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Evaluation of manganese dioxide deposition on lead-based electrowinning anodes

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ABSTRACT

In this study, the initial stages of the MnO_2 electrodeposition on different lead-based electrowinning anodes (Pb–MnO_2 and PbAg) in sulfuric acid electrolyte solutions were investigated. The MnO_2 deposition and its preliminary effects on the oxidation of the anodes were studied using electrochemical techniques including potentiostatic polarization and linear potential sweep voltammetry. The potentiostatic polarizations were accompanied by chemical analysis of the electrolyte to investigate the manganese oxidation rates on the anodes. Scanning electron microscopy (SEM) was employed to characterize the deposited MnO_2 layers. The presence of MnO_2 particles on the Pb–MnO_2 composite anode contributed to the deposition of a very uniform, dense, and stable MnO_2 layer. The effects of the MnO_2 composite particles in the composite anode on the current distribution, Mn^{3+} disproportionation rate and Mn^{2+} oxidation rate, were proposed as the possible causes of the observed properties of the MnO_2 layer on this anode. The MnO_2 layer on the Pb–MnO_2 anode grew quickly during the initial stages. This layer became smoother over the course of polarization. Although the oxidation of the anodes was hindered by the deposited MnO_2 layer, this effect was more significant on the composite anode than the conventional PbAg anode. This was attributed to different properties of the MnO_2 layers deposited on these anodes.

1. Introduction

Manganese ions are usually encountered as an impurity in the zinc electrowinning electrolyte. Part of manganese originates with the zinc ore. It might also be introduced to the electrolyte during the leaching process through the addition of manganese dioxide or potassium permanganate in order to oxidize iron impurities (Ivanov and Stefanov, 2002; Zhang and Cheng, 2007).

Manganese ions are oxidized on the anodes during the electrowinning process, resulting in the formation of an MnO_2 layer on the anode as well as the MnO_2 particles in the electrolyte, which are also known as cell mud (Zhang and Cheng, 2007). Manganese and its oxidation product can influence different aspects of the zinc electrowinning process such as cathodic current efficiency and anode oxidation. For instance, the co-deposition of MnO_2 particles with zinc on the cathode causes formation of Zn/MnO_2 galvanic pairs, resulting in anodic dissolution of zinc and less current efficiency (Mackinnon and Brannen, 1991; Zhang and Hua, 2009). Permanganate (MnO_4^-) ions can also have a negative effect on the cathodic current efficiency, which was verified by Ivanov and Stefanov (2002) through using separate electrode compartments. Moreover, performances of Pb-based electrowinning anodes, including their potential and oxidation rate, might be influenced by the MnO_2 deposited layer.

The mentioned effects of the manganese oxidation products strongly depend on the properties of the anodic MnO_2 deposited layer. MnO_2 cell mud formation, for example, is determined by the physical properties and mechanical stability of the layer. Detachment of the MnO_2 layer catalyzes the formation of MnO_2 particles in the electrolyte through the Guyard reaction (reaction (1)) (Ladbury and Cullis, 1959; Polissar, 1934; Tompkins, 1942; Yu and O'Keefe, 2002).

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+ \qquad (1)$$

It has been previously reported that the MnO_2 layer deposition and its properties depend on the type of anode material and its chemical composition (Mohammadi et al., 2014; Yu and O'Keefe, 2002).

Lead–silver anodes (PbAg) have been widely used in the zinc electrowinning process since the silver alloying element improves the corrosion resistance and electrocatalytic activity of lead. However, the significant cost associated with alloying lead anodes with silver has motivated companies and research centers to find an alternative for PbAg anodes (Lander, 1958; Cekerevac et al., 2010; Yanqing et al., 2010). Lead-based composite anodes containing MnO_2 particles have exhibited promising catalytic activity for oxygen evolution and superior corrosion resistance in the zinc electrowinning operating conditions (Mohammadi and Alfantazi, 2013; Mohammadi et al., 2013a; Schmachtel et al., 2009; Li et al., 2014).

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The authors showed that the MnO_2 layer deposited on the Pb–MnO_2 composite anode was different from those deposited on the lead-based alloys of Pb, PbAg, and PbCa (Mohammadi et al., 2014; Mohammadi and Alfantazi, 2015). The layers deposited on the composite anode were uniform and compact, which significantly inhibited the formation of the MnO_2 cell mud in the electrolyte (Mohammadi and Alfantazi, 2015). Needless to say, the initial stages of the MnO_2 deposition process determine the properties of a deposited MnO_2 layer (Duan et al., 2012). Therefore, the observed difference in the properties of the MnO_2 layers deposited on the Pb–MnO_2 and PbAg anodes can be the result of the initial stages of the deposition process. However, no comprehensive study on the initial stages of the deposition of the MnO_2 layer on the Pb–MnO_2 composite anodes has yet been performed.

In this study, the electrodeposition and properties of the MnO_2 layer on the Pb–MnO_2 composite anode were investigated and compared with those on the PbAg anode using chemical–electrochemical techniques. The possible reasons for the observed differences were also explored. Furthermore, the effects of this layer on the oxidation rate of the mentioned lead-based anodes were examined.

2. Experimental

2.1. Sample preparation

The Pb–MnO_2 composite anode was prepared through single-action pressing of the Pb/MnO_2 powder mixture. Manganese dioxide and lead particles with diameters less than 100 μm and 44 μm from Baker & Adamson and Sigma-Aldrich were used respectively to fabricate the composite anodes. Disk-shaped samples with a diameter of 16 mm were pressed at a 4-t load for 5 min in a stainless steel mold. The components of the stainless steel mold are schematically shown in Fig. 1(a). The likelihood of this process affecting the size of the composite particles is unknown. This phenomenon is not an objective of this study, but can be an area of further investigation. Based on the corrosion performance of the anodes, the composite anode containing 10 wt.% MnO_2 was used in this study (Mohammadi and Alfantazi, 2013). Fig. 1(b) shows cross section of the composite anode, revealing a uniform distribution of the composite particles in the lead matrix. A rolled PbAg anode (composition: 0.746 wt.% Ag, 0.003 wt.% Sn, <0.01 wt.% Ca, <100 ppm Al, <100 ppm Fe, <100 ppm Mg) was also used in this study.

2.2. Electrochemical and chemical measurements

Electrochemical experiments were performed in a water-jacketed glass container and a standard three-electrode cell. A Silver/silver chloride electrode (Ag/AgCl, E = 199 mV vs. SHE) and a platinised titanium were used as the reference and counter electrodes, respectively. The temperature of the electrolyte was maintained at 37 ± 1 °C by a Cole–Parmer heater and water circulating system. All the potentials in this paper are reported versus the Ag/AgCl reference electrode. A Gamry Reference 600 potentiostat was utilized to perform the electrochemical experiments including cyclic voltammetry, potentiostatic, and linear sweep voltammetry.

The lead-based samples were ground up to 600-grit SiC paper and rinsed in distilled water before each experiment. A 1 cm^2 area of the disk-shaped samples was exposed to the electrolyte. All the electrochemical experiments were performed in a 180 g/L H_2SO_4 (ACS grade, Fisher Scientific) electrolyte containing different concentrations of manganese ions (Mn^{2+}). Manganese ions were introduced into the electrolyte through the addition of $MnSO_4$ (ACS grade, Fisher Scientific). A typical Mn^{2+} concentration in the zinc electrowinning electrolyte is in the range of 3–7 g/L (Sinclair, 2005). Based on this, a Mn^{2+} concentration range of 0–6 g/L was chosen in this study. The sulfuric acid concentration in the electrolyte and the electrolyte temperature were chosen according to the typical operating conditions of most zinc electrowinning plants (Sinclair, 2005).

The electrolyte samples were taken during the potentiostatic polarization of the anodes in Mn^{2+}-containing electrolytes. These samples were used to measure the amount of manganese oxidation products (Mn^{3+} and MnO_2 mud) by potentiometric titrations using Metrohm 999 Titrando auto-titrant. The electrolyte reacted with ferrous ammonium sulfate in order to reduce Mn^{3+} ions and MnO_2 by ferrous through reactions (2a) and (2b), respectively. Then the leftover ferrous ions were back titrated by a permanganate solution through reaction (3). Mn^{2+} oxidation rates were calculated from the amount of consumed ferrous ions to reduce Mn^{3+} and MnO_2.

$$Mn^{3+} + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+} \tag{2a}$$

$$MnO_2 + 2Fe^{2+} + 4H^{+} \rightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O \tag{2b}$$

$$MnO_4^{-} + 5Fe^{2+} + 8H^{+} \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O \tag{3}$$

All the electrochemical and chemical experiments were repeated at least two times to ensure that the obtained data are reproducible. Scanning Electron Microscopy (SEM, Hitachi S-3000 N) was used occasionally to study the morphology of the MnO_2 anodic layer deposited on the anodes.

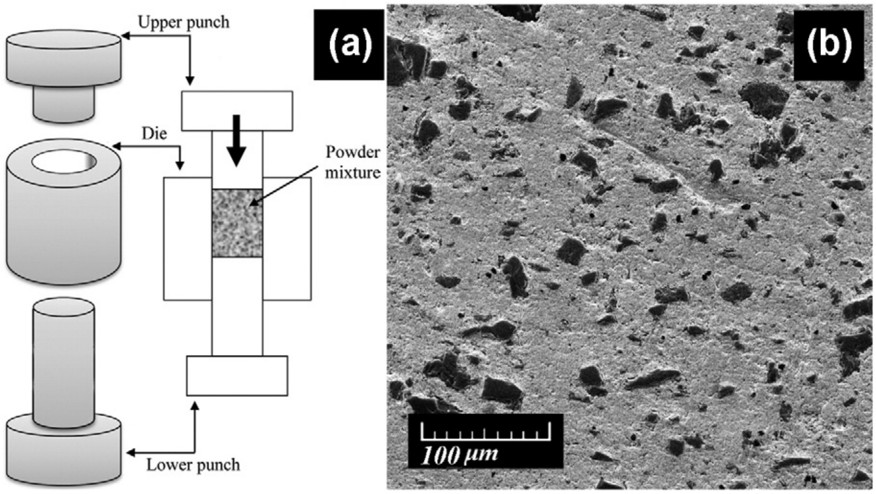

Fig. 1. Schematic of a pressing mold components (a) and cross sectional SEM image of the Pb–MnO_2 anode (b).