



Article Al₂O₃ Coatings on Zinc for Anti-Corrosion in Alkaline Solution by Electrospinning

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Abstract: The severe corrosion accompanied with hydrogen evolution reaction has become the main obstacle restricting the utilization of zinc as an electrode in alkaline batteries. Al_2O_3 coating helps control the corrosion of zinc in alkaline solution. Herein, a stable Al_2O_3 coating is fabricated through facile electrospinning from $Al(NO_3)_3$ as an efficient anti-corrosion film on zinc. The electrospinning technique facilitates uniform dispersion of Al_2O_3 particles, therefore the corrosion inhibition efficiency could be up to 88.5% in this work. The Al_2O_3 coating prevents direct contact between zinc and the alkaline solution and minimize hydrogen evolution. Further, the effects of the thickness of Al_2O_3 coating on corrosion behavior of zinc are investigated through hydrogen evolution reaction, Tafel polarization, and impedance test. The results show that the thicker Al_2O_3 coating possessed better corrosion inhibition efficiency due to the higher corrosion resistance and lower porosity. The 18 µm Al_2O_3 coating on zinc provides corrosion current density of 60.6 mA/cm², while the bare zinc substrate delivers as much as 526.3 mA/cm². This study presents a promising approach for fabricating Al_2O_3 coating for corrosion-resistant applications.

Keywords: anti-corrosion; electrospinning; Al₂O₃ coating

1. Introduction

Recently, metal–air batteries are considered as the renewable energy for many devices [1–4]. Zinc is one of the most widely used electrodes because of its abundance, low cost, and environmental compatibility [5–7]. Aqueous alkaline electrolyte (KOH, NaOH) is generally applied in Zn-air batteries, and the electrolyte concentration is commonly fixed at 4–6 M [8–10]. However, the parasitic hydrogen evolution reaction (HER) during discharge is a major defect that leads to the degradation in the electrochemical performance of batteries [11–13].

Many efforts were conducted to overcome this defect. One method is adding some inhibitors into the alkaline electrolyte [14,15]. Zinc oxide, indium hydroxide, sodium stannate, and citrate are found to be effective in inhibiting the self-corrosion in alkaline solutions [16,17]. Another way is alloying elements such as Mg, Ga, Mn, In, Sn, Zr, and Ti in zinc due to their low melting temperatures and high hydrogen evolution overpotential [18,19]. The third approach to suppress corrosion is to modify the surface of zinc with coatings [20–22]. Surface coating materials have been found an increasingly wide utilization in the field of anti-corrosion, such as CuO, MgO, Al₂O₃, Bi₂O₃, and In₂O₃, which can prevent the HER and effectively decrease the side reaction [23,24]. Among them, Al₂O₃ coating has been investigated widely for its possible use as an excellent protective film against HER corrosion due

to the excellent corrosion resistance, high mechanical properties, and stable chemical properties [25]. The study by Huai et al. [26] has indicated that the anti-corrosion properties of Al_2O_3 coating is better in alkaline solution than in acid solution. Lee et al. [27] reported that Al_2O_3 coating effectively suppressed the HER of zinc anode during storage in alkaline electrolyte. In addition, they proved that the Al_2O_3 coating could be more effective to control HER than just adding Al_2O_3 powder into alkaline electrolyte [27].

Various strategies of Al_2O_3 coating fabrications have been developed to protect the metal from corrosion. Atomic layer deposition (ALD) of Al_2O_3 on LiCoO₂ was studied by Jung et al. to reduce the surface electrolyte reactions for lithium-ion batteries [28]. Díaz et al. coated Al_2O_3 film on steel by ALD for anti-corrosion [29]. Wongrujipairoj et al. [30] synthesized Al_2O_3 coating on zinc substrate by sol-gel method to suppress the HER of Zn-air battery. Nevertheless, the ALD and sol-gel coating layers are complex and costly. It would be required multi-step treatment or the special design of equipment. Furthermore, there may be uneven distribution of Al_2O_3 concerns during the preparation, which would affect the corrosion inhibition efficiency [31]. Electrospinning has been used as an efficient method for preparing thin films [32,33]. The coating film fabricated through electrospinning possesses smooth surface and uniform distributions of particles [34]. Since past few years, various composite materials have been successfully electrospun into ultrathin coatings from their solutions. However, to the best of our knowledge, there has been little research regarding the fabrication of Al_2O_3 coating through electrospinning technique.

In this study, Al₂O₃ coating has been electrospun from Al(NO₃)₃ to inhibit the corrosion of zinc in alkaline solutions. The surface structure and morphology of the Al₂O₃ coating were characterized by X-ray diffraction and scanning electron microscope (SEM). The corrosion behavior has been investigated through hydrogen evolution test, Tafel polarization, and impedance (EIS). The effect of the coating thickness on anti-corrosion properties is also discussed in this work.

2. Materials and Methods

2.1. Materials

All materials in this study were of analytical grade and used as received without further treatment. Polyacrylonitrile (PAN, $Mw = 150,000 \text{ g} \cdot \text{mol}^{-1}$) was obtained from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Aluminum nitrate (Al(NO₃)₃·9H₂O) and N,N-dimethylformamide solution (DMF) were purchased from Shanghai Lingfeng Chemical Reagent (Shanghai, China). KOH flakes (AR, 99%) and zinc sheet (99.99%) were purchased from Shenyang Kejing (Shenyang, China).

2.2. Preparation of Al₂O₃ Coatings

The precursor solution for electrospinning was prepared by dissolving 3 g of Al(NO₃)₃·9H₂O and 1.5 g of PAN in 10 g of DMF solution. Magnetic stirring was applied for 3 h at 60 °C to obtain a homogeneous precursor solution. Subsequently, the solution was electrospun via a single-capillary electrospinning apparatus. The tip-collector distance, applied voltage, and the flow rate were fixed at 12 cm, 17 kV and 0.15 mL/h, respectively. The electrospun coatings were collected on a rotating drum covered with zinc substrate. The coatings were dried in an oven at 60 °C for 3 h to remove the residual solvent. Then sintered the coatings at 350 °C for 1 h with a heating rate of 5 °C/min in an atmospheric environment to obtain Al₂O₃ coatings. Finally, the coatings is shown in Figure 1. Different thicknesses of Al₂O₃ coatings were tested in this work. The coating thickness was measured with a step profiler (DektakXT, Bruker, Billerica, MA, USA).



Figure 1. Schematic illustration of the preparation of Al₂O₃ coatings. Electrospun Al(NO₃)₃·9H₂O, polyacrylonitrile (PAN) and N,N-dimethylformamide (DMF) mixed solution on zinc substrate (**a**). Heat treated the electrospun films in muffle furnace in an atmospheric environment to obtain Al₂O₃ coatings (**b**).

2.3. Characterization

The morphological structure of the electrospun coatings was investigated through SEM (Su-8010, Hitachi, Tokyo, Japan). The crystalline structures of the samples were characterized using an X-ray diffraction (XRD) instrument (Bruker D8 Advance, Bruker Corp., Billerica, MA, USA) with a Cu-K α radiation of 0.1541 nm as an X-ray source. The pH of solution was measured using a Mettler-Toledo pH meter (SevenMulti, Mettler-Toledo Instruments, Columbus, OH, USA).

2.4. Hydrogen Evolution Tests and Electrochemical Measurementsc

The HER corrosion was investigated by hydrogen evolution tests using a set of hydrogen collection equipment as described in Ref. [35]; 4 M KOH served as corrosive solution due to its common use in Zn-air batteries as alkaline electrolyte. Zinc specimens ($3 \text{ cm} \times 3 \text{ cm}$) with Al₂O₃ coating on both faces were placed in 4 M KOH solution at pH 13.52 for 1.5 h. The temperature was controlled at 298 K using a thermostat water bath. The hydrogen evolution rate was calculated as:

Hydrogen evolution rate $(mL/cm^2/min) =$ Hydrogen volume/Surface area/Time of immersion (1)

The electrochemical tests were carried out with three electrodes system by RST5000 electrochemical workstation (Suzhou, China). The alkaline solution used in this study was 4 M KOH solution. An Hg/HgO and a platinum wire were used as reference and counter electrodes. Potentiodynamic polarization was measured at a scan rate of $1 \text{ mV} \cdot \text{s}^{-1}$. Furthermore, electrochemical impedance spectroscopy (EIS) measurements were also performed using the same electrochemical workstation. The frequency ranged from 100 kHz to 0.01 Hz and the sinusoidal excitation voltage applied to the cells was 10 mV·rms. The samples were immersed in KOH solution for 30 min in order to obtain stable surface state. All the electrochemical tests for every material were repeated at least three times to ensure reproducibility.

3. Results and Discussion

3.1. Morphology Characterization of Coatings

In order to confirm the uniformity of Al_2O_3 coating on the surface of zinc substrate, we conducted SEM analyses of Al_2O_3 coating. The images of the coatings before and after heat treatment are shown in Figure 2a,b, respectively. Figure 2a shows the surface morphology of $(Al(NO_3)_3 + PAN)$ coated on zinc substrate; the nanofibers display a smooth surface and an average diameter of ~400 nm. After heat treatment at 350 °C in air, the diameter was reduced to ~220 nm (Figure 2d) and the nanofibers became a little rougher and thinner, due to the removal of the bound water and the decomposition of



Al(NO₃)₃·9H₂O. In addition, the organic components of PAN would be decomposed and burned at 250 °C [5,36]. A possible formation mechanism of Al₂O₃ nanofibers is proposed in Figure 2c.

Figure 2. SEM images of the Al_2O_3 coatings made by electrospinning technique before (**a**) and after heat treatment (**b**). Sketch illustrating the formation mechanism of the Al_2O_3 nanofiber coatings (**c**). The diameter distribution of Al_2O_3 nanofibers (**d**).

XRD was used to monitor the components of the prepared coatings (Figure 3). Characteristic diffraction peaks at around $2\theta = 37.4^{\circ}$, 45.8° , 61.55° , and 67.2° were observed in the pattern of the nanofibers, representing the (311), (400), (511), and (440) reflections of cubic γ -Al₂O₃ [30]. This observation is consistent with reported data (JCPDS Card 10-425). A peak of $2\theta = 17^{\circ}$ contributed to the orthorhombic PAN (110) [37] reflection could also be found because small amount of PAN did not decompose completely. No other peaks were observed for the coatings, suggesting that unique advantages of better control over the chemistry of the Al₂O₃ coatings offered by electrospinning.



Figure 3. XRD patterns of the Al₂O₃ coatings on zinc substrate.

3.2. Hydrogen Gas Evolution Tests

The need to suppress hydrogen evolution is critical for zinc in alkaline solution. In order to study the coating effect on HER, the hydrogen volume evolved from the zinc substrate coated with Al_2O_3

coating were measured in a volumetric method. Figure 4 shows the volumetric amount of hydrogen spontaneously evolved from zinc substrate modified with Al_2O_3 coating in 4 M KOH during 1.5 h at elevated temperature of 298 K. The bare zinc has the highest H_2 evolution rate, compared with zinc substrate coated with Al_2O_3 . It is obvious that Al_2O_3 coating plays an important role in retarding the spontaneous corrosion reaction of bare zinc immersed in alkaline solution. As can be seen in Figure 4, the volume of H_2 gas decreased with the increase of coating thickness. It shows that zinc modified with $18 \ \mu m \ Al_2O_3$ coating has the best hydrogen evolution rate.



Figure 4. Hydrogen evolution rates of the bare and different thicknesses of Al₂O₃-coated zinc substrates in 4 M KOH solutions.

3.3. Electrochemical Measurements

To clarify the effect of coating thicknesses on H_2 evolution behavior, the polarization behavior of different thickness coatings were measured with a three-electrode system. Polarization curves obtained for zinc substrate coated with Al₂O₃ in 4 M KOH solution are plotted in Figure 5a. The curves show similar behaviors but different corrosion parameters, including Tafel slopes b_a and b_c , corrosion potential (E_{corr}), corrosion current density (I_{corr}), and corrosion inhibition efficiency (η %). The parameters by Tafel extrapolation method are listed in Table 1. It is evident that the Tafel slope of the anode decreased obviously. The polarization curves indicate the Al₂O₃ coatings have obvious passivation behavior, and the stable passivation widens with increasing the coating thickness. For the case of 18 µm Al₂O₃ coating, it can be seen that the anodic current decreases at higher potential. This is mainly due to the formation of Al(OH)₃ adsorbed on the coating surface and attainment of a passive region. When the potential increases to a certain degree, the passive coating begins to be destroyed. The corrosion current densities decrease with the increase of coating thicknesses. The corrosion current density of bare zinc, 526.3 mA/cm², is much higher than of the zinc substrate modified with 18 µm Al_2O_3 coating, 60.6 mA/cm². It is worthwhile to notice that the corrosion current density is reduced by almost one order after the surface is modified on zinc substrate. The corrosion inhibition efficiency is calculated using the following formula:

$$\eta\% = (I_{corr} - I_{corr(inh)}) / I_{corr} \times 100\%$$
⁽²⁾

where I_{corr} and $I_{corr(inh)}$ are the corrosion current densities without and with the Al₂O₃ coating, respectively. As shown in Table 1, compared with bare zinc, the corrosion inhibition efficiency of zinc coated with 18 µm Al₂O₃ film reached 88.5%, which is higher than previous studies by Lee (82%) [27],

who modified zinc with Al₂O₃ coating by sol-gel process. The polarization resistance can be obtained from the potentiodynamic polarization curves [38]:

$$R_p = \frac{B}{i_{corr}} \text{ and } B = \frac{b_a b_c}{2.303(b_a + b_c)}$$
(3)



Figure 5. The polarization curves obtained for the bare and different thicknesses of Al_2O_3 -coated zinc substrates in 4 M KOH solutions (a). Plots of the porosity as a function of the coating thicknesses calculated from Equation (4) (**a**) and SEM (**b**).

Table 1. Corrosion parameters from polarization curves and electrochemical impedance spectroscopy

 (EIS) fitting parameters form Nyquist plots.

	Polarization							Impedance			
Samples	$-E_{corr}$	Icorr	b_a	$-b_c$	η%	R_p	P_R %	R _e	R _{ct}	n	С
	mV	mA/cm ²	mV/dec	mV/dec	-	$\Omega \cdot cm^2$	-	Ω·cm ²	$\Omega \cdot cm^2$	-	×10 ⁻⁵ F·cm ²
Bare zinc	1399	526.3	1160	840	-	577	100	25.7	620	0.83	1.69
Al ₂ O ₃ 6 μm	1416	209.4	1004	793	60.2	1476	39.1	26.5	1598	0.85	1.53
Al ₂ O ₃ 12 μm	1421	124.7	927	785	76.3	2475	23.3	26.9	2569	0.86	1.31
Al ₂ O ₃ 18 μm	1436	60.6	871	770	88.5	5106	11.3	29.3	5167	0.85	0.83

It can be seen in Table 1 that the thicker coatings get lower current density and higher corrosion resistance. It is established that a lower corrosion current density denotes lower corrosion rate and better corrosion resistance [39].

The coating quality is an important factor that influences the anti-corrosion effect. Defects, pores, or pinholes present in the coating may reduce the corrosion inhibition efficiency. This is hereafter defined as the total coating porosity, which can be calculated from the polarization resistance [40,41]:

$$P_R = \frac{R_P^0}{R_p} \times 100\% \tag{4}$$

where P_R , R_p^0 and R_p correspond to the total coating porosity, polarization resistance of the uncoated and coated zinc substrate, respectively. Table 1 shows the resulting coating porosity values obtained from Equation (4). We also measured the surface porosity of the coatings from SEM by using Image software (Java version) image processing as shown in Figure 5b. The surface porosity calculated from SEM is a little smaller than the total coating porosity calculated from Equation (4). Apparently, the coating porosity decreases with increasing thickness. The observed decrease of porosity with increasing thickness of Al₂O₃ coating is consistent with the view that fewer defects are existed in the thicker coating. Defects are assumed to connect the bulk alkaline solution to the surface of zinc substrate where the electrochemical reactions proceed. Therefore, polarization resistance would be higher for the substrate modified by thicker coatings.

Figure 6 shows the Nyquist plots for zinc substrate with different thickness Al₂O₃ coatings in 4 M KOH solutions. The equivalent circuits of the EIS plots are shown in the insert, and the fitting values of the impedance parameters are listed in Table 1. The equivalent circuit includes the electrolyte resistance, R_e , measured at high frequency, and the charge transfer resistance, R_{ct} , found at the low-frequency intercept. It can be seen that R_{ct} increases in the following order: Bare zinc < zinc with 6 μ m Al₂O₃ coating < zinc with 12 µm Al₂O₃ coating < zinc with 18 µm Al₂O₃ coating, indicating that Al₂O₃ coating can effectively increase the resistance value of R_{ct} in KOH solution. As depicted in Table 1, the resistance of bare zinc is only 620 $\Omega \cdot cm^2$, while the resistance of zinc with 18 µm Al₂O₃ coating reaches up to 5167 Ω ·cm² (almost one order of magnitude higher than bare zinc). With the increase of the coating thickness, more micro fibers coated the surface of zinc substrate. Thus, it is more difficult for the ions to pass through the coating and touch the zinc substrate. The charger transfer resistance R_{ct} obtained at the low frequency corresponds well to the polarization resistance calculated from the Tafel tests as shown in Table 1. As shown in Figure 6, the EIS plots consist of a capacitive loop for all the cases. The decrease of the capacitance (C) with increasing the thickness of the coating is also consistent with the decrease of porosity. This is due to the fact that the double layer capacitance is directly related to the exposed surface area. "n" represents the roughness of the surface. There is no obvious change in the surface roughness of zinc substrate after modified with thicker Al₂O₃ coatings. This indicates that the electrospun fibers are distributed uniformity. As the coating thickens on the zinc substrate, the resistance increased and the porosity reduced. KOH solution penetrated into the coating more difficultly, making the anti-corrosion effect of the coating improve further. The findings indicated that the barrier of coating to corrosive medium became stronger. All these results illustrated that the thicker Al₂O₃ coatings had better anti-corrosion property.



Figure 6. Nyquist plots obtained by EIS for the bare and different thicknesses of Al₂O₃-coated zinc substrates in 4 M KOH solution. Inset: The equivalent circuit model for fitting the impedance data.

4. Conclusions

The Al_2O_3 coating was fabricated by electrospinning from $Al(NO_3)_3$ and coated onto zinc substrate to inhibit the corrosion. The XRD confirmed that Al_2O_3 coating film was well formed. The anticorrosion properties of Al_2O_3 coatings with different thicknesses were evaluated by H_2 evolution, Tafel, and EIS in KOH solution. The coating thickness had a significant influence on the anti-corrosion behavior. The thicker Al_2O_3 coating possessed better corrosion resistance, lower porosity, and better corrosion inhibition efficiency. The corrosion inhibition efficiency reached 88.5%. The corrosion current density was 60.6 A/cm², which was one order of magnitude smaller than the bare zinc. The results indicate that Al_2O_3 coatings show promise as a good candidate for the corrosion protection of reactive metals.

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