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Electrochemical performance of a Pb/Pb-MnO_2 composite anode in sulfuric acid solution containing Mn^{2+}

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ABSTRACT

The influence of Mn^{2+} on oxygen evolution kinetics and corrosion behaviour of Pb/Pb-MnO_2 composite anode in sulfuric acid electrolyte was investigated using SEM, XRD, and several electrochemical methods. The results indicate that a high concentration of Mn^{2+} (e.g. 3.0 g L^{-1}) in the electrolyte resulted in the formation of a MnO_2 layer on the surface of the anode. This layer decreased the oxygen evolution activity of the anode, but at the same time made the underlying PbO_2 layer more compact and flat, effectively improving the anodic corrosion resistance. When the Mn^{2+} concentration was low (e.g. 0.1 g L^{-1}), no MnO_2 layer was formed but the structure of the PbO_2 anodic layer was modified. As a result, the oxygen evolution activity and corrosion resistance were both significantly improved. In addition, Mn^{2+} in the electrolyte did not change the kinetic mechanism of oxygen evolution reaction. The reaction was exclusively controlled by the formation and adsorption of first intermediate, and the adsorption resistance played a dominant part in the whole reaction resistance.

1. Introduction

In the zinc electrowinning industry Pb-Ag alloys are widely used as the anode material (Aromaa and Evans, 2007; Felder and Prengaman, 2006). However, this alloy has several disadvantages, such as high anodic over-potential, Pb contamination of the cathode zinc, short-circuits resulting from lead distortion, and high consumption of silver. Therefore, recently composite anodes of lead and an active dispersed phase have been widely studied (Chang et al., 2007; Dobrev et al., 2009; Hrussanova et al., 2002; Hrussanova et al., 2004a, 2004b; Muaiani et al., 1999; Schmachtel et al., 2009; Stefanov and Dobrev, 2005). Such anodes couple the high electrocatalytic activity of the dispersed phase and good chemical stability of lead matrix. As a result, the oxygen evolution activity (Chang et al., 2007; Muaiani et al., 1999; Schmachtel et al., 2009) and corrosion resistance (Dobrev et al., 2009; Hrussanova et al., 2002; Stefanov and Dobrev, 2005) of the lead matrix were significantly improved. Based on its fairly low material and preparation cost compared with conventional Pb-Ag alloys, such composite anodes are promising alternatives to the present cast lead anodes.

When these composite anodes are applied in industry, the first key problem which needs to be recognized is the influence of Mn^{2+}. This additive is a double-edge sword in the traditional zinc electrowinning electrolyte with the casted or rolled Pb-Ag alloy as anode materials (Kruphowa et al., 1977; Verbaan and Mullinder, 1981; Zhang and Cheng, 2007). The Mn^{2+} can be oxidized to form a compact and strongly adhesive MnO_2 anodic layer during the electrolysis, which effectively reduces the corrosion of anodes and minimizes the contamination of cathodic zinc by lead (MacKinnon and Brannen, 1991; Newnham, 1992; Saba and Elsherief, 2000; Schierle and Hein, 1993). The MnO_2 slimes also adsorb detrimental ionic impurities, such as Cu^{2+}, Co^{2+}, Ni^{2+}, Sb^{3+} (Ivanov, 2004; Ivanov and Stefanov, 2002), and decrease the effect of Cl^{-} (Kelsall et al., 2000).

On the other hand, the complex oxidation and reduction reactions among manganese ions of different valences will considerably decrease the current efficiency (Cathro, 1991; MacKinnon and Brannen, 1991). Also, the MnO_2 layer can passivate the anodic surface and retard the oxygen evolution (Rerolle and Wiart, 1996). Furthermore, Yu and O'Keefe (2002) studied the electrochemical impact of Mn^{2+} to Pb-Ag and Pb-Ca-Sn anodes and found that the presence of Mn^{2+} depolarizes anodic reactions and decreases PbO_2 formation. Cachet et al. (1999) studied the influence of Mn^{2+} on oxygen evolution on lead anodes, and stated that the kinetics for lead and lead-silver anodes were affected in the presence of Mn^{2+}.

Previous studies investigated the electrochemical performance of the co-deposited Pb/Pb-MnO_2 composite anode in sulfuric acid solution and found that its oxygen evolution activity and corrosion rate were largely improved by the association of lead and MnO_2 particles (Li et al., 2010; Li et al., 2011). The current paper presents further electrochemical studies to investigate the influence of Mn^{2+} in the electrolyte on the oxygen evolution behaviour and corrosion resistance of this kind of Pb/Pb-MnO_2 composite anode.

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2. Experimental details

Pb-MnO$_2$ composite coatings were electrochemically co-deposited on 1 cm^2 casted pure lead substrate. The basic composition of the deposition bath was as follows: 120–150 g L^{-1} Pb(BF$_4$)$_2$; 30–40 g L^{-1} HBF$_4$; 12–15 g L^{-1} H$_3$BO$_3$; 0.5 g L^{-1} gelatin; 0.2 g L^{-1} diethanolamine (DEA) and 80–120 g L^{-1} MnO$_2$ (in suspension). The experiments were conducted in a 250 mL beaker, where up-faced horizontal cathode was used to guarantee MnO$_2$ particles were incorporated in the deposit. The plating temperature and agitation rate were controlled at 35 ± 0.5 °C and 400 ± 20 rpm using a DF-101S constant temperature magnetic stirrer. The cathodic current density was maintained at 40 mA cm^{-2} for 60 min producing a 1 × 1 cm deposit 200–300 μm thick containing 6–8 wt.% MnO$_2$. All solutions were prepared with analytical reagents and double-distilled water, and the MnO$_2$ particles used were 2–7 μm γ-MnO$_2$ of high purity (> 95%, HUI-TONG CO. LTD).

The electrochemical measurements for the Pb/Pb-MnO$_2$ composite anodes were performed in 160 g L^{-1} H$_2$SO$_4$ solution with different contents of Mn^{2+} at 35 ± 0.5 °C using a standard three-electrode system. A platinum plate of 4 cm^2 and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials shown in the figures are against SCE. The constant current density used during galvanostatic electrolysis was 50 mA cm^{-2} which is equivalent to the 500 A m^{-2} used in industry. The anode potential was measured using a high impedance input ($5 \times 10^{12}\,\Omega$) multimeter during the 72 h electrolysis. After electrolysis, cyclic voltammograms, Tafel parameters and electrochemical impedance spectroscopy (EIS) were immediately carried out on the anodic layers using an EG&G Princeton applied research model 2273 potentiostat/galvanostat controlled using PowerSuite software. The scanning range of the voltammograms was − 1.0–2.1 V at a sweep rate of 10 mV s^{-1}. The quasi-stationary polarization curve for Tafel measurement was recorded from 1.7 to 2.0 V with a scanning rate of 0.2 mV s^{-1}. The frequency interval of EIS measurement was from 10^5 to 10^{-2} Hz and the AC Amplitude is 5 mV rms.

The corrosion resistance of the Pb/Pb-MnO$_2$ composite anode was measured by the ionic equilibrium method. The corrosion of lead-based anode in H$_2$SO$_4$ solution is mainly caused by the dissolution of lead. Other parts also include the formation of sedimentary anode slime, which can be neglected in such laboratory experiments due to the short duration (Lai et al., 2010). As there is little lead deposited on the platinum cathode, the corrosion resistance can be evaluated by the concentration of Pb^{2+} in the electrolyte during the electrolysis. The Pb^{2+} concentration in the electrolyte was measured by atomic absorption spectroscopy (Hitachi, Z-5000).

In addition, JSM-6360F Scanning Electron Microscope (SEM) and TTR-III X-ray Diffraction (XRD) were used to detect the microscopic morphology and phase composition of the Pb/Pb-MnO$_2$ anode before and after electrolysis, respectively.

3. Results and discussion

3.1. Galvanostatic polarization

Fig. 1 shows the influence of Mn^{2+} in electrolyte on the galvanostatic polarization curves of the composite anodes. As described in an earlier work (Li et al., 2010, 2011), there is a “potential valley” on the polarization curve at the very beginning of electrolysis due to the formation of a stable surface. Over the 72 h polarization time the layers came to an equilibrium state and the behaviour of the anode became consistent.

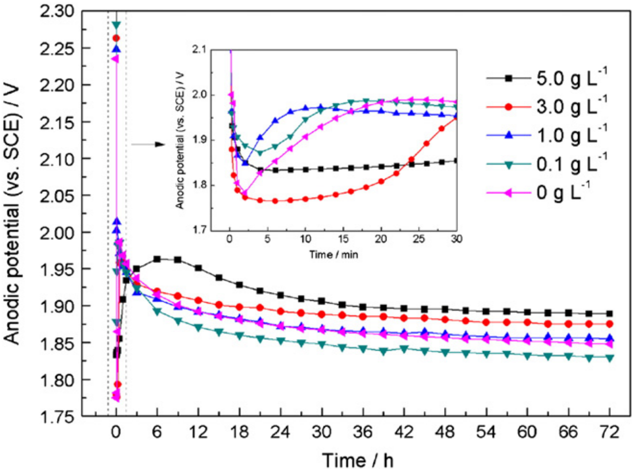

Fig. 1. Influence of Mn^{2+} concentration in the electrolyte on the anodic potential of Pb/Pb-MnO$_2$ composite anode during the 72 h galvanostatic polarization.

As shown in the inset of Fig. 1, in the electrolytes with high Mn^{2+} content (e.g. 3 g L^{-1} and 5 g L^{-1}), the time to stability was extended. This may be due to the more ready formation of a MnO$_2$ layer by oxidation of Mn^{2+} in solution, which to some extent aided retention of the MnO$_2$ particles in the deposit. During the following electrolysis, this MnO$_2$ layer gradually became thick, rigid and cracked, and then covered most of the PbO$_2$ surface (visually observed), and as a result the anodic potential markedly increased. When the MnO$_2$ layer became thick enough, it began to break off bit by bit and drop into the electrolyte in the form of anodic slime. Low-concentration Mn^{2+} (1.0 g L^{-1} or 0.1 g L^{-1}) had very little influence on the polarization curve at the beginning. In the prolonged electrolysis, there was no apparent MnO$_2$ layer formed on the anodic surface, and powdery MnO$_2$ slime was found to gradually deposit in the cell bottom. When the Mn^{2+} concentration decreased to 0.1 g L^{-1}, the stable anodic potential to some extent reduced. This is probably due to the influence of Mn^{2+} on the structure and composition of the anodic layer.

3.2. Surface morphology and phase composition

Fig. 2 shows the microscopic morphology of a fresh composite anode and the surface after 72 h galvanostatic polarization in an electrolyte without Mn^{2+}. On the fresh surface, pyramidal crystal grains of lead with clearly outlined boundaries can be observed, and the surface is relatively heterogeneous, which makes the specific surface area of the composite anode considerably larger than the geometric area. Moreover, individual particles partially embedded in lead matrix can also be observed, and were found to be Mn-rich by EDS. When the anode was polarized for 72 h, although the macro surface was still smooth and flat, the microscopic morphology was relatively loose and porous. Such a structure will not protect the inner lead base from further corrosion with increasing time of electrolysis.

The MnO$_2$ layer formed at high Mn^{2+} content after 72 h electrolysis was rigid, cracked and weakly adherent to the PbO$_2$ surface. It should be noted that this MnO$_2$ layer is quite different from MnO$_2$ layers formed on traditional cast or rolled Pb-Ag anode, where the MnO$_2$ layers are smooth, compact and firmly combined with the PbO$_2$ substrate (MacKinnon and Brannen, 1991; Yu and O'Keefe, 2002). Fig. 3(a) and (b) shows the surface morphology of Pb/Pb-MnO$_2$ anode after the weakly adherent MnO$_2$ surface layer was removed using flowing DI-water. Compared with that formed in the absence of Mn^{2+}, the PbO$_2$ layer was a hard, compact and flat surface, which can be expected to protect the lead substrate. When the Mn^{2+} content was 1.0 g L^{-1} (Fig. 3 (c)) or 0.1 g L^{-1} (Fig. 3 (b)), even though there was no apparent MnO$_2$ layer formed on anode surface, the anodic layer also became more compact and flat compared with that without Mn^{2+}. In the electrolyte with 0.1 g L^{-1} Mn^{2+}, the anodic surface was relatively ordered and the structure of the fresh