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Effects of polyaniline on electrochemical properties of composite inert anodes used in zinc electrowinning

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Abstract: In order to search for a suitable anode material used in zinc electrowinning in place of Pb−Ag alloy, Al/Pb−PANI (polyaniline)−WC (tungsten carbide) composite inert anodes were prepared on aluminum alloy substrate by double pulse electrodeposition (DPE) of PANI and WC particles with Pb^{2+} from an original plating bath. Thereafter, anodic polarization curves, cyclic voltammetry curves and Tafel polarization curves for the composite inert anodes obtained under different PANI concentrations in the original plating bath were measured, and the microstructural features were also investigated by scanning electron microscopy (SEM). The results show that Al/Pb−PANI−WC composite inert anode obtained under PANI concentration of 20 g/L in the original plating bath possesses uniform microstructures and composition distributions, higher electrocatalytic activity, better reversibility of electrode reaction and corrosion resistance in a synthetic zinc electrowinning electrolyte of 50 g/L Zn^{2+}, 150 g/L H_2SO_4 at 35 °C. Compared with Pb−1%Ag alloy, the overpotential of oxygen evolutions for the composite inert anode are decreased by 185 mV and 166 mV, respectively, under 500 A/m^2 and 1000 A/m^2.
Key words: composite inert anodes; double pulse electrodeposition; anodic polarization curves; cyclic voltammetry curves; Tafel polarization curves; microstructures

1 Introduction

Zinc is mainly extracted from its sulfide ores, oxide ores or other secondary resources by means of electrowinning process for hydrometallurgy. Generally, the electrode materials used in zinc electrowinning must meet the following requirements of good electroconductivity, mechanical strength and electrocatalytic activity, excellent corrosion resistance and long service life. At present, only Pb−Ag alloy anode in which Ag content ranges form 0.5% to 1.0% (mass fraction), is used extensively in zinc electrowinning, but it also has some shortages of higher overpotential of oxygen evolution, worse conductivity and mechanic performance [1−5]. The overpotential of oxygen evolution, current efficiency and corrosion rate for Pb−Ag−Sb, Pb−Ca−Sn, Pb−Ag−Ca and Pb−Co alloy anodes used in zinc electrowinning were investigated and some valuable results have been obtained [6−8].

PANI particle has been intensively researched in recent years owing to its high conductivity, good electrocatalytic activity and environment stability, and has a large variety of applications in the fields of light-emitting materials, electronic device materials, chemical sensor materials and electrode materials [9−13]. WC particle can increase distortion resistance and decrease overpotential of oxygen evolution in zinc electrowinning when deposited into matrix metal Pb or metal oxidation PbO_2. Compared with direct current electrodeposition (DCE), pulse electrodeposition (PE) with higher instantaneous current density can increase cathodic activation polarization and decrease cathodic concentration polarization, which is easier to make out

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metal matrix composite materials in the fine grained structures by means of relaxation of pulse current [14−18]. In order to search for a suitable anode material used in zinc electrowinning in place of Pb−Ag alloy, a new kind of Al/Pb−PANI−WC composite inert anode was prepared by double pulse electrodeposition (DPE) and it has been found to a potential anode material. In this research, effects of PANI concentrations in an original plating bath on electrochemical properties and microstructural features for the composite inert anodes were studied.

2 Experimental

2.1 Preparation of composite inert anodes

Al/Pb−PANI−WC composite inert anodes were prepared on aluminum alloy substrate by DPE from an original plating bath. The dimensions of plating cell were 80 mm(L)×60 mm(W)×130 mm(H); a pair of electrolytic lead sheets with dimensions of 30 mm(L) × 3 mm(W) × 100 mm(H) were used as electrodepositing anodic materials, and were connected with anodic wire of DPE supply; aluminum alloy sheet with dimensions of 30 mm(L)×2 mm(W)×60 mm(H) was used as cathodic material, and was connected with cathodic wire of DPE supply; the electrode spacing between anodic material and cathodic material was 40 mm.

The original plating bath compositions used for electrodepositing Al/Pb−PANI−WC composite inert anodes were as follows: 180 g/L $Pb(AC)_2$, 220 mL/L HBF_4, 20 g/L H_3BO_3, 1.0 g/L gelatin, 0.2 g/L thiourea, 5 mL/L polyethylene glycol, 20 g/L WC and 0−25 g/L PANI. The plating temperature was maintained at 35 °C, the plating pH value was about 1.0. The waveforms of DPE supply used for electrodepositing the composite inert anode from the original plating bath were as follows: forward and reverse pulse duty cycles were 10% and 30% respectively, forward and reverse pulse average current densities were 4 A/dm^2 and 0.4 A/dm^2 respectively, and forward and reverse pulse working time were 200 ms and 20 ms, respectively. The electrodeposition time was 1.5 h. Thereafter, the composite inert anodes were used for measuring of electrochemical properties and surface microstructural features.

To guarantee better dispersion of PANI and WC particles in the original plating bath and in the composite inert anodes, the original plating bath was dispersed by ultrasonic device with 2 A for 30 min before DPE. After that, the mechanical stirring was used for the original plating bath in DPE experiments and the stirring speed was controlled at 150 r/min.

2.2 Measurement and analysis

The electrochemical workstation (CHI760C) with three-electrode system was used for measuring the anodic polarization curves, cyclic voltammetry curves and Tafel polarization curves for the composite inert anodes in a synthetic zinc electrowinning electrolyte of 50 g/L Zn^{2+}, 150 g/L H_2SO_4 at 35 °C. The auxiliary electrode was graphite, the reference electrode was a saturated calomel electrode, the working electrode was the composite inert anode and the working areas were 1.0 cm^2. The working electrode and auxiliary electrode were connected with KCl agar salt bridge, and their electrode spacing was 30 mm. Scanning electron microscope (SEM, XL30 ESEM-TEP+EDAX) was used for determining surface microstructures and composition distributions of the composite inert anodes.

3 Results and discussion

3.1 Anodic polarization curves and kinetic parameters of oxygen evolution

At a constant scan rate of 5 mV/s, anodic polarization experiments for Al/Pb−PANI−WC composite inert anodes obtained under different PANI concentrations in the original plating bath, were carried out in a synthetic zinc electrowinning electrolyte of 50 g/L Zn^{2+}, 150 g/L H_2SO_4 at 35 °C, and the results are shown in Fig. 1.

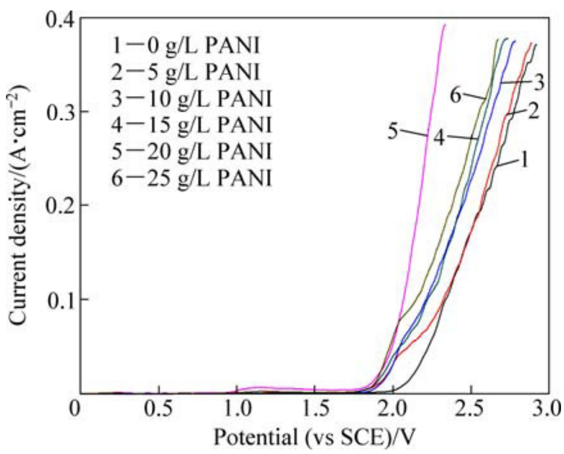

Fig. 1 Anodic polarization curves for composite inert anodes obtained under PANI concentrations in original plating bath

As shown in Fig. 1, the relationships of PANI concentrations in the original plating bath and anodic polarization curves have identical characteristics in the potential ranges of 0−2.9 V, but PANI concentrations in the original plating bath have no obvious effects on the initial anodic behavior for the composite inert anodes in the potential ranging from 0 V to 1.8 V. It can also be seen that the potentials of oxygen evolution for the composite inert anodes obtained under PANI concentrations of 0 g/L and 5 g/L in the original plating bath, are higher in the potential ranging from 1.8 V to