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Abstract

The corrosion and oxygen evolution behaviors of Pb-Ag-RE alloy anodes in Cl^--free and 500 mg/L Cl^--containing H_2SO_4 solutions were comparatively investigated using constant current polarization, SEM, XRD, EIS, and Tafel scans. The results indicate that the oxide film formed on the Pb-Ag-RE anode in Cl^--containing electrolyte exhibits crater-like pores, with numerous corrosion pits distributed across the alloy substrate, manifesting distinct localized corrosion characteristics. Furthermore, the presence of Cl^- decreases the PbO_2 content in the anode surface oxide film, suppresses the generation and adsorption of oxygen evolution reaction intermediates, and thereby increases the charge transfer resistance of the oxygen evolution reaction. Consequently, 500 mg/L Cl^- exerts detrimental effects on both the corrosion resistance and oxygen evolution activity of Pb-Ag-RE alloy anodes, suggesting that the Cl^- concentration in the electrolyte should be minimized in industrial production.

Full Text

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Effect of Chloride Ions on the Electrochemical Behavior of Pb-Ag-RE Alloy Anodes*

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Abstract Galvanostatic polarization, SEM, XRD, EIS, and Tafel scanning were used to comparatively investigate the corrosion behavior and oxygen evolution behavior of Pb-Ag-RE alloy anodes in H_2SO_4 solutions without Cl^- and containing 500 mg/L Cl^-. The results show that the oxide film formed on the Pb-Ag-RE anode in the Cl^--containing electrolyte exhibits "volcanic-vent" -like pores, and a large number of corrosion pits are distributed on the alloy substrate, showing obvious localized corrosion characteristics. In addition, the presence of Cl^- reduces the content of PbO_2 in the oxide film on the anode surface, inhibits the formation and adsorption of intermediates in the oxygen evolution reaction, and thereby increases the charge-transfer resistance of the oxygen evolution reaction. Therefore, 500 mg/L Cl^- adversely affects both the corrosion resistance and oxygen evolution activity of Pb-Ag-RE alloy anodes; in industrial production, the concentration of Cl^- in the electrolyte should be reduced as much as possible.

Key words Pb-Ag-RE alloy, lead-based anode, electrowinning, chloride ion, localized corrosion, oxygen evolution reaction

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EFFECTS OF CHLORIDE ION ON THE ELECTROCHEMICAL BEHAVIOR OF Pb-Ag-RE ALLOY ANODE

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ABSTRACT Corrosion and oxygen evolution behavior of Pb-Ag-RE alloy anode has been comparatively investigated in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^- by galvanostatic polarization, SEM, XRD, EIS and Tafel scanning. The results show that anodic layer on Pb-Ag-RE anode formed in electrolyte with Cl^- exhibits 'volcanic vent'-like holes, and the metallic substrate in this electrolyte shows obvious localized corrosion feature with large numbers of corrosion pits. In addition, the presence of Cl^- decreases the amount of PbO_2 on the surface of anodic layer. It also inhibits the formation and adsorption of oxygen evolution intermediates, and further enhances the charge transfer resistance of oxygen evolution reaction. Therefore, Cl^- is detrimental to the corrosion resistance and oxygen evolution reactivity of Pb-Ag-RE alloy anode. Consequently, the Cl^- concentration in electrolyte should be reduced as low as possible during industrial operation.

KEY WORDS Pb-Ag-RE alloy, lead-based anode, electrowinning, chloride ion, localized corrosion, oxygen evolution reaction

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In the hydrometallurgy and electrodeposition processes for nonferrous metals (such as Zn, Cu, Co, Ni, and Mn), sulfuric acid electrolyte is commonly used. Lead-based alloys, because of their good stability under working conditions of high-concentration sulfuric acid solutions and high current densities, are widely used as oxygen-evolution anodes[^1,^2]. In the initial stage of service, a protective oxide film layer can form on the lead-based alloy anode. This film layer can greatly slow the further oxidative corrosion of the alloy substrate; therefore, the anode has relatively good stability and corrosion resistance[^3]. Studies[^4] have shown that the corrosion resistance of lead-based alloy anodes is affected by the structure and composition of the oxide film layer, while the structure and composition of the oxide film layer are essentially determined by the microstructure of the lead-based alloy and the properties of the electrolyte.

To improve the performance of lead-based anodes, their microstructure can be regulated and the composition of the electrolyte controlled. For regulating the microstructure of lead-based alloys, there are mainly three approaches: first, optimizing the types and contents of alloying elements[^5,^6]; second, controlling the cooling regime during alloy casting[^7]; and third, mechanical processing and heat treatment[^8]. For controlling the electrolyte composition, some beneficial metal ions (such as Mn^{2+} and Co^{2+})[^1,^9] can be added, while ions harmful to the electrochemical performance of lead-based anodes, such as F^-, should be reduced as much as possible.

In the Zn electrowinning industry, the electrolyte generally contains about 500 mg/L Cl^-. With the increasing complexity of mineral compositions and the accumulation of Cl^- in industrial circulating solutions[^10], the Cl^- concentration in some electrolytes can even reach 1000 mg/L[^11]. Therefore, both in China and abroad, increasing attention has been paid to the effect of Cl^- on the performance of lead-based anodes during electrolysis. Fraunhofer[^12] found that Cl^- participates in the precipitation of Pb^{2+} to form $PbCl_2$; at higher potentials, $PbCl_2$ is oxidized to PbO_2, and Cl_2 may also evolve together with O_2. Ivanov et al.[^13] reviewed the effects of Cl^- on the performance of Pb and lead-alloy anodes, reporting that when the Cl^- concentration is 100 mg/L, the corrosion of Pb-Ag anodes is comparable to that in electrolyte without Cl^-, whereas pure Pb anodes undergo severe corrosion even in electrolytes with low Cl^- concentrations. A Cl^- concentration of 500 mg/L can markedly aggravate corrosion of Pb-Ag anodes. Hampson et al.[^14] found that Cl^- decreases the stability of SO_4^{2-} in the film layer, reduces the quality of the oxide film layer, and inhibits the passivation process; at the same time, Cl^- can reduce the oxygen-evolution overpotential. Liu et al.[^10] also considered that Cl^- reduces the protective performance of the film layer and accelerates its dissolution. Cifuents et al.[^15] found that, during Cu electrodeposition, when the Cl^- concentration is below 100 mg/L, Cl^- can reduce Pb weight loss and corrosion. Tunnicliffe et al.[^9]

also reported that Cl^- can reduce corrosion of Pb-Ag anodes because $AgCl_2$ generated during service can envelop the oxide film layer and improve its corrosion resistance. Therefore, whether Cl^- is beneficial or harmful to lead-alloy anodes remains inconclusive and requires further study.

In this work, the corrosion behavior and oxygen-evolution behavior of Pb-Ag-RE alloy anodes in H_2SO_4 solutions without Cl^- and containing Cl^- were comparatively studied. The effects of Cl^- on the anode potential, oxide film morphology and phase composition, corrosion rate, corrosion morphology of the substrate, and kinetic parameters of the oxygen-evolution reaction of the Pb-Ag-RE alloy were investigated, and the mechanism by which Cl^- affects the electrochemical behavior of Pb-Ag-RE alloy anodes was discussed, providing a reference for regulation of Cl^- concentration in industrial electrolytes for hydrometallurgical electrodeposition.

1 Experimental Methods

1.1 Experimental Materials

The working electrode was a rolled Pb-Ag-RE alloy. Its chemical composition, measured using a PS-6 inductively coupled plasma atomic emission spectrometer (ICP-AES), was Pb-0.45%Ag-0.03%RE (mass fraction). The alloy wire was cut into specimens of 10 mm × 10 mm × 5 mm. After welding a Cu lead wire and sealing with denture-base resin, a working electrode with a working area of 1 cm^2 was obtained. The counter electrode was a Pt electrode with a surface area of 4 cm^2, and the reference electrode was Hg/Hg_2SO_4/saturated K_2SO_4 (0.64 V vs standard hydrogen electrode potential). Unless otherwise specified, all potentials in this paper are referenced to this reference electrode.

Two H_2SO_4 solutions (160 g/L), one without Cl^- and the other containing 500 mg/L Cl^-, were used to simulate industrial electrolytes. The electrolytes were prepared from analytically pure H_2SO_4, analytically pure HCl, and deionized water. The electrolyte temperature was controlled at (35$±$1) °C. Before electrochemical testing, the working electrode was polished to a bright finish with SiC abrasive paper and then rinsed clean with deionized water for later use.

1.2 Testing Methods

A 1470 E electrochemical workstation was used to record the anode potential of the Pb-Ag-RE anode during 72 h of galvanostatic polarization (500 A/m^2, the current density used in the Zn electrowinning industry) in the two H_2SO_4 solutions. After galvanostatic polarization, an oxide film layer formed on the anode surface. The morphology and phase composition of the oxide film layer were examined using a MIRA 3 scanning electron microscope (SEM) and a D/max 2500 X-ray diffractometer (XRD), respectively. To study the influence of Cl^- on the corrosion rate and corrosion characteristics of the Pb-Ag-RE anode, ICP-AES was used to measure the change in Pb^{2+} concentration in

the electrolyte with galvanostatic polarization time. The polarized anode was immersed for 5 min in a boiling alkaline glucose solution (20 g/L glucose + 100 g/L NaOH) to dissolve and remove the oxide film layer on the anode surface; the corrosion morphology of the alloy-anode substrate was then observed by SEM.

To explore the effect of Cl^- on the oxygen-evolution behavior of the Pb-Ag-RE anode, electrochemical impedance spectroscopy (EIS) and Tafel scanning were performed immediately after 72 h of galvanostatic polarization (500 A/m^2) of the Pb-Ag-RE anode. In the EIS test, the bias potential was the stable anode potential at the end of galvanostatic polarization, the AC amplitude was 10 mV, and the frequency range was 100 kHz–0.1 Hz. The Tafel potential scan range was 1.20–1.45 V, and the scan rate was 0.166 mV/s.

2 Experimental Results and Discussion

2.1 Anode Potential

Figure 1 shows the Pb-Ag-RE alloy anode in two H_2SO_4 solu-

During galvanostatic polarization, the anode potential changed with time. As can be seen from Fig. 1, the presence of Cl^- in the electrolyte had no obvious effect on the trend of the potential variation of the Pb-Ag-RE anode. At the initial stage of polarization, the anode potential decreased rapidly. In this stage, rapid growth of the $PbSO_4$ layer mainly occurred. As the $PbSO_4$ layer thickened and its coverage increased, the resistance of the oxide film layer increased; therefore, the potential showed a brief rebound. With further extension of the polarization time, the anode potential decreased slowly. This is because part of the poorly conductive $PbSO_4$ in the film layer transformed into the more conductive PbO_2, and PbO_2 is favorable for the formation of active sites for oxygen evolution, reducing the polarization degree of the oxygen-evolution reaction. Therefore, the anode potential gradually decreased. In the H_2SO_4 solution containing 500 mg/L Cl^-, the anode potentials of Pb-Ag-RE were all lower than those in the electrolyte without Cl^-. After 72 h of polarization, the anode potential in the Cl^--containing electrolyte was about 20 mV lower.

2.2 Oxide film layer

The morphology and phase composition of the anodic oxide film layer affect the corrosion rate of the alloy substrate. This is because, on the one hand, the film layer physically isolates the substrate from the electrolyte, and the porosity and compactness of the film layer affect the diffusion and mass transfer of the electrolyte within the film layer, thereby influencing corrosion of the substrate. On the other hand, according to the theory of Pavlov and Dinev[1], newly generated oxygen at the oxide film/electrolyte interface is transported from this interface toward the substrate/film interface, while oxygen vacancies are transported in the opposite direction. Finally, oxygen reacts with Pb, while

[1]16

Fig. 1 Anodic potential variation of Pb-Ag-RE anode during galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^-

Figure 1: Fig. 1 Anodic potential variation of Pb-Ag-RE anode during galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^-

oxygen vacancies participate in electron transfer at the oxide film/electrolyte interface. Therefore, the phase composition of the oxide film layer also affects the solid-state transport of newly generated oxygen in the film layer, and thus affects the oxidation-corrosion rate of the substrate. In addition, because the film/electrolyte interface is the site where the oxygen-evolution reaction occurs, the phase composition of the film surface affects the number and distribution of active sites for the oxygen-evolution reaction; meanwhile, the surface area of the film layer also affects the rate of the heterogeneous reaction. Therefore, the oxide film layer largely determines the oxygen-evolution activity of the anode. In summary, it is necessary to study the influence of Cl^- on the morphology and phase composition of the oxide film layer formed on the Pb-Ag-RE alloy anode during polarization.

2.2.1 Morphology Figure 2 shows SEM images of the oxide film layers formed on the Pb-Ag-RE anode after 72 h of galvanostatic polarization in two electrolytes. Figure 2a exhibits a typical coral-like morphology. This morphological feature is mainly caused by two factors: first, the film layer is continuously flushed by O_2 bubbles generated by the oxygen-evolution reaction; second, part of the $PbSO_4$ and PbO_2 on the film surface transform into each other, and because their molar volumes differ, shrinkage and expansion of the film during transformation lead to relatively low compactness. In the Cl^--containing electrolyte, the oxide film layer shows different characteristics, as shown in Fig. 2b. Many "crater" -like pores appear in the film layer. Around these pores, the film layer exhibits a gelatinous state, which is consistent with the report by Fraunhofer[2]. These regions are flatter and denser than the film layer obtained in the electrolyte without Cl^-. It should be noted that the pores in Fig. 2a are caused by the unevenness of the film layer; most of these pores do not penetrate into the interior of the film layer. By contrast, the "crater" -like pores in Fig. 2b extend deep into the film layer, which will intensify corrosion of the substrate.

Fig. 1 Anodic potential variation of Pb-Ag-RE anode during galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^-

Fig. 2 SEM images of anodic layers on Pb-Ag-RE anode obtained through 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- (a) and with 500 mg/L Cl^- (b)

2.2.2 Phase composition Figure 3 gives the XRD patterns of the oxide film layers formed on the Pb-Ag-RE anode after 72 h of polarization in two H_2SO_4

[2]12

Fig. 2 SEM images of anodic layers on Pb-Ag-RE anode obtained through 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- (a) and with 500 mg/L Cl^- (b)

Figure 2: Fig. 2 SEM images of anodic layers on Pb-Ag-RE anode obtained through 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- (a) and with 500 mg/L Cl^- (b)

Fig. 3 XRD patterns of anodic layers on Pb-Ag-RE anode formed through 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^-

Figure 3: Fig. 3 XRD patterns of anodic layers on Pb-Ag-RE anode formed through 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^-

solutions. It can be seen from Fig. 3 that the oxide film layers formed in the two electrolytes are mainly composed of β-PbO_2 and α-PbO_2. No obvious [[unclear: continuation cut off at bottom of page]]

Fig.3 XRD patterns of anodic layers on Pb-Ag-RE anode formed through 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^-

distinct characteristic peaks of $PbSO_4$ and non-stoichiometric PbO or basic $PbSO_4$ and other substances. This is because the amounts of these phases on the surface of the film layer are relatively small or they are covered by the surface PbO_2 layer. In the oxide film layer formed in the Cl^--containing electrolyte, the characteristic peak intensity of α-PbO_2 is even lower. Hampson et al.[14] considered that this is because the presence of Cl^- accelerates dissolution of the film layer, resulting in a decrease in film thickness. It is worth noting that characteristic peaks of metallic Pb can be observed in the XRD patterns, indicating that the film layer is not compact and that part of the lead alloy substrate is exposed. Another explanation is that, because the film layer is relatively thin, X-rays penetrate the film layer and detect signals from the substrate. The characteristic peaks of Pb in the film layer in the Cl^--containing electrolyte are more pronounced and have greater intensity. This is because the presence of Cl^- creates many "crater"-like pores in the film layer, reducing the compactness of the film layer and exposing more of the substrate. In addition, Cl^- may also reduce the thickness of the film layer, leading to the detection of more phase signals from the substrate.

2.3 Corrosion characteristics

2.3.1 Pb^{2+} concentration During the oxidative corrosion process of the anode, Pb first dissolves into the electrolyte in the form of Pb^{2+}. Because the solubility of $PbSO_4$ is very low, Pb^{2+} combines with $SO_4{}^{2-}$ to precipitate on

Fig. 4 Variation of Pb^{2+} concentration in electrolyte during 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^-

Figure 4: Fig. 4 Variation of Pb^{2+} concentration in electrolyte during 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^-

the anode surface in the form of $PbSO_4$. The $PbSO_4$ on the anode surface is further oxidized to PbO_2, ultimately leading to formation of the film layer. In addition, dissolved Pb^{2+} in the solution also migrates toward the cathode under the action of the electric field, is reduced, precipitates, and becomes incorporated into the cathode product, causing contamination of the cathode product. In general, the corrosion products of Pb are mainly the anodic oxide film layer, Pb^{2+} in the electrolyte, and impurity Pb in the cathode product. Although Pb^{2+} in the electrolyte accounts for only a small proportion of the corrosion amount of Pb, the corrosion condition of the lead-based alloy can still be inferred from changes in the Pb^{2+} concentration in the electrolyte. Figure 4 shows the variation of Pb^{2+} concentration in the two electrolytes with polarization time during galvanostatic polarization. In 160 g/L H_2SO_4 solution, according to the solubility product of $PbSO_4$, the saturation concentration of Pb^{2+} can be calculated to be approximately 0.078 mg/L

Fig.4 Variation of Pb^{2+} concentration in electrolyte during 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^-

(25 °C, standard atmospheric pressure). As can be seen from Fig. 4, the Pb^{2+} concentration in the electrolyte containing 500 mg/L Cl^- increases rapidly. When the polarization time is 36 h, the Pb^{2+} concentration reaches 0.09 mg/L (greater than the saturation concentration of Pb; this is related to the test temperature being higher than 25 °C). After the polarization time exceeds 48 h, the Pb^{2+} concentration remains unchanged and reaches saturation. In the Cl^--free electrolyte, the Pb^{2+} concentration increases more slowly, and only approaches saturation after polarization has continued for 72 h. Therefore, the presence of Cl^- accelerates the dissolution of Pb^{2+} at the initial stage of polarization and accelerates corrosion of the alloy substrate.

2.3.2 Corrosion of the substrate Corrosion of the lead-based alloy occurs at the interface between the alloy substrate and the oxide film layer. Therefore, observing the corrosion morphology of the alloy substrate helps in understanding the corrosion laws and characteristics of the alloy. After immersion in boiling sucrose solution for 5 min, the oxide film layer dissolved and the alloy substrate was exposed. Although the sucrose solution also caused slight corrosion of the alloy substrate during removal of the oxide film layer, the corrosion morphology of the alloy substrate during the galvanostatic polarization process could essentially be retained, as shown in Fig. 5. Figure 5a shows the corrosion morphology of the substrate of the Pb-Ag-RE anode in the Cl^--free electrolyte. It can be

seen from Fig. 5a that the substrate is relatively flat; although there are a small number of corrosion pores, the corrosion is generally relatively uniform. In the electrolyte containing 500 mg/L Cl^-, however, the corroded substrate is uneven, with numerous corrosion pits and pores, showing pronounced localized corrosion characteristics (Fig. 5b). Therefore, the presence of Cl^- intensifies pitting corrosion of the Pb-Ag-RE alloy. In the Cl^--containing electrolyte in Fig. 2b, the oxide film layer has many "crater"-like pores, and the appearance of these pores is related to pitting corrosion of the substrate. In areas of the substrate that are prone to corrosion, as corrosion products accumulate, the internal pressure in the film layer increases and exerts outward compressive stress, thereby causing pores or cracks to appear in the film layer. In many engineering fields, Cl^- can promote corrosion of materials, mainly because Cl^- ions have a small radius and strong complexing ability. In the Cl^--containing electrolyte, many pores form in the oxide film layer; Cl^- diffuses and electromigrates rapidly within the film layer, thereby causing the Pb-Ag-RE

Fig. 5 Corrosion morphologies of the substrate of Pb-Ag-RE anode after 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- (a) and with 500 mg/L Cl^- (b)

the corrosion of the alloy substrate was aggravated.

2.4 Oxygen evolution behavior

During service, lead-based alloy anodes mainly undergo the oxygen evolution reaction. Equations (1)-(3) give the oxygen evolution mechanism of a widely accepted lead anode in sulfuric acid solution, where S denotes the oxygen evolution active sites on the surface of the oxide film layer[^17]. The oxygen evolution activity of lead-based alloy anodes not only affects the anode potential and electrical energy consumption, but also has a certain influence on the corrosion of the anode. Therefore, it is necessary to study the influence of Cl^- on the oxygen evolution behavior of Pb-Ag-RE alloy anodes. In this study, EIS and Tafel tests were used to investigate the oxygen evolution behavior.

$$S + H_2O \rightarrow S - OH_{ads} + H^+ + e^- \quad (1)$$

$$S - OH_{ads} \rightarrow S - O_{ads} + H^+ + e^- \quad (2a)$$

$$2S - OH_{ads} \rightarrow S - O_{ads} + S^+ + H_2O \quad (2b)$$

$$S - O_{ads} \rightarrow S + 1/2O_2 \quad (3)$$

2.4.1 EIS

The EIS of Pb-Ag-RE anodes after polarization for 72 h in the two electrolytes is shown in Fig. 6. The complex-plane impedance plots obtained in the two electrolytes each have only one capacitive arc, corresponding to an RC circuit composed of the double-layer capacitance and charge-transfer resistance in parallel. In the high-frequency region, an inductive arc appears; this is caused by charge relaxation of electroactive species unevenly distributed on the anode surface[^18]. The equivalent circuit shown in Fig. 6 was used to fit the impedance data, and the fitting results are given by the curves in Fig. 6. Because the oxygen-evolution active sites on the surface of the oxide film layer are unevenly distributed, a constant phase element (CPE) was used in the fitting process to replace the ideal capacitor. Its impedance Z_{CPE} can be expressed as follows[^18]:

$$Z_{\mathrm{CPE}} = Q^{-1}(j\omega)^{-n} \tag{4}$$

where Q is the capacitance, ω is the phase angle, and n is used to characterize the deviation of the CPE from an ideal capacitor; when $n = 1$, it represents a pure capacitor. Brug et al.[^19] pointed out that the value of the double-layer capacitance C_{dl} can be calculated from Eq. (5):

$$Q = (C_{\mathrm{dl}})^{n}\left[(R_{\mathrm{u}})^{-1} + (R_{\mathrm{ct}})^{-1}\right]^{(1-n)} \tag{5}$$

where C_{dl} is the double-layer capacitance, R_{u} is the uncompensated resistance, and R_{ct} is the charge-transfer resistance. The values of Q, R_{u}, R_{ct}, and n are obtained by equivalent-circuit fitting, and the value of C_{dl} is obtained from Eq. (5). The specific results are shown in Table 1.

Fig. 6 EIS of Pb-Ag-RE anode after 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^- (Bias potential is 1.38 V in electrolyte without Cl^- and 1.36 V in electrolyte with 500 mg/L Cl^-) and electrical equivalent circuits (inset) used to fit the impedance data (L—inductance, R_{u}—uncompensated resistance, CPE—constant phase element, R_{ct}—charge transfer resistance)

From Table 1, it can be seen that the χ^2 values of the two EIS fitting results are both on the order of 10^{-4}, indicating that the fitting accuracy meets the requirements. Table 1 also shows that, in the Cl^--containing electrolyte, the uncompensated resistance R_{u} is slightly greater than that in the Cl^--free electrolyte. This may be due to the incorporation of a small amount of high-resistance (4×10^7-$5 \times 10^7\ \Omega \cdot \mathrm{cm}$) $PbCl_2$ into the oxide film layer grown in the Cl^--containing electrolyte. The double-layer capacitance C_{dl} of the anode in the Cl^--containing electrolyte is smaller than C_{dl} in the Cl^--free electrolyte, indicating that, during polarization in the Cl^--containing electrolyte, fewer oxygen-evolution reaction

intermediates are adsorbed at the oxide-film/electrolyte interface. This is because the PbO_2 content on the surface of the anode oxide film formed in the Cl^--containing electrolyte is lower, resulting in fewer oxygen-evolution active sites. In addition, from the morphology of the oxide film layer, it can be seen that the Cl^--containing electrolyte ···

Table 1 Impedance parameters determined by fitting the EIS data shown in Fig. 6

Electrolyte	L	R_u	Q	C_{dl}	n	R_{ct}	χ^2
	10^{-7} H · cm^2	Ω · cm^2	10^{-2} F · cm^{-2}	10^{-2} F · cm^{-2}		Ω · cm^2	
Without Cl^-	1.01	0.593	6.90	5.42	0.919	1.88	3.58×10^{-4}
500 mg/L Cl^-	1.11	0.633	6.64	5.06	0.911	2.26	6.61×10^{-4}

Note: Q—capacity, C_{dl}—double-layer capacity, n—deviation of CPE from ideal capacitor, χ^2—Chi square

The film layer obtained in the solution contains some gel-like regions, resulting in a smaller surface area, which also leads to a smaller C_{dl}. Meanwhile, in the Cl^--containing electrolyte, the charge-transfer resistance R_{ct} of the oxygen evolution reaction is larger. Therefore, the combination of a smaller C_{dl} value and a larger R_{ct} value can demonstrate that the oxygen evolution reaction is less likely to proceed in the Cl^--containing electrolyte. However, the Pb-Ag-RE anode exhibits a lower anodic potential in the Cl^--containing electrolyte. This is because the anodic potential of the lead-based alloy anode is a mixed potential; it is affected not only by the oxygen evolution reaction, but also by other side reactions, such as chlorine evolution and corrosion of the substrate. More severe substrate corrosion in the Cl^--containing electrolyte is one explanation for the lower anodic potential, because the corrosion reaction proceeds at a lower potential and acts to reduce anodic polarization.

2.4.2 Tafel curves

To further investigate the effect of Cl^- on the oxygen evolution behavior of the Pb-Ag-RE anode, Tafel linear-sweep tests were performed after galvanostatic polarization for 72 h. Fig. 7 shows the Tafel curves obtained by scanning from high potential to low potential toward the steady-state potential, and the obtained Tafel curves were corrected according to Eq. (6)[20]:

$$E_{eff} = E_{appl} - iR_u \tag{6}$$

where E_{appl} is the voltage applied between the anode and the reference electrode, i is the current density, and E_{eff} is the actual potential of the anode after

subtracting the voltage drop iR_u caused by the solution resistance between the working electrode and the reference electrode. As can be seen from Fig. 7, in the electrolyte without Cl^-, the Tafel curve exhibits a dual-slope characteristic. After piecewise fitting with Origin, the slopes of the Tafel curve were obtained. In the low-overpotential region, the Tafel slope is 97.5 mV/dec. In the high-overpotential region, the Tafel slope increases to 163.7 mV/dec, indicating that in this potential region the anodic reaction is controlled by the formation and adsorption steps of oxygen-evolution intermediates. In the electrolyte containing 500 mg/L Cl^-, the Tafel curve shows only a single-slope characteristic (slope 169.6 mV/dec), indicating that Cl^- has a relatively large influence on the oxygen evolution reaction mechanism of the Pb-Ag-RE alloy anode. In both the low-overpotential and high-overpotential regions, the oxygen evolution process in the Cl^--containing electrolyte is controlled by the formation and adsorption steps of oxygen-evolution intermediates. In the Cl^--containing electrolyte, Cl^- may compete for adsorption with OH^- and other intermediate active species in the aqueous solution (anions or negatively charged free radicals), leading to a decrease in the oxygen-evolution active intermediates adsorbed at the oxide-film/electrolyte interface, thereby making its Tafel slope slightly larger than that in the electrolyte without Cl^-. This also corresponds to the smaller C_{dl} value in the Cl^--containing electrolyte. Comprehensive analysis of the EIS and Tafel data leads to the conclusion that the presence of Cl^- suppresses the formation and adsorption of oxygen-evolution intermediates, increases the oxygen-evolution charge-transfer resistance, and reduces the oxygen evolution activity of the Pb-Ag-RE alloy anode.

Fig. 7 Tafel curves of Pb-Ag-RE anode after 72 h galvanostatic polarization in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^- (i—current density)

3 Conclusions

(1) In H_2SO_4 solution containing 500 mg/L Cl^-, the Pb-Ag-RE anode exhibits a higher corrosion rate during the initial stage of polarization. The oxide film grown on the Pb-Ag-RE surface contains "crater" -like pores, and the compactness of the film becomes poorer. At the same time, the alloy substrate in the Cl^--containing electrolyte undergoes severe pitting corrosion; therefore, Cl^- accelerates corrosion of the lead-based alloy substrate.

(2) EIS and Tafel tests show that, in the Cl^--containing electrolyte, the formation and adsorption of oxygen-evolution reaction intermediates are suppressed, and the oxygen-evolution charge-transfer resistance increases, resulting in poorer oxygen evolution activity of the Pb-Ag-RE alloy. However, the presence of Cl^- increases the anodic corrosion rate, causing the Pb-Ag-RE alloy to exhibit a lower anodic potential in the Cl^--containing electrolyte.

(3) 500 mg/L Cl^- has adverse effects on both the corrosion and oxygen evolution reactions of the Pb-Ag-RE alloy anode. In industrial production,

the concentration of Cl^- in the electrolyte should be reduced as much as possible.

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Note: Figure translations are in progress. See original paper for figures.