

Effect of impurities in recycling water on Pb-Ag anode passivation in zinc electrowinning process

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Abstract: Effect of impurities in recycling water on Pb-Ag anode passivation in zinc electrowinning process was investigated by linear scan voltammetry. Results show that passivation process would be affected in the presence of Cl^- and F^- in recycling water. It was highly advantageous to take H_2SO_4 concentration as 180 g/L, Mn^{2+} concentration as 3–5 g/L and F^- less than 42 mg/L. However, passivation process would not be affected when Cl^- concentration was less than 13 mg/L without any other ions, or when mass ratio of Mn^{2+} to Cl^- existing in electrolyte was 8, where Cl^- concentration could reach up to 625 mg/L.

Key words: zinc electrowinning process; Pb-Ag anode; passivation; impurities; recycling water

1 Introduction

Nonferrous metals industry shares huge water consumption in China [1–2]. A large amount of acidic sulfate wastewater containing heavy metals from non-ferrous metal industry was discharged, which would lead to the lavishness of water resource and seriously affect safety of residential drinking water due to persistent pollution of toxic heavy metals [3–5].

Although water consumption per ton of product has presently been declined in non-ferrous metal smelter in China, water recycling ratio is still less than 85%. The only way to solve this problem is to improve the recycling ratio of purified water and to achieve zero discharge of wastewater [6]. Various methods have been developed to treat heavy metal-containing wastewater. For example, limestone neutralization process is conventionally applied for its advantages such as low investment, mature technique, simple and convenient operation. However, the purified water produced by this method may result in some problems for high concentrations of Ca^{2+} , SO_4^{2-} , F^- , Cl^- and so on, which would influence and limit the reutilization of industrial wastewater [7–8].

There are many parameters which influence Pb-Ag anode passivation in zinc electrowinning process, such as substrate metal, contents of Ag, Ca and Sr in anode, component of electrolyte, potential, current density, temperature and pretreatment of electrode [9–11]. Components of electrolyte, such as concentrations of H_2SO_4 , Mn^{2+} and Cl^- , are decisive factors because they affect process of Pb-Ag anode passivation and performance of passivation layer directly [12–14]. Impurities in reused water may influence zinc electrowinning process, and then lead to decreasing quality of zinc. Therefore, it is of great significance to establish main indexes for recycling process of purified water. For example, after heavy metal-containing wastewater from Zhuzhou Smelter Group, Hunan province, China, was treated by biologics, which was exploited by our research group, concentrations of Zn, Cd, Pb, Cu and As of purified water reached Water Quality Standard for Drinking Water Sources (CJ 3020—93). However, removal of main anions including SO_4^{2-} , Cl^- and F^- was not so remarkable, which may result in another problem: purified water with chloride ions and fluoride ions may affect Pb-Ag anode passivation process when reused to zinc electrowinning process. Therefore, it is of considerable interest to investigate and

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establish main indexes of Pb-Ag anode passivation in zinc electrowinning process.

Objective of this work is to investigate effect of impurities, such as concentrations of H_2SO_4 , Mn^{2+} , Cl^- and F^- , on passivation process of Pb-Ag anode in zinc electrowinning process.

2 Experimental

2.1 Electrolytes

Reagents used in this study included H_2SO_4 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, KCl , NaOH , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, NaCl and NaF , and electrolytes were prepared from analytical grade chemicals and double-distilled water.

2.2 Experiment of linear scan voltammetry

Linear scan voltammetry was carried out in a three-electrode system consisting of a lead-silver electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum sheet (1 cm×1 cm) as counter electrode. Open circuit potential—time curves were recorded before experiments of linear scan voltammetry.

Lead-silver electrode was prepared in laboratory. Lead-silver wire was collected from Zhuzhou Smelter Group, Zhuzhou City, Hunan Province, China. In brief, a lead-silver wire with diameter of 6 mm was inserted into a glass tube with 15 cm in length and 2 cm in diameter. Epoxy resin adhesive was filled into the glass tube to fix lead-silver wire. Circular cross-section of one end of lead-silver wire exposed outside and the other end extended. After 24 h, the exposed surface of the lead-silver wire was polished with 12 μm -abrasive paper, dipped in acetone for 30 min and washed with double-distilled water, and the final product was regarded as working electrode (Pb-Ag anode).

Experiments were thermostated at 313 K in thermostat water bath. Scan rate was set as 1 mV/s over the potential range from stable potential to 2.0 V, while stable potential was determined by open circuit potential—time curves. Potentials described in this study were all recorded vs SCE.

2.3 Effect of different indexes on Pb-Ag anode passivation process

Effect of H_2SO_4 concentration on Pb-Ag anode passivation process was investigated using ZnSO_4 solution with a zinc concentration of 50 g/L as base electrolyte. H_2SO_4 concentrations were adjusted to 0, 50, 100, 150, 180 and 210 g/L, respectively.

Effect of Mn^{2+} concentration on Pb-Ag anode passivation process was studied on the basis of H_2SO_4 – ZnSO_4 solution, in which concentration of Zn^{2+} was 50 g/L, concentrations of H_2SO_4 were 50 g/L and

180 g/L, respectively. Mn^{2+} concentrations were 0, 0.5, 1.5, 3, 4 and 5 g/L, respectively.

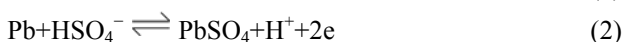
Effects of Cl^- concentration, $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio and F^- concentration on Pb-Ag anode passivation process were investigated on the basis of H_2SO_4 – ZnSO_4 solution, in which concentration of Zn^{2+} was 50 g/L, H_2SO_4 was 180 g/L. Conditions of experiments were controlled as follows: Cl^- concentrations were controlled as 0, 13, 105, 203, 253, 302 and 407 mg/L; Mn^{2+} concentrations were 3.0 g/L; $\text{Mn}^{2+}/\text{Cl}^-$ mass ratios were 1, 3, 5, 8 and 10; F^- concentrations were 0, 24, 42, 52 and 64 mg/L.

3 Results and discussion

3.1 Effect of H_2SO_4 concentration on Pb-Ag anode passivation process

3.1.1 Effect of H_2SO_4 concentration on open circuit potential—time curves

Effect of H_2SO_4 concentration on open circuit potential—time curves of Pb-Ag anode can be sketched in Fig. 1. Changes of potential could be classified into three stages: stable stage, unstable stage and stable stage. Corrosion potential of Pb-Ag anode shifted negatively with the gradual increase of H_2SO_4 concentration, while the trend of negative shift became smoother at higher H_2SO_4 concentrations. The reason was that the whole system could be regarded as a corrosion cell when the applied current was zero. In anode of corrosion cell, following reactions occurred at higher H_2SO_4 concentrations [15]:



Anode surface was separated from the solution with PbSO_4 , which covered Pb-Ag anode surface owing to its low solubility in H_2SO_4 solution. Coverage of PbSO_4 on anode surface increased with reaction time and when

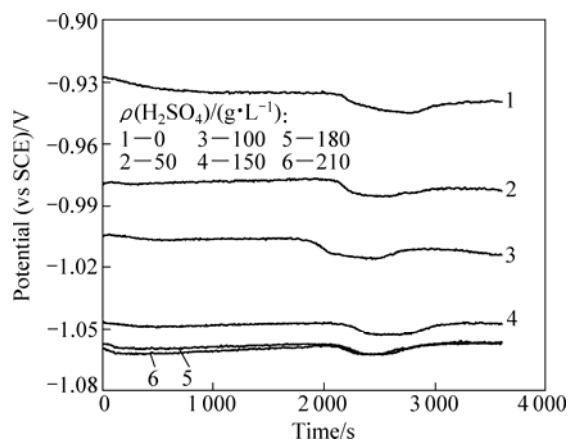


Fig. 1 Open circuit potential—time curves of Pb-Ag anode at different H_2SO_4 concentrations

Pb-Ag anode surface was completely covered by PbSO_4 , corrosion process reached stable state, that is to say, the corrosion potential was stable.

3.1.2 Effect of H_2SO_4 concentration on anodic polarization curves

Anodic polarization curves of Pb-Ag anode at different H_2SO_4 concentrations are depicted in Fig. 2, and the fitting parameters are listed in Table 1. It appears clearly that anode polarization curves can be divided into four regions. From corrosion potential (φ_{corr}) to passivating potential (φ_p) is the first region named as active dissolution region, in which dissolution current of Pb-Ag anode increased with potential. In the second region, from φ_p to activation potential (φ_F), which is named as transition region, condition on Pb-Ag anode surface was rapidly changed and anodic current decreased sharply from φ_p . The third region began from φ_F . In this region Pb-Ag anode surface was in the state of passivation and dissolution current was very small. Thus, it is named as passivation region. And then when potential was over passivation potential (φ_{tr}), it came into the fourth region (over passivation region). This region has characteristics similar to the first region, that is, current increased with the enhancement of potential.

Decrease of current in Fig. 2 indicates that PbSO_4 crystal formed and grew rapidly on anode surface, and then metal was oxidized gradually in the sulfate layer. Owing to high over potential generated by oxygen evolution on surface of PbO_2 layer, when potential was

less than $\varphi_{\text{PbO}_2/\text{PbSO}_4}$, the main reaction was the formation of intermediary, such as PbSO_4 crystal and PbO_2 . When potential was more than $\varphi_{\text{PbO}_2/\text{PbSO}_4}$, metals oxidation and oxygen evolution took place synchronously. With the decrease of unoxidized anode surface area, oxidation rate of the anode decreased, while oxygen evolution rate and the anodic polarization current increased with the reaction time, when anodic potential was high enough, current density could be used to express the oxygen evolution rate.

Figure 2 and Table 1 also show that when H_2SO_4 concentration changed from 0 to 100 g/L, φ_p and φ_F shifted negatively, while φ_{tr} shifted positively, so the passivation region extended. Additionally, I_{max} and I_p increased gradually. However, when the concentration of H_2SO_4 was more than 100 g/L, φ_p and φ_F turned to shift positively, which in turn shortened the passivation region, yet I_{max} and I_p increased continuously. When the concentration of H_2SO_4 was 180 g/L, φ_p , φ_F and I_p reached their minimums, while φ_{tr} and $\Delta\varphi$ reached their maximums; values of φ_p , I_{max} , φ_F , φ_{tr} and $\Delta\varphi$ were -0.605 8 V, 0.097 2 mA, -0.493 9 V, 1.129 8 V and 1.623 7 V, respectively. The region of maintaining passivating current was in the domain $10.3\text{--}58.8$ μA .

3.2 Effect of Mn^{2+} concentration on Pb-Ag anode passivation process

3.2.1 Effect of Mn^{2+} concentration on open circuit potential—time curves

Open circuit potential—time curves of Pb-Ag anode at different Mn^{2+} concentrations are depicted in Fig. 3 and Fig. 4. Corrosion potential exhibited a negative shift with the increase of Mn^{2+} concentration. When H_2SO_4 concentration increased from 50 g/L to 180 g/L, the negative shift value of corrosion potential increased. The corrosion principles of Pb-Ag anode in electrolyte with or without Mn^{2+} were similar. When SO_4^{2-} concentration increased, the following equation showed left shift:



So, HSO_4^- concentration in electrolyte increased, which is beneficial to Pb-Ag corrosion.

3.2.2 Effect of Mn^{2+} concentration on anodic polarization curves

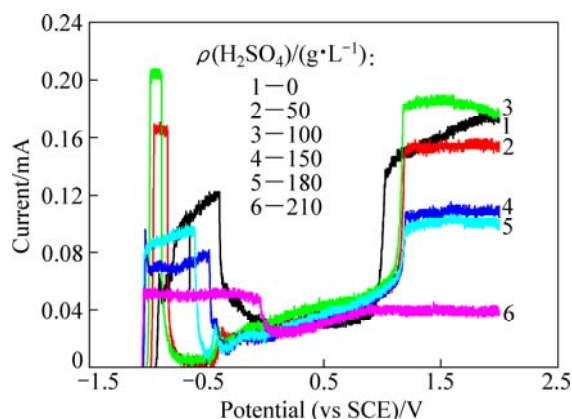


Fig. 2 Anodic polarization curves of Pb-Ag anode at different H_2SO_4 concentrations

Table 1 Fitting parameters of anodic polarization curves of Pb-Ag anode at different H_2SO_4 concentrations

$\rho(\text{H}_2\text{SO}_4)/(\text{g}\cdot\text{L}^{-1})$	φ_p/V	I_{max}/mA	φ_F/V	$\varphi_{\text{tr}}/\text{V}$	$\Delta\varphi/\text{V}$	I_p/mA
0	-0.394 4	0.121 5	-0.029 4	0.930 0	0.959 4	0.030 4
50	-0.948 2	0.168 7	-0.721 8	1.107 7	1.829 5	0.003 1–0.053 9
100	-0.977 3	0.206 6	-0.716 3	1.112 0	1.828 3	0.005 3–0.067 1
150	-0.477 6	0.079 5	-0.326 5	1.124 4	1.450 9	0.012 2–0.056 0
180	-0.605 8	0.097 2	-0.493 9	1.129 8	1.623 7	0.010 3–0.058 8
210	-0.170 1	0.052 0	0.068 9	0.909 5	0.840 6	0.025 3–0.039 8

φ_p , I_{max} , φ_F , φ_{tr} and I_p represent passivating potential, passivating current, activation potential, over passivation potential and maintaining passivity current, respectively; $\Delta\varphi$ represents passivation region from activation potential to over passivation potential.

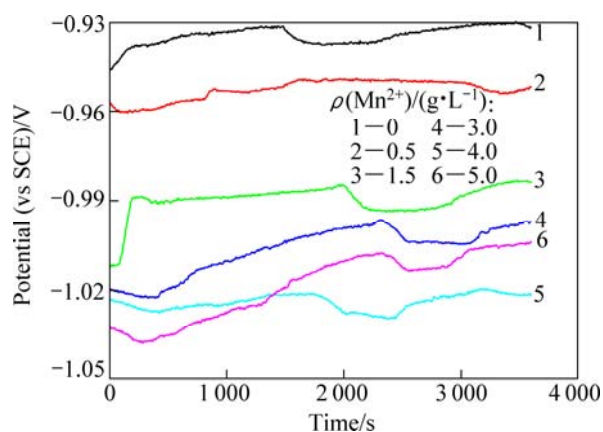


Fig. 3 Open circuit potential–time curves of Pb-Ag anode at different Mn^{2+} concentrations ($\rho(\text{H}_2\text{SO}_4)=50 \text{ g/L}$)

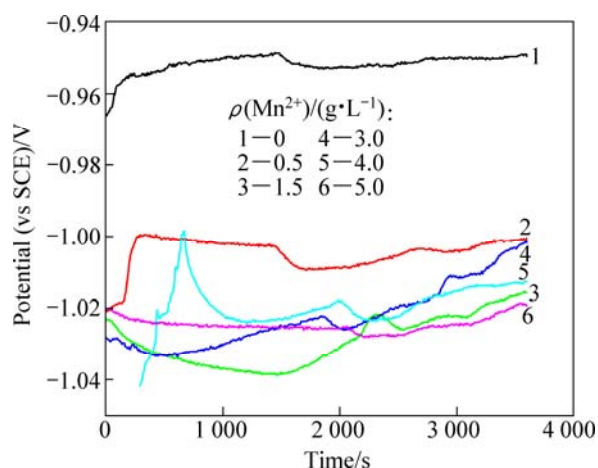


Fig. 4 Open circuit potential–time curves of Pb-Ag anode at different Mn^{2+} concentrations ($\rho(\text{H}_2\text{SO}_4)=180 \text{ g/L}$)

Figures 5 and 6 show anodic polarization curves of Pb-Ag anode at different Mn^{2+} concentrations, and corresponding fitting parameters are listed in Table 2 and Table 3.

When Mn^{2+} existed in electrolyte, ϕ_F showed little change, ϕ_{tr} shifted negatively and I_P increased slightly (Fig. 5 and Fig. 6). Comparison between Fig. 5 and Fig. 6 reveals that when Mn^{2+} concentration was in the range of 1.5–3.0 g/L and H_2SO_4 concentration increased from 50 g/L to 180 g/L, fitting parameters showed following change under the same concentration of Mn^{2+} : ϕ_P shifted negatively, ϕ_F and ϕ_{tr} shifted positively, I_{\max} increased,

passivation region $\Delta\phi$ became wide and I_P decreased. Thus, H_2SO_4 concentration in this work was taken as 180 g/L, that is, $\text{H}_2\text{SO}_4/\text{Zn}^{2+}$ mass ratio was 3.6.

When H_2SO_4 concentration was set as 180 g/L and Mn^{2+} concentration changed from 0.5 g/L to 3.0 g/L, ϕ_P , I_{\max} , ϕ_F , ϕ_{tr} , $\Delta\phi$ and I_P had little change. However, ϕ_P and ϕ_F shifted negatively while ϕ_{tr} shifted positively, I_{\max} and I_P decreased, and passivation region $\Delta\phi$ widened when Mn^{2+} concentration was higher than 3.0 g/L. Consequently, the concentration of Mn^{2+} was chosen as 3–5 g/L in electrolyte.

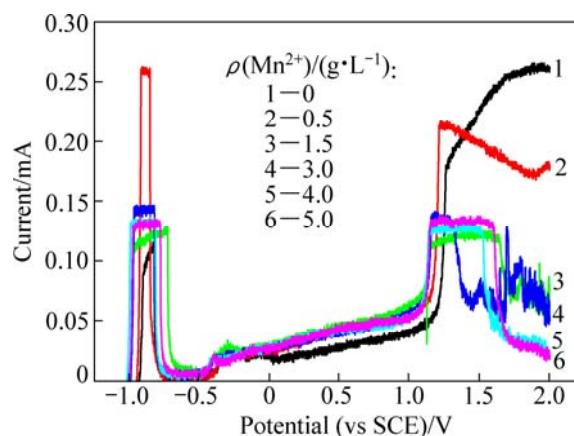


Fig. 5 Anodic polarization curves of Pb-Ag anode at different Mn^{2+} concentrations ($\rho(\text{H}_2\text{SO}_4)=50 \text{ g/L}$)

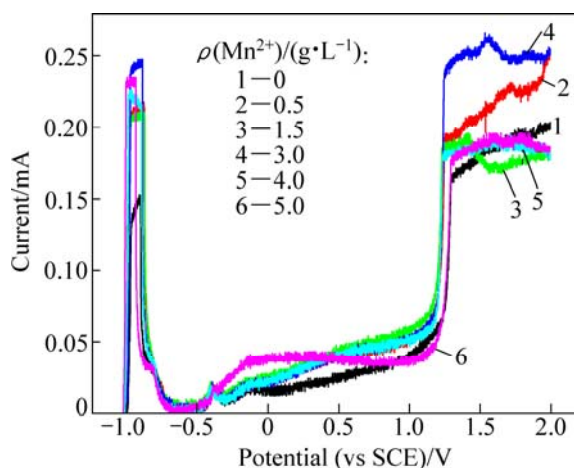


Fig. 6 Anodic polarization curves of Pb-Ag anode at different Mn^{2+} concentrations ($\rho(\text{H}_2\text{SO}_4)=180 \text{ g/L}$)

Table 2 Fitting parameters of anodic polarization curves of Pb-Ag anode at different Mn^{2+} concentrations ($\rho(\text{H}_2\text{SO}_4)=50 \text{ g/L}$)

$\rho(\text{Mn}^{2+})/(\text{g}\cdot\text{L}^{-1})$	ϕ_P/V	I_{\max}/mA	ϕ_F/V	ϕ_{tr}/V	$\Delta\phi/\text{V}$	I_P/mA
0	-0.824 2	0.112 3	-0.733 5	1.162 3	1.895 8	0.004 0–0.052 0
0.5	-0.911 1	0.260 4	-0.758 6	1.067 3	1.825 9	0.004 4–0.055 6
1.5	-0.724 6	0.127 9	-0.658 3	1.041 6	1.699 9	0.006 2–0.061 0
3	-0.821 7	0.146 6	-0.720 9	1.042 7	1.763 6	0.005 2–0.060 0
4	-0.815 2	0.134 5	-0.724 6	1.051 2	1.775 8	0.005 2–0.053 4
5	-0.784 3	0.131 3	-0.691 2	1.022 6	1.713 8	0.006 1–0.051 9

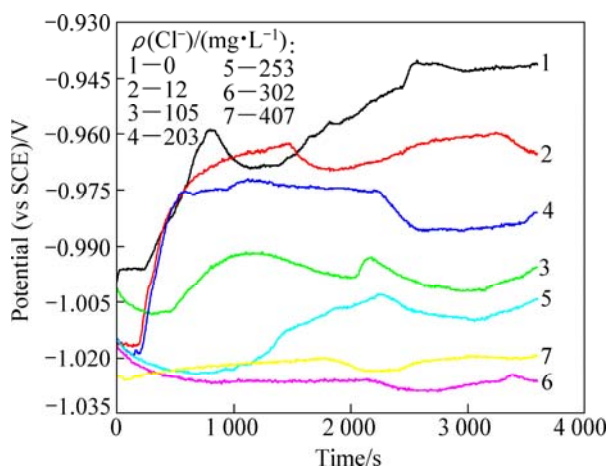
Table 3 Fitting parameters of anodic polarization curves of Pb-Ag anode at different Mn^{2+} concentrations ($\rho(\text{H}_2\text{SO}_4)=180 \text{ g/L}$)

$\rho(\text{Mn}^{2+})/(\text{g}\cdot\text{L}^{-1})$	φ_p/V	I_{\max}/mA	φ_F/V	φ_{tr}/V	$\Delta\varphi/\text{V}$	I_p/mA
0	-0.893 2	0.152 3	-0.696 3	1.148 3	1.844 6	0.003 1–0.041 8
0.5	-0.873 8	0.216 6	-0.676 4	1.105 2	1.781 6	0.003 2–0.048 9
1.5	-0.866 8	0.209 7	-0.676 2	1.104 5	1.780 7	0.005 1–0.056 9
3	-0.883 5	0.247 4	-0.676 9	1.092 9	1.769 8	0.003 4–0.052 8
4	-0.963 4	0.225 7	-0.689 8	1.111 2	1.801 0	0.003 1–0.054 2
5	-0.926 1	0.235 2	-0.689 3	1.116 8	1.806 1	0.001 7–0.039 7

3.3 Effect of Cl^- concentration on Pb-Ag anode passivation process

3.3.1 Effect of Cl^- concentration on open circuit potential—time curves

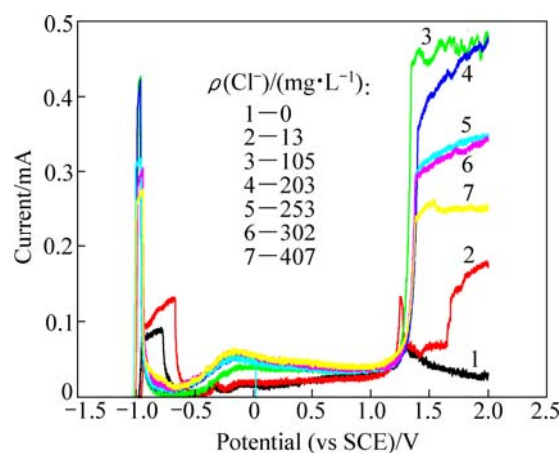
Open circuit potential—time curves of Pb-Ag anode at different Cl^- concentrations are shown in Fig. 7. The negative shift of corrosion potential with increase of Cl^- concentration made passivation process more complex. When Cl^- concentration was higher than 302 mg/L, the time for reaching steady state was shortened. There was an obvious competition on activate adsorption points between Cl^- and HSO_4^- ; moreover, Cl^- accelerated the corrosion process after contacting Pb-Ag anode surface via the surface void of PbSO_4 , and the formed PbCl_2 precipitate was absorbed on Pb-Ag anode surface and made system stable.

**Fig. 7** Open circuit potential—time curves of Pb-Ag anode at different Cl^- concentrations

3.3.2 Effect of Cl^- concentration on anodic polarization curves

Anodic polarization curves of Pb-Ag anode at different Cl^- concentrations are shown in Fig. 8, and fitting parameters are listed in Table 4. When Cl^- concentration changed from 0 mg/L to 13 mg/L, φ_p and φ_F shifted positively, φ_{tr} shifted negatively, $\Delta\varphi$ decreased. I_{\max} increased by 42.2 μA , while I_p changed little. When Cl^- was more than 13 mg/L, φ_p decreased by 0.295 5 V, φ_F declined by 0.280 6 V. Moreover, φ_{tr} changed by 0.038 2 V, which made $\Delta\varphi$ wide. However, I_{\max} increased by 0.295 5 mA, and I_p also increased evidently.

Consequently, passivation process would not be affected only under the condition that Cl^- concentration was less than 13 mg/L when there was only Cl^- existing in electrolyte.

**Fig. 8** Anodic polarization curves of Pb-Ag anode at different Cl^- concentrations

At present, there are two theories for interpretation of metal passivation process destructed by Cl^- ions. One is phase film formation theory: Cl^- pushes O_2 out of the film or passes through the film void. The other is adsorption theory: adsorption capacity of Cl^- is so strong that it takes the place of O_2 and is absorbed on electrode surface. Therefore, protection layer of metal oxides would be replaced by non-protective, soluble metal chloride layer. The following reaction occurs:



CAO [16] considered when Cl^- enriched in solution near the partial surface of metal, it would increase absorption of anion on metal surface, decrease ion resistance of passivation layer and destroy protection ability. On the other hand, it would accelerate the dissolution of passivation layer for complex compounds formed between Cl^- and metal ions.

3.4 Effect of $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio on Pb-Ag anode passivation process

3.4.1 Effect of $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio on open circuit potential—time curves

Open circuit potential—time curves of Pb-Ag anode

at different $\text{Mn}^{2+}/\text{Cl}^-$ mass ratios are shown in Fig. 9. When $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio was less than 3, corrosion potential showed negative shift with the increase of the mass ratio. Corrosion potential and time needed for reaching steady state changed little when $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio was more than 3.

3.4.2 Effect of $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio on anodic polarization curves

Anodic polarization curves of Pb-Ag anode at different $\text{Mn}^{2+}/\text{Cl}^-$ mass ratios are shown in Fig. 10, and fitting parameters are listed in Table 5. It can be seen that when Cl^- existed in electrolyte, φ_p and φ_F shifted negatively while φ_{tr} shifted positively, $\Delta\varphi$ widened, I_{\max} and I_p were less than those without Cl^- .

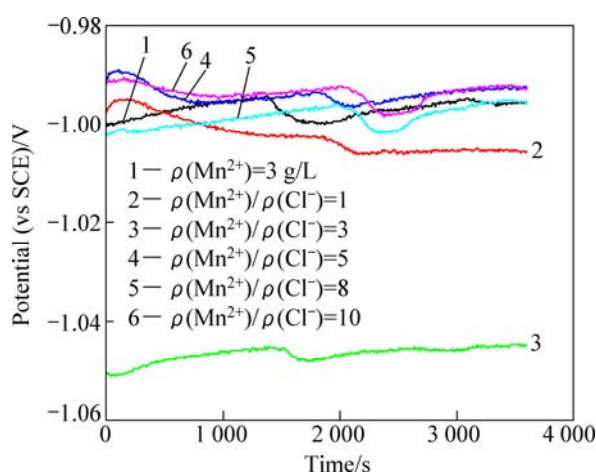


Fig. 9 Open circuit potential—time curves of Pb-Ag anode at different $\text{Mn}^{2+}/\text{Cl}^-$ mass ratios

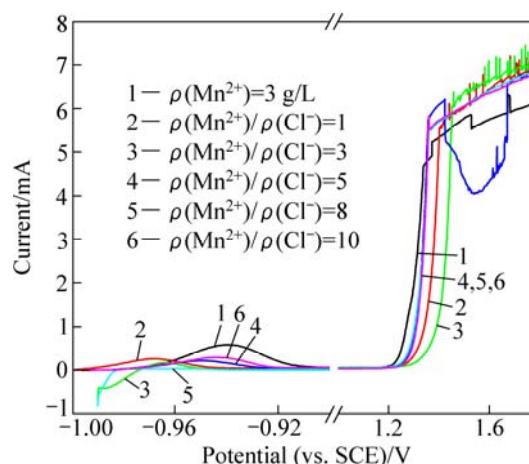


Fig. 10 Anodic polarization curves of Pb-Ag anode at different $\text{Mn}^{2+}/\text{Cl}^-$ mass ratios

When $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio increased from 1 to 3, φ_p , φ_F and φ_{tr} changed positively, $\Delta\varphi$ widened. I_{\max} decreased by 0.088 3 mA, while I_p changed little.

When $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio changed in the range of 3–8, φ_p and φ_F shifted positively, φ_{tr} shifted negatively, $\Delta\varphi$ diminished, and there was a minor increase for I_{\max} and I_p .

When $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio was 8, I_{\max} reached the minimum of 0.030 5 mA, while I_p and $\Delta\varphi$ did not change too much. φ_p , φ_F and φ_{tr} showed negative shift.

When $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio was more than 8, I_{\max} and I_p increased again, φ_p , φ_F and φ_{tr} increased up to -0.944 5 V, -0.918 9 V and 1.224 5 V, respectively. $\Delta\varphi$

Table 4 Fitting parameters of anodic polarization curves of Pb-Ag anode at different Cl^- concentrations

$\rho(\text{Cl}^-)/(\text{g}\cdot\text{L}^{-1})$	φ_p/V	I_{\max}/mA	φ_F/V	φ_{tr}/V	$\Delta\varphi/\text{V}$	I_p/mA
0	-0.797 7	0.088 4	-0.639 7	1.211 4	1.851 1	0.002 1–0.042 8
13	-0.672 1	0.1306	-0.625 7	1.180 6	1.806 3	0.003 1–0.035 7
105	-0.963 2	0.426 1	-0.898 5	1.185 8	2.084 3	0.002 9–0.039 6
203	-0.964 8	0.421 2	-0.906 3	1.218 8	2.125 1	0.009 2–0.044 6
253	-0.967 6	0.316 5	-0.886 0	1.212 4	2.098 4	0.009 1–0.045 8
302	-0.945 4	0.304 6	-0.859 3	1.204 5	2.063 8	0.012 2–0.045 9
407	-0.946 8	0.275 7	-0.865 6	1.157 5	2.023 1	0.012 2–0.047 8

Table 5 Fitting parameters of anodic polarization curves of Pb-Ag anode at different $\text{Mn}^{2+}/\text{Cl}^-$ mass ratios

$\rho(\text{Mn}^{2+})/\rho(\text{Cl}^-)$	φ_p/V	I_{\max}/mA	φ_F/V	φ_{tr}/V	$\Delta\varphi/\text{V}$	I_p/mA
$\rho(\text{Mn}^{2+})=3 \text{ g/L}, \rho(\text{Cl}^-)=0 \text{ g/L}$	-0.939 5	0.583 8	-0.907 8	1.208 5	2.116 3	0.033 5–0.051 9
1	-0.978 4	0.256 1	-0.946 2	1.211 3	2.157 5	0.001 1–0.040 8
3	-0.953 9	0.167 8	-0.936 5	1.281 5	2.218 0	0.000 0–0.049 8
5	-0.949 0	0.213 7	-0.921 3	1.218 6	2.139 9	0.002 9–0.039 7
8	-0.963 5	0.030 5	-0.939 1	1.199 6	2.138 7	0.002 9–0.045 6
10	-0.944 5	0.292 3	-0.918 9	1.224 5	2.143 4	0.006 2–0.033 6

increased by 4.7 mV.

Therefore, the optimal $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio in electrolyte was 8, while Cl^- concentration could be 375 mg/L and Mn^{2+} 3 g/L.

3.5 Effect of F^- concentration on Pb-Ag anode passivation process

3.5.1 Effect of F^- concentration on open circuit potential—time curves

Open circuit potential—time curves of Pb-Ag anode at different F^- concentrations are shown in Fig. 11. The corrosion potential showed negative shift with increase of F^- concentration, while the time needed for reaching steady state increased. As F is the most active halogen, corrosion ability of hydrofluoric acid is great in aqueous solution. Metal fluoride formation would accelerate the dissolution of metal. And PbF_2 precipitate resulted in formation of a protection layer through being adsorbed on surface of Pb-Ag anode, which made the system stable.

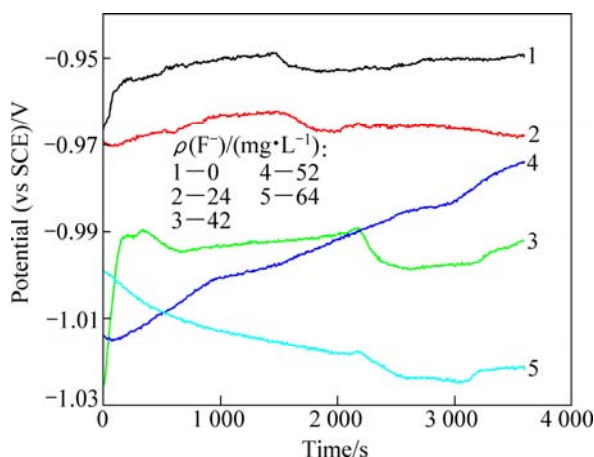


Fig. 11 Open circuit potential—time curves of Pb-Ag anode at different F^- concentrations

3.5.2 Effect of F^- concentration on anodic polarization curves

Anodic polarization curves of Pb-Ag anode at different F^- concentrations are shown in Fig. 12, and fitting parameters are listed in Table 6. ϕ_p and ϕ_F decreased by 0.211 7 V and 0.195 4 V, respectively, I_{\max} enhanced little, ϕ_{tr} fluctuated gently, and $\Delta\phi$ increased by

0.189 7 V with increasing F^- concentration from 0 mg/L to 42 mg/L. However, when F^- concentration was 42 mg/L, I_{\max} enhanced to 0.14 mA, I_p decreased by the range of 0.003 0–0.036 6 mA. Further increasing F^- concentration, ϕ_p and ϕ_F showed positive shift, $\Delta\phi$ diminished while I_{\max} and I_p increased again. Consequently, F^- concentration in electrolyte should be less than 42 mg/L.

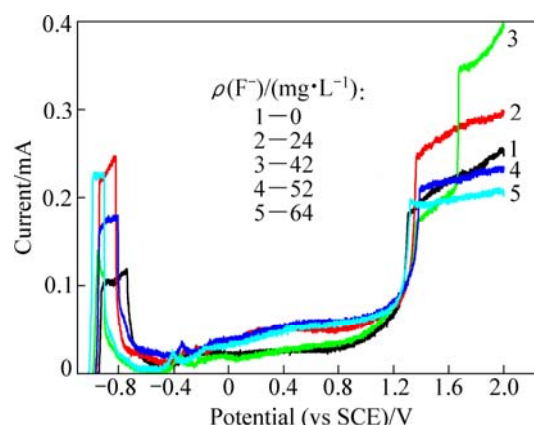


Fig. 12 Anodic polarization curves of Pb-Ag anode at different F^- concentrations

Corrosion mechanism of passivation layer with F^- is in accordant with other halogen ions. Furthermore, due to halogen ion with the smallest radius, F^- could achieve stronger activation and permeability, which made the destruction of passivation layer worse. And the damage to the passivation layer was serious when Pb-Ag anode was in passivation region.

4 Conclusions

1) It was highly recommended for passivation process of Pb-Ag anode when the concentration of H_2SO_4 in electrolyte was 180 g/L, Mn^{2+} was in 3–5 g/L and F^- was less than 42 mg/L.

2) Pb-Ag anode passivation process would not be affected when Cl^- concentration was less than 13 mg/L without any other ions or when $\text{Mn}^{2+}/\text{Cl}^-$ mass ratio was 8, while Cl^- concentration could reach 625 mg/L.

3) Existence of Cl^- and F^- in purified water would affect Pb-Ag anode passivation process.

Table 6 Fitting parameters of anodic polarization curves of Pb-Ag anode at different F^- concentrations

$\rho(\text{Cl}^-)/(\text{g}\cdot\text{L}^{-1})$	ϕ_p/V	I_{\max}/mA	ϕ_F/V	ϕ_{tr}/V	$\Delta\phi/\text{V}$	I_p/mA
0	-0.740 1	0.118 0	-0.632 8	1.148 4	1.781 2	0.009 2–0.030 9
24	-0.821 7	0.247 2	-0.701 8	1.138 1	1.839 9	0.014 1–0.051 9
42	-0.951 8	0.140 0	-0.828 2	1.142 7	1.970 9	0.003 0–0.036 6
52	-0.810 4	0.180 1	-0.651 6	1.148 4	1.800 0	0.021 5–0.059 0
64	0.904 5	0.229 1	-0.743 2	1.145 0	1.888 2	0.005 2–0.058 3

4) From the viewpoint of Pb-Ag anode passivation process, the purified water with SO_4^{2-} , F^- , Cl^- produced by limestone neutralization process could be used to zinc electrowinning.

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回用水中杂质离子对锌电解过程中 Pb-Ag 阳极钝化的影响

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摘 要: 采用线性扫描伏安法研究了回用水中杂质离子对锌电解过程中 Pb-Ag 阳极钝化的影响。结果表明: 回用水中 Cl^- 和 F^- 的存在将会影响电极的钝化过程。当溶液中 H_2SO_4 浓度为 180 g/L, 即酸锌比为 3.6, Mn^{2+} 浓度为 3~5 g/L, F^- 浓度小于 42 mg/L 时有利于 Pb-Ag 阳极钝化; 而当溶液中只存在 Cl^- 时, Cl^- 浓度必须低于 13 mg/L 才不会影响电极的钝化过程; 当溶液中同时存在 Mn^{2+} 和 Cl^- 且锰氯质量比为 8 时, 电极的钝化过程不会受到 Cl^- 的影响, 此时溶液中 Cl^- 的含量最高, 可以达到 625 mg/L。

关键词: 锌电解; Pb-Ag 阳极; 钝化; 杂质; 回用水

(Edited by YANG Hua)