

Article

Corrosion Resistance of the Superhydrophobic Mg(OH)₂/Mg-Al Layered Double Hydroxide Coatings on Magnesium Alloys

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Abstract: Coatings of the Mg(OH)₂/Mg-Al layered double hydroxide (LDH) composite were formed by a combined co-precipitation method and hydrothermal process on the AZ31 alloy substrate in alkaline condition. Subsequently, a superhydrophobic surface was successfully constructed to modify the composite coatings on the AZ31 alloy substrate using stearic acid. The characteristics of the composite coatings were investigated by means of X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electronic microscope (SEM) and contact angle (CA). The corrosion resistance of the coatings was assessed by potentiodynamic polarization, the electrochemical impedance spectrum (EIS), the test of hydrogen evolution and the immersion test. The results showed that the superhydrophobic coatings considerably improved the corrosion resistant performance of the LDH coatings on the AZ31 alloy substrate.

Keywords: magnesium alloy; layered double hydroxide; Mg(OH)₂; superhydrophobicity; corrosion resistance

1. Introduction

Magnesium alloys are being increasingly used as advanced structural and functional materials in the ship, automotive, aerospace and electronics industries, because of their high strength-to-weight ratio. The lower corrosion resistance of the alloys is, however, a limitation on its extensive application [1].

An improvement in corrosion resistance of Mg alloys has usually been achieved by element alloying, post-processing and surface modification [2–4]. Surface modification of Mg alloys includes a variety of approaches: chemical conversion film [5], micro-arc oxidation (MAO) or plasma electrolyte oxidation [6], polymeric coating [7], layer-by-layer film [8] and layered double hydroxide (LDH) coating [9].

Recently, the LDHs have caused great interest as promising alternative conversion coatings for Mg alloys [10–15]. LDHs can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_x(\text{OH})_2]^{x+}(A)^{n-}_{x/2} \cdot m\text{H}_2\text{O}$, where the cations M^{2+} and M^{3+} occupy the octahedral holes in a brucite-like layer and the anion A^{n-} is located in the hydrated interlayer galleries [16]. The LDH materials have caused widespread concern

because of their many applications as precursors to magnetic materials [17], catalysts [18,19] and anion exchangers [20–24].

In the authors' previous studies [14,15], a nano-sized LDH ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) and LDH ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{MoO}_4 \cdot 4\text{H}_2\text{O}$) coatings with ion-exchange and self-healing ability were obtained by the combination of the co-precipitation and hydrothermal treatment on the AZ31 Mg alloy. Those LDH coatings are environmentally friendly and low cost, which can provide protection to the Mg substrate. However, our previous study [15,16] and the other aforementioned study [25] bear in common that dissolution can certainly take place after the exposure of LDH solids to aqueous solutions. The open pores, acting as the channels for the aggressive ions in the solutions during the corrosion process, can be discerned on the outer layer [12–15]. The micro-pores on the outer layer may lead to a decrease in the corrosion resistance of the LDH coatings. Thus, in order to provide long-term protection for magnesium alloys, it is necessary to fabricate a composite coating on the LDH coatings. Our previous investigations have shown that the Zn-Al-LDH/poly(lactic acid) (PLA) coating on Mg alloys exhibited a better corrosion performance in comparison to the LDH coatings [26].

One approach that has been proven effective in protecting Mg alloys from corrosion is to produce a superhydrophobic surface, which also offers the advantage of providing the surface with the functions of self-cleaning and anti-fouling [27,28]. Self-cleaning coatings have been utilized in considerable industry fields. Generally, a self-cleaning surface can be made by means of the preparation of hierarchical structures [29] and self-assembly of organic compounds, such as fluoroalkylsilane with low surface energy [30]. Our group [31] fabricated the superhydrophobic surface on the AZ31 alloy by the combination of the hydrothermal treatment method and post-modification with stearic acid. Gao's group [32] obtained the superhydrophobic surface on the fibrous szaibelyite-coated AZ31 Mg alloy by the integration of hydrothermal synthesis and fluoroalkylsilane (FAS) modification. The resulting coatings exhibited advantageous superhydrophobic properties. Liu [33] also prepared a superhydrophobic surface on an AZ91D Mg alloy by Ni plating, followed by surface modification with stearic acid. Wang *et al.* [34] fabricated a superhydrophobic coating on the magnesium alloy by the combination of MAO and the sol-gel method using tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) as precursors. These coatings have significantly improved the corrosion resistance of Mg alloys. However, the preparation processes of the above-mentioned coatings were either complicated or required expensive raw materials, such as fluoroalkylsilane. Besides, to the best of our knowledge, few attempts have previously been made to create a superhydrophobic LDH surface on magnesium alloys. There is therefore clearly an urgent need to develop a greener and more effective approach to inhibiting the corrosion of Mg alloys.

In this work, we present a simple and efficient process for the fabrication of a superhydrophobic surface on the LDH-coated AZ31 Mg alloy, wherein LDH coatings were used to first prepare a rough microporous structure, which was then modified using an environmentally-friendly long-chain stearic acid with a low surface energy. The structure and composition of the obtained surfaces were characterized by scanning electronic microscope (SEM), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS) tests and Fourier transform infrared (FTIR). Moreover, the anticorrosion behavior of the superhydrophobic surface was described by means of electrochemical measurement, immersion tests and the hydrogen evolution rate in detail. Our research is expected to create some ideas from natural enlightenment to improve the anti-corrosion property of magnesium alloy, while this method can be easily extended to other metal materials.

2. Materials and Methods

2.1. Pretreatment of AZ31 Alloys

AZ31 magnesium alloy (2.5%–3% Al, 0.7%–1.3% Zn, 0.4% Mn, 0.02% Si, Mg, Balance) was used for this work. The substrate surface was ground with SiC papers up to 2000 grit to ensure the same

surface roughness. The substrate was then ultrasonically cleaned in ethyl alcohol and dried under a stream of air.

2.2. Preparation of the Superhydrophobic Coating on AZ31 Alloys

The superhydrophobic coatings were prepared on the AZ31 alloy by a two-step process. Firstly, the Mg-Al-LDH coatings were prepared using a combined co-precipitation and hydrothermal processing technique on the magnesium alloy substrates. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a $\text{Mg}^{2+}/\text{Al}^{3+}$ molar ratio of 3:1 were dissolved in deionized water to obtain Solution A, which was then kept in a three-neck flask. Na_2CO_3 was dissolved in deionized water and then mixed with a certain volume of NaOH to form Solution B. Solution B was then added dropwise into the three-neck flask to form a slurry, which was stirred vigorously in a water bath at a temperature of 338 K for 48 h and then aged for 12 h. Afterwards, the resulting slurry was transferred to a Teflon-lined autoclave in which the pretreated magnesium alloy was immersed. The Teflon-lined autoclave was then heated at 393 K for 36 h. The as-prepared samples were rinsed with deionized water and dried under ambient conditions.

Subsequently, the as-prepared magnesium samples with Mg-Al-LDH coatings were modified with 0.01 M stearic acid (SA) in a mixture of dimethyl formamide (DMF) and water (the volume ratio of DMF to water was 1:1, 2:1, 3:1) designated as LDH/SA1, LDH/SA2 and LDH/SA3, at 99 °C for 0.5 h. Finally, the samples were rinsed with deionized water and dried at room temperature for further characterization.

2.3. Characterization

The morphologies of the coatings were observed using a scanning electronic microscope (FEI, Nano SEM450, FEI Company, Hillsboro, OR, USA). The chemical compositions of the coatings were analyzed by X-ray diffractometer (XRD, D/Max 2500PC, Rigaku Corporation, Tokyo, Japan) with a Cu target ($\lambda = 0.154$ nm), Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS) tests. XPS measurements were carried out on an X-ray photoelectron spectrometer (ESCALAB250, Thermo VG Corporation, East Sussex, UK) with an Al K α X-ray source, and the spectra were referenced to the adventitious C 1s peak (284.6 eV). The FTIR spectra were obtained on a Nicolet iN10 MX (Thermo Fisher Scientific Corporation, Waltham, MA, USA) in the wavenumber range of 700–4000 cm^{-1} with a resolution of 1 cm^{-1} . The water contact angles (CA) were measured using the JC2000C1 contact angle goniometer (Shanghai Zhongchen Digital Technic Apparatus Corporation, Shanghai, China). The volume of water drops was 2 μL . The potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (PARSTAT, 2273, Princeton Instruments Corporation, Princeton, NJ, USA) in a cell with 3.5 wt. % NaCl solution at room temperature. All of the electrochemical tests were conducted in a classical three-electrode system, which consisted 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 polarization curves were recorded with a sweep rate of 2 mV/s. EIS plots were acquired from 100 kHz–10 MHz with a perturbation amplitude of 5 mV. As shown in Figure 1, the hydrogen evolution set-up design was tested by placing the sample with full surface exposure in 3.5 wt. % NaCl solution at 25 °C under an inverted funnel connected to a graduated burette. The water level in the burette was intermittently recorded during the immersion experiment for 336 h.

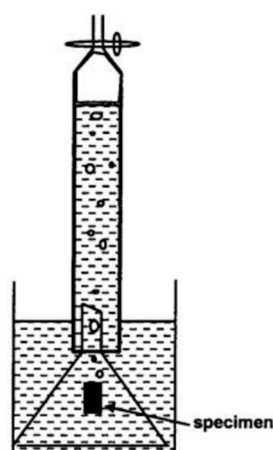


Figure 1. Schematic illustration of the setup for hydrogen evolution.

3. Results and Discussion

3.1. Structure and Composition of the Superhydrophobic Surface

Figure 2 illustrates the XRD patterns of the prepared Mg-Al- CO_3 -LDH coatings by a combined co-precipitation method and the hydrothermal treatment. As can be seen, in addition to the characteristic peaks of the magnesium substrate, the XRD patterns of the obtained coatings showed a typical layered structure characteristic of the LDH with identical peaks corresponding to the (003)/(006) reflections, which illustrates that the LDH coatings are successfully formed on the substrate. It is pointed out that obvious $\text{Mg}(\text{OH})_2$ peaks appeared on the coated samples in addition to those of the MgAl-LDH layer, which means that $\text{Mg}(\text{OH})_2$ was also obtained on the substrate in the coating-forming process under a high temperature in the alkaline condition.

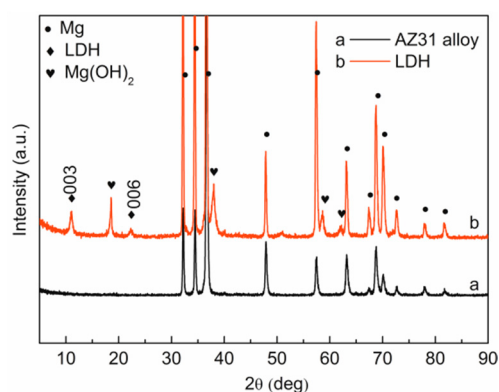


Figure 2. X-ray diffractometer (XRD) patterns of the bare magnesium alloy substrate and layered double hydroxide (LDH) coatings formed on magnesium alloy.

SEM morphologies of the prepared Mg-Al-LDH coating and LDH/SA coatings are shown in Figure 3, and the insets are the contact angles. Figure 3a demonstrates that the Mg-Al-LDH coating is compact over the entire magnesium alloy substrate after the hydrothermal treatment, which is in accord with our previous work [16]. Figure 3b presents the image at higher magnification, demonstrating that the Mg-Al-LDH coating consists of uniform nano-plates that grew roughly vertically on the substrate, with a length of 300–750 nm. Figure 3c–e shows the micrographs of the LDH-coated magnesium alloy surface further treated with SA. It is obvious that the morphologies of the surfaces were drastically changed as compared to the micrographs of the magnesium alloy treated only with hydrothermal

treatment in Figure 3a,b, and many petal-like clusters are present at the porous and rough LDH surface. The platelet-like structure of the LDH coatings was completely covered. From the cross-sectional morphology of the LDH coating in Figure 3f, we can see that the thickness of the LDH coating is about 7.5 μm .

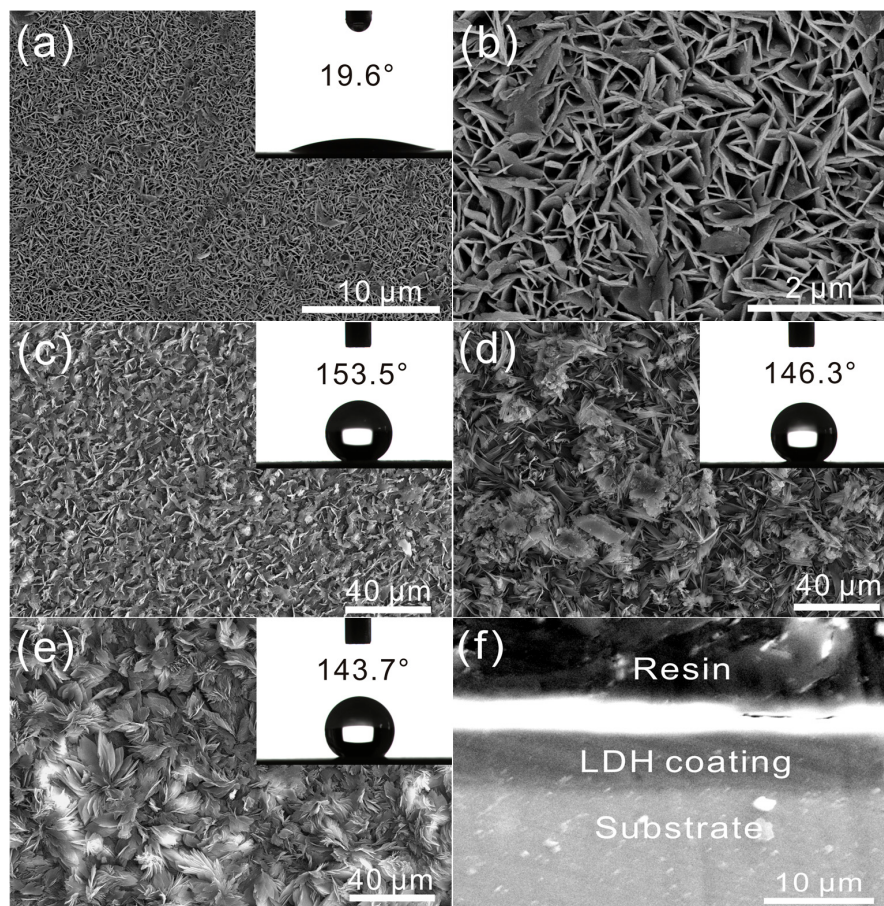


Figure 3. SEM morphologies and contact angle (inset) of the LDH coatings (a); (c–e) the prepared LDH/SA1, LDH/SA2, LDH/SA3 coatings; (b) high magnification view of and (a,f) cross-sectional view of the LDH coatings.

Due to the capillary phenomenon, the LDH surface became much more hydrophilic after the hydrothermal treatment, and the CA is determined to be 19.6° . Interestingly, the surfaces modified with SA possessed a high CA, such that the CAs of the LDH/SA1 coating, the LDH/SA2 coating and the LDH/SA3 coating are 153.5° , 146.3° and 143.7° . The surfaces after being modified with SA exhibited hydrophobic properties. It is clear that the LDH/SA1 coating possessed superhydrophobicity. The water droplets scarcely stuck to the SA-modified surface and rolled off easily, suggesting a superhydrophobic surface acquired for the LDH coating on the AZ31 alloy. The superhydrophobic behavior was attributed to the combination effect of the hierarchical microstructure of the LDH coating, as well as the low surface energy of SA.

The above-mentioned results demonstrated that the superhydrophobic behavior of the dense and uniform LDH/SA composite coatings could avoid their substrate's exposure to the environment by blocking the penetration of aggressive ions effectively. Thus, the LDH/SA composite coatings have a potential to act as an environment-friendly and corrosion-resistant coating on Mg alloys.

Figure 4 shows the typical XPS survey spectra of the LDH/SA1 coating. It can be found that the LDH/SA1 coating is composed of Mg 1s, C 1s, O 1s and Al 2p peaks in Figure 4a. We can see that the peak of Mg 1s at 1302.0 eV can be assigned to $\text{Mg}(\text{OH})_2$ derived from the LDH structure from

Figure 4b. As shown in Figure 4c, the C 1s peaks at 283.1 and 282.9 eV are assigned to $\text{CH}_2\text{-CH}_2$ and C=O groups, which confirms that the SA or magnesium stearate was fixed to the LDH surface. The O 1s (α) peak of 530.2 eV (Figure 4d) is attributed to the C=O group in SA, which fits with the C 1s peaks. Additionally, the peak of O 1s (β) at 530.9 eV is assigned to Mg(OH)_2 , which is consistent with the peak of Mg 1s. The peak of Al 2p at 74.5 eV (Figure 4e) indicates that the Al atom exists in an Al(OH)_3 state, which comes from the LDH structure.

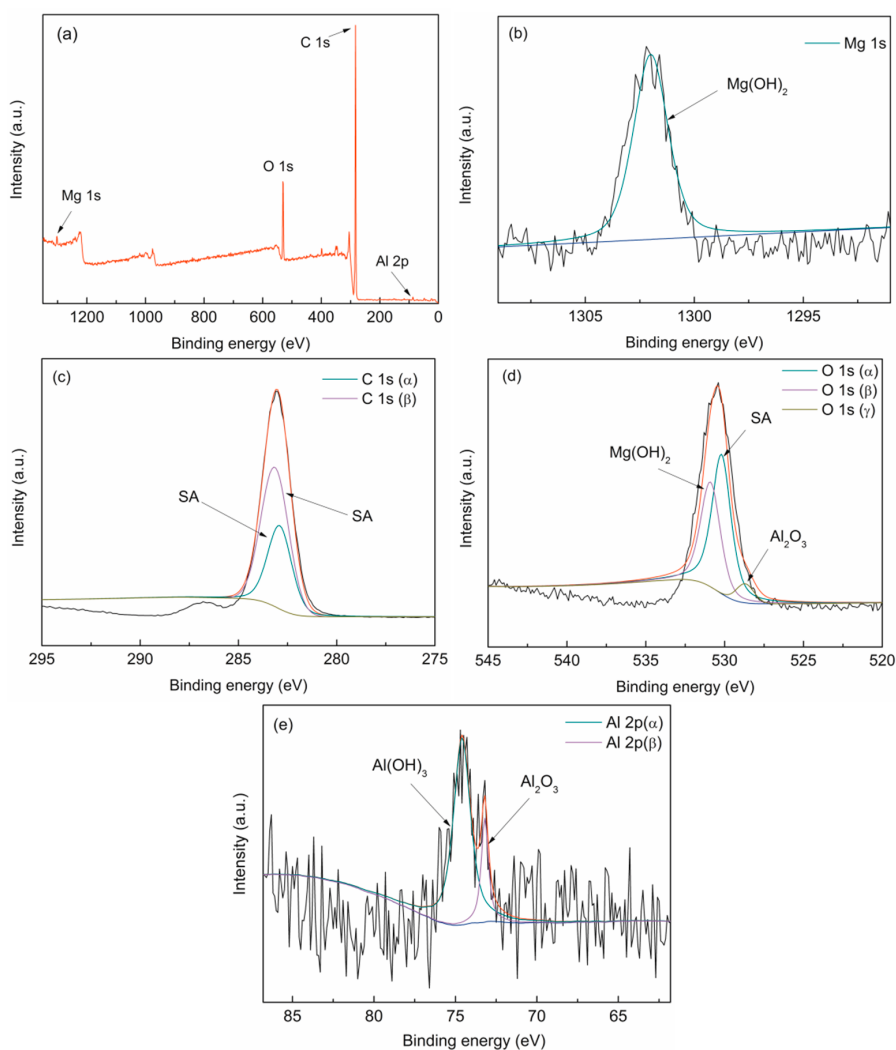


Figure 4. XPS survey spectra of SA1-LDH coating (a); and high-resolution XPS spectra in the Mg 1s (b), C 1s (c), O 1s (d) and Al 2p (e) spectral regions.

The FTIR spectra of the as-prepared Mg-Al-LDH coating and LDH/SA1 composite coatings are designated in Figure 5. The bands corresponding to the H–O–H stretching vibration and the O–H symmetric contraction of the water molecules between layers of the LDH coating and the water molecules absorbed on the LDH surface were at roughly 3696 and 3359 cm^{-1} [16]. The shoulder band at approximately 2931 cm^{-1} corresponds to a $\text{CO}_3^{2-}\text{-H}_2\text{O}$ stretching vibration, suggesting the presence of water molecules hydrogen bonded to the carbonate ions present in the interlayer [35]. The bands at 2913 and 2861 cm^{-1} are attributed to C–H asymmetric and symmetric stretching vibrations [36]. The bands at 1465 cm^{-1} are attributed to the symmetric and asymmetric stretching modes of CO_3^{2-} ion in the interlayer or introduced by CO_2 in the air [37]. The FTIR spectrum of the composite coatings exhibits a characteristic peak at 1539 cm^{-1} , corresponding to carbonyl (C=O) stretching. The absorption peaks are attributed to the functional groups present in SA [38,39].

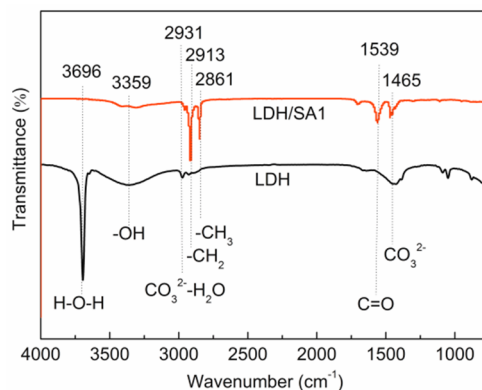


Figure 5. FTIR spectra of the Mg-Al-LDH coating and LDH/SA1 composite coatings.

3.2. Corrosion Resistance of the Superhydrophobic Surface on Magnesium Alloy

The electrochemical test is a commonly-used technique that was employed to investigate the corrosion resistance of the coatings. Figure 6 presents the potentiodynamic polarization curves of the bare magnesium alloy, the Mg-Al-LDH coating and LDH/SA composite coatings in 3.5 wt. % NaCl solution. The results of the potentiodynamic test are summarized in Table 1. It is found that the corrosion potential (E_{corr}) of the LDH-coated sample moved toward the positive direction, and the corrosion current density (I_{corr}) decreased after being sealed by the SA species. The E_{corr} of the AZ31 substrate is about -1.58 V *vs.* SCE. The E_{corr} of the Mg-Al-LDH coated sample was improved up to -1.40 V *vs.* SCE, and the LDH/SA composite coatings are -1.16 , -1.29 and -1.45 V *vs.* SCE for LDH/SA1, LDH/SA2 and LDH/SA3. The E_{corr} mainly describes the thermodynamic property of the materials, so the corrosion resistance cannot be evaluated by E_{corr} . The I_{corr} of the substrate is 4.7×10^{-5} A/cm², and the LDH-coated sample is 3.9×10^{-7} A/cm², while that of the samples modified with SA is 3.4×10^{-10} , 4.8×10^{-9} and 1.7×10^{-8} A/cm² for LDH/SA1, LDH/SA2 and LDH/SA3. The I_{corr} of the Mg-Al-LDH-coated sample increased two orders of magnitude compared to the bare substrate, while the LDH/SA composite coating increased three, two and one orders of magnitude compared to the LDH-coated sample. The values of I_{corr} indicated that the existence of the composite surface improved the corrosion resistance of the Mg-Al-LDH coatings, which is mainly attributed to the effective blocking of the penetration of aggressive ions. Krishna *et al.* [40] formed the cold gas dynamic spray (CGDS) + MAO duplex coating on AZ91D magnesium alloy. The minimum I_{corr} of the duplex coating is 8.0×10^{-7} A/cm², which was higher (nearly three orders of magnitude) than that of the surface fabricated here. The LDH/SA1 composite coating possessed the lowest corrosion current density ($I_{\text{corr}} = 3.4 \times 10^{-10}$ A/cm²) because the superhydrophobic surface can effectively block the penetration of corrosive ions in the electrolyte.

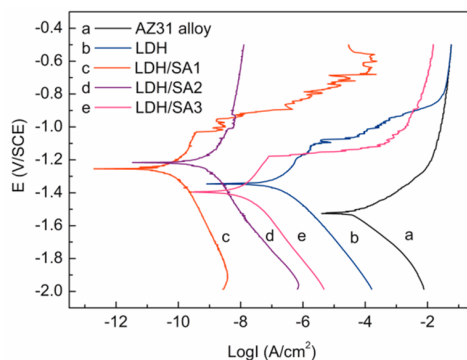


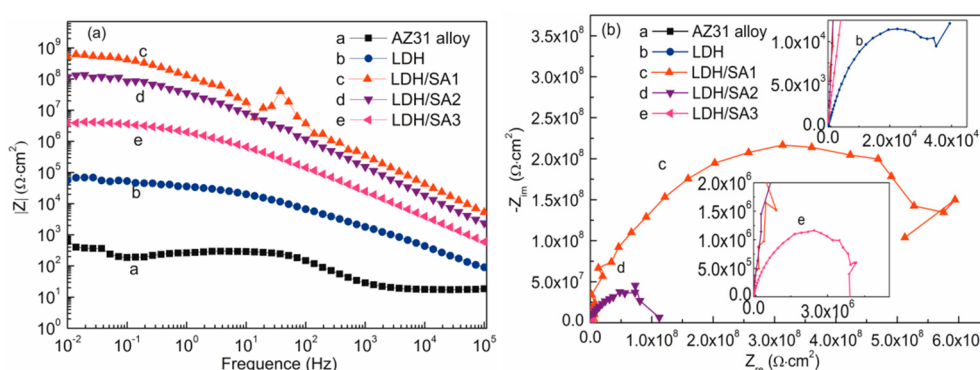
Figure 6. Tafel polarization curves of the bare magnesium alloy: (a,b) the Mg-Al-LDH coating and (c–e) LDH/SA composite coatings in 3.5 wt. % NaCl solution.

Table 1. Corrosion potential (E_{corr}) and corrosion current density (I_{corr}) of the samples. SCE, saturated calomel electrode.

Samples	E_{corr} (V vs. SCE)	I_{corr} (A/cm ²)
AZ31 alloy substrate	−1.58	4.7×10^{-5}
Mg-Al-LDH coating	−1.40	3.9×10^{-7}
LDH/SA1 coating	−1.16	3.4×10^{-10}
LDH/SA2 coating	−1.29	4.8×10^{-9}
LDH/SA3 coating	−1.45	1.7×10^{-8}

Interestingly, there is a significant difference at the anodic branches of the curves (Figure 6). The anodic branch of the sample coated by the Mg-Al-LDH coating (Figure 6b) exhibits some saw-tooth-shaped passivation zones. The repeated rapid increase and decrease in the I_{corr} in the passivation zone indicated that the Mg-Al-LDH coating has a self-healing ability [15,16]. In comparison with the LDH-coated samples, the anodic branches of the LDH/SA1 coating (Figure 6c) exhibited two step-like passivation zones with plenty of breakdown potentials, implying the self-healing ability of the coating. Namely, the SA coating significantly improved the anticorrosion performance of the LDH coating.

In order to further provide the characteristics of the corrosion inhibition effect of LDH/SA composite coatings, EIS was carried out to analyze the corrosion resistance of the coatings. Figure 7a,b show the Bode diagram and Nyquist plot, respectively. It is generally known that a higher Z modulus at the lower frequency and larger radius of the curvature represent a better corrosion resistance on the metal substrates [41,42]. It can be observed from the Bode diagrams that the LDH-coated samples and LDH/SA composite coatings exhibit larger impedance at low frequency compared to the bare Mg alloy sample. Note also that the low frequency impedance for the LDH-coated sample was approximately $10^{5.0} \Omega \cdot \text{cm}^2$, considerably higher than the substrate, which was approximately $10^{3.0} \Omega \cdot \text{cm}^2$. It is worth noting that the impedance (Figure 7a) of the LDH/SA composite coatings at low frequency is larger than that of the LDH-coated sample, which are approximately $10^{9.0}$, $10^{8.0}$ and $10^{7.0} \Omega \cdot \text{cm}^2$ for LDH/SA1, LDH/SA2 and LDH/SA3. Especially, the impedance of the LDH/SA1 coatings is the largest among the three SA-modified LDH coatings. The consequence is in good accordance with the results from the polarization curves in Figure 6.

**Figure 7.** (a) Bode plots and (b) Nyquist plots of the bare magnesium alloy, the Mg-Al-LDH coating and LDH/SA composite coatings.

Concurrently, the Nyquist plot (Figure 7b) is in good agreement with the feature of the Bode diagram. It is usually considered that the larger capacitive loop means a lower corrosion rate. The dimension of the Nyquist plot for the AZ31 substrate is too small to be discerned in comparison with that of the alloy with LDH coating and LDH/SA composite coatings. It can be observed from

the Nyquist plot that the largest radius of curvature for the LDH/SA1 sample indicates the highest corrosion resistance.

The superhydrophobic sample with better EIS performance can effectively prevent the diffusion/penetration of the Cl^- ions to the magnesium alloy substrate, thus reducing the corrosion rate of the magnesium alloy. The results indicate that the corrosion resistance of the substrate is effectively enhanced by the LDH coating and the SA coating. Furthermore, the SA can further improve the corrosion resistance of the LDH-coated sample.

3.3. Hydrogen Evolution

The hydrogen evolution rate (HER) can be calculated by the equation:

$$\text{HER} = V_{\text{H}}/st \quad (1)$$

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

There are two distinct stages for the AZ31 substrate in the HER *vs.* time curves (Figure 8a). In the initial 8 h of immersion in 3.5 wt. % NaCl solution, a continuous increase in HER shows the breakdown of the oxide film and the dissolution of the substrate. The electrochemical reactions are as follows:

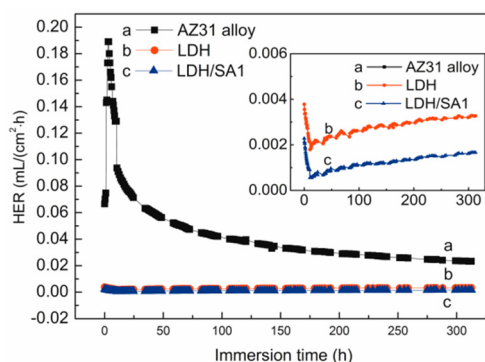


Figure 8. Hydrogen evolution rate (HER) as a function of immersion time for the (a) Mg substrate, (b) Mg-Al-LDH coating and (c) LDH/SA1 composite coating.

After an immersion of 8.5 h, the HER gradually decreased and then kept steady, designating the formation of a thick and dense corrosion product layer on the substrate. When the equilibrium between dissolution and the formation of corrosion products was established, the corrosion rate stabilized.

For the Mg-Al-LDH coating and the LDH/SA1 coating, the HER curves (the inset in Figure 8) were very similar to each other. Firstly, the HERs decreased rapidly in 12 h because of the effective protection of the coatings. When the corrosive medium penetrated into the coatings through the defects onto the surfaces or interface of the coating and the AZ31 substrate, electrochemical corrosion occurred. Thus, the HERs continuously and slowly increased, finally becoming constant due to the formation of corrosion products. The HER of the LDH/SA1 composite coating was lower than that of the Mg-Al-LDH coating in the whole immersion period.

After 312 h of immersion, the HER for the LDH/SA1 coating is $1.67 \times 10^{-3} \text{ mL}/(\text{cm}^2 \cdot \text{h})$ and the Mg-Al-LDH coating $3.27 \times 10^{-3} \text{ mL}/(\text{cm}^2 \cdot \text{h})$, while for the substrate, it is $2.33 \times 10^{-2} \text{ mL}/(\text{cm}^2 \cdot \text{h})$.

This result showed that the HER of the LDH/SA1 coating is the lowest among them and thus has the best corrosion resistance.

3.4. Corrosion Morphology

Figure 9 shows the SEM images of the AZ31 substrate, the LDH coating and the LDH/SA1 coating after immersing in 3.5 wt. % NaCl solution for 14 days. As clearly seen in Figure 9a, the surface of the bare AZ31 alloy suffers severe corrosion damage after immersion. As for the LDH-coated sample, the morphologies of the LDH coatings changed compared to the original Mg-Al-LDH coatings. Some crystals precipitated on the surface of the coating, which may be magnesium hydroxide. Besides, the plate size decreased after immersion, which may be due to the dissolution of the plate; while for the SA-modified LDH coatings, there is LDH/SA composite coatings on the surface after immersion for 14 days (Figure 9c). No LDH plate-like structure appeared after immersion, which suggested that the superhydrophobic surface was very stable. Moreover, many petal-like clusters of the SA-modified coatings have broken, which suggested that the degradation and delamination of the SA coating occurred (Figure 9c). The degradation of the SA coating could be attributed to a local rise in pH and the formation of corrosion products, leading to cracking and delamination.

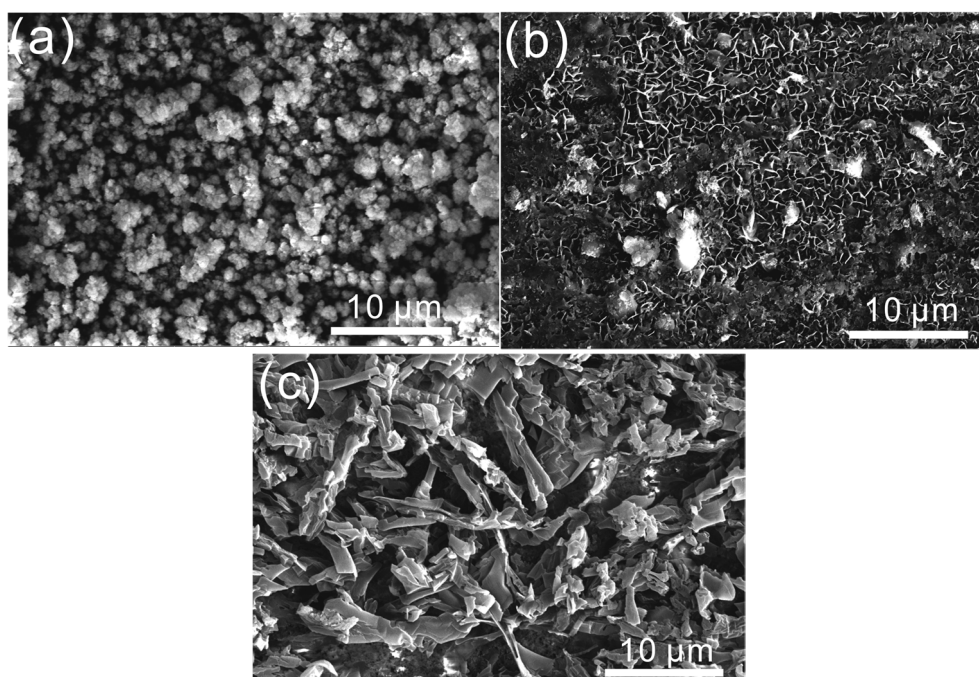


Figure 9. Morphologies of (a) bare AZ31 substrate, (b) the LDH coatings and (c) the superhydrophobic surface after immersing in 3.5 wt. % NaCl aqueous solution for 14 days.

3.5. Corrosion Behavior

The potentiodynamic polarization curves of the LDH coating, the LDH/SA1 composite coatings before and after immersion in 3.5 wt. % NaCl solution were shown in Figure 10. Table 2 lists the E_{corr} and I_{corr} of the LDH coatings and the composite coatings before and after immersion. After immersion for 14 days, the E_{corr} of the coated samples shifted toward negative, and I_{corr} became bigger, as shown in Table 2. The I_{corr} of the LDH/SA1 coatings after being immersed decreased from 3.4×10^{-10} to 9.7×10^{-7} , which was similar to the I_{corr} of the original LDH coating before immersion. The above results demonstrated that some of the petal-like clusters of the SA layer broke during the 14 days immersion process, which is consistent with the SEM morphology shown in Figure 9.

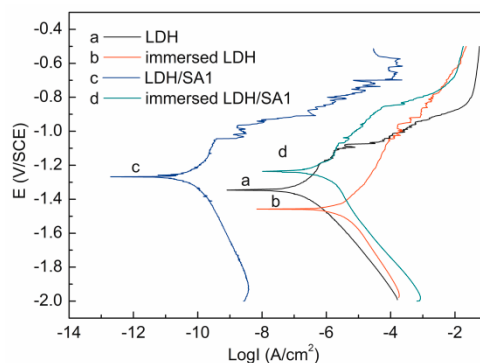


Figure 10. Tafel polarization curves of the LDH coating, the LDH/SA1 composite coatings before and after immersion in 3.5 wt. % NaCl solution.

Table 2. E_{corr} and I_{corr} of the samples.

Samples	E_{corr} (V vs. SCE)	I_{corr} (A/cm ²)
Mg-Al-LDH coating	−1.40	3.9×10^{-7}
Immersed LDH coating	−1.52	4.9×10^{-6}
LDH/SA1 coating	−1.16	3.4×10^{-10}
Immersed LDH/SA1 coating	−1.29	9.7×10^{-7}

During the synthesis process, Mg^{2+} will be released into the electrolyte. Meanwhile, $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-$ will be produced in the solvent. Then, the Mg^{2+} ion may react with $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-$ to generate precipitates, which will result in a drop of SA content on the sample surface. There may exist competing adsorption phenomena between the precipitates and SA. The pH value of 0.01 M SA at 99 °C in different volume ratios of DMF to water is shown in Table 3. As can be seen, the greater the volume ratio of DMF to water, the lower the pH value and, thus, the much greater concentration of $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-$. As is well known, SA has poor solubility in water, which can provide a weak acidic environment, leading to a higher pH value of 6.01. However, SA has good solubility in DMF, which can provide a stronger acidic condition with a pH value of 5.44. That is to say, with the increase of the volume ratio of DMF to water, more precipitates will be produced. Thus, less SA will deposit on the surface of the LDH-coated sample. Therefore, the LDH/SA1 coatings have a better anti-corrosion behavior.

Table 3. The pH value of 0.01 M stearic acid (SA) in different solvents at 99 °C.

Volume Ratio	pH
1:1	6.01
2:1	5.77
3:1	5.44

When the bare AZ31 alloys or hydrothermal-treated samples are immersed in NaCl aqueous solution, Cl^- ions can interact either directly with the substrate or penetrate the LDH coating and interact with them, which rendered the corrosion. Conversely, the superhydrophobic coating capable of trapping a large amount of air and the air that is trapped in the pores of the surface could considerably decrease the direct contact of the surface to corrosive medium, which explains the better corrosion resistance of the superhydrophobic coating.

4. Conclusions

(1) This study demonstrated that a superhydrophobic surface was successfully fabricated on a LDH-coated AZ31 Mg alloy via surface modification with stearic acid. The results of the electrochemical measurements demonstrate that the as-prepared superhydrophobic coating has an excellent anti-corrosion effect in 3.5 wt. % NaCl aqueous solution.

(2) The superhydrophobic behavior was attributed to the combination effect of the high surface roughness of the hierarchical microstructure of the LDH coating, as well as the low surface energy of SA.

(3) HER and photographs of the samples after immersing in 3.5 wt. % NaCl aqueous solution for 14 days exhibited that the superhydrophobic coatings can provide long-term corrosion protection for the AZ31 Mg alloy, which could be ascribed to the compact coating structure and the superior water-repellent property of the modified magnesium alloy surface.

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