Electrochemical properties and microstructure of Al/Pb-Sn anodes during copper electrowinning

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Abstract. Al/Pb-Sn composite anodes used in copper electrowinning are prepared by electrodeposition onto the aluminum substrates in lead methanesulfonate electrolyte. Using potentiodynamic investigations, the information about corrosion resistance and oxygen reaction (OER) potential of these anodes in the lead dioxide region have been measured. The results show that with an increase of Sn content the OER potential and corrosion rate decrease. The SEM observations show that with an increase of Sn content the lead grain size increases. The X-ray diffraction (XRD) analysis show that with an increase of Sn content the phase of β-PbO₂ with lower corrosion rate and OER potential increases.

1. Introduction
To search for a suitable anode alternative to conventional Pb-Ca-Sn anodes which operate at relatively high OER over-potential, resulting in significant energy consumption and corrosion during copper electrowinning, Pb-Sb and Pb-Co alloy anodes and Pb/Pb-Sb, Pb/Pb-Co and Pb/Pb-Co₃O₄ composite anodes have been prepared.

The literature [1-2] pointed that Sb can decrease OER overpotential of anodes for copper electrowinning. As the Sb content is sufficiently low, there is no interconnecting network of Sb and corrosion is reduced. But higher Sb content reduces corrosion resistance of Pb-Sb anodes used in copper electrowinning [3]. Co into Pb (in a concentration of 0.02–0.1%) has long been known to reduce notably the OER over-potential and the corrosion rate of Pb. But the components of Pb and Co cannot mix in liquid-casting condition even in a large temperature range [4]. Co²⁺ into electrolyte increases the electrocatalytic activity and corrosion resistance of anodes but decreases the current efficiency in zinc electrowinning for the difficult formation of lead persulphate [5-6]. For the reason, experiments have been performed to include metallic Co in a anode. Lead-cobalt anodes are obtained by electrodeposition from a lead sulphamate electrolyte onto Pb-Ca [7] or Pb-Ca-Sn [8] plates. A comprehensive study on the behavior of Pb-Co₃O₄ [9-10] composite anodes showed that compared to commonly use metallurgical Pb-5.85Sb and Pb-0.08%Ca-0.74%Sn anodes the Pb-Co₃O₄ composite anode shows a considerable depolarizing effect on the OER. The corrosion rate of Pb-Co₃O₄ composite anode during prolonged polarization 96h under galvanostatic conditions is lower than that of Pb-Sb and Pb-Ca-Sn anodes. But Pb-Co₃O₄ composite anodes are still in the laboratory. Literature [11] points Al/Pb-PANI-WC anode has lower OER potential and corrosion rate, but it only give the electrochemical properties of the fruit surface which is not the best method for characterizing the properties of anodes during metal electrowinning.

Aluminum has a lower cost, density, and electrical resistivity than lead which is probably reduce
the bath voltage and weight used as the substrate of Al/Pb-Sn anodes. In this paper, Al/Pb-Sn composite anodes are obtained by electrodeposition onto aluminum plates in lead methanesulfonate electrolyte. Electrochemical properties and microstructure of Al/Pb-Sn anodes have been researching by potentiodynamic investigations, SEM observations and XRD analysis.

2. Experimental details

2.1. Process method

The Al/Pb-Sn composite anodes materials were obtained by electrodeposition onto 40mm×50mm×3mm aluminum plates in the lead methanesulfonate electrolyte consisted of HCH₃SO₃ 80-120mldm⁻³, and Pb²⁺ 150-200gdm⁻³ from Pb(CH₃SO₃)₂, Sn²⁺ 2-50gdm⁻³. The electrodeposition was carried out at a pH=1-3 and a cathodic current density of Jc=3Adm⁻², and with mechanical bubbling for 5h at 50°C.

The aluminum substrate were pretreated by buffing(mechanical buffing with fibre grinding wheel), degreasing (soak in fatty alcohol-polyoxyethylene ether degreaser at 40°C for 4 to 12h), caustic wash (soak in 12gdm⁻³ NaOH solution at 20-40°C for 120-180 seconds), acid pickling(38gdm⁻³ H₂SO₄ at 20-40°C for 10-30 seconds), zinc immersion (soak in 12gdm⁻³ NaOH, 15gdm⁻³ ZnO, 10gdm⁻³ KNaC₄H₄O₆·4H₂O, 2gdm⁻³ FeCl₃·6H₂O solution at 20-40°C for 60 seconds), acid pickling(3-10s), zinc immersion (at 20-40°C for 50 seconds) and nickel electroplating for 1 minute.

2.2. Measurement and analysis

The electrochemical workstation (CHI760C) with three electrodes were used for measuring CV for Al/Pb-Sn composite anodes in the copper electrowinning electrolyte consisted of Cu²⁺ (50gdm⁻³) and H₂SO₄ (200gdm⁻³) at 40°C. The counter electrode was the platinum plate, and the reference electrode was MSE. The Al/Pb-Sn composite anodes were used as the working electrode. Also, SEM and XRD were used for determining the surface microstructures and anodic layer phase for Al/Pb-Sn composite anodes.

3. Results and discussions

Figure 1 shows the cyclic voltammograms of Al/Pb-0.32%Sn, Al/Pb-0.41%Sn, Al/Pb-0.49%Sn, Al/Pb-0.62%Sn composite anodes after 24h of anodic polarization. It’s obvious from Figure 1 that with an increase of Sn content in Pb-Sn composite the branch is shifted further negatively showing lower OER potential, and the cathode peak d shifted slightly positively, leading to a bigger depolarization region which means that with an increase of Sn content in Pb-Sn composite the corrosion rate of Al/Pb-Sn anodes decrease.

Figure 2 shows the SEM of Al/Pb-0.32%Sn(a), Al/Pb-0.41%Sn(b), Al/Pb-0.49%Sn(c) and Al/Pb-0.62%Sn(d) anodes before anodic polarization. As shown in Figure 2, with an increase of Sn content the Pb grain size increases, showing a higher corrosion rate [10]. The result is contradiction with the corrosion information by CV analysis which is probably due to the content β-PbO₂ phase on anodic layer increase after 24h of anodic polarization (as shown in Figure 3). SEM observations on the fruit surface of Al/Pb-0.32%Sn shows that the Al/Pb-0.32%Sn anode has dense and cubic crystals of lead, possessing a chaotic orientation, but changing to a well-organized orientation gradually when the Sn content increase.
**Figure 1.** Cyclic voltammograms of Al/Pb-0.32%Sn, Al/Pb-0.41%Sn, Al/Pb-0.49%Sn, Al/Pb-0.62%Sn composite anodes after 24h of anodic polarization.

**Figure 2.** SEM of the Al/Pb-0.32%Sn(a), Al/Pb-0.41%Sn(b), Al/Pb-0.49%Sn(c) and Al/Pb-0.62%Sn(d) anodes before anodic polarization

**Figure 3.** XRD of the Al/Pb-0.32%Sn, Al/Pb-0.41%Sn, Al/Pb-0.49%Sn and Al/Pb-0.62%Sn anodes after 24h of anodic polarization.
Figure 3 shows the XRD of Al/Pb-0.32%Sn(1), Al/Pb-0.41%Sn(2), Al/Pb-0.49%Sn(3) and Al/Pb-0.62%Sn(4) anodes after 24h of anodic polarization. The XRD analysis indicates that these anodic layers of Al/Pb-Sn composite anodes are composed of $\alpha$-PbO$_2$, $\beta$-PbO$_2$, and Pb phase. The anodic layer of Pb anode presents a high content of $\alpha$-PbO$_2$ and lower of PbSO$_4$. The existence of Pb phase reveals that the layers are relatively thin. The major phases of Al/Pb-Sn anodes are $\alpha$-PbO$_2$, PbSO$_4$, $\beta$-PbO$_2$, and Pb. With an increase of Sn content, PbSO$_4$ first increases and then decreases while $\beta$-PbO$_2$ increases at the range of 20 from 43 to 50.

4. Conclusions

(1) The result of potentiodynamic investigations deduced that with an increase of Sn content, the corrosion rate and OER potential of Al/Pb-Sn anodes decrease during copper electrowinning.

(2) With an increase of Sn content of Pb-Sn composite the grain size of Pb increases, showing a higher corrosion rate which is contradiction with the corrosion information by CV analysis which is probably due to the content $\beta$-PbO$_2$ phase on anodic layer increase after 24h of anodic polarization.

Acknowledgments

Financial supports for this work from the Baoji science and technology project (14GYGG-2-4).

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