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Effects of current density on preparation and performance of Al/conductive coating/ α -PbO₂-CeO₂-TiO₂/ β -PbO₂-MnO₂-WC-ZrO₂ composite electrode materials

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Abstract: Al/conductive coating/ α -PbO₂-CeO₂-TiO₂/ β -PbO₂-MnO₂-WC-ZrO₂ composite electrode material was prepared on Al/conductive coating/ α -PbO₂-CeO₂-TiO₂ 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/dm² possesses the lowest overpotential (0.610 V at 500 A/m²) for oxygen evolution, the best electrocatalytic activity, the longest service life (360 h at 40 °C in 150 g/L H₂SO₄ solution under 2 A/cm²), and the lowest cell voltage (2.75 V at 500 A/m²). Furthermore, with increasing current density, the coating exhibits grain growth and the decrease of content of MnO₂. Only a slight effect on crystalline structure is observed.

Key words: composite electrode material; A1 substrate; β -PbO₂-MnO₂-WC-ZrO₂; electrochemical co-deposition; current density

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. PbO₂ is usually used as an anode for the electrowinning of metals [5,6]. The traditional PbO₂-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 PbO₂-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.

PbO₂ and MnO₂ composite electrodes have been widely investigated [10]. These composite electrodes are prepared by adding PbO₂ to nano-MnO₂ particles. The modifying effect of PbO2 on MnO2 is based on the introduction of Pb into the MnO₂ lattice. PbO₂ and MnO₂ form the complexes Pb(X) and Mn(Y) (X=IV, II; Y=IV, III) MnO₂ charge–discharge process. in the These compounds undergo co-oxidation and co-reduction, resulting in a complete MnO₂/MnOOH homogeneous redox process. Furthermore, the discharge capacity of MnO₂ can be greatly improved by doping nano-PbO₂ powders to modify MnO₂ electrodes [11]. Metal-based coated anodes with different substrates, such as Ti-based electrodes (Ti/PbO₂, Ti/RuO₂, Ti/IrO₂, Ti/TiO₂/PbO₂, and Ti/SnO₂-Sb₂O₃-MnO₂/PbO₂) [12-16], stainless steel-based electrodes (stainless steel/\u00c3-PbO2-TiO2-Co₃O₄ and stainless steel/PbO₂-CeO₂) [17] and Pb-based electrodes (Pb/Pb-MnO₂) [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 -PbO₂-MnO₂-WC-ZrO₂ composite coating with high catalytic activity was prepared on a previous Al/conductive coating/ α -PbO₂-CeO₂-TiO₂ substrate [18-20] through anodic electrochemical codeposition of PbO₂, MnO₂, nano-ZrO₂, and WC particles in lead nitrate and manganese nitrate acid baths. PbO₂ with high electrical conductivity and MnO₂ with high electrocatalytic activity were successfully compounded. Nano-ZrO₂ 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 -PbO₂-CeO₂-TiO₂/ β -PbO₂-MnO₂-WC-ZrO₂ 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 -PbO₂-CeO₂-TiO₂ deposit, and finally covering the intermediate coating with a top coating consisting of a mixture of β -PbO₂-MnO₂ deposit and WC and ZrO₂ particles. The schematic diagram of the composite electrode materials is shown in Fig. 1.



Fig. 1 Schematic diagram of Al/conductive coating/ α -PbO₂-CeO₂-TiO₂/ β -PbO₂-MnO₂-WC-ZrO₂ 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 -PbO₂ plating bath are as follows: 4 mol/L NaOH with litharge PbO(s) (the soluble PbO species were HPbO₂⁻ anions), pH≥14, anode current density of 1.0 A/dm², mild stirring using a magnetic stirrer, bath temperature of 40 °C, 15 g/L TiO₂ grain (rutile, average particle size of 30 nm), 100 g/L CeO₂ grain (average particle size of 50 nm), and electroplating time of 4 h. The composition and process conditions of the β -PbO₂-MnO₂ plating bath are as follows: 30% Pb(NO₃)₂ (pH=1.5), 80 g/L Mn(NO₃)₂, 50 g/L ZrO₂ 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/dm², mild stirring using a magnetic stirrer, bath temperature of 60 °C, and electroplating time of 2 h. The granularities of the TiO2, CeO2, ZrO2, 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.

2.2 Characterization

An electrochemical workstation (CHI660C) with three electrode systems was used in this experiment. The schematic diagram of the electrochemical test is shown in Fig. 2. The working electrode was the A1/ conductivecoating/a-PbO2-CeO2-TiO2/β-PbO2-MnO2-WC-ZrO anode experimental sample with a working area of 1.0 cm^2 , and the reference electrode used was saturated calomel electrode (SCE; Hg, Hg₂C1₂/saturated KCl). The potential of the mercurous chloride electrode (vs SCE) used in the anodic polarization curves and EIS measurements was 0.231 V (vs NHE) at 40 °C. The counter electrode used was a graphite plate (6 cm^2). All potentials shown in the figures are against SCE.

The anodic polarization curves were obtained in a synthetic electrolyte of 50 g/L Zn^{2+} and 150 g/L H₂SO₄ at 40 °C. Anodic polarization experiments were carried out at a constant scan rate of 5 mV/s from an initial potential of 1.2 V (vs SCE) to a final potential of 2.1 V (vs SCE). Electrochemical impedance measurements were performed in a synthetic electrolyte consisting of 50 g/L Zn^{2+} and 150 g/L H₂SO₄ at 40 °C. The frequency interval was from 10⁵ Hz to 0.1 Hz, and the AC amplitude was 5 mV (root mean square). The applied anodic potential was 1.4 V (vs SCE). The impedance data were converted into Nyquist data format and then fitted to appropriate simulative circuits. The surface morphology of the composite coating was characterized by SEM (XL30 SEM, Philips, Holland). The chemical compositions were obtained by EDXS (Phoenix, EDAI, USA). The phase composition of the films was studied by XRD using Cu K_a radiation (D8ADVANCE, Bruker, Germany).

3 Results and discussion

As shown in Fig. 3, cyclic voltammetric curves for the Al/conductive coating/ α -PbO₂-CeO₂-TiO₂ electrodes

were measured at 60 °C in the potential range from 0 to 2.1 V (vs SCE) at a constant scan rate of 5 mV/s in different baths: 1) 30% Pb(NO₃)₂ (pH 1.5); 2) 100 g/L Mn(NO₃)₂ + 15 g/L HNO₃ + 20 g/L KNO₃; 3) 30% $Pb(NO_3)_2 + 80 g/L Mn(NO_3)_2 (pH 1.5)$. Before recording CV curve, the Al/conductive coating/ α -PbO₂-CeO₂-TiO₂ electrode was kept in each bath until achieving steady open-circuit-potential. And the potential of mercurous chloride electrode (vs SCE) used in cyclic voltammetric curves is 0.215 V (vs NHE) at 60 °C. The potential of the beginning deposition of MnO_2 is approximately 1.0 V (vs SCE). The potential of the beginning deposition of β -PbO₂-MnO₂ is nearly 1.0 V (vs SCE), and that of β -PbO₂ is approximately 1.25 V (vs SCE). The beginning deposition potentials of MnO₂ and β -PbO₂-MnO₂ are almost the same and lower than those of β -PbO₂. Based on the standard redox potentials [28], the anodic deposition of MnO₂ should proceed more easily than the deposition of PbO₂.

$$Mn^{2+}+2H_2O=MnO_2+4H^++2e$$

(1)

$$Pb^{2+}+2H_2O=PbO_2+4H^++2e$$

 $\varphi^{\Theta}(V) = 1.228 - 0.1182 \text{pH} - \ln\alpha_{[\text{Mn}^{2+}]}$ Pb²⁺+2H₂O=PbO₂+4H⁺+2e $\varphi^{\Theta}(V) = 1.449 - 0.1182 \text{pH} - \ln\alpha_{[\text{Pb}^{2+}]}$ (2)

where φ^{Θ} is the standard redox potential against NHE, and $\alpha_{[Mn^{2+}]}$ and $\alpha_{[Pb^{2+}]}$ are the activities of the $[Mn^{2+}]$ and $[Pb^{2+}]$ ion, respectively.

Equilibrium reactions (1) and (2) show that the standard equilibrium potential of MnO₂ is 0.221 V lower than that of PbO₂. When E < 1.5 V (vs NHE), MnO₂ electrodeposition predominates. Thus, lower potentials are required for the deposition of pure MnO₂. However, upon the decrease of Mn²⁺ in solution, the amount of deposited PbO₂ increases during the electrodepositing process. This phenomenon is more obvious as Mn^{2+} is further reduced. The presence of Pb²⁺ and/or formation of PbO₂ may increase the overpotential of MnO₂ deposition.



Fig. 2 Schematic diagram of electrochemical test



Fig. 3 Cyclic voltammograms on A1/conductive coating/ α -PbO₂-CeO₂-TiO₂ at 60 °C in different baths: 1-30% Pb(NO₃)₂ (pH=1.5); 2-100 g/L Mn(NO₃)₂ + 15 g/L HNO₃ + 20 g/L KNO₃; 3-30% Pb(NO₃)₂ + 80 g/L Mn(NO₃)₂ (pH=1.5)

3.1 Chemical composition

Figure 4 shows the effects of current density on the chemical compositions of β -PbO₂-MnO₂-WC-ZrO₂ composite coatings. Figure 4(a) shows the effect on WC and nano-ZrO₂ contents, and Fig. 4(b) shows the effect on PbO₂ and MnO₂ contents.



Fig. 4 Influence of current density on chemical compositions of composite coatings: (a) Mass fractions of WC and ZrO₂; (b) Mass fractions of PbO₂ and MnO₂

The contents of WC and nano- ZrO_2 in the composite coatings increase with the increase in current density and reach the highest value (6.61% and 3.51%, respectively) when the current density is 1 A/dm². When the current density is higher than 1 A/dm², the contents of WC and nano- ZrO_2 in the composite coatings slowly decrease with increasing current density. PbO₂ content monotonously increases and MnO₂ content monotonously decreases with the increase in current density.

This phenomenon may be explained as follows. In the first case ($J \le 1$ A/dm²), as the deposition rates of PbO₂ and MnO₂ increase, the capture probability of the particles becomes higher. In the second case $(J>1 \text{ A/dm}^2)$, the content of particles in the coating remains nearly constant or decreases when the deposition rate reaches its limiting value [29]. The high current density causes the simultaneous reactions of Pb2++Mn2+ oxidation and oxygen evolution. In this current density region, oxygen evolution significantly contributes to the partial current, thus decreasing the current efficiency of PbO₂ and MnO₂ formation. In other words, oxygen has sufficient time to hinder the co-deposition of particles with PbO2 and MnO₂. Ultimately, the content of particles in the composite decreases with increasing current density in the higher-current density region. The content of WC particles in the composite coatings is higher than that of nano-ZrO₂ particles. WC is thermodynamically unstable and is easily oxidized in the presence of water or oxygen at room temperature. WC powder is easily oxidized on the surface, and the oxidized surface layer mainly consists of WO₃. The zeta-potential of the WC powder is highly negative in the pH range of 3 to 11. This behavior is typical of an acidic oxide with a very low isoelectric point. The surface of the WO₃ particle can adsorb hydrates and -OH groups. The presence of these surface groups can result in a negative surface charge according to the following reaction [30]:

$$\equiv W - OH \Longrightarrow W - O^{-} + H^{+}$$
(3)

In this case, the increase in WC and MnO_2 contents in PbO₂ is due to the specific adsorption of Pb²⁺ and Mn²⁺ on the WC particles. The zero-charge pH value (pH₀) of ZrO₂ is approximately 6.82 [31]. Thus, the migration possibility of nano-ZrO₂ particles to the anode surface is weak. The higher current density results in a higher deposition overpotential, which is favorable to PbO₂ deposition and adverse to MnO₂ deposition. This process ultimately results in the increased PbO₂ content and the decreased MnO₂ content with increase in current density [28].

3.2 Anode polarization curves and EIS

Figure 5(a) shows the anodic polarization curves of the Al/conductive coating/ α -PbO₂-CeO₂-TiO₂/ β -PbO₂-

 $MnO_2-WC-ZrO_2$ composite electrode materials obtained by anodic deposition at different current densities in 50 g/L Zn²⁺ and 150 g/L H₂SO₄ solution at 40 °C. A change in the oxygen evolution potential of the composite electrodes obtained at different current densities was clearly observed. As shown in Fig. 5(a), over the studied polarization range, the polarization curve of composite electrode obtained at 2.5 A/dm² presented the highest oxygen evolution potential whereas that of composite electrode obtained at 1.0 A/dm² presented the lowest oxygen evolution potential at a current density of 500 A/m²(0.05 A/cm²).

The relationship curve of the JR_s -corrected overpotential for oxygen evolution, η , and the logarithm for current density, lg*J*, was also employed in this research (Fig. 5(b)). The overpotential data (η) used for the fitted Tafel lines of oxygen evolution were obtained from part of the anodic polarization curves (about 1.7 V to 2.1 V, vs SCE) using the following formula [8,13,25]:

$$\eta = E + 0.231 \,\mathrm{V} - 1.240 \,\mathrm{V} - JR_{\rm s},\tag{4}$$

where *E* (vs SCE) is the potential of oxygen evolution obtained in the anodic polarization curves, 0.231 V (vs SHE) is the potential of the SCE, 1.240 V (vs NHE) is the reversible potential of oxygen evolution calculated from the Nernst equation using a synthetic zinc electrowinning electrolyte of 50 g/L Zn²⁺ and 150 g/L H₂SO₄ at 40 °C, *J* is the Faradaic current, and R_s is the electrolyte resistance between the reference and working electrodes.

Figure 5(b) shows the JR_s -corrected Tafel lines $(\eta$ -lg J) of the anode samples obtained at different current densities. The lines mainly present a double-slope behavior except the line of composite electrode obtained at 2.5 A/dm². These slope values and the potential intercepts of the five lines were separately analyzed using Origin 7.5 software and the results are displayed in Table 1. The η under a specific current density was calculated using the Tafel formula [32] and is listed in Table 1.

$$\eta = a + b \lg J \tag{5}$$

where η and J represent the overpotential of oxygen evolution and the Faradaic current, respectively, and a and b are constants obtained by linear fitting of the relationship curve of η (Formula (4)) and lg J in Origin 7.5 software. Variables a_1 and b_1 correspond to a low potential area, whereas a_2 and b_2 correspond to a high potential area. In this work, η values under specific current densities and the electrode surface (exchange) current density were calculated in the low potential area $(a_1 \text{ and } b_1)$.

The electrode surface (exchange) current density, J_0 , was calculated using the Tafel equation (5) when $\eta=0$ [24].



Fig. 5 Anodic polarization curves and Tafel lines for anode samples: (a) Anodic polarization curves; (b) Simulated Tafel lines

Table 1 Overpotentials and kinetic parameters of oxygen evolution for composite electrode prepared at different current densities

Current density/ _ (A·cm ⁻²)	Overpotential of oxygen evolution, η /V										2
	500 A/m ²	600 A/m ²	700 A/m ²	800 A/m ²	900 A/m ²	1000 A/m ²	a_1	b_1	a_2	b_2	$J_0/(\mathrm{A}\cdot\mathrm{cm}^{-2})$
0.5	0.688	0.709	0.726	0.741	0.754	0.766	1.024	0.258	1.213	0.499	1.070×10^{-4}
1.0	0.610	0.638	0.662	0.682	0.700	0.716	1.067	0.351	1.208	0.545	9.123×10^{-4}
1.5	0.700	0.722	0.741	0.757	0.771	0.784	1.062	0.278	1.277	0.551	1.510×10^{-4}
2.0	0.781	0.801	0.818	0.833	0.846	0.858	1.114	0.256	1.234	0.405	4.450×10^{-5}
2.5	0.880	0.902	0.921	0.937	0.951	0.964	1.243	0.279			3.510×10^{-5}

As shown in Table 1, J_0 mainly presented a declining trend with increasing current densities during electrodeposition. The J_0 of composite electrode obtained at 2.5 A/dm² was the lowest (3.510×10^{-5} A/cm²) and was the highest in the anode sample obtained at 1.0 A/dm² (9.123×10⁻⁴ A/cm²). According to electrochemical theory, the electrode polarization and the reversibility of electrode reactions may be evaluated by J_0 ; generally, a higher J_0 implies that the electrode is not easily polarizable, electrode reversibility is improved, and the electrode reaction easily occurs.

The η values of the anode samples obtained at 1.0 A/dm² during electro-deposition were 0.610, 0.638, 0.662, 0.682, 0.700, and 0.716 V at 500, 600, 700, 800, 900, and 1000 A/m², respectively, corresponding to decreases of 270, 264, 259, 255, 251, and 248 mV, respectively, compared with anode samples obtained at 2.5 A/dm² during electro-deposition. In summary, with increasing current densities during electro-deposition, the potential (vs SCE) and η mainly present rising trends whereas the J_0 demonstrates a declining trend.

As shown in Fig. 5 and Table 1, at a fixed current density, the A1/conductive coating/ α -PbO₂-CeO₂-TiO₂/ β -PbO₂-MnO₂-WC-ZrO₂ electrodes deposited at 1 A/dm^2 show the lowest potential and overpotential and possess the best electrocatalytic activity. The electrocatalytic activity of the anode depends on electronic and geometric factors [33]. At a given current density, the corresponding electrode potential is a result of multiple factors affecting the OER kinetics (e.g. anode kind. electrode morphology, and electrolyte). Furthermore, the limiting catalytic activity is reached when the content of WC and nano-ZrO₂ particles is at maximum (Fig. 4(a)). The overpotential mainly increases as the MnO₂ amount decreases in the composite coating (Fig. 4(b)). Therefore, the incorporated MnO₂ can improve the catalytic activity of the composite coating.

EIS measurements were performed by applying an AC voltage of 5 mV over the frequency range of 10⁵ Hz to 10^{-1} Hz. The results analyzed by Zsimpwin software are shown in Figs. 6(a) and (b)). Apparently, an electrochemical responsive semicircle and a straight line are observed simultaneously. Thus, the electrochemical process was controlled by both the electrochemical reaction and the diffusion step. An equivalent circuit model [34] is proposed in Fig. 6(c). In the equivalent circuit, R_s stands for the electrolyte resistance, C_{dl} stands for the double layer capacitance, $R_{\rm ct}$ represents the charge transfer resistance in the electrochemical process, CPE stands for the constant phase element of the interface between electrode and electrolyte, R_a is equivalent resistance associated with the adsorption of intermediate, and W_0 is the Warburg resistance of the diffusion step. Table 2 shows the simulation result by Zsimpwin software. The charge transfer resistances $R_{\rm ct}$ are 1.983 and 5.659 $\Omega \cdot {\rm cm}^2$ when the composite electrode is obtained at 0.5 and 2.5 A/dm², respectively. The charge transfer resistance of composite electrode obtained at 0.5 A/dm² is the minimum. However, the composite coating obtained at 0.5 A/dm² presents large cracks which also fall off easily (Fig. 7(a')). The charge transfer resistance of composite electrode obtained at 1 A/dm² is the minimum (3.135 $\Omega \cdot {\rm cm}^2$) except that of composite electrode obtained at 0.5 A/dm². Furthermore, the composite coating obtained at 0.5 A/dm². Furthermore, the composite coating obtained at 1.0 A/dm² presents the compact microstructures.



Fig. 6 Experimental EIS patterns and electrical equivalent circuit for composite electrode materials: (a) Nyquist diagrams; (b) Bode plots; (c) Electrical equivalent circuit used to simulate impedance data for OER on composite electrode materials

The experimental (scatters) and simulated (lines) Bode patterns for Al/conductive coating/ α -PbO₂-CeO₂-TiO₂/ β -PbO₂-MnO₂-WC-ZrO₂ composite electrode materials obtained at different current densities (corresponding to Fig. 6(a)) are shown in Fig. 6(b). The experimental and simulated data reach a very good agreement.

3.3 Microscopic structure and phase composition

Figure 7 shows the morphologies of the β -PbO₂-

 MnO_2 -WC-ZrO₂ composite coatings obtained by anodic deposition at different current densities with 200- and 10000-time magnifications.

The surface morphologies of the coatings are considerably different from one another. Coarse grains and numerous agglomerations are observed on the surface. The grains mainly consist of square-, triangular-,

Table 2 Equivalent circuit simulation results for composite coatings obtained at different current densities in Zn^{2+} 50 g/L, H_2SO_4 150 g/L solution

Current density/ $(A \cdot dm^{-2})$	$R_{\rm s}/(\Omega \cdot {\rm cm}^{-2})$	$C_{\rm dl}/(\rm F\cdot cm^{-2})$	$R_{\rm ct}/(\Omega \cdot {\rm cm}^{-2})$	$CPE/(\Omega^{-1} \cdot cm^{-2} \cdot s^n)$	п	$R_{\rm a}/(\Omega \cdot {\rm cm}^{-2})$	$W_0/(\Omega \cdot \mathrm{cm}^{-2})$
0.5	0.136	9.232×10^{-5}	1.983	2.567×10^{-2}	0.80	2.332	0.056
1.0	0.155	3.017×10^{-5}	3.135	4.764×10^{-4}	1.0	0.7878	0.043
1.5	0.120	7.242×10^{-5}	3.520	1.703×10^{-4}	0.81	6.658	0.065
2.0	0.120	4.584×10^{-5}	3.724	7.540×10^{-4}	1.0	1.768	0.027
2.5	0.080	3.772×10^{-4}	5.659	9.656×10 ⁻³	0.95	7.4	0.050



Fig. 7 Influence of current density on surface microstructures of composite coatings: (a, a') 0.5 A/dm²; (b, b') 1.0 A/dm²; (c, c') 1.5 A/dm² (a', b' and c' are higher magnification of a, b and c, respectively)

3400

rectangular-shaped and subgrains with different orientations [35]. The subgrain size increases with increasing current density. The exact change in subgrain size depends on the composition on the surface, which determines the stacking fault energy [36]. More solid particle contents are obtained at higher current density. A coating morphology with no obvious cracks is obtained at the current density of 1 A/dm². Appropriately, increasing the current density is beneficial to the absorption between the coating and particles. The highest content of solid particles on the coating is achieved at a current density of 1 A/dm^2 , resulting in the maximal dispersion effect of the composite coating. Consequently, the inner stress of the coatings is eliminated and the cracks between coatings are reduced or even completely covered. Therefore, the current density should be controlled appropriately at 1 A/dm².

Figure 8 shows the XRD patterns for the β -PbO₂-MnO₂-WC-ZrO₂ composite coatings prepared at different current densities. Attribution of the peaks is performed using the JCPDS cards. The surface layer of β -PbO₂-MnO₂-WC-ZrO₂ is mainly composed of β -PbO₂ (JCPCDS card 41–1492), α -PbO₂ (JCPCDS card 45-1416), and MnO₂ (JCPCDS card 24-0735) with a small amount of WC (JCPCDS card 51-0939) and ZrO₂ (JCPCDS card 37-1484). The current density does not change the phase in the composite coating but changes their relative abundances. The highest contents of WC and nano-ZrO₂ are obtained at 1 A/dm², resulting in minimum peak intensity. The reason may be that the high content of WC and nano-ZrO₂ can modify the crystal structure of the composite coating by decreasing its grain size.



Fig. 8 XRD patterns of composite coating at different current densities

3.4 Service life

Figure 9 shows the accelerated life tests of the composite electrodes obtained at different current densities in 150 g/L H_2SO_4 solution under 2 A/cm² at

40 °C. The composite electrode material was subjected to accelerated life tests to compare their electrochemical stability. For composite electrode materials obtained at 2.5 A/dm² after 20 h, the cell voltage rapidly increased. A sharp potential increase was observed during the last few hours. The conductive composite oxide film and aluminum substrate were thus eroded. Therefore, the composite electrode materials obtained at 2.5 A/dm² had a service life of 20 h under accelerated life test conditions.



Fig. 9 Accelerated life tests of composite coating obtained at different current densities in 150 g/L H_2SO_4 solution under 2 A/cm^2 at 40 °C

Electrode deactivation includes metal base passivation, film consumption, film detachment, and mechanical damage [17,37]. The β -PbO₂-MnO₂-WC-ZrO₂ composite coatings disappeared at the end of the accelerated life test. Examination of the surface of the failed electrode shows that some areas of the aluminum substrate were exposed to the solution and showed pitting corrosion. Furthermore, a black deposit was observed at the cell bottom. The new composite electrode deactivation was the result of film detachment. The composite electrode materials obtained at 1 A/dm^2 displayed excellent stability under accelerated life test conditions up to 360 h. A sharp potential increase was also observed for composite electrode materials obtained at 1 A/dm². This result indicates that the service life of the composite electrode materials obtained at 1 A/dm² is approximately 360 h, which is longer than that of composite electrode materials obtained at 0.5, 1.5, 2, and 2.5 A/dm^2 under the same conditions. Moreover, no black deposit was observed at the cell bottom, and no area of the aluminum substrate was exposed to the solution. Thus, no film detachment occurred, and the film and substrate exhibited good bonding. The most likely reason for electrode deterioration is film consumption during the test [17].

The composite electrode obtained at 1 A/dm^2

presents the best electrochemical stability. To assess the actual life, an evaluation is conducted using the method proposed by CHEN et al [37]. In this method, a simple relationship between the electrode service life (L_s) and the current density (J) is proposed as follows:

$$L_{\rm s} = 1/J^m \tag{6}$$

where *m* ranges from 1.4 to 2.0. Assuming a lower *m* of 1.4 for the composite electrode, the predicted service life is 7 a at a current density of 50 mA/cm².

3.5 Cell voltage

The electrolysis conditions used in this experiment are as follows: 50 g/L Zn^{2+} , 4 g/L Mn^{2+} (or without Mn²⁺), 150 g/L H₂SO₄, 40 °C temperature, 3 cm cathode-anode distance, 500 A/m² current density, and 24 h electrolytic time. The measured cell voltage is shown in Table 3. The A1/conductive coating/ α -PbO₂- CeO_2 -TiO₂/ β -PbO₂-MnO₂-WC-ZrO₂ obtained at 1 A/dm² possesses the lowest cell voltage with and without Mn²⁺. This result shows that the composite electrode has superior advantages over the conventional Pb-1%Ag alloy with regard to reducing cell voltage [8,9,17,38]. The possible reasons are as follows. Firstly, the surface layer of composite electrode was composed of β -PbO₂, MnO₂, WC and ZrO₂. These solid particles and β -PbO₂ possess higher catalytic activity for oxygen evolution [17]. Secondly, intermediate layer of composite electrode was composed of α -PbO₂, CeO₂ and TiO₂. The intermediate layer improves the adhesion of surface layer and undercoating. And finally, the lower cell voltage may be due to the good electric conduction of the aluminum substrates.

Table 3 Cell voltages of different electrodes in $ZnSO_4$ - H_2SO_4 solution

	Cell voltage/V			
Electrode	$7n^{2+}50 \alpha/I$	Zn ²⁺ 50 g/L,		
Lietuoue	$\Sigma II = 50 \text{ g/L},$	Mn ²⁺ 4 g/L,		
	H ₂ SO ₄ 150 g/L	H ₂ SO ₄ 150 g/L		
Pb	3.81	3.61		
Pb-1%Ag	3.14	3.34		
Al/conductive coating/				
a-PbO ₂ -CeO ₂ -TiO ₂ /β-PbO ₂ -	2.75	2.83		
MnO ₂ =6.61WC=3.51%ZrO ₂				

4 Conclusions

1) Good catalytic activity of A1/conductive coating/ α -PbO₂-CeO₂-TiO₂/ β -PbO₂-MnO₂-WC-ZrO₂ inert node was successfully prepared by composite electrodeposition of MnO₂, PbO₂, WC, and ZrO₂ particles on A1/conductive coating/ α -PbO₂-CeO₂-TiO₂. The composite coating possesses the best combination property at current density of 1 A/dm^2 .

2) With increasing current density, the coating exhibits grain growth and the content of MnO_2 is reduced. However, the crystalline structure is only slightly affected. The highest content of solid particles is observed at the current density of 1 A/dm², indicating the maximal dispersion effect of the composite coating. Thus, the inner stress of the coatings is eliminated and the cracks between coatings are reduced or even completely covered.

3) At a fixed current density, the A1/ conductive coating/ α -PbO₂-CeO₂-TiO₂/ β -PbO₂-MnO₂-WC-ZrO₂ electrodes deposited at 1 A/dm² exhibit the lowest potential and overpotential and possess the best electrocatalytic activity.

4) The composite electrode obtained at the current density of 1 A/dm² has the longest service life. At high current density (2 A/dm²), its lifetime reaches 360 h. The cell voltage is 0.4 V lower than that of the Pb–1% Ag alloy anode in 50 g/L Zn²⁺, 4 g/L Mn²⁺, and 150 g/L H₂SO₄.

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电流密度对 Al/导电涂层/α-PbO₂-CeO₂-TiO₂/β-PbO₂-MnO₂-WC-ZrO₂复合电极材料制备和性能的影响

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摘 要:通过电化学氧化共沉积技术在 A1/导电涂层/α-PbO₂-CeO₂-TiO₂ 基体上,制备了 A1/导电涂层/α-PbO₂-CeO₂-TiO₂/β-PbO₂-MnO₂-WC-ZrO₂复合阳极材料。通过能量色散 X 射线光谱(EDXS)、阳极极化曲线、暂稳态极 化曲线(Tafel)、交流阻抗谱(EIS)、扫描电子显微镜(SEM)以及 X 射线衍射(XRD)等方法研究电流密度对复合阳极 材料的化学组分、电化学活性和稳定性的影响。研究结果表明:在电流密度为 1 A/dm²条件下制备的 A1/导电涂 层/α-PbO₂-CeO₂-TiO₂/β-PbO₂-MnO₂-WC-ZrO₂复合材料具有最低的析氧过电位(0.610 V,条件: 500 A/m²),最 好的电化学活性,最长的使用寿命(360 h,条件: 150 g/L H₂SO₄, 2 A/cm², 40 °C)以及最低的槽电压(2.75 V,条件: 500 A/m²)。而且,随着电流密度的增加,涂层晶粒逐渐增大,MnO₂含量也逐渐降低,晶体结构几乎没有变化。 关键词:复合电极材料;铝基体;β-PbO₂-MnO₂-WC-ZrO₂;电化学共沉积;电流密度

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