

Article

Influence of Rare Earth Samarium/Ytterbium Salt on Electrochemical Corrosion Behavior of Aluminum-Based Anode for Batteries

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Highlights:

- $\text{Sm}(\text{OAc})_3$ and $\text{Yb}(\text{OAc})_3$ were used as new corrosion inhibitors for aluminum-based anodes for batteries.
- The potential effect of mixed rare earth salts was preliminarily explored.
- Electrochemical noise test illustrated the transient process of self-corrosion.
- 3D microscopic morphology of the electrode surface was constructed.

Abstract: In this work, effects and mechanism analysis of samarium acetate and ytterbium acetate on enhancing the electrochemical corrosion performance of aluminum-based anode for aluminum-air batteries in 3.5 wt.% NaCl are studied by methods such as weight loss tests, electrochemical measurements, anode galvanostatic discharge tests and microscopic morphology analysis. The results show that samarium acetate and ytterbium acetate are ideal electrolyte additives, and exhibit obvious inhibitory effects on the self-corrosion of 7075 aluminum alloy. The optimal concentration is 200 mg/L. Moreover, corrosion inhibitors mainly reduce the self-corrosion speed of aluminum by suppressing the microcathodic reaction, thereby promoting the improvement of the discharge performance of aluminum-air batteries. Simultaneously, it is found that after mixing samarium acetate and ytterbium acetate in different proportions, the two rare earth salts have a mutual adjustment effect. By adding different rare earth salt components, the battery capacity densities of the anode are improved by 9.6% to 16.3%. Finally, a possible model is presented to illustrate the impact mechanism of different additives on the self-corrosion process and discharge performance of aluminum-air batteries.

Keywords: aluminum-based anode; aluminum-air battery; rare earth salts; electrochemical corrosion; inhibitory additives



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1. Introduction

The rapid economic development and huge energy consumption have led to rapid reduction in fossil fuels and the massive production of carbon dioxide. In recent years, research on new energy sources has made excessive gains and will accelerate the conversion of fossil fuel energy to clean energy. As a new type of high-energy chemical power source, aluminum-air batteries fabricated from aluminum-based anode materials have the characteristics of high capability density, abundant sources, inexpensive and long service life. In addition to being used in marine activities, it can also provide electricity for areas where power supply cannot be guaranteed, such as mountainous areas, pastoral areas, and forest areas. It can also be used as a lighting power source for underground operations

such as mines and tunnels, and as a new power source for vehicles. The application prospects are very broad.

However, the urgent problems of aluminum-based anode cannot be ignored [1,2]. The self-corrosion phenomenon of aluminum is serious. There is a negative difference effect, which reduces the utilization rate of the aluminum-based anode. In addition, the reaction product $\text{Al}(\text{OH})_3$ has adhesive properties. If the corrosion products cannot be effectively separated and removed, they will cause capacity loss and affect the discharge performance of the battery. Moreover, although the energy density of aluminum-air batteries is high, the actual specific power is low, especially in neutral solutions such as 3.5% NaCl. The existence of corrosion directly threatens the service life of aluminum-air batteries, which increases the maintenance cost and wastes resources. One of the effective ways to prevent aluminum anode corrosion is to use corrosion inhibitors, which have the advantage of not requiring special devices, being easy to operate and at lower cost.

Restraining the self-corrosion process of aluminum-based anodes ought not to degrade the dischargeability of batteries [3]. Some inorganic salts are the first corrosion inhibitors used for aluminum alloys in corrosive media, such as seawater. To date, studies have found some substances that can effectively slow down the corrosion of aluminum alloys, including nitrite, sulfate, chromate [4], molybdate [5], permanganate [6], phosphate [2] and silicate [7]. These inorganic salts can effectively suppress the corrosion of aluminum alloys in seawater media. However, their environmental pollution and damage defects are gradually being recognized. Therefore, corrosion inhibitors are also developing in the direction of green [8] and environmental protection [9]. Among them, rare earth corrosion inhibitors have attracted much attention because of their high efficiency, low toxicity, and low harm to the environment and human body. Research has found that trace amounts (in mM, ppm or mg) [10–13] of rare earth salts can have a strong inhibitory effect on aluminum corrosion.

Hinton [14,15] was the first to conduct related research on rare earth salts as inhibitors of aluminum corrosion, and they found that the presence of low-concentration rare earth metal salts can greatly decrease the corrosion rate of aluminum alloys. After that, the corrosion phenomena of pure aluminum and its alloys in various media containing rare earth salts have been tested successively [10–13,16,17], in which obvious corrosion inhibition effects of La^{3+} and Ce^{3+} have been found, and there is an additional concentration peak. Allachi [18,19] investigated the inhibition performance of Ce^{3+} on AA6060 aluminum alloy in NaCl solution, and the results showed that Ce^{3+} can have a good corrosion suppressive effect, in which the corrosion inhibition efficiency can reach 80%. Julie-Anne Hill [2] found that $\text{Ce}(\text{dpp})_3$ had a good inhibitory effect on AA7022, AA7075 and AA7050 aluminum alloys in the chloride electrolyte, obviously reducing the corrosion rate of each alloy. In addition, many scholars [20–27] have studied the influence of rare earth compounds on aluminum or aluminum alloys in neutral/alkaline solutions. Among them, Rosero-Navarro [22] deemed that the corrosion inhibition effect of cerium nitrate in 3.5% NaCl was basically equivalent to chromate on the same time scale. Venkatasubramanian [23] believed that hydroxides/oxides of Ce(III) and La(III) were deposited on the second phase in 0.6 M NaCl, reducing the galvanic effect of aluminum alloy matrix, thereby inhibiting corrosion. Bore [21] and Peter [26] used Ce^{3+} to mix the second additive to study its effect on the electrochemical properties of aluminum alloys, and proved that Ce^{3+} can synergistically repress corrosion with organic additives. These investigations have proved that Ce^{3+} and La^{3+} have pretty good effect on the corrosion inhibition of aluminum alloys. To date, however, research on rare earth corrosion inhibitors has mainly focused on cerium and lanthanum compounds. Little or no attention has been paid to other rare earth salts. At the same time, there are very few studies on the relative effects of mixed rare earth additives as corrosion inhibitors on aluminum alloys.

In this research, the corrosion features and discharge properties of aluminum anodes in 3.5 wt.% NaCl containing samarium/ytterbium acetate were studied comprehensively. The corrosion inhibition effect of rare earth salts was examined by using the weight loss test.

The potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) were tested to investigate the electrochemical behaviors of the aluminum anode in 3.5 wt.% NaCl with dissimilar additives. The discharge properties of the anode were tested at a galvanostatic density of $20 \text{ mA} \cdot \text{cm}^{-2}$. Scanning electron microscopy (SEM) was used to detect the surface micromorphology and tissue of the aluminum anode. Through systematic experiments, the corrosion inhibition influence of samarium/ytterbium acetate on commercial 7075 aluminum alloy was evaluated, and the potential effect of the mixture was explored by mixing both in different ratios.

2. Experimental

2.1. Materials

The anode sample was a merchant 7075 aluminum alloy, provided by Shanghai Shengshuo Metal Material Group Co., Ltd (Shanghai, China). $\text{Sm}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ and $\text{Yb}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ were provided by Jining Tianyi New Materials Co., Ltd (Jining, China). All chemicals are analytically pure grade. Moreover, 3.5 wt.% NaCl solutions containing different rare earth salts were prepared in deionized water as electrolyte solutions.

Using wire cutting technology to cut 7075 aluminum alloy into small lumps for corrosion testing and electrochemical measurement. All samples were polished with metallographic sandpaper of different particle sizes (600#, 800#, 1200# and 2000#) in turn, polished with diamond paste, washed with deionized water, ultrasonically rinsed in absolute ethanol, and finally air-dried. All experiments in this research were performed at $25 \pm 1^\circ\text{C}$. Each test was performed at least three times, during which two comparative specimens were prepared.

2.2. Self-Corrosion Assessment

The self-corrosion behavior was evaluated by weight loss test. The initial mass (m_0) of each post-treatment ($10 \text{ mm} \times 10 \text{ mm} \times 2 \text{ mm}$) was weighed with an analytical balance (FA1004B) (Shanghai Youke Instrument Co., Ltd, Shanghai, China) with an accuracy of 0.1 mg. The samples were tied with a sufficiently thin polyester rope, and then suspended in a wide-mouth bottle containing an adequate amount of 3.5 wt.% NaCl containing different additives. After 8 days, the specimens were taken out, gently scrubbed with a soft brush in deionized water, and then ultrasonically cleaned with absolute ethanol for 5 min to eliminate the corrosion products on the surface. Then the specimens were ultrasonically cleaned in absolute ethanol for 15 min, dried with cold air, and weighed to obtain the remaining mass (m_1). Each measurement was repeated three times to guarantee error within 3%. The corrosion rate was calculated using the following formula [28]:

$$v = \frac{m_0 - m_1}{S \cdot t} \quad (1)$$

where v is the corrosion rate (in $\text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$), S and t are the surface (in cm^2) and time of immersion (in h), respectively.

2.3. Electrochemical Measurements

The equipment used for electrochemical testing was CS350 electrochemical workstation (Wuhan Corrtest Instrument Corp., Ltd, Wuhan, China). The electrolytic cell device adopted a three-electrode system, which consisted of a saturated calomel electrode (SCE), a metal platinum electrode and a commercial 7075 aluminum alloy. An effective exposed area of 1 cm^2 was reserved after epoxy sealing.

The connected three-electrode device was allowed to stand for approximately 30 min to make the system in a stable state. The AC impedance spectrums (EISs) were tested in the frequency range from 100 kHz to 0.1 Hz at open circuit potential (OCP) with a sinusoidal potential perturbation of 5 mV in amplitude. The sampling frequency and the potential interval were 2 Hz and 0.5 mV, respectively. The potential scanning range of polarization curve measurements was $-0.3 \text{ V} \sim +0.3 \text{ V}$ with the scanning rate 1 mV/s . The data of

electrochemical tests were fitted by CView (CView 2.6.0.1, Scribner Associates Inc, Southern Pines, NC, USA) and ZView software (ZView 3.0.0.14, Scribner Associates Inc, Southern Pines, NC, USA) separately [29].

For the electrochemical noise (EN) tests [30], the approach mentioned by Balaskas was adopted [31]. In short, in this means two 7075 electrodes and a saturated calomel electrode (SCE) were used as the working electrode and reference electrode, respectively. The CS350 electrochemical workstation was equipped with a zero-resistance ammeter (ZRA) to keep the potential difference between the electrodes at zero. The noise test time for each group was 24 h, and the noise test frequency was 4 Hz.

2.4. Anode Galvanostatic Discharge Test

Galvanostatic discharge test as a widely applied method by many researchers was executed to test the effect of the rare earth samarium/ytterbium salt on the anode discharge properties [3,32–34]. During the anode galvanostatic discharge test, the system was first allowed to stand for 30 min to stabilize, and then tested at a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ for 90 min.

2.5. Surface Micromorphology

A total of 7075 aluminum alloy specimens ($20 \text{ mm} \times 10 \text{ mm} \times 5 \text{ mm}$) were soaked in 3.5 wt.% NaCl with different additives. Then the specimens were cleaned with deionized water and air dried. The microscopic morphologies of sample surfaces were observed by scanning electron microscopy (SEM, S-3400N, Hitachi Company, JEOL, Tokyo, Japan).

3. Results and Discussion

3.1. Self-Corrosion Assessment

The weight loss test is a convenient and effective measurement to assess the corrosion speed of metallic materials [35]. The self-corrosion rates of different post-processed specimens calculated from the loss of weight in 3.5 wt.% NaCl are listed in Figure 1. As shown in Figure 1, as the concentration of samarium acetate increases, the self-corrosion rate of 7075 aluminum alloys slows down, indicating that the presence of Sm^{3+} has a certain protective effect. Similarly, after adding ytterbium acetate, the self-corrosion rate of 7075 aluminum alloy decreased evidently. In addition, the concentrations of Sm^{3+} and Yb^{3+} that achieved the best protective effect were both 200 mg/L , and the self-corrosion inhibition efficiencies were 69.2% and 77.8%, respectively. Furthermore, the mixtures of two rare earth salts with a total consistence of 200 mg/L were tested, in which the ratios of the two components were 2:1, 1:1, and 1:2. For the mixed corrosion agent, when the proportion of $\text{Sm}(\text{OAc})_3$ is relatively small, the self-corrosion inhibition effect of the mixed additive is better.

3.2. Potentiodynamic Polarization

Potential polarization tests were used to analyse the anodic oxidative dissolution and cathodic hydrogen reduction of 7075 aluminum alloy in 3.5 wt.% NaCl containing different consistencies of samarium acetate and ytterbium acetate. The results are presented in Figure 2a,b. Electrochemical parameters include corrosive potential E_{corr} ($\text{V}_{\text{vs.SCE}}$), corrosive current density i_{corr} ($\text{mA}\cdot\text{cm}^{-2}$), anode Tafel slope β_a ($\text{V}\cdot\text{dec}^{-1}$) and cathode Tafel slope β_c ($\text{V}\cdot\text{dec}^{-1}$) (listed in Table 1). The calculation formula of corrosion inhibition efficiency (η) is [36,37]:

$$\eta\% = \frac{i_{\text{corr}} - i_{\text{corr}(\text{inh})}}{i_{\text{corr}}} \times 100\% \quad (2)$$

where i_{corr} and $i_{\text{corr}(\text{inh})}$ are the corrosion current densities for aluminum electrodes in 3.5 wt.% NaCl without and with additives, respectively.

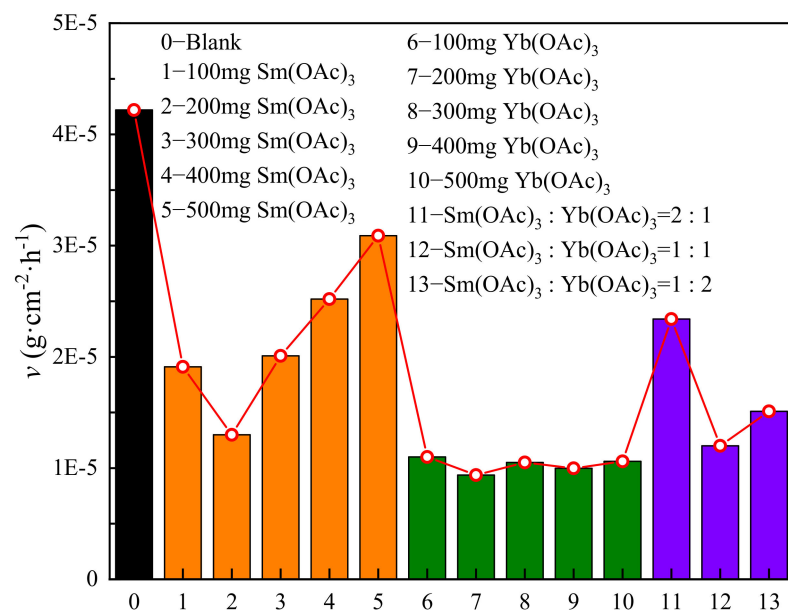


Figure 1. Self-corrosion rate of 7075 samples immersed in 3.5 wt.% NaCl with different additives for 8 days.

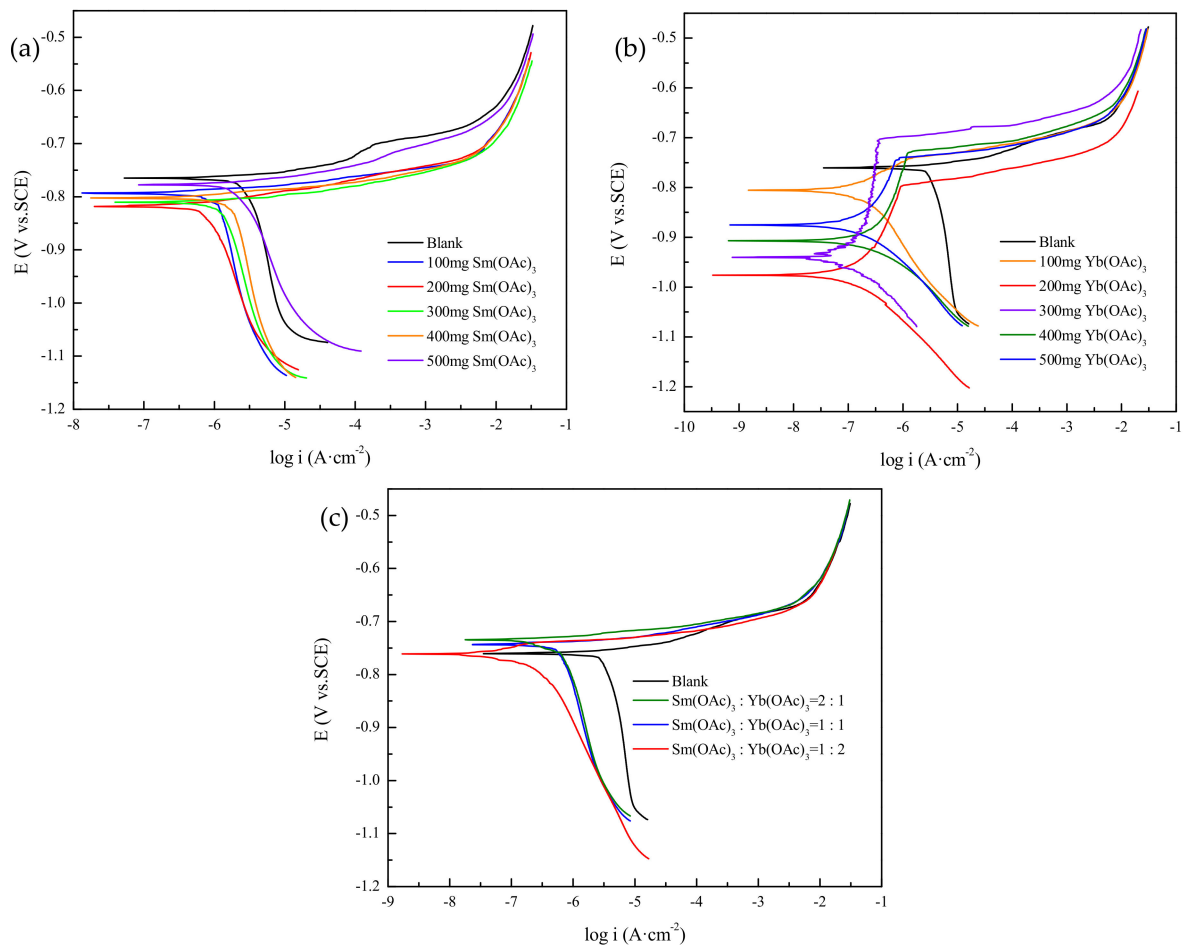
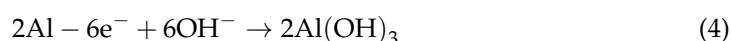
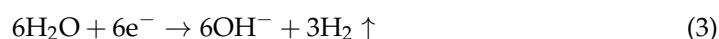


Figure 2. Potentiodynamic polarization curves of aluminum anode in 3.5 wt.% NaCl with different additives: (a) samarium acetate, (b) ytterbium acetate, and (c) mixed corrosion inhibitors.

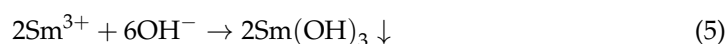
Table 1. Electrochemical parameters obtained from polarization curves for aluminum anode in 3.5 wt.% NaCl solution with different additives.

Additives	E_{corr} /V _{vs.SCE}	i_{corr} /mA · cm ^{−2}	β_a /mV · dec ^{−1}	β_c /mV · dec ^{−1}	η /%
Blank	−0.76583	2.9533×10^{-3}	20.806	−540.37	–
100 mg/L Sm(OAc) ₃	−0.79335	1.2659×10^{-3}	16.066	−484.27	57.14
200 mg/L Sm(OAc) ₃	−0.81594	8.2035×10^{-4}	23.893	−352.82	72.22
300 mg/L Sm(OAc) ₃	−0.81196	1.4113×10^{-3}	18.913	−517.36	52.21
400 mg/L Sm(OAc) ₃	−0.80301	1.8396×10^{-3}	18.798	−612.11	37.71
500 mg/L Sm(OAc) ₃	−0.77832	2.6513×10^{-3}	24.083	−371.14	10.23
100 mg/L Yb(OAc) ₃	−0.80609	2.6236×10^{-4}	88.136	−181.94	91.12
200 mg/L Yb(OAc) ₃	−0.97694	1.6906×10^{-4}	257.93	−114.69	94.28
300 mg/L Yb(OAc) ₃	−0.94258	2.5989×10^{-4}	376.93	−120.86	91.20
400 mg/L Yb(OAc) ₃	−0.90535	2.6041×10^{-4}	321.28	−105.02	91.18
500 mg/L Yb(OAc) ₃	−0.87452	2.4086×10^{-4}	261.95	−118.68	91.84
$\rho(\text{Sm}):\rho(\text{Yb}) = 2:1$	−0.74296	6.6488×10^{-4}	12.535	−443.76	77.49
$\rho(\text{Sm}):\rho(\text{Yb}) = 1:1$	−0.73405	6.8027×10^{-4}	14.389	−441.63	76.97
$\rho(\text{Sm}):\rho(\text{Yb}) = 1:2$	−0.76340	2.9971×10^{-4}	19.724	−241.79	89.85

Figure 2a shows that all the curves exhibit similar outlines, and the cathodic and anodic sections are nearly parallel, which indicates that samarium acetate (Sm(OAc)₃) does not change the principium of the cathode reduction. Compared with the electrolyte without any inhibitor, the corrosive potential moved in a more negative direction, and the cathode branch produced a leftward displacement when Sm(OAc)₃ was added. It is visible from Table 1 that the anode Tafel slope β_a has a small change range, while the cathode Tafel slope β_c almost increases to varying degrees before and after the corrosion inhibitor is added, indicating that the cathode reaction is suppressed significantly. Combining the above results, it is preliminarily believed that Sm(OAc)₃ is an ideal cathodic corrosion inhibitor [38–40] for aluminum alloys to resist corrosion in 3.5 wt.% NaCl. Generally, the self-corrosion reaction of aluminum in the electrolyte solution is a result of the emergence of corrosion microcathode regions and the water reduction reaction:



Therefore, Sm(OAc)₃ in 3.5 wt.% NaCl can be deemed to carry out the following reaction:



The oxide or hydroxide of samarium deposits on the external of aluminum and decreases the contact area, which is similar to the deposition protection mechanism of cerium and lanthanum [12,35,40–43]. Obviously, the repression of the cathode reaction makes the electrons in the anodic region accumulate excessively, thus generating a more negative potential. In addition, the corrosion current density of aluminum was reduced in the electrolyte by adding Sm(OAc)₃, and the inhibition efficiency was improved. The corrosion inhibition efficiency gradually enhanced as the consistence of Sm³⁺ subjoined when the additive density of Sm(OAc)₃ was within the scope of 0 mg/L~200 mg/L. In the range of 200 mg/L~500 mg/L, inhibitory function gradually weakened with the further increase in concentration. This shows that Sm³⁺ has an efficiency peak of corrosion suppression at 200 mg/L, which can reach 72.22%. It proves that Sm³⁺ can achieve a better corrosion inhibition rate than 65.7% of Ce³⁺ [35,44].

Figure 2b indicates that the polarization curves of the anode zone are almost parallel. After adding ytterbium acetate (Yb(OAc)₃), the current density did not increase significantly

but showed a flat passivating zone with the increasing of overpotential in the anodic polarization zone. This can be attributed to the deposition of $\text{Yb}(\text{OH})_3$ or Yb_2O_3 on the surface of the aluminum alloy to form a passivating film in the meantime. This is similar to the conclusion drawn by Peter Rodič, who suggested that cerium-based sediments hinder the progress of cathodic reaction, lowering the corrosion rate of the aluminum alloy [45]. The protective film reduces the active points on the metallic surface, thereby delaying the self-corrosion reaction of hydrogen evolution in the electrolyte solution. This is analogous to the protection mechanism of samarium acetate mentioned earlier. Besides, the corrosion potential moved to a negative value after adding $\text{Yb}(\text{OAc})_3$ compared with the blank group (listed in Table 1). Simultaneously, β_a and β_c both increased significantly, which was a typical feature the inhibition mechanism of rare earth salts. In addition, the difference in β_c between different concentrations was not obvious. Therefore, it is reasonable to consider ytterbium acetate as an effective mixed type inhibitor that restrains the cathodic process and simultaneously promotes the anodic reaction (Al dissolution) [46]. In the range of less than 200 mg/L, inhibition efficiency enhances as the concentration of Yb^{3+} increases and reaches a peak of 94.28% at 200 mg/L. Based on this, $\text{Yb}(\text{OAc})_3$ is considered as an ideal corrosion inhibitor for aluminum anodes. Once the concentration is more than 200 mg/L, the self-corrosion current value will not change much as the concentration increases, and the corrosion inhibition effect tends to be stable. This shows that the continuous increase in the Yb^{3+} concentration cannot produce a better corrosion inhibition effect.

According to the above analysis, it can be judged that the optimal concentrations of samarium acetate and ytterbium acetate are both 200 mg/L in 3.5 wt.% NaCl. Moreover, the corrosion inhibition impact of ytterbium acetate is significantly stronger than that of samarium acetate. To explore the difference between the two rare earth salts before and after mixing, the anode electrochemical behaviors of 7075 aluminum alloy in 3.5 wt.% NaCl containing $\text{Sm}(\text{OAc})_3$ and $\text{Yb}(\text{OAc})_3$ in varying proportions were analysed, in which 200 mg/L is used as the total concentration of mixed rare earth additives. The consequents are shown in Figure 2c and Table 1, and in light of these data, nearly overlapping anode curves can be found. There is also no passivation zone after adding different proportions of mixed corrosion inhibitors. It is preliminarily believed that samarium acetate in mixed additives plays a regulatory role. At the same time, the cathode Tafel slope β_c increases significantly, and the self-corrosion current decreases markedly. It shows that the mixture of two additives can effectively curb the process of a cathode but has little effect on the reaction of an anode. At the same time, the suppression efficiency is basically inversely proportional to the content of samarium acetate for the mixed rare earth additive with a total concentration of 200 mg/L, which is regarded as a rule for the time being. Combined with the polarization curves, it is reasonable to believe that the samarium acetate in the mixture has a regulating effect and can compensate for the deficiency of the protection mechanism of ytterbium acetate.

3.3. Electrochemical Impedance Spectroscopy

To further investigate the corrosion behavior of aluminum in 3.5 wt.% NaCl with different additives, electrochemical impedance spectroscopy (EIS) was measured. Nyquist plots of 7075 aluminum immersed in different electrolyte components are exhibited in Figure 3. Besides, the equivalent electric circuit (EEC) displayed in Figure 4a was used to fit the EIS data to analyse the features of alloy surface [47,48]. R_s represents the solution resistance, R_f and R_{ct} are due to the surface film resistance, which can be associated with the corrosion process occurring on the electrode surface. CPE_f and CPE_{dl} are constant-phase elements, representing the capacitance of surface film and the double layer capacitance, respectively. The impedance of CPE is derived from the following formula:

$$Z_{\text{CPE}} = \frac{1}{Q(j\omega)^n} \quad (7)$$

where Q and C have similarities under a definite deviation, j is the virtual root, ω is the angular frequency and n is the phase offset, which is connected with the degree of external non-uniformity [49,50].

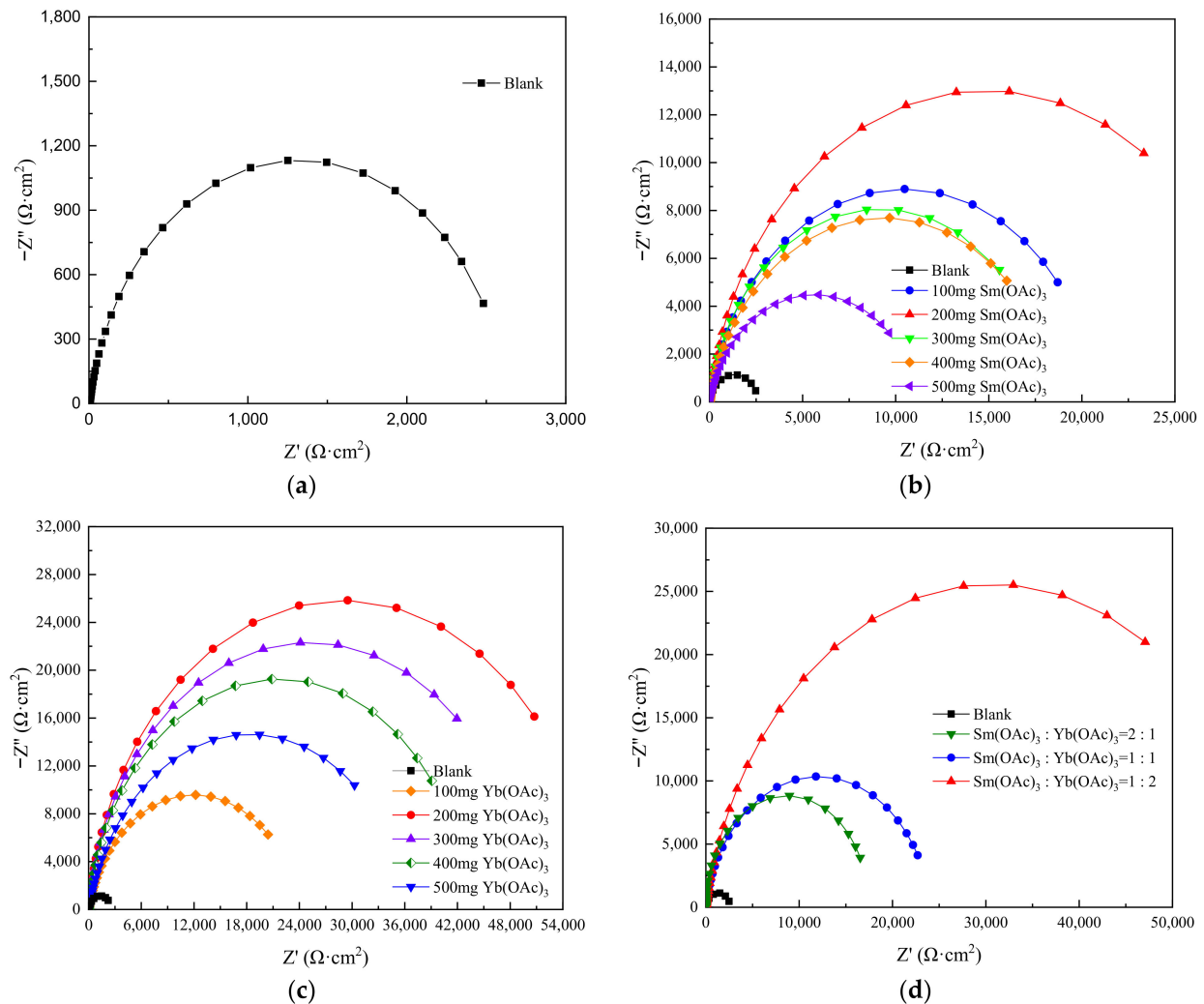


Figure 3. Nyquist plots of aluminum anode in 3.5 wt.% NaCl with different additives: (a) blank, (b) samarium acetate, (c) ytterbium acetate, and (d) mixed corrosion inhibitors.

The fitting results of Bode plots are revealed in Figure 4b–e, which are in good agreement with the original data within 10% of errors, demonstrating that the established EEC model is appropriate. Because both passivated and corroded zones exist on metallic surfaces, a two-time-constant model (Figure 4a) was set up. The passivated zone stands for the oxide layer on the 7075 aluminum surface, while the corroded zone indicates the breakdown of the oxide layer [35]. The fitting parameters of the EIS spectra are listed in Table 2.

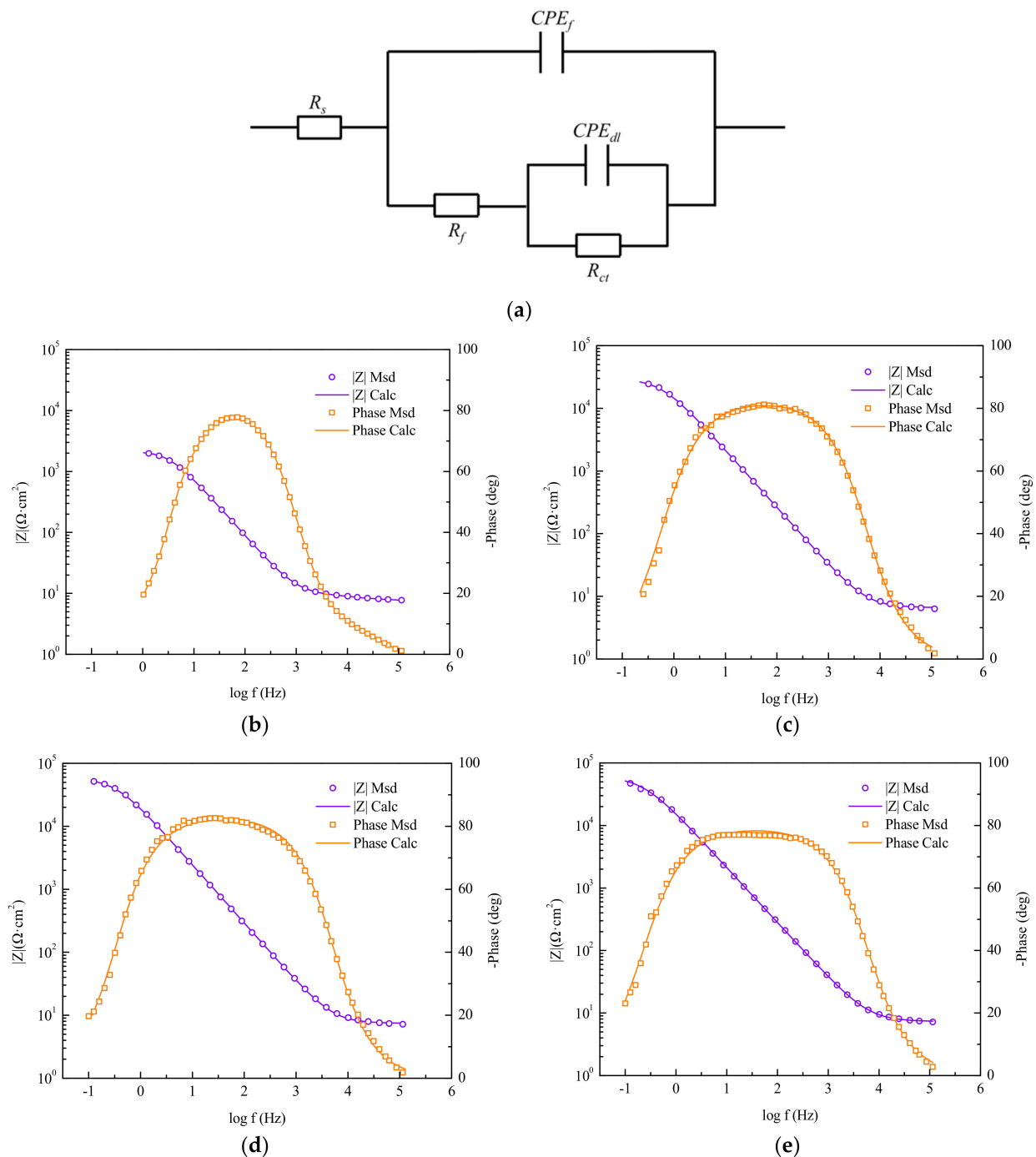


Figure 4. (a) Equivalent circuit diagram and corresponding fitting results of Bode plots: (b) blank, (c) 200 mg/L $\text{Sm}(\text{OAc})_3$, (d) 200 mg/L $\text{Yb}(\text{OAc})_3$, (e) $\text{Sm}(\text{OAc})_3:\text{Yb}(\text{OAc})_3 = 1:2$.

From Figure 3a–d, it is clear that 7075 aluminum alloy only exhibits a capacitive arc in the high frequency region regardless of whether corrosion inhibitors are added or not in 3.5 wt.% NaCl. The larger capacitive arc radius signifies a greater impedance for the charge to pass through the interface, which means a better corrosion resistance of the alloy. Compared with the blank one, it can be clearly seen that the capacitive arc radius in the high-frequency area boosts, and both R_f and R_{ct} in Table 2 show an increasing trend after adding different additives. Moreover, it is worth noting that the arc radius of the capacitive reactance first increases and then decreases as the concentration of samarium/ytterbium acetate increases, and both reach the maximum value at 200 mg/L. The R_f representing the surface film resistance reaches a maximum value at the concentration of 200 mg/L. Coelho

studied CeCl_3 and discovered that R_f dropped sharply, coinciding with the sharp increase in thickness, suggesting that excessive cerium deposition was unfavorable to the performance of protective film [51]. This is similar to the phenomenon in this study. Furthermore, the fitted R_{ct} values are extremely analogical to those measured by Snihirova [52] with cerium nitrate, indicating that it is more difficult for the corrosive medium (Cl^-) to contact the base aluminum under this circumstance, which greatly restrains the pitting corrosion caused by chloride ions and the reduction reaction of water. Accordingly, the anodic corrosion rate is reduced. This is completely coincident with the conclusions drawn from polarization curve tests.

Table 2. Electrochemical parameters extracted from modeling the Nyquist and Bode diagrams for aluminum anode in 3.5 wt.% NaCl solution with different additives.

Additives	$R_s/\Omega \cdot \text{cm}^2$	CPE_f		$R_f/\Omega \cdot \text{cm}^2$	CPE_{dl}		$R_{ct}/\Omega \cdot \text{cm}^2$
		$Y_0 (\text{S} \cdot \text{s}^n \text{cm}^{-2})$	n		$Y_0 (\text{S} \cdot \text{s}^n \text{cm}^{-2})$	n	
Blank	8.306	2.967×10^{-5}	0.947	2268	0.98×10^{-3}	1.000	16
100 mg/L $\text{Sm}(\text{OAc})_3$	4.458	1.395×10^{-5}	0.899	20,900	1.25×10^{-3}	0.913	81
200 mg/L $\text{Sm}(\text{OAc})_3$	6.605	1.041×10^{-5}	0.917	29,696	1.45×10^{-3}	0.647	152
300 mg/L $\text{Sm}(\text{OAc})_3$	3.542	1.065×10^{-5}	0.918	19,865	1.23×10^{-3}	0.895	104
400 mg/L $\text{Sm}(\text{OAc})_3$	3.422	1.391×10^{-5}	0.875	18,751	1.15×10^{-3}	0.923	93
500 mg/L $\text{Sm}(\text{OAc})_3$	6.403	1.866×10^{-5}	0.854	11,295	1.09×10^{-3}	0.934	84
100 mg/L $\text{Yb}(\text{OAc})_3$	3.398	4.444×10^{-5}	0.859	22,957	3.06×10^{-3}	0.941	161
200 mg/L $\text{Yb}(\text{OAc})_3$	7.455	8.770×10^{-5}	0.927	57,996	3.61×10^{-3}	0.547	245
300 mg/L $\text{Yb}(\text{OAc})_3$	7.455	8.730×10^{-5}	0.925	50,798	3.57×10^{-3}	0.961	236
400 mg/L $\text{Yb}(\text{OAc})_3$	7.142	1.012×10^{-5}	0.923	44,284	3.50×10^{-3}	0.911	231
500 mg/L $\text{Yb}(\text{OAc})_3$	7.450	2.208×10^{-5}	0.864	33,902	3.51×10^{-3}	0.900	197
$\rho(\text{Sm}):\rho(\text{Yb}) = 2:1$	3.140	2.160×10^{-5}	1.000	17,408	1.33×10^{-3}	0.931	89
$\rho(\text{Sm}):\rho(\text{Yb}) = 1:1$	7.301	1.186×10^{-5}	0.904	24,105	1.31×10^{-3}	0.926	90
$\rho(\text{Sm}):\rho(\text{Yb}) = 1:2$	7.301	1.207×10^{-5}	0.884	61,507	3.74×10^{-3}	0.609	47

For the mixed rare earth additives with a total concentration of 200 mg/L, Figure 3d and Table 2 show that the capacitive arc radius and the protective film resistance R_f gradually increase with the decreasing samarium acetate content, and they reach a maximum when the ratio of samarium acetate to ytterbium acetate is 1:2. This fully proves the rationality and accuracy of the analysis of polarization data.

3.4. Image Assisted Electrochemical Noise

The anticorrosion properties of $\text{Sm}(\text{OAc})_3$ and $\text{Yb}(\text{OAc})_3$ on 7075 aluminum and their potential interaction were appraised by EN tests. Figure 5a displays the temporal evolution of noise current for 7075 aluminum electrodes submerged in 3.5% NaCl with different additive compositions. The diagram indicates that the noise current fluctuation of the 7075 aluminum electrode without inhibitor is relatively large, while the current fluctuations for electrodes with different inhibitors are significantly reduced. In particular, the noise current of the aluminum electrode without inhibitor fluctuated greatly in the range of $4.58 \mu\text{A} \cdot \text{cm}^{-2}$ during the first two hours, which magnified to $11.08 \mu\text{A} \cdot \text{cm}^{-2}$ in 2~4 h, and maintained the current fluctuation range at approximately $2.29 \mu\text{A} \cdot \text{cm}^{-2}$ at 24 h. In contrast, the noise-current values of all electrodes with inhibitors were significantly reduced. In the case of adding $\text{Sm}(\text{OAc})_3$ in a corrosive environment, the noise-current volatility was significantly reduced. Compared with the blank group, the fluctuation value of the first two hours of the test dropped to $0.91 \mu\text{A} \cdot \text{cm}^{-2}$, correspondingly decreased to $2.25 \mu\text{A} \cdot \text{cm}^{-2}$ in 2~4 h and dropped to $0.35 \mu\text{A} \cdot \text{cm}^{-2}$ at 24 h. In addition, the average noise current showed a lower value compared with the blank group, which showed a decreasing trend in the first three hours of soaking and tended to stabilize after 3 h. The overall noise curve of the electrode containing $\text{Yb}(\text{OAc})_3$ was abnormally stable with minimal fluctuation and had an average noise current of $0.3 \mu\text{A} \cdot \text{cm}^{-2}$ within 0~24 h. The electrodes

submerged in $\text{Sm}(\text{OAc})_3 + \text{Yb}(\text{OAc})_3$ revealed noise-current values in the $0.44 \mu\text{A}\cdot\text{cm}^{-2}$ scope during the first two hours, $0.45 \mu\text{A}\cdot\text{cm}^{-2}$ in 2~4 h and $0.53 \mu\text{A}\cdot\text{cm}^{-2}$ at 24 h. The samples submerged with $\text{Sm}(\text{OAc})_3 + \text{Yb}(\text{OAc})_3$ had analogous behavior to the case with $\text{Sm}(\text{OAc})_3$ addition, including the noise-current value and curve volatility.

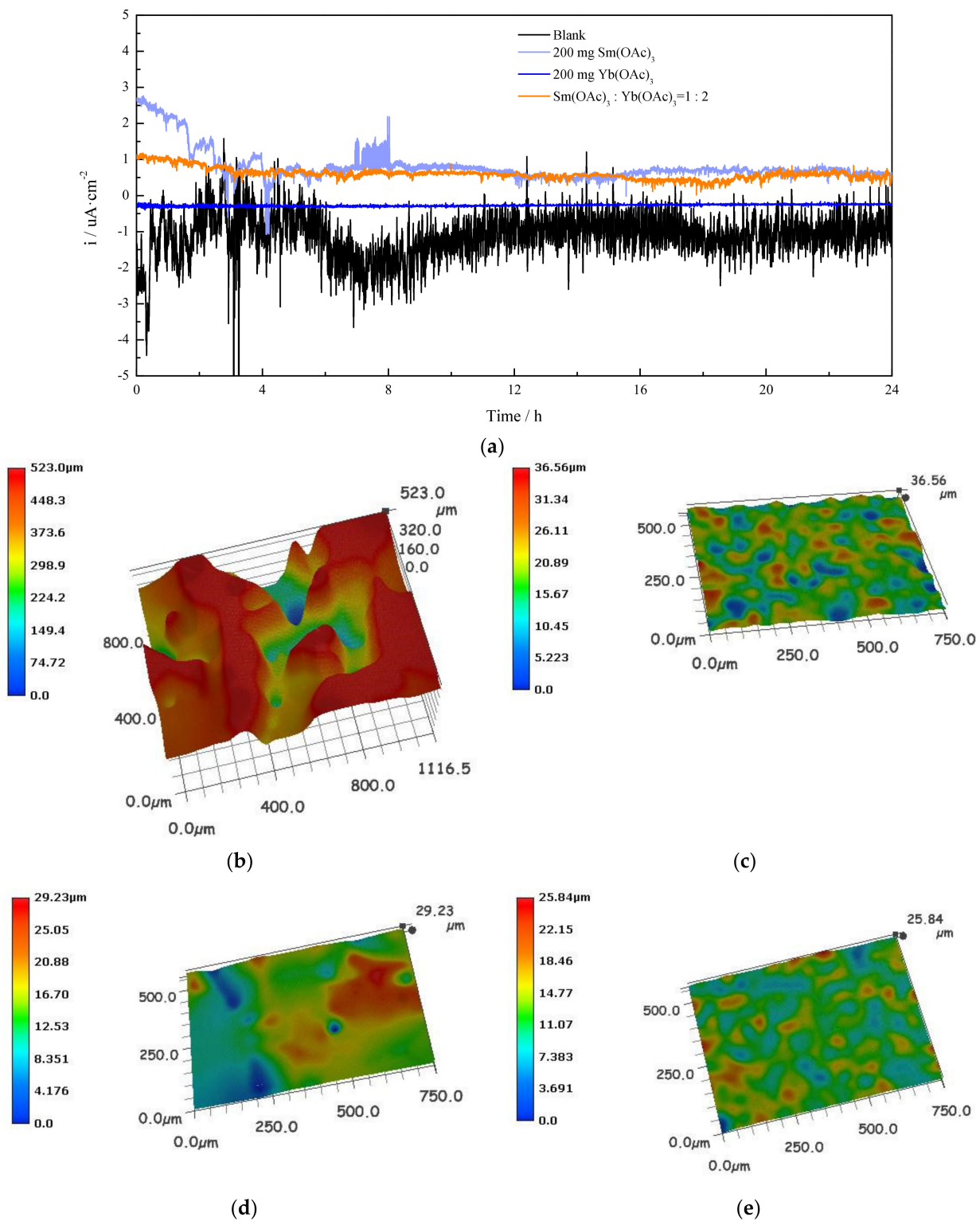


Figure 5. (a) Time evolution diagram of noise current and 3D microscopic morphology characteristics after electrochemical noise test: (b) blank, (c) 200 mg/L $\text{Sm}(\text{OAc})_3$, (d) 200 mg/L $\text{Yb}(\text{OAc})_3$, and (e) $\text{Sm}(\text{OAc})_3 : \text{Yb}(\text{OAc})_3 = 1 : 2$.

The existence of chlorine in the electrolyte increased the possibility of local breakdown of the passivation film on the electrode surface, which would cause fluctuations in current and potential. Namrata [53] and Iman [54] suggested that the exposure of naked metal surface to the chloride medium was due to the formation of tiny pits by the rupture of the passive film. As shown in Figure 5a, the blank group without corrosion inhibitor showed multiple sharp transient peaks with peak heights ranging from $2.29 \mu\text{A}\cdot\text{cm}^{-2}$ to $11.08 \mu\text{A}\cdot\text{cm}^{-2}$. Some previous researches believed that these transient peaks represented the phenomenon of pitting corrosion caused by the damage of the passivation on the electrode surface at different times [55–57]. This showed that the exterior of the aluminum electrode in 3.5 wt.% NaCl without any inhibitors was destroyed by Cl^- at almost every moment, and then corrosion pits were generated. Similarly, there were several prominent spikes for the aluminum electrode in the environment containing $\text{Sm}(\text{OAc})_3$ for 2~5 h and 7~9 h, indicating that pitting corrosion occurred at this point in time. However, the fluctuation of the curve tended to be stable after 9 h, unveiling that $\text{Sm}(\text{OAc})_3$ promoted the corrosive process to stabilize, which was a slow but beneficial effect for aluminum electrodes. The corrosion inhibition effect gradually increased as time passed. In comparison, the noise-current curve did not show obvious peak points in the environment containing $\text{Yb}(\text{OAc})_3$, and the current signal had small and symmetrical fluctuations above and below the average value. It could be considered that the aluminum electrode was in a stable and uniform corrosion state throughout, which revealed a rapid and positive effect on the aluminum electrode resulting from $\text{Yb}(\text{OAc})_3$. In the trial test of mixing samarium acetate and ytterbium acetate, it was found that the volatility and current value of the curve were significantly reduced compared to the blank. At the same time, compared with a single $\text{Sm}(\text{OAc})_3$, the current value shown in the curve was not much different, and there was no obvious transient spike, which means that the existence of $\text{Yb}(\text{OAc})_3$ reduced the incidence of pitting corrosion and improved the early unstable performance defects for $\text{Sm}(\text{OAc})_3$. In addition, the $E_{\text{RMS}}/i_{\text{RMS}}$ value was obtained by fitting the four sets of data to find the root mean square (RMS), and their values corresponded to the order of the curves in Figure 5a as follows: $1762.5 \Omega\cdot\text{cm}^2$, $8227.4 \Omega\cdot\text{cm}^2$, $2.06 \times 10^5 \Omega\cdot\text{cm}^2$ and $5.07 \times 10^4 \Omega\cdot\text{cm}^2$. The magnitude relationship of $E_{\text{RMS}}/i_{\text{RMS}}$ corresponds well to the curve phenomenon.

The 3D microscopic morphology of the sample surface after the electrochemical noise experiment recorded by a high-speed microscope (KEYENCE (China) Co., Ltd, Shanghai, China) is shown in Figure 5b–e, where the blue area represents the bottom of the pitting pit and the red area represents the original plane. Figure 5b shows that the 7075 Al surface is severely pitted in 3.5 wt.% NaCl without any additives. According to the 3D topography, the surface is uneven and shaped like a rift, with the deepest pit depth reaching $523.0 \mu\text{m}$. This graph fully proves the penetration and destructiveness of chlorion to the passivating layer on aluminum surface, which leads to corrosion spots on the electrode surface, and the pits have the characteristics of deep depth, large diameter, and uneven distribution. Figure 5c shows that corrosion develops from pitting to uniform corrosion after adding samarium acetate to the electrolyte solution. The result shows that the green area becomes obviously wider and continuous, and the depth of pitting pores is obviously reduced with the deepest being only $36.56 \mu\text{m}$. However, it should be recognized that there are defects in the protective effect of samarium acetate, and the $\text{Sm}(\text{OH})_3$ formed by it cannot completely cover the entire electrode surface, or there are weak areas, which is reflected in the figure as the corrosion pits distributed on the aluminum surface in a star shape. Figure 5d shows that after adding ytterbium acetate, the blue area on the anode surface is significantly reduced, and the depth of pitting pores is reduced to $29.23 \mu\text{m}$. It further reduces the number and depth of corrosion pits, but its regional corrosion is obvious, which will lead to polarization. Figure 5e shows that the plane height difference is only $25.84 \mu\text{m}$ after adding a mixture of $\text{Sm}(\text{OAc})_3$ and $\text{Yb}(\text{OAc})_3$. Simultaneously, the pitting corrosion becomes very insignificant and the surface area becomes more uniform compared to two single corrosion inhibitors, which proves that the two inhibitors have a regulatory effect on each other.

3.5. Anode Galvanostatic Discharge Test

For further elucidating the effects of additives on aluminum anode working in 3.5 wt.% NaCl, the discharge performance was examined by constant current method. Attention should be paid to the fact that adding corrosion inhibitors to electrolytes should not affect the performance of aluminum-air batteries during working discharge. The voltage-time curves are displayed in Figure 6. The battery capacity densities with different additives are calculated by Formula (8) [44] and counted in Table 3.

$$Cd = \frac{I \cdot t}{\Delta m} \quad (8)$$

where Cd is the capacity density of the battery anode (in $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$), I and t represent discharge current (in mA) and continuous discharge time (in h), respectively, Δm refers to the mass of the anode material lost (in g).

Table 3. The constant current ($20 \text{ mA} \cdot \text{cm}^{-2}$) discharge test data and battery capacity density calculation with different additives.

Additives	$\Delta m/\text{g}$	$Cd/\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$
Blank	0.0171	1754.4
200 mg/L $\text{Sm}(\text{OAc})_3$	0.0156	1923.1
200 mg/L $\text{Yb}(\text{OAc})_3$	0.0153	1960.8
$\rho(\text{Sm}):\rho(\text{Yb}) = 2:1$	0.0165	1818.2
$\rho(\text{Sm}):\rho(\text{Yb}) = 1:1$	0.0164	1829.3
$\rho(\text{Sm}):\rho(\text{Yb}) = 1:2$	0.0147	2040.8

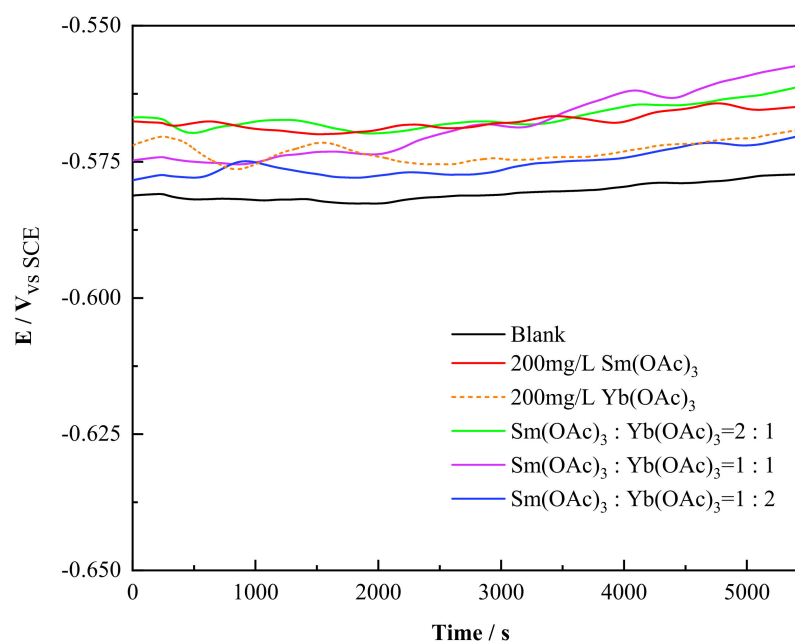


Figure 6. Galvanostatic discharge curves of 7075 anodes in different electrolytes at a current density of $20 \text{ mA} \cdot \text{cm}^{-2}$.

As shown in Figure 6, all the curves show a similar trend. The battery voltage was relatively stable for the first 1 h, and then increased slightly with the discharge time, mainly due to the deposition and exfoliation of discharge products [49]. It led to the polarization of the anode and changes in solution composition. After adding the corrosion inhibitor, the discharge voltage was no more than 15 mV higher than that of the blank one, and the voltage fluctuation was less than 5 mV compared with the blank, highlighting that the addition of corrosion inhibitor only had a small impact on the discharge properties of

aluminum anode, which met the requirements of practical applications. At the same time, it can be seen that when the ratio of $\text{Sm}(\text{OAc})_3$ to $\text{Yb}(\text{OAc})_3$ is 2:1 and 1:2, the discharge curves are relatively stable, and when the ratio is 1:1, the discharge curve is basically within the bounds of these two curves. With the passage of time, the voltage gradually rose and the discharge became precarious, pointing to a large change in surface state, which might put down to the emulative adsorption of $\text{Sm}(\text{OH})_3$ and $\text{Yb}(\text{OH})_3$ on the anode surface. At the same time, it can be inferred that the lower the amount of $\text{Sm}(\text{Ac})_3$, the better the total discharge effect for a mixed corrosion inhibitor with a certain total mass.

Table 3 shows that the battery capacity density after adding corrosion inhibitors was improved by 9.6% to 16.3% compared with that of blank one. Among them, the mixed corrosion inhibitor of 200 mg/L $\text{Yb}(\text{OAc})_3$ and the mass ratio of 1:2 have a very obvious effect on the improvement of battery capacity. This shows that these two inhibitors have obvious effects on improving the anode discharge performance of the battery.

3.6. Surface Microstructure

The SEM images of 7075 aluminum alloy in 3.5 wt.% NaCl were also analyzed to further study the effect of different additives on the change of surface morphology of anodes after soaking (shown in Figure 7). The scratches on the external surface in Figure 7a are caused by mechanical polishing during pretreatment. The smoother surface in Figure 7b relative to the raw sample is ascribed to the accumulation of dense intermediates, which lead to greater polarization of the anode and hinder the discharge process of the Al-air battery. At the same time, the large white bright spots observed on the external surface are considered to be attached corrosion products. Figure 7c reveals that the particle size of the corrosion products on the surface of 7075 aluminum becomes finer after adding samarium acetate, indicating that the presence of Sm^{3+} can significantly restrain the corrosion of 7075 and prevent the anode area from being covered, which is beneficial to improve the discharge activity. Figure 7d manifests that the anode surface after adding ytterbium acetate is relatively more uniform and the pitting hole diameter is smaller, testifying that Yb^{3+} has a more apparent impact on the polarization process of the aluminum anode. At the same time, dark dots are believed to be the result of microgrooves formed by aluminum surface corrosion. Compared with the blank group in Figure 7b, there are smaller corrosion pits and fewer corrosion products, representing that ytterbium acetate inhibits the corrosion of 7075 Al to a certain degree. Figure 7e represents the mixed inhibitor group containing samarium acetate and ytterbium acetate. It displays that white small dots and grayish-brown blocks are deposited on the surface of the aluminum anode, which may be oxides or hydroxides of samarium/ytterbium on the surface. These factors will promote to form a denser and steadier protective film. Combining the above results, the surfaces of the alloy after adding mixed additives are smoother and more homogeneous, and there are fewer corrosion points. It means that the corrosion of 7075 anode has been markedly repressed.

3.7. Modeling Hypothesis

Figure 8 exhibits the mechanism of action models for different additives. Electrochemical corrosion of 7075 Al anode germinates promptly when it comes into contact with 3.5 wt.% NaCl, which can be split into an anodic course (dissolution of aluminum) and a cathodic course (ionization and reduction of water). Undoubtedly, the ideal way to reduce anodic self-corrosion is to suppress the cathodic process.

The aforementioned experiments prove that samarium acetate is a desirable cathode inhibitor. The protective coating consists of oxides or hydroxides of samarium, which muffles aluminum self-corrosion by suppressing the hydrogen evolution reduction in microcathode region and has almost no impact on the dissolution reaction in anode region. Similarly, Ajit Kumar [10,11] confirmed that the oxide/hydroxide sediments of lanthanum and cerium were formed on cathodic intermetallic loci at low inhibitor consistence and over the entire surface at high consistence by SEM. Experimental data manifested that the corrosion potential value of 7075 electrode in 3.5 wt.% NaCl containing samarium

acetate moved to a more negative position. The samarium covering layer did not reduce the reactivity of aluminum anode, while the insufficient amount of OH^- results from the inhibited water reduction in cathodic area made it more difficult to form corrosion products. Eventually, much freer Al^{3+} migrated into the matrix solution.

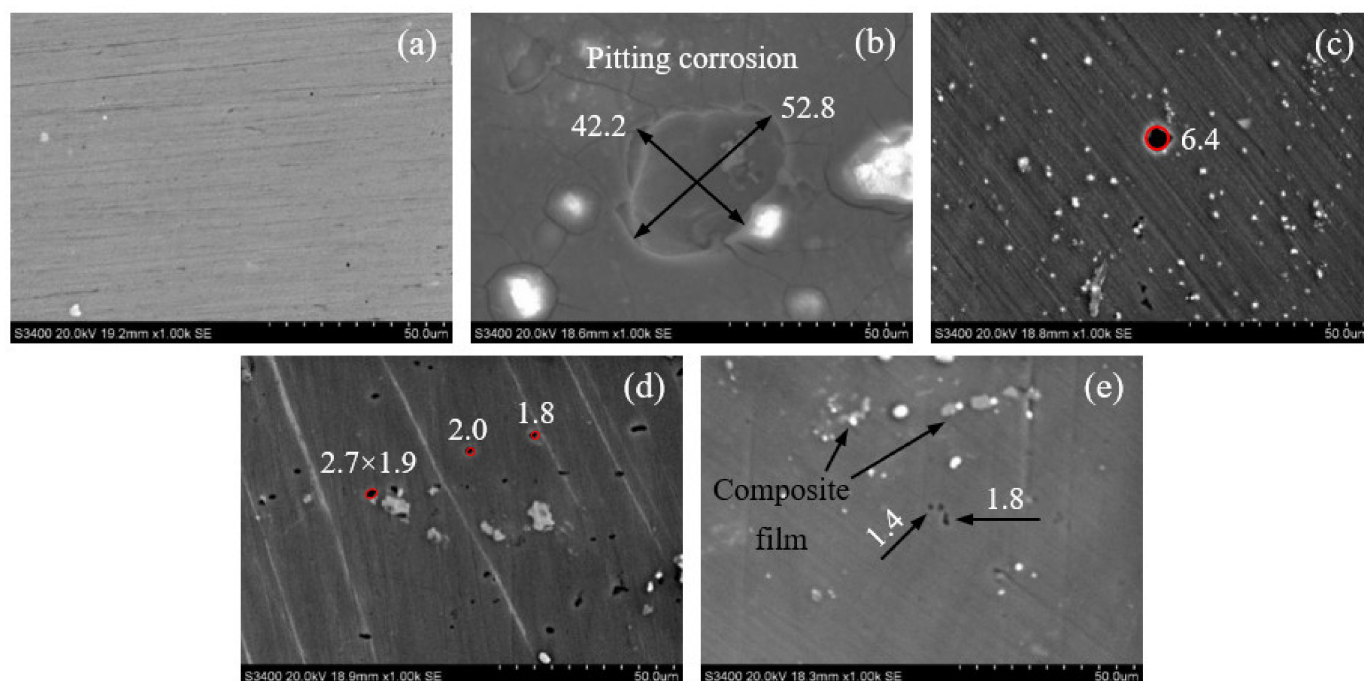


Figure 7. SEM images of 7075 aluminum alloy surface: (a) unimmersed surface, (b) without inhibitors, (c) 200 mg/L $\text{Sm}(\text{OAc})_3$, (d) 200 mg/L $\text{Yb}(\text{OAc})_3$, and (e) 200 mg/L hybrid inhibitors ($\text{Sm}^{3+}:\text{Yb}^{3+} = 1:2$).

Similarly, the protective layer formed by ytterbium acetate is composed of ytterbium oxide or hydroxide, which inhibits the hydrogen evolution reaction in the microcathode region more obviously than the samarium protective layer. More specifically, ytterbium acetate can significantly promote the dissolution reaction in the anode zone. It is proven that it is a mixed inhibitor that can not only inhibit the cathodic reaction but also promote the dissolution of the anode. Compared with samarium acetate, it can achieve better corrosion inhibition effects. The reason can put down to that the ytterbium covering layer is denser than the samarium protective layer.

The protective layer of rare earth compounds generated by corrosion inhibitors changes the microscopic characteristics of aluminum surface [24], curbs the adsorption of intermediates and releases the discharge active sites. Accordingly, the discharge property of Al-air battery is remarkably enhanced. In addition, the suppression of the self-corrosive cathode reaction also allows more electrons released from anode dissolution to be transferred to the working air cathode, which helps us to obtain higher output power during discharge, thereby increasing the capacity density of Al-air battery.

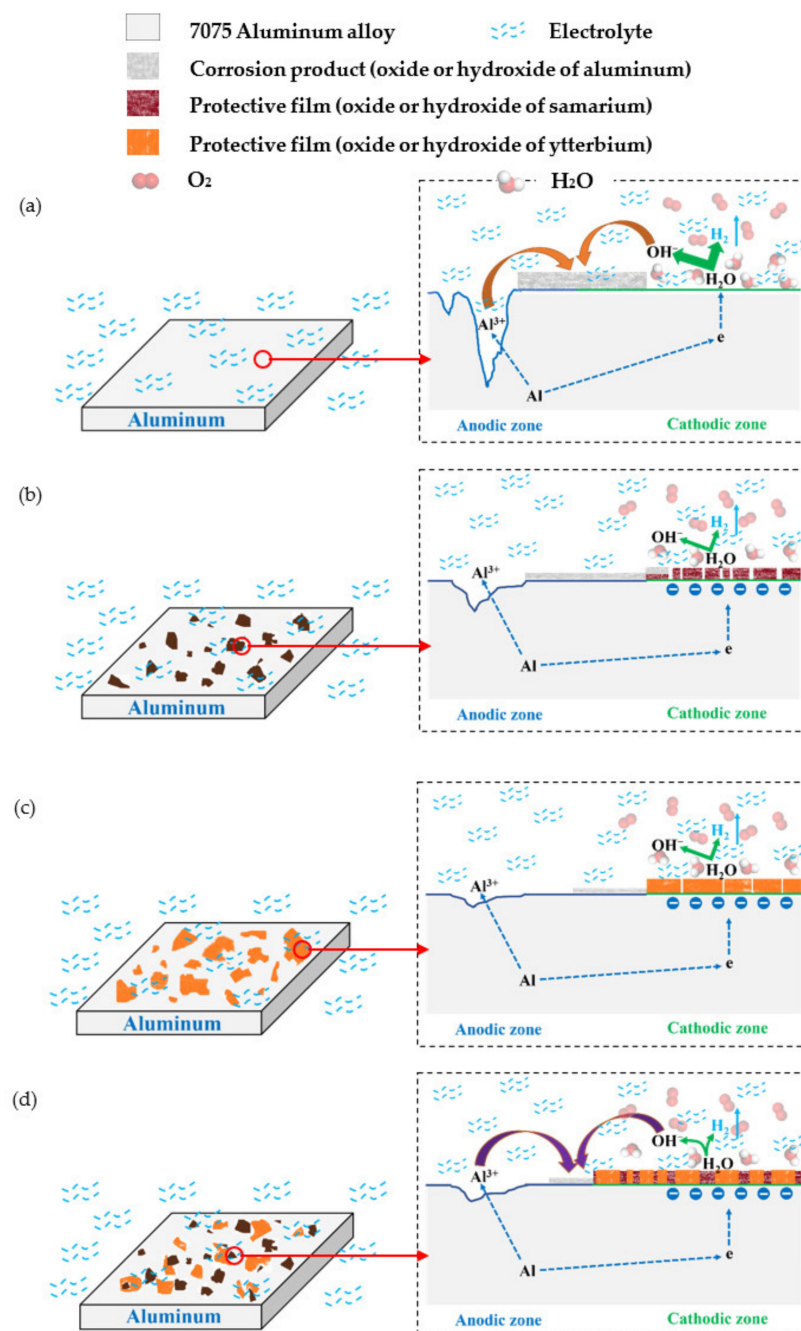


Figure 8. Hypothetical model of the influence mechanism of different additives on 7075 Al corrosion behavior and discharge performance: (a) blank; (b) Sm(OAc)₃; (c) Yb(OAc)₃; (d) Sm(OAc)₃ + Yb(OAc)₃.

4. Conclusions

This paper studies the effects of rare earth salts as electrolyte additives in Al-air batteries on the electrochemical and discharge characteristics of 7075 aluminum anodes.

- (1) Weight loss test and electrochemical test showed that both Sm(OAc)₃ and Yb(OAc)₃ achieved their best corrosion inhibition effects at 200 mg/L in 3.5 wt.% NaCl. The best corrosion inhibition efficiencies were 72.22% and 94.28%, respectively. Combining with surface microstructure analysis, these two corrosion inhibitors were mainly deposited on aluminum surface through the hydroxide or oxide of samarium/ytterbium, which slowed down the reaction process of corroding the microcathode zone, thereby inhibiting the self-corrosion of aluminum alloy.

- (2) $\text{Sm}(\text{OAc})_3$ had little effect on the electrochemical activity of aluminum anode as a cathodic inhibitor, and its corrosion inhibition effect gradually increased as time went by, while the performance of $\text{Yb}(\text{OAc})_3$ to improve the anode activity was closer to that of the hybrid type. The capacity density of the anode was improved by 9.6% to 16.3% after adding rare earth salts, which can be increased from $1754.4 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ to $2040.8 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ at most.
- (3) $\text{Yb}(\text{OAc})_3$ exhibited excellent corrosion inhibitory effects during the course of this study, but it easily passivated the anode, which was unfavorable for the battery in the actual discharge process. However, in the subsequent experimental study of the mixed rare earth salt, it was found that the doped rare earth salt can not only achieve the corrosion inhibition effect which is not inferior to that of ytterbium acetate, but it also does not cause anode passivation and can obtain good comprehensive performance.

A trace amount (200 mg/L) of rare earth samarium/ytterbium salt can have a strong corrosion inhibition effect on aluminum alloys. Taking a vehicle aluminum-air battery weighing 100 kg as an example, as long as no more than 15 g of rare earth salt is added to the electrolyte, the requirements for corrosion resistance of the battery's aluminum-based anode can be met. Rare earth salt has the characteristics of low cost, low toxicity, high efficiency and easy operation in the actual use process, and it is a green corrosion inhibitor with techno-economic feasibility. Therefore, in future work, we will try to refine and screen the mix and match of different rare earth salts to obtain the most cost-effective corrosion inhibitor composition.

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