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### Behavior of arsenic in zinc electrowinning

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**Abstract**: The effects of arsenic on the cathode polarization process in zinc electrowinning, its kinetics equation, parameters and polarization mechanism were studied by multiple electrochemistry approaches. The experimental results show that, if  $[As^{3+}] = 3$  mg/L, electrowinning first enters into stationary passivation range, and then enters into precipitation range, which indicates that the depolarization function of impurity arsenic is zinc electrowinning.

Key words: zinc electrowinning; arsenic; cathode polarization; kinetics equation; parameters

### **1** Introduction

Due to its low cost and abundance, zinc is widely used in the production of brass, galvanized steel, sacrifice anodes and primary and secondary batteries. The electrolytic recovery of zinc is one of the oldest industrial processes, whose importance lies in the great worldwide demand for this metal that currently reaches an overall production of 9 million tones per year[1]. However, even though the electrolytic processing of zinc has been in practice for many years, there still exist problems in the cathodic process.

The electrolytic recovery of zinc in industrial processes is carried out in a medium containing Zn( ) in  $H_2SO_4$  solution, in addition to trace amounts of metallic impurities. Aluminum is used as the cathode because it does not form alloys with zinc, thus facilitating zinc separation at the end of the electrolysis, and its density is low. There are reports[2–6] on impurities during zinc reduction process due to low current efficiencies and bad cathode.

On the other hand, laboratory scale research has shown interesting results. For example, WEI et al[7] studied the effects of impurities on current efficiency in zinc electrowinning, and the acceptable concentration of impurities is decreased a great deal when the acid concentration is high. The studies on others impurity[8–10] only discussed the current efficiency and cathode quality at the end of electrolysis without analyzing the phenomena and mechanism occurring during the deposition that may be important in the overall cathodic process. For example, LU et al[11] studied the effect of cobalt ion on the cathodic process in zinc electrowinning and its kinetics through multiple approaches. LIANA et al[12] studied comparatively the influence of Cd, Fe and Cu on zinc electrowinning, and the results show that zinc deposition is destroyed by the codeposition of Cd and Cu and hindered by ferrous.

In this work, the cathodic polarization curves of the zinc electrowinning process with adding arsenic in a sulfuric acid medium are studied with steady and transient state methods, and the kinetic parameters of electrochemistry are obtained. The influent mechanism of arsenic effect on zinc electrowinning is studied using EMPA result.

#### 2 Experimental

#### 2.1 Apparatuses and reagents

Apparatuses employed in the experiments were CMEM-1 electrochemistry instrument, L23-100 X-Y function recorder and EPMA-100 electron microprobe analyzer.  $ZnSO_4 \cdot 7H_2O$ ,  $As_2O_3$  and  $H_2SO_4$  were analytical reagents.

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## 2.2 Electrowinning experiments and testing conditions

The experiments were carried out in a three electrode cell a platinum electrode with an area of  $1 \text{ cm}^2$ was used as the cathode, a Pb-Ag alloy electrode was used as auxiliary electrode, and a saturated calomel electrode was used as the reference electrode. In the process of measuring the cathodic polarization curves, the ratio of cathode surface area to anode surface area was greater than 100. This ensures that the anodic process has a negligible influence on the cathodic deposition process since the anodic current density of polarization and anodic polarization potential were less than the cathodic polarization potential. The electrolyte was prepared with redistilled water, H<sub>2</sub>SO<sub>4</sub> and ZnSO<sub>4</sub>·7H<sub>2</sub>O containing 150 g/L H<sub>2</sub>SO<sub>4</sub> and 60 g/L Zn. During the experiments, the temperature of the electrolytic vessel was held fixed by means of an HHS-6 thermostatic bath[13].

The potential between the cathode and the reference electrode and current in the deposition process were marked by X-Y function instrument. The cathode deposition current was transformed as cathode deposition current density, the cathode reduction potential was expressed as cathode actual reduction potential. The cathode polarization curve was the relation curve between reduction potential and current density of cathode deposition process gained by dealing these data.

#### **3 Results and discussion**

In the research of cathode polarization curve, the cathode polarization curve of different As concentrations under different temperature is measured. The scanning rate is 30 mV/s.

# **3.1** Cathode polarization curves of different As concentrations at different temperatures

Figs.1-5 show the cathode polarization curves of different As concentrations at different temperatures. At the same temperature, the figures show that the current density increases and the reduction potential decreases slightly with increasing As<sup>3+</sup> concentration. From 20 to , the limiting current density of passivation point 60 increases from 50 to 80 mA/ $cm^2$ , its increasing amplitude is notable. The reason is that zinc-hydrogen microcell is shaped in electrolyte, and the measured current is the sum of microcell and zinc cathode. The current density of zinc-hydrogen microcell increases with increasing temperature, the precipitation of arsenic is violent, and so the harm of zinc electrowinning is largened. The phenomena of metal ions' sparsity in cathode portion is further adjusted by increasing temperature, but it is seen from the figures of cathode polarization curve that

precipitation of impurity, corrosion and resolution are increased, and overpotential is decreased, the deposition potential of hydrogen is moved towards positive. Furthermore, increasing temperature led to enlarge the consuming of energy resource, and bring negative effect on zinc deposition. So, the zinc electrolyte temperature is popularly controlled in the range of 40-50 . If [As<sup>3+</sup>] 3 mg/L, the electrowinning first enters into stationary passivation range, and then enters into precipitation range. It is indicated that the depolarization function of impurity arsenic is to zinc electrowinning. The reason is that the cathode deposition of arsenic is so easy, and its overpotential is not high too. Arsenic could occur electrochemistry reaction with acid in electrolyte, besides the reaction at the surface of electrode[2-3]. In the situation of higher acidity, arsenic forms poisonous AsH<sub>3</sub>[4-5].

 $As+3H^++3e=AsH_3$ 

 $HAsO_2+6H^++6e=AsH_3+2H_2O$ 

According to Ref.[14], the reactions in the cathode of microcell are



**Fig.1** Cathode polarization curves of different As<sup>3+</sup> concentrations at 20



**Fig.2** Cathode polarization curves of different As<sup>3+</sup> concentrations at 30



**Fig.3** Cathode polarization curves of different As<sup>3+</sup> concentrations at 40



**Fig.4** Cathode polarization curves of different As<sup>3+</sup> concentrations at 50



**Fig.5** Cathode polarization curves of different As<sup>3+</sup> concentrations at 60

 $As_2O_3+12H^++12e=2AsH_3+3H_2O$  $6Zn=6Zn^{2+}+12e$ 

The formed AsH<sub>3</sub> gas will be adsorbed on the surface of the cathode and act as an insulating layer and

inhibit zinc deposition at this location, which leads to the zinc deposition reaction achieving a dynamic equilibrium. Therefore, a passivation stable state is apparent in the polarization curve. The presence of arsenic has an adverse effect on zinc electrowinning, not only in terms of the current efficiency per unit area, but also because the quality of the zinc cathode decreases greatly. The quality of cathodic zinc is shown in EMPA shape figure.

The polarization current is different from that of steady state. The reason is that the measuring time of steady state is longer than that of transient state, when the scanning rate of steady state is 0.1 mV/s. The electrode is transferred from platinum plate to zinc plate, and the state of electrode surface is hardly kept accordance, because of the effect of accumulation collect on electrode surface. The impurity in ZnSO<sub>4</sub> solution has enough time to diffuse to the surface of electrode because of long measuring time. After 8 h electrowinning with addition of arsenic impurity, the surface of zinc is shriveled and becomes unstable. It is owing to the fact that minute hydrogen bubble is absorbed on the surface of zinc electrode, furthermore continues zinc deposition contained plentiful gas, come into being the state of looseness and nigrescence, and is dissolved by sulfate in the electrolyte. Fig.6 shows EMPA images of cathodic product. After added arsenic impurity, crystal shape of zinc presents blade, specific surface area increases, and



**Fig.6** EPMA images of cathode zinc: (a) Pure ZnSO<sub>4</sub>; (b) With As impurity

current density of unit area decreases compared with electrowinning product from pure  $ZnSO_4$  solution. These results in that current efficiency of zinc electrowinning quickly decreases, and surface roughness of zinc cathode increases.

# 3.2 Kinetic parameters of As effect on zinc electrowinning

According to cathode polarization curves measured by steady state method (see Fig.7), the dynamic parameters are analyzed. But the results of polarization curves of steady state and transient state are not accordance. Its reason is that the scanning rate of transient polarization curve is fast, and the quantity of zinc deposition on the surface of platinum plate is very small. But the scanning rate of steady polarization curve is slow, and the quantity of zinc deposition on the surface of platinum plate is big and platinum plate is covered because of long time. In addition, the impurity in ZnSO<sub>4</sub> solution has enough time to diffuse to the surface of electrode. This results in current density of steady polarization curve decreasing[7]. It is known from Tafel function that



Fig.7 Steady cathode polarization curves of As at 40

$$\eta = a + b \lg j \tag{1}$$

where  $\eta$  and j are known,  $\lg j$  and  $\eta$  are shown in Fig.8, intercept *a* and slope *b* can be known from Fig.8. So the electrowinning kinetic function of pure ZnSO<sub>4</sub> solution is  $\eta$ =0.207+0.142lg *j*, and the electrowinning kinetic function of ZnSO<sub>4</sub> solution containing arsenic 5 mg/L is  $\eta$ =0.224+ 0.150lg *j*.

Because of  $b=2.3RT/(\alpha nF)$  in Eq.(1), these factors are satisfied with Buter-volmer function among net current density  $j_c$  of zinc deposition, overpotential  $\eta$ , exchange current density  $j_0$  and charge transfer coefficient  $\alpha$  and  $\beta$ [15]:

$$j_{\rm c} = j - j^{\rm o} = j^0 \left[ \exp(\frac{\alpha nF}{RT} \eta_{\rm c}) - \exp(-\frac{\beta nF}{RT} \eta_{\rm c}) \right]$$
(2)



**Fig.8** Relationship between  $\lg j$  and  $\eta$  of steady state

Table 1 Dynamic parameters

Solution	а	b	α	$j_0$	п
ZnSO <sub>4</sub> solution	0.207	0.142	0.490	0.035	0.890
Adding 5 mg/L As	0.224	0.150	0.440	0.032	0.940

$$\eta_{\rm c} = \varepsilon_{\rm e} - \varepsilon_{\rm m} \tag{3}$$

$$\varepsilon_{\rm e} = \varepsilon^0 + \frac{RT}{nF} \lg a(\operatorname{Zn}^{2+}) = -0.751 \,\mathrm{V} \tag{4}$$

The electron transfer number n, exchange current density  $j_0$  and charge transfer coefficient  $\alpha$  are figured out through above equations. From this, the limit of electrowinning reaction rate can be figured out at given conditions, consequently the speed of electrode reaction can be compared, so it is propitious to progressing production process[15].

#### 4 Conclusions

1) The current density increases and the reduction increasing As<sup>3+</sup> potential little decreases with concentration. From 20 , limiting current to 60 density of passivation point increases from 50 to 80 mA/cm<sup>2</sup>; its increasing amplitude is notable. The zinc electrolyte temperature is popularly controlled in the . If  $[As^{3+}]$  3 mg/L, electrowinning scope of 40-50 first enters into stationary passivation range, and then enters into precipitation range. The depolarization function of impurity arsenic is to zinc electrowinning.

2) After adding arsenic impurity, the crystal shape of zinc presents blade, specific surface area increases, and current density of unit area decreases by compared with electrowinning product from pure  $ZnSO_4$  solution. And the current efficiency of zinc electrowinning quickly decreases, and surface roughness of zinc cathode increases because of existence of arsenic.

3) The electrowinning kinetic equation of  $ZnSO_4$  solution adding 5 mg/L arsenic is  $\eta$ =0.262+0.15lg *j*, and

electron transfer number  $\eta$  is 0.94, exchange current density  $j_0$  is 0.032, charge transfer coefficient  $\alpha$  is 0.44.

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