Oxygen evolution and corrosion behavior of low-MnO$_2$-content Pb-MnO$_2$ composite anodes for metal electrowinning

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A B S T R A C T

In this study, the oxygen evolution and corrosion behavior of Pb-MnO$_2$ composite anodes produced by powder pressing with low MnO$_2$ content (1–7 wt%) were systematically investigated in H$_2$SO$_4$ solution and compared to pure Pb and Pb–Ag (1 wt%) anodes. Galvanostatic polarization, weight loss, and ionic equilibrium techniques were employed to evaluate the electrocatalytic activity and corrosion resistance of the composite anodes. The results demonstrated that Pb-MnO$_2$ composite anodes presented lower potential than that of the Pb–Ag anode during a 72 h polarization period, and the potential of composite anodes decreased as MnO$_2$ fraction increased. The corrosion resistance of composite anodes was higher than that of the Pb–Ag anode. The surface morphology and phase composition of the anodic layer after 72 h polarization were examined with scanning electron microscopy (SEM) and X-ray diffraction (XRD) and the results indicated that anodic layers on Pb-MnO$_2$ composite anodes were both thinner and denser than that of the Pb–Ag anode, confirming excellent corrosion resistance in H$_2$SO$_4$ solution electrolysis.

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1. Introduction

The oxygen evolution reaction (OER) is an important counter reaction for metal reduction during the electrowinning of non-ferrous metals such as Zn, Cu, Ni, Co, Cr, and Mn (Rerolle and Wiart, 1996). Water oxidation reaction produces acid, expressed as follows (Alamdari et al., 2012):

$$H_2O(1) \rightarrow 0.5O_{2(g)} + 2H^+_{(aq)} + 2e^- \quad E^0 = 1.229\,V\,vs.SHE \quad (1)$$
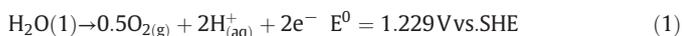
Lead-based alloy anodes are often used to produce high-purity zinc, as they have advantageous corrosion resistance properties in acidic sulfate solutions. There are still several inherent problems for lead-based alloys, however, including high OER over-potential, cathodic product contamination due to anode dissolution, poor mechanical properties, and over-consumption of Ag (Albert et al., 1997; Ivanov et al., 2000b; Li et al., 2011; Yanqing et al., 2010).

In effort to solve these problems, different metal elements were added to the Pb anode. These element additions can be classified into three main groups (Alamdari et al., 2012; Bagshaw, 1995; Ivanov et al., 2000a): 1) Ag, Co, Pt, or low levels of Au, Cu, Ni, or Fe which can improve the electrochemical catalytic activity of the lead-based alloy anodes by forming a stable oxidation layer on the anode surfaces; 2) Tl, In, Sn, Bi or Sb, which can enhance corrosion resistance by transforming the structure of the protective layer; and 3) alkaline and alkaline-earth metals, such as Li, Na, Ca, and Ba, which affect the adsorption processes and refine the grain size as the Pb alloy melt crystallizes. Unfortunately, OER over-potential is still rather high when the anode is supplemented with metal elements (Hui et al., 2010); for this reason, reducing the OER over-potential has been the subject of many recent studies (including, of course, this one,) on the electrowinning of non-ferrous metals (Chen et al., 2013; Cifuentes et al., 2011; Dobrev et al., 2009; Mohammadi et al., 2011).

In effort to minimize the OER over-potential of lead-based alloys, many previous researchers have attempted to fabricate another form of anode called "dimensionally stable anodes" (Brungs et al., 1996; Moats, 2008), borrowed from the chlor-alkali industry (Hayfield, 1998a, 1998b; Kim Chandler et al., 1997), which are already commonly utilized in the electroplating (Cobley et al., 2001) and sewage treatment industries (Chen, 2004). These anodes are typically made by coating titanium mesh or plate with mixed metal oxides of Ru, Ir and several other noble metals (Aromaa and Forsén, 2006; Chmiola et al., 2003; de Oliveira-Sousa et al., 2000; Hu et al., 2004; Ma et al., 2006; Moats, 2008; Song et al., 2008). Wider usage of these anodes remains limited, however, because they are not suited to employment for the lengthy duration necessary in zinc electrowinning – after several days, unavoidable MO$_2$ deposits block the surface and affect the electrocatalytic activity of the dimensionally stable anodes (Jaimes et al., 2015; Kim et al., 2006).

Conductive lead matrix composites with active dispersed MnO$_2$ particles have been investigated extensively for the oxygen evolution reaction (ORE) in non-ferrous metals electrowinning (Lai et al., 2012a, 2012b; Li et al., 2011; Mohammadi and Alfantazi, 2013; Mohammadi et al., 2013; Schmachtel et al., 2009a; Schmachtel et al., 2009b). Pb-

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MnO_2 composite anodes are fairly cost effective, and have shown favorable conductivity properties of the lead matrix and excellent electrocatalytic activity of MnO_2 (Li et al., 2011; Mohammadi and Alfantazi, 2013; Schmachtel et al., 2009a). The Pb-MnO_2 composite anodes are considered one of the most promising alternatives to the Pb–Ag anode for several reasons (Lai et al., 2012a), however, research on Pb-MnO_2 anodes has mostly focused on those with high MnO_2 content (5–20 wt%) and presents mostly cyclic potentiodynamic polarization curves. To the best of our knowledge, there exist only very few studies in the literature that have used galvanostatic assessment to validate their findings, and no prior studies investigating low-MnO_2 composite anodes. Porosities and cracks in cold-pressed samples increase alongside the number of MnO_2 particles (Mohammadi et al., 2013), reducing the resultant material's mechanical properties and increasing fabricating cost – thus making low-MnO_2 composite anodes quite worth investigating.

2. Experiment

2.1. Preparation

Pb-MnO_2 composite anodes were fabricated using lead powder with particles less than 75 μm in diameter (99.95%, Xingyuan High-pure Co. Ltd.) and high-purity MnO_2 (>85%, Xilong Co. Ltd.) with particle diameters less than 250 μm. Fig. 1 shows the XRD spectrum of the MnO_2 powder, which has low crystallinity and consists of ε-MnO_2, α-MnO_2, and γ-$Mn(O,OH)_2$. The structure of this MnO_2 powder is very similar to the MnO_2 particles synthesized by (Kim et al., 2006). The MnO_2 and lead particles were combined in a plastic tube which was fixed on a blender mixer at a rotation rate of 50 r/min for 24 h. Sample mixtures with different MnO_2 contents (1, 2, 3, 5, or 7 wt%) were then pressed under 4425 kg/cm^2 at room temperature for 5 min in a stainless steel mold. For comparison, Pb–Ag (1 wt%) and pure lead anodes were produced by melt casting using the same stainless steel mold.

Compactness of pressed samples is an important factor that can be calculated as follows:

$$C = \frac{V_b}{V_t} \times 100\% \tag{2}$$

where C is the compactness of the pressed samples, and V_t and V_b are the true specific volume and bulk specific volume of the samples, respectively. V_t was measured by vernier caliper, and V_b was calculated as follows:

$$V_b = x \times M/\rho_{MnO_2} + (1-x) \times M/\rho_{Pb} \tag{3}$$
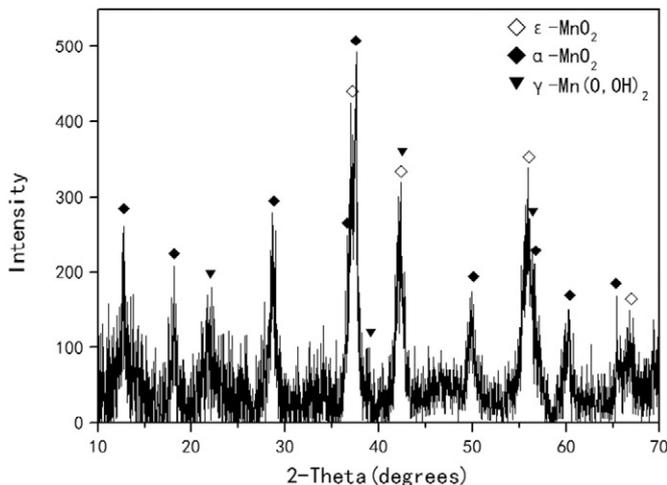

Fig. 1. XRD spectrum of MnO_2 powder.

where x and M stand for the mass fraction of MnO_2 and the mass of the sample. Table 1 shows the compactness trends of the samples with increasing MnO_2 mass fractions. According to Table 1, compactness of the samples decreased as MnO_2 fraction increased.

The as-prepared samples, including Pb and Pb–Ag, were converted into electrodes in the following stepwise manner:

1) Insulated copper wire was soldered to the samples at one circular section.
2) The electrode was enclosed in epoxy resin, leaving the surface of the other circular section (12 mm diameter) free.
3) After 12 h of curing time, each anode was polished with 200 and 400 mesh sandpaper to ensure uniform surface roughness and complete exposure of the anode circular section. The samples were washed by deionized water after every step.

2.2. Electrochemical measurements

The chronopotentiometry experiment was performed in a square glass electrolytic cell containing 160 g/L H_2SO_4 solution at 25 °C. The standard three-electrode system was used. Mercurous sulfate electrode (MSE, E = 0.616 V vs. SHE) and graphite flake were used as the reference electrode and counter electrode, respectively. The experiment was performed at a constant current density of 50 mA/cm^2 for 72 h using a potentio-galvano-scanner (Wenking PGS 81), and the anode potential values were measured with a high-ohmic input multimeter and recorded by computer every 30 s.

2.3. Corrosion rate measurements

In this experiment, "anode corrosion" referred to dissolution of the anodes and anode slime sloughing off the anode surface. Ionic equilibrium and weight loss methods were adopted to measure the corrosion rate as accurately as possible. Before and after 72 h of constant current polarization, the anodes were washed by deionized water and dried in an oven at 70 °C × 6 h, then weighed (0.1 mg accuracy). The concentrations of Pb and Mn in the electrolyte were measured with inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 7000DV, accuracy 1 ppb) to compare the corrosion resistance of the sample anodes. Every 24 h during 72 h polarization period, a 10 mL sample of the electrolyte was removed for analysis.

2.4. Morphology and phase measurements

Microscopic morphologies of the anode surface were observed after 72 h of galvanostatic polarization with a scanning electron microscopy (SEM, JSM6480LV). X-ray diffraction (MAC Science Co. Ltd.) was also used to detect the phases formed on the anode surface after 72 h of galvanostatic polarization.

3. Results and discussion

3.1. Galvanostatic polarization

In order to compare the electrochemical activity among samples, each anode was measured by chronopotentiometry for 72 h at 25 °C and a current density of 50 mA/cm^2. Fig. 2 shows the differences in potential among Pb, Pb–Ag, and different Pb-MnO_2 anodes during 72 h galvanostatic polarization. According to Fig. 2(b), the initial potentials of composite anodes decreased rapidly for 10 min, then gradually increased until

Table 1
Compactness of the fabricated samples.

MnO_2 fraction/wt%	1	2	3	5	7
Compactness/%	97.4	95.4	95.0	91.9	90.2