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Anodic behavior and microstructure of Pb-Ca-0.6%Sn, Pb-Co_3O_4 and Pb-WC composite anodes during Cu electrowinning

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ABSTRACT

Plumbum-Wolfram Carbide (Pb-WC) and Pb-Co_3O_4 composite anodes were prepared by electrodeposition from a lead mathanesulfonate electrolyte for Cu electrowinning. By means of the cyclic voltammograms (CV) and Electrochemical Impedance Spectroscopy (EIS), the mechanism of the anodic processes playing on the surface of Pb-Ca-0.6%Sn, Pb-WC and Pb-Co_3O_4 composite anodes had been measured. Cyclic voltammograms analysis revealed the corrosion rate of the anodic layer in PbO_2 region. EIS analysis pointed out that the reaction kinetics varied a lot during electrolysis for it is a process indicating the formation and stabilization of anodic layer. At the very beginning of galvanostatic electrolysis, the reaction oxygen evolution (OER) was Pb to $PbSO_4$ and α-PbO_2. On the anodic layer after 24 h electrolysis, the more β-PbO_2 appears, and the adsorption resistance took a dominant part in the whole impedance. SEM observed the microstructures of the conventional Pb-Ca-0.6%Sn, Pb-WC and Pb-Co_3O_4 composite anodes before and after 24 h electrolysis, and X-Ray Diffraction (XRD) analysis showed the phase after 24 h electrolysis of the three anodes for Cu electrowinning.

1. Introduction

Conventional Pb-Ca-Sn anodes for Cu electrowinning operate at relatively high oxygen over-potential, resulting in significant energy consumption and corrosion. The association of the conducting aluminum matrix and actives dispersed phase has been wildly studied as a new type of composite anodes for Cu electrowinning with a lower OER potential.

The classical anode for Cu electrowinning is Pb-6%Sb alloy anode. Sb is a favorable metal for lowering the OER potential on Pb but it has been found that the corrosion rate increases with an increase of the Sb content [1–3]. Some researches point that cobalt ion can reduce the OER potential and corrosion rate of anodes for metal electrowinning. Adding Co^{2+} into electrolyte increases the electrocatalytic activity and corrosion resistance of anodes, but decrease the current efficiency in zinc electrowinning for the difficult formation of lead persulphate [4,5]. For this reason, experiments have been performed in order to include metallic cobalt in the anodes. Cobalt does not form an alloy with lead and that is why a third component is used for the inclusion of Co in the Pb alloy Pb-Co. Sn is the component that forms an alloy with Co, with Ag, and with Pb [6]. Lead-cobalt anodes are obtained by electrodeposition from a lead ammonium sulphamate electrolyte onto Pb-Ca [7]or Pb-Ca-Sn [8] plates. A comprehensive study on the behavior of Pb-Co_3O_4 composite anode by the authors [9] showed that the Pb-Co_3O_4 composite anode shows a considerable depolarizing effect on the oxygen evolution reaction compared to commonly used metallurgical Pb-5.85Sb and Pb-0.08%Ca-0.74%Sn anodes. The corrosion resistance of Pb-Co_3O_4 composite anode during prolonged polarization 96 h under galvanostatic conditions is higher than that of Pb-Sb and Pb-Ca-0.6%Sn anodes. WC is used as electrolysts for photoelectrochemical cell and anode for zinc electrowinning [10,11]. Co_3O_4 is applied in lithium-ion battery with a highest specific capacitance [12,13].

Aluminum has a lower cost, density and electrical resistivity than lead which are probably to reduce the bath voltage, cost and weight of the aluminum-based anodes for Cu electrowinning [10].

Cyclic voltammograms analysis shows the information about the change of anodic potentiodynamic and the formation during the beginning galvanostatic electrolysis. EIS analysis has been widely applied in the studies of oxygen evolution process on metal-oxide anodes and also can discuss the importance of the electrochemical adsorption behaviors of chemisorbed intermediates

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involved in the electrocatalytic multistep mechanism of OER at electrodeposited α-PbO_2 and β-PbO_2 electrodes [14].

In this paper, Al/Pb-WC, Al/Pb-Co_3O_4, Pb/Pb-WC and Pb/Pb-Co_3O_4 composite anodes were obtained by electrodeposition from a lead methanesulfonate electrolyte. Cyclic voltammograms and EIS carried out a copper sulfate electrolyte. By means of cyclic voltammograms and EIS analysis, the mechanism of the anodic processes playing on the surface of Al/Pb-WC and Al/Pb-Co_3O_4 composite anodes during Cu electrowinning have been measured. After 24 h of galvanostatic electrolysis, the SEM observations and XRD analysis showed the microstructure and phase of the conventional Pb-Ca-0.6%Sn, Pb-WC and Pb-Co_3O_4 composite anodes.

2. Theories of CV and EIS

In this paper, the cyclic votammograms of Pb-Ca-0.6%Sn, Al/Pb-Co_3O_4, Pb/Pb-WC, Pb/Pb-Co_3O_4 and Al/Pb-WC anodes after 24 h of galvanostatic electrolysis are nonreversible, so the function (1) by A. J. Bard and L. R. Faulkner [15] can be used in this case. Classic Butler-Volmer kinetics model which is necessary before equations can be derived for most electrochemical approaches apply in this part, then a plot of ln $k_f(E)$ versus E should be liner with a slope $-\alpha F/_{RT}$. Based on R. A. Marcus' and P. Siddarth's [16] researches and Frank-Condon principle, equation (2) can be obtained and α depends on potential in a particular way.

$$\ln k_f(E) = \ln D_o^{1/2} - \ln \frac{[I_1 - I(t)]}{i(t)}, \tag{1}$$

$$\alpha = \frac{1}{2} + \frac{F\left(E' - E^{\Theta}\right)}{2\lambda}, \tag{2}$$

$$\lambda = \lambda_i + \lambda_0, \tag{3}$$

$$\lambda = 2\Delta G_f^{\neq}, \tag{4}$$

where $k_f(E)$ is the potential-dependent rate constant as a function of potential E, E is an electrode versus a reference at different scanning speed v, k_f is heterogeneous rate constant for reduction, D_o is diffusion coefficient of O, $I(t)$ is current semi-integral, I_1 is limit value of $I(t)$, $i(t)$ is experimental current; F is the faraday constant, E' is electron energy, E^{Θ} is standard potential of an electrode or couple, α is transfer coefficient; Reorganization energy for electron transfer λ can be obtained by equation (3), λ_i represents the contribution from reorganization of species O, and λ_0 that from reorganization of the solvent. Considering electrode reaction and ignoring self-exchange reaction and λ_i, equation (4) can be obtained; $\Delta G_f^{\neq}$ is standard Gibbs free energy of forward action.

Fig. 1 shows the electrical equivalent circuit to simulate impedance. As shown in Fig. 1, C_{dl} represents the double-layer capacitance, and R_s represents the uncompensated solution resistance. By theoretical calculation, in this case, R_fC_f takes in to count the capacitive response of oxide layer and R_f, C_f represents the resistance and capacitance of the oxide layer, respectively. In the simulation, Constant Phase Elements (CPEs) are used instead of capacitors (C_{dl} and C_a) to fit the experimental data. Moreover, the double layer capacitance C_{dl} is coupled with the uncompensated solution resistance R_s and the charge transfer resistance R_t according to the following equation (5) [17]:

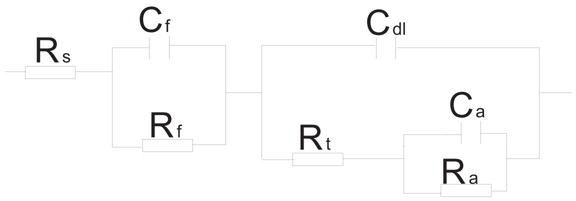

Fig. 1. Electrical equivalent circuit used to simulate the impedance data.

$$Q_{dl} = (C_{dl})^n \left[(R_s)^{-1} + (R_t)^{-1}\right]^{(1-n)}. \tag{5}$$

In This case, C_{dl} is calculated with Q_{dl} value obtained from the CNLS (Classical Nuclear Location Signal) fit [18,19]. Q_{dl} parameters can be used to describe the variation of adsorption pseudo-capacitance C_a during the electrolysis, which actually reflect the variation of intermediate and phase coverage on the anodic layer [20,21]. The consideration above based on that when n is close to 1, the Q parameters adequately describe the pseudo-capacitance [22,23].

3. Experimental details

3.1. Anodes

The composite materials were obtained by electro-deposition on to 40 × 50 × 2 mm aluminum plates and Pb-Ca-0.6%Sn plates. The coatings were deposited from a standard lead methanesulfonate electrolyte containing organic additives: Organic additive is 50–100gdm^{-3}, 150-200gdm^{-3} $Pb(CH_3SO_3)_2$, 50-150gdm^{-3}Co_3O_4, 50-150gdm^{-3}WC. The electrodeposition was carried out at pH values in the range of 1–2 at a cathodic current density Jc = 2Adm^{-2} and with mechanical bubbling for 24 h at 40 °C. The content of the Co_3O_4 and WC in the composite coatings measured by AAS (Atomic Absorption Spectroscopy) was in the range of 14%–15%.

The aluminum-matrix was pretreated by buffing (mechanical buffing with fibre grinding wheel), degreasing (soak in fatty alcohol-polyoxyethylene ether degreaser at 40 °C for 4–12 h), caustic wash (soak in 12gdm^{-3} NaOH solution at 20–40 °C for 120–180 s), acid pickling (38gdm^{-3} H_2SO_4 at 20–40 °C for 10–30 s), zinc immersion (soak in 12gdm^{-3} NaOH, 15gdm^{-3} ZnO, 10gdm^{-3} $KNaC_4H_4O_6 \cdot 4H_2O$, 2gdm^{-3} $FeCl_3 \cdot 6H_2O$ solution at 20–40 °C for 60 s), acid pickling (3–10s), zinc immersion (at 20–40 °C for 50 s) and nickel electroplating in $NiSO_4$ electrolyte (100gdm^{-3} $NiSO_4$, 15gdm^{-3} NaCl, 25gdm^{-3} H_3BO_3, 100gdm^{-3} $C_6H_5Na_3O_7$) for 1 min.

The Pb-Ca-0.6%Sn matrix was pretreated by degreasing, mechanical polishing and etching. Anodic etching at current at a current density of 1000Am^{-2} for 30 min in boiling 10% oxalic acid.

3.2. CV and EIS method

The cyclic voltammograms and EIS of the Pb-Co_3O_4, Pb-WC anodes and conventional Pb-Ca-0.6%Sn anode (a geometric area of 1 cm^2) were obtained at the beginning 0 h, 12 h and 24 h of galvanostatic electrolysis, when the PbO_2 layer had already been formed. The galvanostatic electrolysis was performed at 20 mAcm^{-2} in a glass cell at constant temperature of 40 °C.

An electrochemical workstation (CHI760C) with three electrode systems was used for measuring cyclic voltammetry curves and EIS characterization for Pb-Co_3O_4, Pb-WC anodes and conventional Pb-Ca-0.6%Sn anode in the synthetic Cu electrowinning electrolyte as follows: Cu^{2+}50gdm^{-3}, H_2SO_4 200gdm^{-3}, temperature 40 °C. The counter electrode was platinum plate and the reference electrode was Mercurous Sulfate Electrode (MSE) with a potential $E_{MSE} = +0.64V$. The Pb-Co_3O_4 and Pb-WC composite anodes and