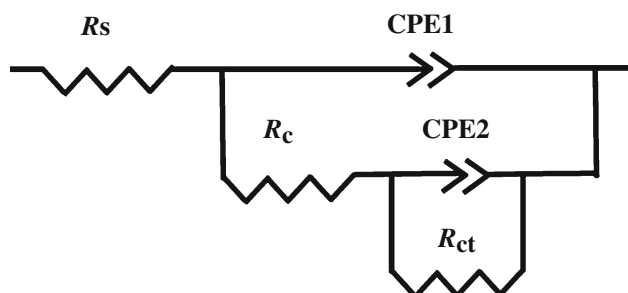


Fig. 5: Equivalent electrical circuit used for numeric fitting of EIS data

Table 3: Parameters of different samples (PAS1, PAS2, and PAS3) obtained from the fitting of the experimental impedance spectra with the equivalent circuit and calculated from polarization curves

Sample	R_c (ohm cm^2)	R_{ct} (ohm cm^2)
PAS1-0 d	7142 ± 269.4	3885 ± 183.4
PAS1-4 d	5257 ± 204.6	1942 ± 23.9
PAS1-7 d	8369 ± 314.6	9887 ± 353.3
PAS2-0 d	3821 ± 130.8	2939 ± 112.7
PAS2-4 d	2636 ± 55.6	677 ± 10.6
PAS2-7 d	6865 ± 242.5	5865 ± 212.7
PAS3-0 d	10,591 ± 426.1	6455 ± 239.7
PAS3-4 d	8664 ± 326.9	3502 ± 126.7
PAS3-7 d	9194 ± 342.9	14,314 ± 608.9

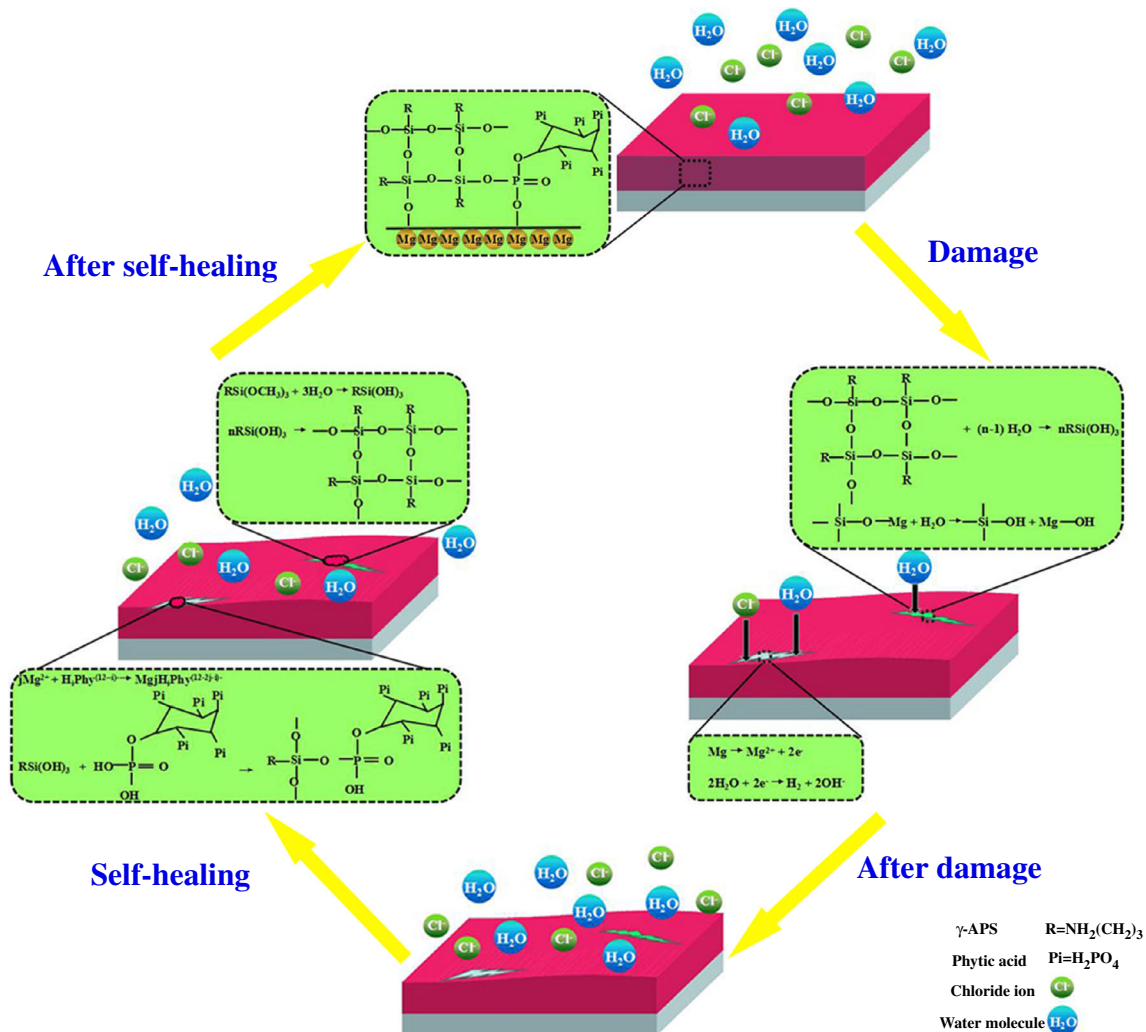


Fig. 6: Schematic illustration of “self-healing” process for phytic acid/ γ -APS hybrid coating coated AZ31 magnesium alloy after immersion in SBF and main reactions

corrosion resistance. This phenomenon was the consequence of the chelating ability of phytic acid from the hybrid coating, promoted by water permeation raising local pH value, followed by fast chelating with released magnesium ions from the substrate precipitated in the

defect. Besides, dense Si–O–Si network in the coating improved during the water permeation process. These results may suggest that the hybrid coatings exhibited “self-healing” ability during the relatively lengthy immersion period to some extent.^{16,53–60}

In order to better understand the “self-healing” process for phytic acid/ γ -APS hybrid coating coated AZ31 magnesium alloy after immersion in SBF, a possible schematic illustration is shown in Fig. 6. According to Metrok and Hu’s theory,^{14,16} because of the existence of silane component in hybrid coating, the destruction process easily occurred, due to the fact that water molecules damaged the coating’s intrinsic Si–O–Si or Si–O–Mg structure. However, the self-healing hybrid coatings of phytic acid/silane still contained hydrolyzable alkoxy groups (–OCH₃), and they could rebuild their original structure. When the alkoxy groups were in contact with water molecules, they would hydrolyze and yield silanols, which could condense to form Si–O–Si or Si–O–Mg structure, and the newly obtained network structure increased the crosslinking degree of the coatings. The competition between the destruction and reconstruction processes determined whether the self-healing phenomenon would occur. The results from polarization curves, Nyquist plots, and immersion tests indicated that the reconstruction process was dominant; therefore, the formation of Si–O–Si bonds in hybrid coatings during immersion test may act as the healing agent for these coatings. Besides, some reactive groups in the structure of phytic acid would react with magnesium ions released from alloy substrate to form insoluble magnesium phytic acid that healed the defects or cracks in hybrid coatings.^{51–60} Therefore, the phytic acid/silane hybrid coating showed “self-healing” ability during the immersion of 2 weeks in SBF solution, which can provide good protection for magnesium alloy substrates.

Conclusions

A series of “self-healing” phytic acid/ γ -APS hybrid coatings was successfully prepared on AZ31 magnesium alloys, which could provide effective protection for magnesium alloy substrates. According to the results from SEM, EDS, immersion test, and electrochemical test, it can be concluded that the hybrid coating PAS3 prepared in alkaline solution (pH value \sim 8.0) was dense and homogeneous, and it showed the least mass loss of 8.3 ± 0.4 wt% among all the coatings after 14-day immersion. In addition, after the long-term immersion in SBF, the decrease in mass loss, the amount of cracks on the surfaces of coatings, and the increase in charge transfer resistance, results indicated that phytic acid/ γ -APS hybrid coating exhibited the self-healing ability.

Acknowledgments Authors acknowledge the financial support by National Nature Science Foundation of China (Grant Nos. 51372166, 51572186, and 81271954) and Tianjin Natural Science Foundation (Grant No. 15JCYBJC47500). The authors acknowledge Mr. Chang Lin for his help in the experimental work via Tianjin-Hainan University

innovation fund cooperation project (Grant No. 2016XZC-0043).

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