Effect of Chloride Ions on the Electrochemical Behavior of Pb-Ag-RE Alloy Anodes (Postprint)

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Abstract

The corrosion behavior and oxygen evolution behavior of Pb-Ag-RE alloy anodes in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^- were comparatively investigated using constant current polarization, SEM, XRD, EIS, and Tafel analysis. The results indicate that the oxide film formed on the Pb-Ag-RE anode in Cl^--containing electrolyte exhibits "crater"-shaped pores, with numerous corrosion pits distributed on the alloy substrate, demonstrating distinct characteristics of localized corrosion. Furthermore, the presence of Cl^- reduces the PbO_2 content in the anode surface oxide film, inhibits the generation and adsorption of oxygen evolution reaction intermediates, and consequently increases the charge transfer impedance of the oxygen evolution reaction. Therefore, 500 mg/L Cl^- exerts adverse effects on both the corrosion resistance and oxygen evolution activity of Pb-Ag-RE alloy anodes, and the concentration of Cl^- in the electrolyte should be minimized in industrial production.

Full Text

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Abstract

The corrosion and oxygen evolution behavior of Pb-Ag-RE alloy anodes in H_2SO_4 solution without Cl^- and with 500 mg/L Cl^- was comparatively investigated using galvanostatic polarization, SEM, XRD, EIS, and Tafel scanning. The results demonstrate that the anodic layer formed on Pb-Ag-RE anodes in

Cl^--containing electrolyte exhibits "volcanic vent" -like holes, with numerous corrosion pits distributed across the alloy substrate, indicating pronounced localized corrosion characteristics. Furthermore, the presence of Cl^- reduces the PbO_2 content in the surface oxide layer, inhibits the formation and adsorption of oxygen evolution reaction intermediates, and consequently 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, suggesting that Cl^- concentration in industrial electrolytes should be minimized.

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

Introduction

Hydrometallurgical electrowinning of non-ferrous metals (such as Zn, Cu, Co, Ni, and Mn) commonly employs sulfuric acid electrolytes, with lead-based alloys widely used as oxygen-evolving anodes due to their stability under high-concentration sulfuric acid and high current density conditions [1,2]. During initial service, lead-based alloy anodes form a protective oxide layer that significantly retards further oxidation corrosion of the alloy substrate, imparting good stability and corrosion resistance [3]. Research [4] indicates that the corrosion resistance of lead-based alloy anodes is governed by the structure and composition of the oxide layer, which is fundamentally determined by the alloy' s microstructure and electrolyte properties.

Performance improvement of lead-based anodes can be achieved through two primary approaches: controlling the alloy microstructure and regulating electrolyte composition. Microstructure control includes optimizing alloy element types and contents [5,6], controlling cooling rates during casting [7], and mechanical processing/heat treatment [8]. Electrolyte composition can be modified by adding beneficial metal ions (such as Mn^{2+} and Co^{2+}) [1,9] while minimizing harmful species like F^-.

In zinc electrowinning, electrolytes typically contain approximately 500 mg/L Cl^-. With increasingly complex mineral compositions and Cl^- accumulation in industrial recycle streams [10], some electrolytes can reach Cl^- concentrations up to 1000 mg/L [11]. Consequently, the impact of Cl^- on lead-based anode performance has garnered significant attention. Fraunhofer [12] reported that Cl^- precipitates with Pb^{2+} to form $PbCl_2$, which oxidizes to PbO_2 at higher potentials, potentially co-evolving Cl_2 with O_2. Ivanov et al. [13] reviewed Cl^- effects on Pb and lead alloy anodes, noting that at 100 mg/L Cl^-, Pb-Ag anode corrosion was comparable to Cl^--free electrolytes, while pure Pb anodes corroded severely even at low Cl^- concentrations. At 500 mg/L, Cl^- markedly accelerated Pb-Ag anode corrosion. Hampson et al. [14] found that Cl^- reduces sulfate stability in the oxide layer, degrades film quality, inhibits passivation, and decreases oxygen evolution overpotential. Liu et al. [10] similarly reported that Cl^- reduces the protective properties of the oxide layer and accelerates its dissolution. Conversely, Cifuentes et al. [15] observed that Cl^- below 100 mg/L reduced Pb weight loss and corrosion during Cu electrowinning, while Tunnicliffe et al. [9] reported that Cl^- decreased Pb-Ag anode corrosion due to $AgCl_2$ formation that surrounded and protected the oxide layer. Thus, whether Cl^- is beneficial or detrimental remains inconclusive, necessitating further investigation.

This work comparatively studied the corrosion and oxygen evolution behavior of Pb-Ag-RE alloy anodes in Cl^--free and Cl^--containing H_2SO_4 solutions, examining the effects of Cl^- on anode potential, oxide layer morphology and phase composition, corrosion rate and substrate morphology, and oxygen evolution kinetics parameters. The underlying mechanisms of Cl^- influence on electrochemical behavior are discussed to provide guidance for controlling Cl^- concentration in industrial hydrometallurgical electrowinning electrolytes.

1.1 Experimental Materials

Rolled Pb-Ag-RE alloy was used as the working electrode. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, PS-6) determined its composition as Pb-0.45%Ag-0.03%RE (mass fraction). Alloy samples were wire-cut into 10 mm × 10 mm × 5 mm specimens, welded with Cu wire, and sealed with denture base resin to obtain working electrodes with 1 cm^2 exposed area. A Pt electrode (4 cm^2) served as the counter electrode, and Hg/Hg_2SO_4/saturated K_2SO_4 (0.64 V vs. standard hydrogen electrode) as the reference electrode. All potentials reported herein refer to this reference electrode unless otherwise specified.

Two H_2SO_4 solutions (160 g/L) were prepared using analytical-grade H_2SO_4, analytical-grade HCl, and deionized water to simulate industrial electrolytes: one Cl^--free and one containing 500 mg/L Cl^-. Electrolyte temperature was maintained at (35 ± 1) °C. Prior to electrochemical testing, working electrodes were polished with SiC sandpaper, rinsed with deionized water, and prepared for experimentation.

1.2 Test Methods

A 1470E electrochemical workstation recorded the anode potential of Pb-Ag-RE anodes during 72 h galvanostatic polarization at 500 A/m^2 (the current density used in industrial Zn electrowinning). After polarization, the formed oxide layers were characterized using a MIRA 3 scanning electron microscope (SEM) for morphology and a D/max 2500 X-ray diffractometer (XRD) for phase composition.

To investigate Cl^- effects on corrosion rate and characteristics, ICP-AES measured Pb^{2+} concentration in the electrolyte as a function of polarization time.

Polarized anodes were immersed in boiling sugar-alkali solution (20 g/L glucose + 100 g/L NaOH) for 5 min to dissolve the oxide layer, followed by SEM examination of the alloy substrate corrosion morphology.

To explore Cl^- effects on oxygen evolution behavior, electrochemical impedance spectroscopy (EIS) and Tafel scanning were performed immediately after 72 h galvanostatic polarization at 500 A/m^2. EIS measurements were conducted at the stable anode potential from the later polarization stage, with 10 mV AC amplitude and frequency range of 100 kHz-0.1 Hz. Tafel scans were performed from 1.20-1.45 V at 0.166 mV/s.

2.1 Anode Potential

Figure 1 [Figure 1: see original paper] shows the anode potential variation of Pb-Ag-RE alloy anodes during galvanostatic polarization in the two H_2SO_4 solutions. The presence of Cl^- does not significantly affect the potential trend. During initial polarization, the anode potential decreases rapidly, corresponding to rapid $PbSO_4$ layer growth. As the $PbSO_4$ layer thickens and coverage increases, the oxide layer impedance rises, causing a brief potential recovery. With further polarization, the potential decreases gradually as poorly conductive $PbSO_4$ transforms into more conductive PbO_2, which facilitates oxygen evolution active site formation and reduces polarization. In 500 mg/L Cl^- solution, the Pb-Ag-RE anode potential is consistently lower than in Cl^--free electrolyte, being approximately 20 mV lower after 72 h polarization.

2.2 Oxide Film Layer

Anode oxide layer morphology and phase composition significantly influence alloy substrate corrosion rate. The layer provides physical isolation between substrate and electrolyte, where porosity and density affect mass transfer and thus corrosion. According to Pavlov and Dinev’ s theory [16], newly generated oxygen at the oxide layer/electrolyte interface transports toward the substrate/layer interface while oxygen vacancies migrate in the opposite direction, ultimately oxidizing Pb. Therefore, phase composition affects solid-state oxygen transport and corrosion rates. Since the layer/electrolyte interface hosts the oxygen evolution reaction, surface phase composition influences active site density and distribution, while surface area affects heterogeneous reaction rates. Consequently, the oxide layer largely determines anode oxygen evolution activity, necessitating investigation of Cl^- effects on its morphology and phase composition.

2.2.1 Morphology Figure 2 [Figure 2: see original paper] presents SEM images of oxide layers formed on Pb-Ag-RE anodes after 72 h galvanostatic polarization. In Cl^--free electrolyte (Fig. 2a), the layer exhibits typical coral reef-like morphology resulting from continuous O_2 bubble scouring during oxygen evolution and volume changes during $PbSO_4/PbO_2$ interconversion, yielding low density. In Cl^--containing electrolyte (Fig. 2b), the layer shows numerous "volcanic vent" -like holes with gelatinous surrounding regions, consistent with Fraunhofer's report [12]. These areas appear flatter and denser than the Cl^--free layer. Notably, holes in Fig. 2a result from surface roughness and are largely non-penetrating, whereas the "volcanic vent" holes in Fig. 2b penetrate deeply into the layer, exacerbating substrate corrosion.

2.2.2 Phase Composition Figure 3 [Figure 3: see original paper] shows XRD patterns of oxide layers formed after 72 h polarization. Both layers consist primarily of β-PbO_2 and α-PbO_2. Characteristic peaks for $PbSO_4$, non-stoichiometric PbO , or basic lead sulfates are absent, likely due to low surface content or coverage by surface PbO_2. The α-PbO_2 peaks are weaker in the Cl^--containing electrolyte, which Hampson et al. [14] attributed to accelerated layer dissolution and reduced thickness. Metallic Pb peaks are visible, indicating a non-dense layer exposing substrate or thin film allowing X-ray penetration to detect substrate signals. The Pb peaks are more pronounced and intense in the Cl^--containing electrolyte, reflecting the "volcanic vent" holes that reduce layer density and expose more substrate, possibly also indicating reduced layer thickness.

2.3 Corrosion Behavior

2.3.1 Pb^{2+} Concentration During anodic corrosion, Pb dissolves as Pb^{2+} in the electrolyte. Due to low $PbSO_4$ solubility, Pb^{2+} combines with ${SO_4}^{2-}$ to deposit as $PbSO_4$ on the anode surface, which further oxidizes to PbO_2, forming the oxide layer. Dissolved Pb^{2+} also migrates to the cathode under the electric field, reducing and depositing as impurity in the cathode product. Although Pb^{2+} represents a small fraction of total corrosion products, its concentration change reflects alloy corrosion. Figure 4 [Figure 4: see original paper] shows Pb^{2+} concentration variation during polarization. In 160 g/L H_2SO_4, the saturated Pb^{2+} concentration is approximately 0.078 mg/L at 25 °C. In 500 mg/L Cl^- electrolyte, Pb^{2+} concentration rises rapidly, reaching 0.09 mg/L at 36 h (exceeding saturation due to higher test temperature) and stabilizing after 48 h. In Cl^--free electrolyte, Pb^{2+} increases slowly, approaching saturation only after 72 h. Thus, Cl^- accelerates initial Pb^{2+} dissolution and alloy substrate corrosion.

2.3.2 Corroded Substrate Lead alloy corrosion occurs at the substrate/oxide layer interface, making substrate morphology observation crucial for understanding corrosion mechanisms. After 5 min immersion in boiling sugar-alkali solution, the oxide layer dissolves, exposing the substrate. Although the solution causes slight substrate corrosion during removal, the polarization-induced morphology is largely preserved (Fig. 5 [Figure 5: see original paper]). In Cl^--free electrolyte (Fig. 5a), the substrate appears relatively flat with uniform corrosion and few pits. In 500 mg/L Cl^- electrolyte (Fig. 5b), the substrate is uneven with numerous corrosion pits and holes, exhibiting clear localized corrosion features. The "volcanic vent" holes in the oxide layer (Fig.

2b) correlate with substrate pitting. In corrosion-prone regions, accumulated corrosion products increase internal pressure, extruding and cracking the layer. Chloride promotes corrosion in many engineering applications due to its small ionic radius and strong complexation ability. In Cl^--containing electrolytes, the porous oxide layer facilitates rapid Cl^- diffusion and electromigration, accelerating Pb-Ag-RE alloy substrate corrosion.

2.4 Oxygen Evolution Behavior

Lead-based alloy anodes primarily undergo oxygen evolution during service. Equations (1)-(3) present the widely accepted oxygen evolution mechanism in sulfuric acid, where S represents active sites on the oxide layer surface [17]. Anode oxygen evolution activity affects not only potential and energy consumption but also corrosion. Therefore, Cl^- effects on Pb-Ag-RE anode oxygen evolution behavior were investigated using EIS and Tafel tests.

2.4.1 EIS EIS spectra measured after 72 h polarization are shown in Figure 6 [Figure 6: see original paper]. Both electrolytes exhibit a single capacitive arc corresponding to the parallel RC circuit of double-layer capacitance and charge transfer resistance. An inductive arc appears in the high-frequency region, attributed to charge relaxation of non-uniformly distributed electroactive species [18]. Impedance data were fitted using the equivalent circuit shown in Figure 6. Due to non-uniform active site distribution, a constant phase element (CPE) replaced ideal capacitance, with impedance Z_{CPE} expressed as [18]:

[Equation for Z_{CPE} would appear here]

where Q is capacitance, ω is angular frequency, and n characterizes deviation from ideal capacitance (n = 1 for pure capacitance). Brug et al. [19] indicated that double-layer capacitance C_{dl} can be calculated using:

[Equation for C_{dl} would appear here]

where C_{dl} is double-layer capacitance, R_u is uncompensated resistance, and R_{ct} is charge transfer resistance. Fitting yielded Q, R_u, R_{ct}, and n values, from which C_{dl} was calculated (Table 1).

Both fits exhibit ^{2} values on the order of 10^{-4}, confirming satisfactory accuracy. In Cl^--containing electrolyte, uncompensated resistance R_u is slightly higher, likely due to embedded high-impedance $PbCl_2$ (40\$$\times10^{\{6\}-50\times10}$\{6\}\$ $\Omega\cdot$cm) in the oxide layer. The double-layer capacitance C_{dl} is smaller in Cl^--containing electrolyte, indicating fewer adsorbed oxygen evolution intermediates at the oxide layer/electrolyte interface. This results from lower PbO_2 content on the anodic layer surface, reducing active sites. Additionally, the gelatinous regions on the Cl^--formed layer decrease surface area, further reducing C_{dl}. The charge transfer resistance R_{ct} is larger in Cl^--containing electrolyte. Combined with smaller C_{dl} and larger R_{ct}, oxygen evolution is less favorable. However, Pb-Ag-RE anodes exhibit lower potentials in Cl^--containing electrolyte because the anode potential is a mixed potential influenced by side reactions such as chlorine evolution and substrate corrosion, which occur at lower potentials and reduce anodic polarization.

2.4.2 Tafel Analysis Tafel linear sweep tests were conducted after 72 h polarization to further investigate oxygen evolution behavior. Figure 7 [Figure 7: see original paper] shows Tafel curves obtained from high-to-low potential quasi-steady-state scanning, corrected according to [20]:

[Equation for potential correction would appear here]

where E_{appl} is the applied voltage between anode and reference electrode, and E_{eff} is the actual anode potential after IR_u drop compensation. In Cl^--free electrolyte, Tafel curves exhibit dual slopes: 97.5 mV/dec at low overpotential and 163.7 mV/dec at high overpotential, indicating control by oxygen evolution intermediate formation and adsorption. In 500 mg/L Cl^- electrolyte, a single slope of 169.6 mV/dec appears, suggesting Cl^- significantly alters the oxygen evolution mechanism. In both potential regions, the process is controlled by intermediate formation and adsorption. Chloride may compete with OH^- and other active species (anions or negatively charged radicals) for adsorption sites, reducing adsorbed intermediates and yielding a slightly larger Tafel slope that corresponds to the smaller C_{dl} value. Combined EIS and Tafel analysis concludes that Cl^- inhibits oxygen evolution intermediate formation and adsorption, increases charge transfer resistance, and reduces Pb-Ag-RE alloy anode oxygen evolution activity.

3 Conclusions

1. In 500 mg/L Cl^- H_2SO_4 solution, Pb-Ag-RE anodes exhibit higher initial corrosion rates. The anodic layer develops “volcanic vent” -like holes with reduced density, while the alloy substrate suffers severe pitting. Therefore, Cl^- accelerates lead-based alloy substrate corrosion.
2. EIS and Tafel tests demonstrate that Cl^- inhibits oxygen evolution intermediate formation and adsorption, increases charge transfer resistance, and reduces Pb-Ag-RE alloy oxygen evolution activity. However, accelerated corrosion in Cl^--containing electrolyte results in lower anode potentials due to mixed potential effects from side reactions.
3. 500 mg/L Cl^- adversely affects both corrosion and oxygen evolution reactions of Pb-Ag-RE alloy anodes. Industrial operations should minimize electrolyte Cl^- concentration.

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