Hydrometallurgy 141 (2014) 31–35

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

The effects of additives on the electrowinning of zinc from sulphate solutions with high fluoride concentration

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ARTICLE INFO

Article history:
Received 12 March 2013
Received in revised form 25 August 2013
Accepted 7 September 2013
Available online 19 September 2013

Keywords:
Zinc electrowinning
Acidic sulphate electrolytes
Fluoride
Additives
Deposit morphology

ABSTRACT

Effects of additives on zinc electrowinning from zinc sulphate aqueous solution with a higher concentration fluoride (300 mg L^{-1}) have been investigated based on the measurements of polarization curves (PC), cyclic voltammetry (the working electrode was made from pure aluminum, a graphite rod was used as counter and a saturated calomel electrode (SCE) as the reference electrode) and zinc electrodeposition experiments, in which gelatin, boric acid, citric acid and aluminum sulfate served as additives and were added into the electrolytes alone or in combination with different dosages. Zinc deposit morphology on aluminum cathode surface after zinc electrowinning was observed using SEM (scanning electron microscopy). The results indicated that all additives within a certain concentration scope increased nucleation overpotential, stimulated cathodic polarization and promoted electrodepositing with fine-grained zinc. The nucleation overpotential increased from 124 mV to 183 mV in addition of 5 mg L^{-1}. Finer-grained zinc deposits, lower specific power consumption (maximum reduction from 3129 kWh t^{-1} to 2192 kWh t^{-1}) and higher current efficiency (86.2% to 96.2%) were available by these additives combination.

1. Introduction

A contemporary method for zinc production is its extraction from acid zinc sulphate aqueous solution by electrolysis with aluminum cathodes and anodes made of lead–silver (~1 wt.% Ag) alloy, more than 80% of world zinc production is obtained by electrowinning (Muresan et al., 1996a,b). As well-known, zinc electrowinning process is particularly sensitive to detrimental impurities in the electrolyte solution, which is a major problem to increase electrolytic zinc quality and current efficiency. Above all in the presence of fluoride ions larger than 100 mg L^{-1}, the current efficiency will be obviously decreased and zinc deposits will become loose, in addition to accelerating the corrosion of aluminum cathode making zinc stripping more difficult and shortening the service life of aluminum electrode (Xue et al., 1991). Adding some additives into zinc sulphate electrolytes is an effective alternative method to depress the detriment originated from fluoride ions. Appropriate amounts of additives are indispensable to promote the formation of fine-grained, smooth and compact zinc deposits and to inhibit the discharge of H^+ ions in zinc electrowinning process due to zinc re-dissolution (Cachet and Wiart, 1990; Ivanov and Stefabov, 2002; Muresan et al., 1996a,b).

Organic additives, in particular glues (Robinson and O'Keefe, 1976), are commonly used to promote deposit growth and to minimize the adverse effects of the impurities. Nevertheless the operating current density in zinc industry is normally limited to about 300–600 A m^{-2}. A considerable saving of capital investment together with reductions in operating costs is expected if the operating current density could be increased whilst maintaining high current efficiency and electrolytic zinc quality.

A number of organic compounds exhibit better performance than the traditional glues. Mathieu et al. (Mathieu et al., 1988) have studied the effect of 2-butyne-1, 4-diol and shown its beneficial effect on improving current efficiency. MacKinnon et al. have tested that tetrabutylammonium chloride (TBAC1) could improve surface morphology and current efficiency (Mackinnon et al., 1987). Fray and Thomas (Thomas and Fray, 1981) claimed that they could operate at a current density of 2000 A m^{-2} using TBAC1. In addition, 2-picoline (Das et al., 1996), hydrooxyethylated-butyne-2-diol-1, 4 (EAA), triethylbenzylammonium chloride (TEBA) (Ivanov, 2004; Stefabov and Ivanov, 2002), 1-butyl-3-methylimidazolium hydrogen sulfate-[BMIM]HSO_4 (Zhang and Hua, 2009, 2012), and perfluorinated surfactant (Cachet and Wiart, 1999), as additives to improve the electrodeposition characteristics of zinc from acidic sulphate electrolytes have been investigated. However, these unusual and costly additives might be uneconomic. Furthermore, it is uncertain that these additives can play the same role in the presence of a higher concentration fluoride as well.

In our present work, in the presence of a higher concentration fluoride, the effects of several usual and cheap additives, such as gelatin, boric acid, citric acid and aluminum sulphate used alone or in combination (two or more additives) on the morphology and the purity of zinc

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http://dx.doi.org/10.1016/j.hydromet.2013.09.007

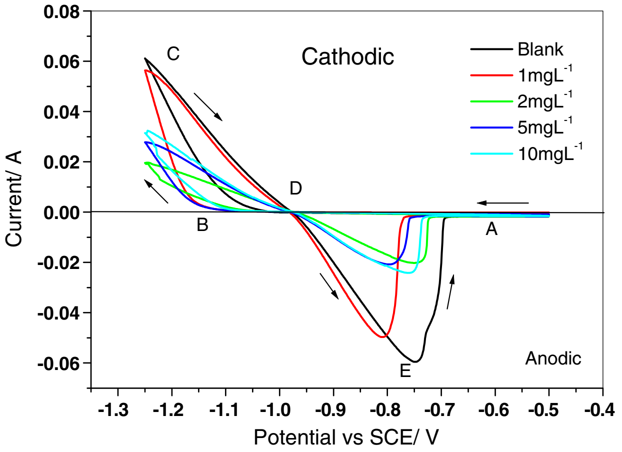

Fig. 1. Cyclic voltammograms of simulated zinc sulphate electrolyte added gelatin only. The scan rate was 10 mV s^{-1}.

deposits, as well as on the polarization were investigated in detail, based on electrochemical measurements and zinc electrowinning experiments.

2. Experimental methods

All chemical reagents were of analytical grade (AR) and all solutions were prepared with distilled water. Sodium fluoride (NaF), manganese sulfate ($MnSO_4$), zinc sulfate ($ZnSO_4$) and sulfuric acid (H_2SO_4), gelatin, boric acid, citric acid and aluminum sulphate were used in this work without further purification. Simulated zinc sulfate aqueous solutions, which contained 50 g L^{-1} Zn^{2+}, 150 g L^{-1} H_2SO_4, 5 g L^{-1} Mn^{2+}, 300 mg L^{-1} F and various additives types with different concentrations from 1 mg L^{-1} to 10 mg L^{-1}, were prepared and used in electrochemical measurements. A CHI660D electrochemical workstation (Shanghai CH Instruments Company in China) served as the analysis of cyclic voltammetry and potentiodynamic polarization. All measurements were performed in a three-electrode plexiglass cell with 50 mL electrolyte. The working electrode was made from pure aluminum with an effective area of 0.30 cm^2. A graphite rod was used as counter and a saturated calomel electrode (SCE) as the reference electrode.

Cyclic voltammetric experiments were carried out at 30 °C under atmospheric condition and scanned at a constant scan rate of 10 mV s^{-1} from the initial potential of −0.50 V to the final potential of −1.25 V.

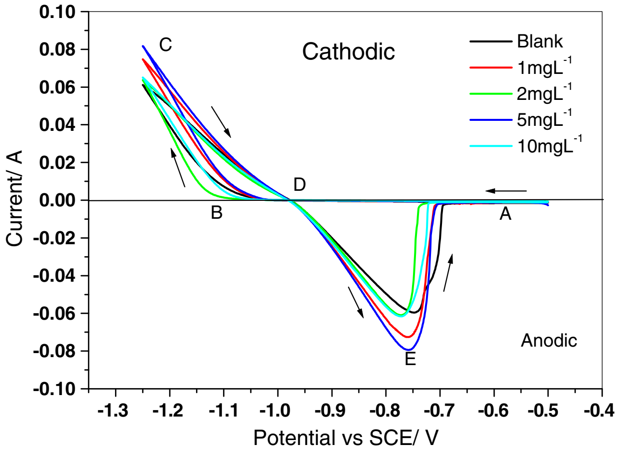

Fig. 2. Cyclic voltammograms of simulated zinc sulphate electrolyte added boric acid only. The scan rate was 10 mV s^{-1}.

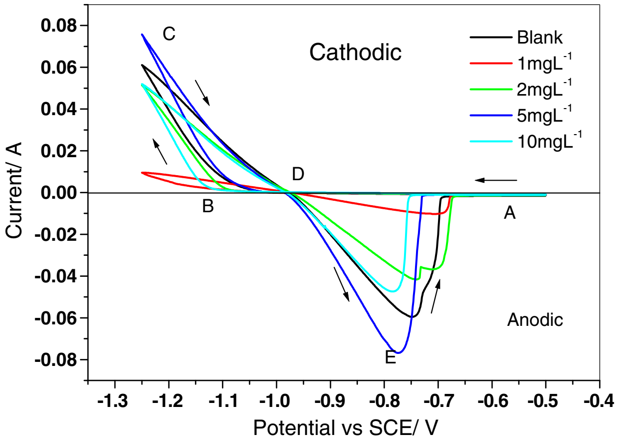

Fig. 3. Cyclic voltammograms of simulated zinc sulphate electrolyte added citric acid only. The scan rate was 10 mV s^{-1}.

After the cyclic voltammetric tests, the potentiodynamic polarization measurements were studied from ca. −1.05 V to −1.30 V with a constant rate of 5 mV s^{-1}. All potentials were recorded with respect to the SCE. Before each experiment, the aluminum sheet electrode was polished successively with fine grade emery paper, degreased with anhydrous alcohol in an ultrasonic bath for 10 min, washed with distilled water and finally dried with filter paper.

Small-scale galvanostatic electrolysis experiments were performed in a plexiglass cell with 250 mL electrolyte. A pure aluminum sheet and two parallel Pb–Ag plates were used as the cathode and anode respectively. The distance between cathode and anode was 2 cm, and zinc was deposited on both sides of the cathode onto a total area of 8 cm^2. All the electrowinning experiments were performed at a constant current density of 500 A m^{-2} for 1.5 h at 35 °C. After electrolysis, the cathode was removed from the cell and washed thoroughly with distilled water and dried. Faraday's law was used to calculate the current efficiency by weight. The surface morphology of the zinc deposits on the aluminum surface was observed by SEM (Inspect, FEI Corporation).

3. Results and discussion

3.1. Cyclic voltammetry

The cyclic voltammograms for various additives alone and the combined recorded for zinc electrowinning are depicted in Figs. 1–5. The cyclic voltammetric scans on the aluminum electrode were initiated at −0.5 V vs SCE (point'A'in Fig. 1), scanned in the cathodic direction

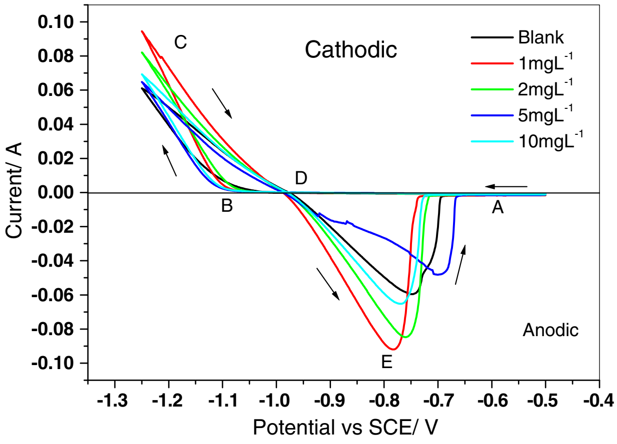

Fig. 4. Cyclic voltammograms of simulated zinc sulphate electrolyte added $Al_2(SO_4)_3$ only. The scan rate was 10 mV s^{-1}.