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## Corrosion resistance mechanism of a novel porous Ti/Sn-Sb-RuO<sub>x</sub>/β-PbO<sub>2</sub> anode for zinc electrowinning

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### ABSTRACT

Sn-SbO<sub>x</sub>, Sn-Sb-RuO<sub>x</sub>, and β-PbO<sub>2</sub> coatings were successfully deposited on a titanium substrate by using the thermal deposition and electrodeposition methods, and their electrochemical properties were investigated in detail. The Sn-Sb-RuO<sub>x</sub> interlayer played a very important role in enhancing the stability of the PbO<sub>2</sub> coating electrodeposited at a low current density. The scanning electron microscopy results showed that the cracks in the Sn-Sb-RuO<sub>x</sub> coating were larger than those in the Sn-SbO<sub>x</sub> coating. Moreover, the Ti/Sn-Sb-RuO<sub>x</sub>/β-PbO<sub>2</sub> coating had many large pits with pore diameters in the range of 50–180 μm and pore depths of < 18.4 μm. The electrodeposition mechanism of β-PbO<sub>2</sub> was investigated by cyclic voltammetry. Compared to the compact β-PbO<sub>2</sub> anode, the porous β-PbO<sub>2</sub> anode showed superior electrocatalytic activity and electrochemical stability. A service life of 96 h was achieved for this anode under the accelerated-life-test conditions at a current density of 1 A/cm<sup>2</sup> in a solution of 150 g/L H<sub>2</sub>SO<sub>4</sub> and 1 g/L Cl<sup>-</sup>.

### 1. Introduction

In Zn electrowinning (EW), oxygen evolution is the predominant anodic reaction, and the overpotential of the anode materials determines the cell voltage/energy consumption of the process. Traditional lead-based anodes typically contain alloying constituents such as Ag [1], Ca [2], Co [3], Nd [4], Zr [5], and MnO<sub>2</sub> [6]. These anodes have been widely used in Zn EW for more than a century because of their low cost and easy availability. However, lead-based anodes usually suffer high overpotential for the oxygen evolution reaction (OER), leading to high cell voltage and energy consumption. Furthermore, the high corrosion rate of lead anodes can also contaminate the cathode metals, leading to the degradation of the quality of Zn produced and a decrease in the production as well. Moreover, the impurities and additives present in EW electrolytes also impose some restrictions on the application of lead-based catalytic anodes for Zn EW operations. For example, the presence of manganese hinders the operation of catalytic anodes during EW by the deposition of poorly conductive manganese oxides. These oxides gradually cover the anode surface, resulting in an increase in the cell voltage [7].

In order to overcome the abovementioned limitations of lead-based anodes, efforts have been made to develop improved anodes for Zn EW.

One straight forward approach to reduce the oxygen evolution overpotential is to replace the conventional lead alloy anodes with dimensionally stable anodes (DSAs). The modification of titanium electrodes by a metallic oxide may lead to the preparation of the well-known DSAs. Noble metal oxides such as RuO<sub>2</sub> [8] and IrO<sub>2</sub> [9] obtained by the thermal decomposition of metal chloride salts are excellent oxygen and chlorine evolution catalysts. By optimizing the EW conditions, the cell voltage can be reduced by 0.3–0.55 V [10]. However, when RuO<sub>2</sub>-based anodes are used in the presence of H<sub>2</sub>SO<sub>4</sub> electrolytes, the formation of RuO<sub>4</sub> is feasible at potentials > 1.3 V. This can cause the dissolution of the active layer. On the other hand, IrO<sub>2</sub> anodes offer better stability than RuO<sub>2</sub> anodes. IrO<sub>2</sub> can be oxidized to IrO<sub>4</sub><sup>2-</sup>, and dissolves in the electrolyte at a higher potential (~0.6 V higher) than that required for RuO<sub>2</sub> oxidation. As a result, IrO<sub>2</sub> shows better resistance to corrosion (under the oxygen evolution conditions) than RuO<sub>2</sub> [11]. Meanwhile, when used for long durations for Zn EW, IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> coatings slowly dissolve in the electrolyte [12], and Ir(IV) ions gradually accumulate on the cathode surface, thus increasing the hydrogen evolution and decreasing the current efficiency [13].

However, oxide coatings can also be obtained by anodic electrodeposition. It is possible, for example, to prepare PbO<sub>2</sub>-coated metals, which are regarded as “low-cost DSAs”. These metals show high

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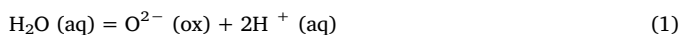
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electrical conductivity, good electrochemical stability, and chemical stability against corrosion and are relatively inexpensive [14]. PbO<sub>2</sub>-coated metal anodes offer some advantages over the conventional Pb-Ag anodes such as the obviated need for preconditioning, improved quality of electrolytic Zn, good corrosion resistance to chlorine (or even the removal of chloride ions in the electrolyte), and less anode slime [15]. These advantages make PbO<sub>2</sub>-coated metal anodes promising alternatives to Pb-Ag anodes for Zn EW. However, PbO<sub>2</sub>-coated metal anodes produce high cell voltages during the electrolytic process [16]. To overcome this limitation, PbO<sub>2</sub> is deposited on Ti substrates, which are sometimes doped with ZrO<sub>2</sub> [17], Mn<sub>3</sub>O<sub>4</sub> [18], carbon nanotubes [19], and RuO<sub>2</sub> [20].

The stability of DSA catalytic anodes is another crucial parameter for Zn EW. In general, the deactivation of DSA anodes can be attributed to the consumption of the active oxide coating components and the formation of a passive interlayer between the coatings and the substrate [21]. For DSA anodes, passivation generally occurs by the reaction of titanium substrates with the O<sup>2-</sup> ions in water according to the following reaction:



O<sup>2-</sup> ions are driven towards the substrate by the electric field in the coating film. The migration rate of O<sup>2-</sup> ions is strongly affected by the electric field strength. Hence, the smaller the electric field strength, the lower is the migration rate. Low conductivity causes a quick migration of O<sup>2-</sup> ions towards the substrate because the electric field strength is inversely proportional to the conductivity. Finally, the quick O<sup>2-</sup> migration accelerates the formation of an insulating TiO<sub>2</sub> layer at the interface between the titanium substrate and the coating, leading to electrode passivation [22]. Generally, for plant-scale Zn EW operations, approximately 2 mg/L of fluoride is added to the electrolyte to minimize the attack on the titanium anodes. Higher levels of fluoride aggravate the corrosion of titanium anodes by forming [TiF<sub>6</sub>]<sup>2-</sup> [23].

PbO<sub>2</sub> shows poor adhesion on Ti substrates. This can be attributed to the formation of an insulating TiO<sub>2</sub> layer between the PbO<sub>2</sub> coating and the Ti substrates during anodic polarization in aqueous media. To overcome this issue, various efforts have been made to develop novel substrates modified by various pre-treatments and undercoats from different media. SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>3</sub> [24], SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub>-RuO<sub>2</sub> [25], and IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> [26] have been utilized as the interlayer for PbO<sub>2</sub> films. The use of these interlayers can further increase the chemical stability of the electrodes while enhancing their electrocatalytic activity. Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>5</sub>-RuO<sub>2</sub>/α-PbO<sub>2</sub>/β-PbO<sub>2</sub> electrodes show a lifetime of up to 59 h under the accelerated-life-test conditions at a current density of 4 A/cm<sup>2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution [25].

In terms of the electrocatalytic activity, porous β-PbO<sub>2</sub>-coated DSAs have attracted immense attention because of their higher electrochemically active surface areas than those of compact β-PbO<sub>2</sub>-coated ones [27]. Porous lead oxide coatings [28] are prepared by the anodic deposition of lead(II) ions under a large current density to trigger a vigorous OER on the surface. Then, the oxidation of lead ions occurs, thereby forming porous β-PbO<sub>2</sub> with oxygen bubbles as the templates. Another approach to prepare porous PbO<sub>2</sub> electrodes is to use porous Ti substrates. The electrodes obtained using this approach show a three-dimensional porous structure. However, these methods cannot produce electrodes suitable for industrial applications where heavy thermal loads and very high current densities are employed. The preparation of porous Ti/Sn-Sb-RuO<sub>x</sub>/β-PbO<sub>2</sub> anodes with superior electrochemical properties is still a major challenge.

Herein, we propose a novel method to fabricate porous β-PbO<sub>2</sub> anodes at low current densities on Ti/Sn-Sb-RuO<sub>x</sub> substrates. The stability of the surface morphology and electrochemical performance of the resulting porous β-PbO<sub>2</sub> anode were investigated and compared with those of a Ti/Sn-SbO<sub>x</sub>/β-PbO<sub>2</sub> anode. In addition, the cavitation and corrosion resistance mechanisms of the porous PbO<sub>2</sub> layer during

Zn EW were also discussed.

## 2. Experiments

### 2.1. Preparation of electrodes

#### 2.1.1. Pre-treatment of titanium substrate

First, the titanium substrate was pre-treated following a four-step process [29]. First, the titanium plates (TA1) with the dimensions of 20 mm × 20 mm × 1 mm were immersed in a 10 wt.% NaOH solution at 70 °C for 30 min and were then washed with deionized water to remove grease or oil. The cleaned titanium plates were etched in mixed acid (V<sub>HF</sub>/V<sub>HNO<sub>3</sub></sub>/V<sub>H<sub>2</sub>O</sub> = 1:4:5) for 3 min to remove the oxide layer and then washed with deionized water. Next, the further cleaned titanium plates were etched in 20 wt.% HCl solution at 90 °C for 120 min to form a rough surface. Finally, the pre-treated titanium substrate was stored in a solution of ethanol and 2% oxalic acid at room temperature.

#### 2.1.2. Preparation of the Sn-Sb-RuO<sub>x</sub> interlayer

A mixture of 3.0 M SnCl<sub>4</sub>·5H<sub>2</sub>O, 0.50 M SbCl<sub>3</sub> and 0.60 M HCl in n-butanol solution used as the precursor for the preparation of the Sn-SbO<sub>x</sub> interlayer. A mixture of 3.0 M SnCl<sub>4</sub>·5H<sub>2</sub>O, 0.50 M SbCl<sub>3</sub>, 0.60 M HCl and 0.375 M RuCl<sub>3</sub>·3H<sub>2</sub>O in n-butanol was used as the precursor for the synthesis of Sn-Sb-RuO<sub>x</sub> interlayer. The pre-treated titanium substrates were then painted with the precursor solutions using a brush. After drying at 120 °C for 2 min, the substrates were heated at an annealing temperature of 500 °C for 10 min. The sheets were then air-cooled to room temperature and were brushed again. The entire procedure was repeated eight times and the samples were heated at the same annealing temperature for 1 h with the total oxide loading of about 8–10 g/m<sup>2</sup>.

#### 2.1.3. Preparation of the porous β-PbO<sub>2</sub> layer

The electrodeposition method was used to form the β-PbO<sub>2</sub> coating on the surface of the interlayer. An aqueous solution of 0.8 M Pb(NO<sub>3</sub>)<sub>2</sub>, 0.1 M HNO<sub>3</sub>, and 0.015 M Fe(NO<sub>3</sub>)<sub>3</sub> was prepared. The Ti/Sn-Sb-RuO<sub>x</sub> coating was employed as the anode and a titanium mesh of the same size as the cathode. The current density was maintained at 20 mA/cm<sup>2</sup>. The gap between the anode and the cathode was 20 mm. The deposition was carried out at 60 °C for 2 h under mild stirring using a magnetic stirrer. The same procedure was used for the electrodeposition of the Ti/Sn-SbO<sub>x</sub> coating.

### 2.2. Characterization of electrodes

An electrochemical workstation (CS350, corrtest, China) with three electrodes was used for obtaining the anodic polarization curves, cyclic voltammetry curves, and Nyquist plots of the electrodes in an electrolyte solution of 50 g L<sup>-1</sup> Zn<sup>2+</sup> 150 g L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. A temperature of 40 °C was maintained. The experimental samples with a working area of 1.0 cm<sup>2</sup> were used as the working electrode. The remaining areas were sealed with epoxy resin. A mercurous chloride electrode (SCE): Hg, Hg<sub>2</sub>Cl<sub>2</sub>/sat. KCl was used as the reference electrode. A 6 cm<sup>2</sup> platinum plate was used as the counter electrode. The scanning rates for the anodic polarization and cyclic voltammetry measurements were 10 and 5 mV/s, respectively. The frequency interval of the electrochemical impedance spectroscopy (EIS) measurements ranged from 10<sup>5</sup> to 0.3 Hz, and the AC amplitude was 5 mV (root mean squared). The applied anodic potential was 1.8 V (SCE). The impedance data were converted into Nyquist data and were then fitted to appropriate simulative circuits.

The surface morphology of the anodic oxide layer was examined via scanning electron microscopy (SEM, XL30 ESEM, Philips, Holland). The chemical compositions were obtained through energy dispersive X-Ray spectroscopy (EDS, Phoenix, EDAI, USA). The phase composition of the films was studied using X-ray diffraction (XRD, D8Advance, Bruker,

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