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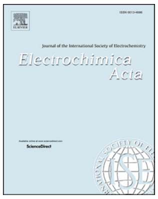

Effect of ionic liquid additives on oxygen evolution reaction and corrosion behavior of Pb-Ag anode in zinc electrowinning

Nabil Sorour [a, *], Chaoran Su [a], Edward Ghali [a], Georges Houlachi [b]

[a] Department of Mining, Metallurgical and Materials Eng., Laval University, Québec, G1V 0A6, Canada
[b] Hydro-Québec Research Institute (LTE), Shawinigan, QC, G9N 7N5, Canada

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ABSTRACT

Three ionic liquid salts, 1-Ethyl-3-methylimidazolium chloride [EMIM]Cl, 1-Ehyl-3-methylimidazolium bromide [EMIM]Br, and 1-Ehyl-3-methylimidazolium ethyl sulfate [EMIM]ESO_4 were chosen as additives in order to examine their effects on the oxygen evolution reaction (OER) and corrosion of Pb-0.7%Ag anode in zinc electrowinning. Results of 24 h of anodic polarization showed that the presence of these additives depolarized the OER. A reduction of 25 mV of anodic potential was obtained by addition of 5 mg L^{-1} of [EMIM]ESO_4 to that obtained from free-addition electrolyte. Corrosion measurements employing linear polarization technique revealed that corrosion rate of Pb-0.7%Ag was decreased by ~25–42% by the addition of [EMIM]ESO_4 or [EMIM]Br. Corrosion current was found to be decreased in the order of [EMIM]ESO_4 < [EMIM]Br < Gelatin ≤ Blank < [EMIM]Cl. Electrochemical impedance spectroscopy demonstrated that addition of ILS to the zinc sulfate electrolyte increased the charge transfer resistance of the anodic dissolution reaction except for [EMIM]Cl. Zero resistance ammeter and scanning reference electrode techniques showed the same corrosion tendency obtained from other techniques and proved that no localized corrosion was observed in the presence of Cl ions.

1. Introduction

Lead has been used since many decades as anode material in the zinc electrowinning industry. However, pure lead is a weak material that tends to creep and deform during operation [1]. In addition, it has significant shortcomings during electrolysis, such as high overpotential of oxygen evolution reaction (OER), low corrosion resistance and lead contamination of cathodic zinc [2,3]. The OER overpotential could be reduced if lead is alloyed with specific elements. Small amounts of silver (0.3–1.0%) alloyed with lead were found to decrease the overpotential by 80–120 mV compared to that of pure lead [4]. Also, the benefits of silver on improving the corrosion resistance of the anode during electrolysis cannot be neglected [5].

Two main reactions occur on the lead-based anode during zinc electrodeposition, the evolution of oxygen gas and the formation of $PbSO_4$ (Eqs. (1) and (2)) [6].

$$H_2O \rightarrow 2H^+ + 2e^- + \frac{1}{2}\,O_{2(g)} \quad E^o = \ 1.23 \text{ V vs SHE} \tag{1}$$

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^- \quad E^o = \ 0.35 \text{ V vs SHE} \tag{2}$$

The oxidation of water to oxygen is theoretically possible at 1.23 V, but production of oxygen is only observed at potentials higher than the equilibrium potential for the $PbSO_4/PbO_2$ (Eq. (3)). Therefore, the evolution of oxygen gas requires overpotential.

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + H_2SO_4 + 2H^+ + 2e^- \quad E^o = \ 1.685 \text{ V vs SHE} \tag{3}$$

Approximately, 60% of the consumed energy during the zinc electrowinning process is used for the anodic reactions [7]. Although many studies and attempts have been carried out on improving the anode material, they mainly focused on lead-based alloys and metal-based coated anode such as Ti and Ni [8–11]. Mixed metal oxides (MMO) anodes are being recently developed to reduce the overpotential of OER. Results using MMO anodes with different oxides (TiO_2 - Ta_2O_5 - IrO_2 - RuO_2) were obtained in terms of voltage reduction and service life [12,13]. However, more work is required to improve and evaluate the electrochemical performance and corrosion resistance of these anodes in the electrowinning industry.

A low cost method to improve the performance of lead-based anode is to use appropriate additives. Cachet et al. [14] have

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* Corresponding author.
E-mail address: nabil.sorour.1@ulaval.ca (N. Sorour).

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examined the effect of Mn^{2+} and Co^{2+} ions on the kinetics of Pb and Pb-Ag anodes. Addition of low concentrations of Mn^{2+} (<5 g L^{-1}) enhanced the kinetics of Pb-Ag anode and decreased the overpotential of OER. The formed MnO_2 layers on the anode surface enhanced the formation of β-PbO_2 more than α-PbO_2. The glassy deposit of MnO_2 β-PbO_2 was found to have more catalytic effect on the OER and exhibited advanced protecting properties against corrosion of lead-based anode [15]. Although Mn^{2+} showed a beneficial effect on the anodic behavior, it was found that these ions have a negative effect on the cathodic process. The formed MnO_4^- ions catalyze the hydrogen evolution reaction resulting in low cathodic current efficiency [16,17]. The addition of Co^{2+} reduced the electrode polarization, mainly for the pure Pb anode more than for the Pb-Ag. The formation of Co^{3+} after oxidation of Co^{2+} at the anode catalyzed the oxidation of water and decreased the charge transfer resistance of this reaction [18]. It has been shown that addition of cobalt to acidic zinc electrolyte reduced the formation of PbO_2 and decreased Tafel slope from 120 to 62–68 mV decade^{-1}, giving an indication of its catalytic effect on OER [14]. However, still the high cost of cobalt and its negative effect on the cathodic current efficiency are obstacles for the industrial applications.

Several organic additives have been widely examined during the cathodic process. Many studies have been conducted on the effect of these additives on cathodic polarization, current efficiency, morphology, and quality of zinc deposit [19]. However, there are few studies on the effect of additives on the anodic behavior. Among these additives, ionic liquids salts (ILS), which showed a good performance on the cathodic reactions and morphology of deposited zinc [20,21]. Different concentrations of 1, 3, 5, 10 and 40 mg L^{-1} of ILS additives were examined during zinc electrodeposition, addition of 3–5 mg L^{-1} was found to increase the cathodic current efficiency (CE) and reduce the overpotential. CE was increased by ~0.8–2.0% by addition of $[EMIM]MSO_4$ or [EMIM] Br. Cathodic overpotential was reduced as well by 10–15 mV in absence of impurities for these two additives. In addition, a maximum reduction of lead contamination in zinc deposit from 26.5 ppm to 5.1–5.6 ppm was obtained from adding same ILS additives to zinc sulfate electrolyte [20]. Moreover, it was found that ILS compounds in the form of imidazolium-based have been recently used as organic solvents due to their high conductivity. The experimental studies showed that the length of cation alkyl chain and the anionic part affect the electrolytic conductivity [22].

The effect of ILS consisting of different cationic groups on the cathodic polarization and zinc deposit has been examined in our previous studies [20,23]. So it is interesting to study the effect of similar ILS additives on the anodic process. Three additives, 1-Ethyl-3-methylimidazolium chloride [EMIM]Cl, 1-Ehyl-3-methylimidazolium bromide [EMIM]Br, and 1-Ehyl-3-methylimidazolium ethyl sulfate $[EMIM]ESO_4$ were chosen to study their effects on the OER and corrosion behavior of Pb-0.7%Ag anode in acidic zinc sulfate electrolyte. These additives are compared to blank electrolyte and gelatin as standard additive. Electrochemical methods such as galvanostatic polarization, potentiodynamic polarization, electrochemical impedance spectroscopy, zero resistance ammeter and scanning reference electrode were conducted in this research paper.

2. Experimental

2.1. Electrolytes and electrodes preparation

The standard electrolyte (blank) was prepared from 60 g L^{-1} of Zn^{2+} ($ZnSO_4.7H_2O$) and 180 g L^{-1} of H_2SO_4 (98%). Chemicals were dissolved in double distilled water in 1L doubled-glazed beaker. The beaker was connected to thermostatic water circulator bath model Isotemp 6200H7 - Fisher Scientific. The operating temperature of solution was maintained at 38 ± 0.5 °C. The used additives were dissolved separately in distilled water then added to the solution to complete 1 L of volume; while gelatin was dissolved using resonator for 6 h before addition. Additives were added individually at concentration of 5 mg L^{-1}. Chemicals were supplied from VWR and Sigma-Aldrich Canada, in compliance with the purity standards set by American Chemical Society (ACS).

One plate of 1 cm^2 of Pb-0.7%Ag and one plate of pure aluminum (99.99%) were connected individually to electric wire using two components conductive silver adhesive. The prepared electrodes were dried then casted in acrylic resin in order to have only 1 cm^2 of exposed surface area. Both anode (Pb-0.7%Ag) and cathode (Al) were polished using several grits of 320, 600, and 1200 of SiC papers then washed with distilled water, ethanol and dried before immersion into the electrolyte. The electrodes were assembled in three-electrode cell with a distance of 2 cm between anode and cathode. A saturated silver chloride electrode Ag/AgCl (0.202 V vs SHE) was used as reference electrode.

2.2. Galvanostatic and potentiodynamic polarizations

The three-electrode cell was connected to Galvanostat/Potentiostat Gamry Reference 3000 - USA. Electrodeposition was conducted at 50 mA cm^{-2} for 24 h at a galvanostatic mode. The anodic potential was monitored every 10 s and results were plotted using Echem Analyst software. The anodic potentiodynamic polarization experiments were carried out from initial potential of 1.7 V to a final potential of 2.0 V vs Ag/AgCl at constant scan rate of 5 mV s^{-1}. All results were carried out in duplicates; triplicate tests were also conducted when required.

2.3. Surface examination

After 24 h of galvanostatic polarization at 50 mA cm^{-2}, the anode was washed by distilled water then dried. The morphology of the anode surface was examined under scanning electron microscope (SEM) model JEOL JSM-840a. The crystallographic structure of oxide film was determined using X-ray diffractometer model Siemens - D5000.

2.4. Electrochemical corrosion measurements

After 24 h of polarization, the anode was held for 2 h of decay at open circuit potential (OCP). This is followed by linear polarization (LP) and electrochemical impedance spectroscopy (EIS) tests. LP measurements were carried out at ±20 mV with respect to corrosion potential (E_{corr}) at constant scan rate of 0.166 mV s^{-1} and EIS tests were carried out at frequency range from 100 kHz to 0.01 Hz with an amplitude of 5 mV. The EIS data were examined using Gamry Echem Analyst based on the appropriate equivalent electrical circuit. After 24 h of electrolysis, two identical anodes were connected to zero resistance ammeter (ZRA) mode for 2 h controlled by Gamry model PC4/750 - USA. Also, after galvanostatic polarization, the anode was scanned employing scanning reference electrode technique (SRET) using EG&G Instruments model SVP100 - UK. The surface of specimen was adjusted and levelled in parallel with the surface of the Persoex tripod. The probe was lowered using the Z-axis control to negative direction to a distance of $\approx$50–100 μm from the specimen surface. The specimen was connected to the negative input of the apparatus while the probe was connected to the positive one for free corrosion measurement mode. The signal was adjusted at 20 mV of sensitivity and vibrating amplitude of 20 μm pp. Each scan lasted 15 min for a total period of 2 h. All corrosion tests were performed at least in duplicates to assure a good reproducibility.