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Effects of current density on preparation and performance of Al/conductive coating/α-PbO_2–CeO_2–TiO_2/β-PbO_2–MnO_2–WC–ZrO_2 composite electrode materials

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Abstract: Al/conductive coating/α-PbO_2−CeO_2−TiO_2/β-PbO_2−MnO_2−WC−ZrO_2 composite electrode material was prepared on Al/conductive coating/α-PbO_2−CeO_2−TiO_2 substrate by electrochemical oxidation co-deposition technique. The effects of current density on the chemical composition, electrocatalytic activity, and stability of the composite anode material were investigated by energy dispersive X-ray spectroscopy (EDXS), anode polarization curves, quasi-stationary polarization (Tafel) curves, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), and X-ray diffraction (XRD). Results reveal that the composite electrode obtained at 1 A/dm^2 possesses the lowest overpotential (0.610 V at 500 A/m^2) for oxygen evolution, the best electrocatalytic activity, the longest service life (360 h at 40 °C in 150 g/L H_2SO_4 solution under 2 A/cm^2), and the lowest cell voltage (2.75 V at 500 A/m^2). Furthermore, with increasing current density, the coating exhibits grain growth and the decrease of content of MnO_2. Only a slight effect on crystalline structure is observed.

Key words: composite electrode material; A1 substrate; β-PbO_2−MnO_2−WC−ZrO_2; electrochemical co-deposition; current density

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1 Introduction

Electrocatalytic oxidation co-deposition technology has been intensively studied [1,2] because of its many distinctive advantages [3,4], including environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation and cost effectiveness. PbO_2 is usually used as an anode for the electrowinning of metals [5,6]. The traditional PbO_2-coated metal anode used for electrowinning zinc possesses some advantages over conventional Pb−1% (mass fraction) Ag anode, such as the obviated need for preconditioning, higher quality of electrolytic zinc, good corrosion resistance toward chlorine or even removal of the chloride ion in electrolyte, less anode slime, higher output of precipitated zinc and longer lifetime of the anode at higher current density [7]. However, the PbO_2-coated metal anode has high cell voltage in electrolytic process.

Manganese dioxide electrodes have been widely investigated as electrowinning zinc anodes [8,9]. Manganese dioxide anodes in acidic sulfate-based electrolytes possess excellent electrocatalytic activity and corrosion resistance. Manganese dioxide is not easily dissolved, does not pollute the cathode deposit during the

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electrolysis process, and produces a high-purity cathode product. However, this electrode material has poor conductivity and mechanical properties, which limits its wide application in various industries.

PbO_2 and MnO_2 composite electrodes have been widely investigated [10]. These composite electrodes are prepared by adding PbO_2 to nano-MnO_2 particles. The modifying effect of PbO_2 on MnO_2 is based on the introduction of Pb into the MnO_2 lattice. PbO_2 and MnO_2 form the complexes Pb(*X*) and Mn(*Y*) (*X*=IV, II; *Y*=IV, III) in the MnO_2 charge–discharge process. These compounds undergo co-oxidation and co-reduction, resulting in a complete MnO_2/MnOOH homogeneous redox process. Furthermore, the discharge capacity of MnO_2 can be greatly improved by doping nano-PbO_2 powders to modify MnO_2 electrodes [11]. Metal-based coated anodes with different substrates, such as Ti-based electrodes (Ti/PbO_2, Ti/RuO_2, Ti/IrO_2, Ti/TiO_2/PbO_2, and Ti/SnO_2−Sb_2O_3−MnO_2/PbO_2) [12–16], stainless steel-based electrodes (stainless steel/β-PbO_2−TiO_2−Co_3O_4 and stainless steel/PbO_2−CeO_2) [17] and Pb-based electrodes (Pb/Pb−MnO_2) [8,9], have been widely studied. Whereas the cost of titanium is higher than that of other electrode materials, stainless steel has lower electroconductivity than copper, aluminum, lead, iron and so on. Lead has poor mechanical properties. In this work, an aluminum substrate is used because of its low cost, low specific gravity, and excellent electrical conductivity and mechanical properties.

To further improve the electrocatalytic activity for oxygen evolution and reduce the overpotential of oxygen evolution, a β-PbO_2−MnO_2−WC−ZrO_2 composite coating with high catalytic activity was prepared on a previous Al/conductive coating/α-PbO_2−CeO_2−TiO_2 substrate [18−20] through anodic electrochemical co-deposition of PbO_2, MnO_2, nano-ZrO_2, and WC particles in lead nitrate and manganese nitrate acid baths. PbO_2 with high electrical conductivity and MnO_2 with high electrocatalytic activity were successfully compounded. Nano-ZrO_2 and WC particles with high electrocatalytic activity were successfully incorporated [21−26]. This work was focused on the influences of current density on the chemical composition, electrocatalytic activity, and stability of the composite anode material.

2 Experimental

2.1 Preparation

Al/conductive coating/α-PbO_2−CeO_2−TiO_2/β-PbO_2−MnO_2−WC−ZrO_2 composite electrode materials were synthesized by applying a conductive undercoating to an A1 substrate, covering the undercoating with an intermediate coating consisting of the α-PbO_2−CeO_2−TiO_2 deposit, and finally covering the intermediate coating with a top coating consisting of a mixture of β-PbO_2−MnO_2 deposit and WC and ZrO_2 particles. The schematic diagram of the composite electrode materials is shown in Fig. 1.

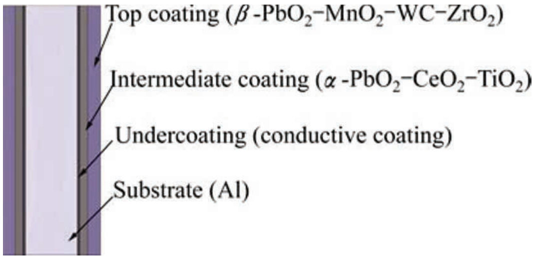

Fig. 1 Schematic diagram of Al/conductive coating/α-PbO_2−CeO_2−TiO_2/β-PbO_2−MnO_2−WC−ZrO_2 composite electrode materials

The substrates were 25 mm×50 mm×2 mm aluminum (1060) plates, both sides of which were roughened by sand-blasting, degreased and chemically etched, and then coated by a conductive material. The conductive coating consisted of waterborne resins (40%, mass fraction), conductive fillers (25%), and solvents (35%). The waterborne resins were either acrylic or polyurethane. The conductive fillers consisted of silver powder (5%) and copper powder (95%). The solvent was a mixture of ethanol (60%) and ethyl acetate (40%). The procedure was performed as follows: first, the conductive coating solution was applied to the substrate by brushing; second, the substrate was surface dried under infrared lamp; and finally, the substrate was dried in an electric drying oven at 423 K for 2 h. The conductive undercoating produced in this work was approximately 20 μm to 30 μm thick. The details were presented in Ref. [27]. The composition and process conditions of the α-PbO_2 plating bath are as follows: 4 mol/L NaOH with litharge PbO(s) (the soluble PbO species were $HPbO_2^-$ anions), pH≥14, anode current density of 1.0 A/dm^2, mild stirring using a magnetic stirrer, bath temperature of 40 °C, 15 g/L TiO_2 grain (rutile, average particle size of 30 nm), 100 g/L CeO_2 grain (average particle size of 50 nm), and electroplating time of 4 h. The composition and process conditions of the β-PbO_2−MnO_2 plating bath are as follows: 30% $Pb(NO_3)_2$ (pH=1.5), 80 g/L $Mn(NO_3)_2$, 50 g/L ZrO_2 particles (average particle size of 20 nm), 40 g/L WC (average particle size of 3 μm), anode current density of 0.5−2.5 A/dm^2, mild stirring using a magnetic stirrer, bath temperature of 60 °C, and electroplating time of 2 h. The granularities of the TiO_2, CeO_2, ZrO_2, and WC particles were analyzed by LS900 laser grain size analyzer (OMEC Technology Co., Ltd., Zhuhai, China). The plating bath was dispersed for 30 min by an ultrasonic device before electrodeposition to assure particle dispersion in the oxide substrate.