

Effect of Current Density on Preparation and Properties of TF/ β -PbO₂ in MSA Media

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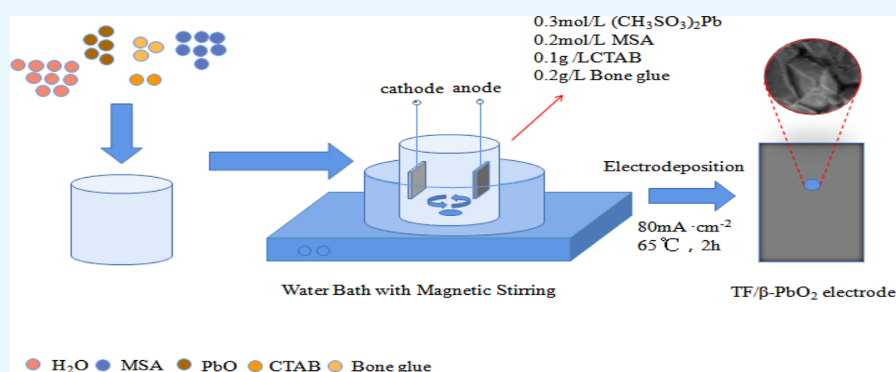
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ABSTRACT: The lead-based alloy and DSA anodes have drawbacks, such as poor corrosion resistance, easy peeling of coating, low electrocatalytic activity, and environmental pollution in electrode preparation processes. In this study, titanium foam/ β -PbO₂ (TF/ β -PbO₂) was prepared by electrodeposition in methanesulfonic acid (MSA) media. The current efficiency and the deposition rate were 89.7% and 5.36 v/($\mu\text{m}\cdot\text{min}^{-1}$) at the best current density of 80 mA·cm⁻², respectively. The TF/ β -PbO₂ was characterized by electrochemical tests, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The cyclic voltammetry (CV) test shows that the anodic peak potential of the optimum TF/ β -PbO₂ was as low as 2.135 V and anodic voltammetry charge was up to the maximum value of 3.564×10^{-2} C. The linear sweep voltammetry (LSV) test indicates that exchange current density of the optimum TF/ β -PbO₂ reached the maximum value of 8.284×10^{-6} A·cm⁻². CV and LSV tests indicate that the optimum TF/ β -PbO₂ had a high electrocatalytic activity. Electrochemical impedance spectroscopy test Tafel polarization curves show that the optimum TF/ β -PbO₂ had better corrosion resistance. The XRD test shows that the crystal was mainly β -PbO₂ of the optimum TF/ β -PbO₂ surface and the current density affected the preferential growth of the crystal surface of PbO₂. SEM tests show that grains of the optimum TF/ β -PbO₂ coating prepared were tightly bound and uniform in size.

1. INTRODUCTION

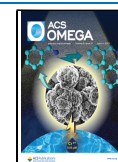
The lead dioxide (PbO₂) electrode is widely used owing to its low cost, good conductivity, and mechanical properties. Meanwhile, the PbO₂ electrode has been noticed for its good chemical stability in acidic solutions and high oxygen evolution overpotential.^{1–3} At present, the PbO₂ electrode is mainly based on lead alloy, which is easily corroded and then causes the pollution of the electrolyte. TF is a kind of foam structure composed of a titanium pore skeleton. It has some properties, such as light, high strength, sound absorption, heat insulation, vibration reduction, damping, impact energy absorption, and electromagnetic shielding. It can be used not only as a structural material but also as a functional material, which has attracted extensive attention. Moreover, TF has a three-dimensional structure and large specific surface area. It combines with the coating well and reduces the internal stress between the substrate and the coating. Therefore, it can make the life of the electrode longer.

At present, the main plating solutions for PbO₂ electrodeposition are the fluoroborate, nitrate, and perchlorate systems.^{4–6} Fluoroborate and perchlorate plating solutions are gradually eliminated due to the disadvantages of strong corrosiveness, difficult treatment of the waste plating solution, and serious environmental pollution. Cu²⁺, F⁻, or other ions need to be added for the preparation of a better PbO₂ coating in a nitrate-plating solution,⁷ which easily causes pollution of the plating solution. Fortunately, MSA has attracted attention in electrodeposition and electrolysis recently.⁸ It has some properties including low toxicity, high saturation metal salt

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solubilities, high conductivity, wider operating window, and ease of effluent treatment.⁹ Velichenko¹⁰ found that the coatings can be obtained at a high deposition rate in MSA. And Protsenko¹¹ demonstrated the formation of lead coatings, which were electrodeposited from an electroplating bath containing MSA. Unfortunately, there is no literature on the electrodeposition of PbO₂ using MSA as a medium and TF as the matrix. Furthermore, current density is one of the most important factors for the preparation of TF/ β -PbO₂. Therefore, it has a great significance for studying the effect of current density on the preparation of the TF/ β -PbO₂ electrode.

In this work, PbO₂ was electrodeposited using MSA as a solution and TF as the matrix. The effects of current density on the surface micromorphology and preferred orientation of TF/ β -PbO₂ were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrocatalytic activity and anticorrosion performance of TF/ β -PbO₂ electrode were investigated by cyclic voltammetry (CV), linear sweep voltammetry (LSV), Electrochemical impedance spectroscopy (EIS), and Tafel.

2. EXPERIMENTAL SECTION

2.1. Preparation of TF/ β -PbO₂. In this work, TF with a bore diameter of 30 μ m and size of 1 \times 1.5 cm² was used. The TF was first cleaned with ethanol solution by ultrasonication for 30 min and then heated in a 1 M sodium hydroxide solution at 90 $^{\circ}$ C for 30 min to remove oil fouling. Then, the TF was boiled in a 10% oxalic acid solution for 60 min and washed in an ethanol solution. Finally, the TF was dried after washed with deionized water. The stainless-steel sheet was washed in absolute ethyl alcohol solution and 1 M hydrochloric acid solution for 30 min to remove oil fouling. Then, the stainless-steel sheets were washed with deionized water, polished, and dried. All chemicals used in the study were of analytical reagent grade lead oxide, cetyl trimethyl ammonium bromide (CTAB), bone glue, and MSA with deionized water. Figure 1 shows the schematic diagram of experimental equipment.

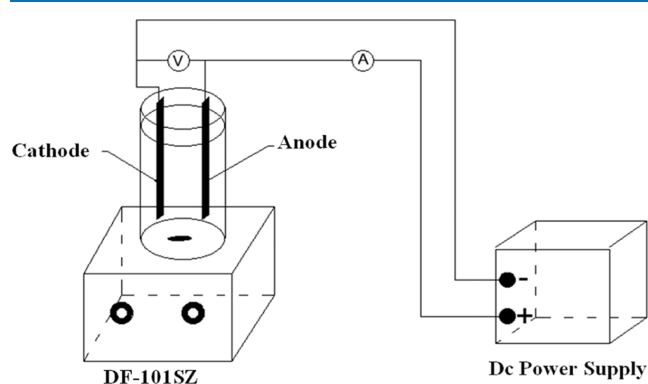


Figure 1. Electrodeposition of TF/ β -PbO₂ schematic diagram of experimental apparatus.

2.2. Characterization. All electrochemical tests were conducted by a CHI660E electrochemical workstation, which was composed of three electrodes. The working electrode was the TF/ β -PbO₂ electrode with 1.5 cm² effective area. The reference electrode was a saturated calomel electrode and the auxiliary electrode was a platinum electrode. The effects of current density on the performance and surface microstructure

of the TF/ β -PbO₂ were studied by XRD, SEM, CV, LSV, EIS, and Tafel, respectively. CV curves were measured at a scan rate of 60 mV/s starting from 0 to 2.3 V. The EIS test at open-circuit potential conditions and AC potential with an amplitude of 10 mV and normally, a frequency range of 0.1 Hz–100 kHz. The anodic polarization curve was obtained by the LSV test at a scan rate of 60 mV/s starting from 0.4 to 2.0 V. The Tafel curve test potential range is -0.5 – 0.5 V and scanning rate is 0.01 V·s⁻¹.

3. RESULTS AND DISCUSSION

3.1. Effect of Current Density on Current Efficiency and Deposition Rate for the Preparation of TF/ β -PbO₂. TF/ β -PbO₂ were prepared in MSA solutions under different current densities. The current efficiency and deposition rate are calculated by eqs 1 and 2, respectively.

$$\eta = \frac{60m}{41.46It} \times 100\% \quad (1)$$

where η is the current efficiency, %; m is the weight of deposited PbO₂, g; I is the current, A; and t is the electrodeposition time, min.

$$v = m/\rho st \quad (2)$$

where v is the deposition rate, μ m·min⁻¹; ρ is the density of PbO₂, 9.375 g·cm⁻³; and s is the working area of anode sample, cm².

Figure 2 shows the effect of current density on the preparation of TF/ β -PbO₂. It can be seen that the current

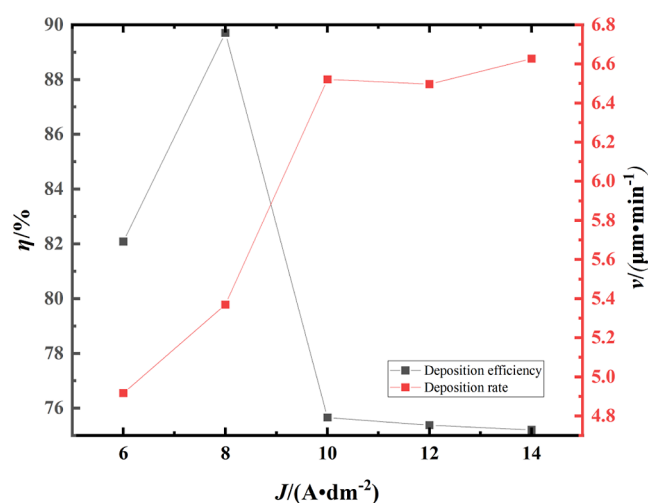


Figure 2. Effect of current density on the current efficiency and deposition rate.

efficiency initially increased from 82.1 to 89.7% with an increase of current density from 60 to 80 mA·cm⁻². However, the current efficiency decreased with a further increase of current density. When the current density was up to 100 mA·cm⁻², the current efficiency was 75.5%. This is mainly because the increase of oxygen evolution rate under high current density. Meanwhile, with the increase of current density, the deposition rate of PbO₂ also increased. The deposition rate of PbO₂ increased slowly when hydrogen evolution occurred in the cathode at a high current density. When the current density was 80 mA·cm⁻², the current efficiency and deposition rate of

the TF/ β -PbO₂ were 89.7% and 5.36 v/ $\mu\text{m}\cdot\text{min}^{-1}$, respectively.

3.2. Cyclic Voltammetry Curve of TF/ β -PbO₂. Figure 3 shows the CV curve of TF/ β -PbO₂ prepared under different

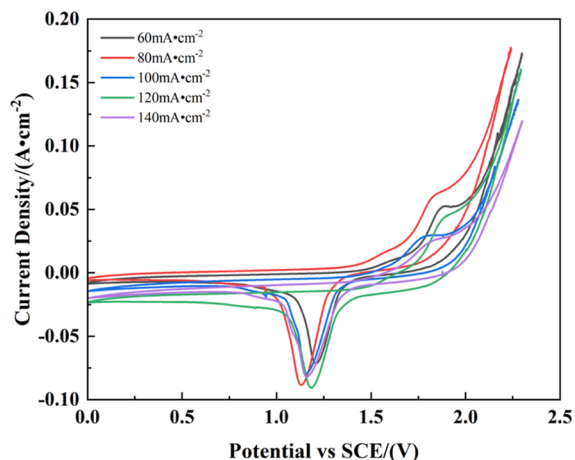


Figure 3. CV curves of TF/ β -PbO₂ prepared under different current densities.

current densities. Moreover, the values of anode peak potential, peak current, and voltammetry charge calculated by the graphical integration method are shown in Table 1.

Table 1. E_p , i_p , and q^* of TF/ β -PbO₂ Prepared at Different Current Densities

J (mA·cm ⁻²)	i_p (10 ⁻² A)	E_p (V)	q^* (10 ⁻² C)
60	6.128	2.211	1.264
80	6.189	2.135	3.564
100	6.176	2.153	1.124
120	6.141	2.186	2.189
140	6.158	2.152	1.133

All TF/ β -PbO₂ electrodes showed a gradient in 1.5–2.3 V, which is due to the oxygen evolution reaction and Pb²⁺ → PbO₂ reaction.¹² Moreover, the Pb³⁺ → Pb²⁺ reaction leads to a reduction peak in 1.0–1.25 V.^{13,14} Figure 1 also shows the area of reduction peak was the largest using a current density of 80 mA·cm⁻². It indicates that the electrode had better electrocatalytic activity.

The TF/ β -PbO₂ electrode had a small anodic peak potential of $E_p = 2.135$ V and a large anode voltammetry charge of 3.564×10^{-2} C using a current density of 80 mA·cm⁻², which are shown in Table 1. Under the same oxygen evolution potential (1.5–2.3 V), the TF/ β -PbO₂ has a large oxygen evolution current. It indicates that the oxide of the TF/ β -PbO₂ was transformed into a high valence state before the oxygen evolution reaction. It had good electrocatalytic activity for the oxygen evolution reaction due to many high valence oxide active sites were generated on the surface of TF/ β -PbO₂. Meanwhile, TF/ β -PbO₂ had a low oxygen evolution potential and a large anodic voltammetry charge. It shows that the TF/ β -PbO₂ had more high valence oxide active sites, larger electrocatalytic active surface area, and better electrocatalytic activity.^{15–17}

3.3. Anodic Polarization Curve of TF/ β -PbO₂. Figure 4 shows the anodic polarization curve of TF/ β -PbO₂. The oxygen evolution potential of TF/ β -PbO₂ electrode changed

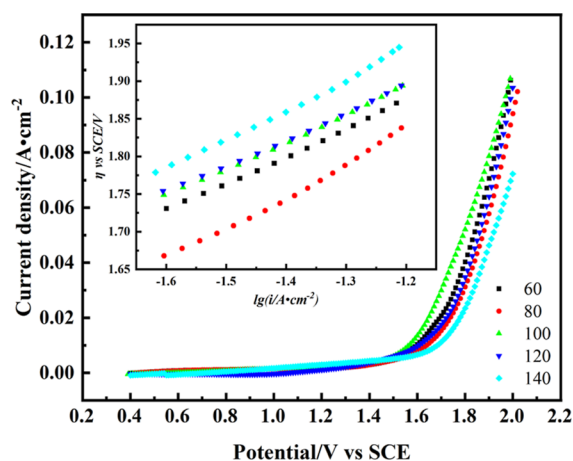


Figure 4. Anodic polarization curves of TF/ β -PbO₂ prepared under different current densities.

with the change of current density. When the current density was 80 mA·cm⁻², the TF/ β -PbO₂ electrode had a relatively high oxygen evolution potential, which was 2.012 V. However, with the increasing of current density, the electrode with a current density of 140 mA·cm⁻² had a relatively low oxygen evolution potential of 2.007 V. The difference between the lowest oxygen evolution potential and the highest oxygen evolution potential was 5 mV.

Figure 4 also shows the Tafel curve of TF/ β -PbO₂ in different current densities. The data are shown in Table 2. The

Table 2. Tafel Fitting Data of TF/ β -PbO₂ Prepared at Different Current Densities

J (mA·cm ⁻²)	η (V)	a	b	I_0 (A·cm ⁻²)
60	1.098	1.097	0.258	5.239×10^{-6}
80	1.071	1.065	0.264	8.284×10^{-6}
100	0.976	1.039	0.232	6.166×10^{-6}
120	1.012	1.048	0.258	5.103×10^{-6}
140	1.055	1.027	0.313	5.262×10^{-6}

TF/ β -PbO₂ has a better electrocatalytic activity when the current density was 80 mA·cm⁻². The reason is that the higher the exchange current density, the stronger the electrocatalytic activity of the electrode.^{18,19}

3.4. EIS of TF/ β -PbO₂. When the potential was higher than 1.5 V, TF/ β -PbO₂ had a strong oxygen evolution reaction. It led to many bubbles that adhere to the electrode surface and effect the stability of the electrode surface. At the same time, when the potential was smaller than 1.5 V, the oxygen evolution rate of the electrode was slow. Therefore, in order to research the kinetic characteristics of oxygen evolution of TF/ β -PbO₂ in different current densities, 1.5 V was selected for EIS. Figure 5 shows the Nyquist plot of TF/ β -PbO₂ in different current densities. It can be seen that TF/ β -PbO₂ electrodes in different current densities showed good uniformity in a sulfuric acid solution. It indicates that the anode materials had good stability in an electrolytic solution.

When the current density was higher than 80 mA·cm⁻², the capacitive loop of TF/ β -PbO₂ became larger. However, the capacitive loop of TF/ β -PbO₂ was the smallest using a current density of 80 mA·cm⁻². It shows that the energy to overcome for the oxygen evolution reaction in a sulfuric acid solution was small when TF/ β -PbO₂ had a small capacitive loop. So, the

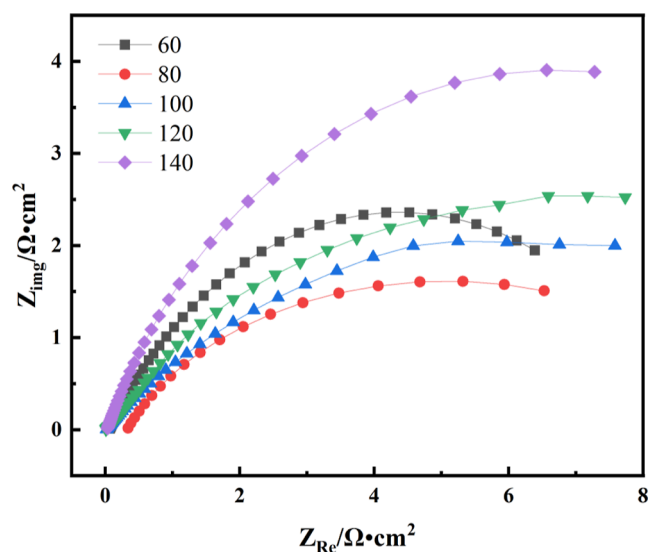


Figure 5. EIS curves of TF/ β -PbO₂ prepared under different current densities.

electrode reaction rate was fast and the electrocatalytic activity was high.^{20,21}

Figure S1 shows the corresponding Bode plot. It shows that the anode material prepared under different current densities has a wave peak, which indicates that the oxygen evolution reaction of the anode material has a time constant in an electrolytic sulfuric acid solution, and there is a state variable in the corresponding system. The state variable corresponds to the capacitive reactance arc on the Nyquist diagram, and the capacitive reactance arc is caused by the state variable through the charge and discharge relaxation in the circuit.

The equivalent circuit of the TF/ β -PbO₂ prepared with different current densities is shown in Figure 6 and the

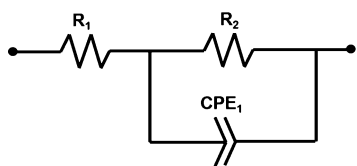


Figure 6. Equivalent circuits of TF/ β -PbO₂ prepared at different current densities.

parameters are listed in Table 3. It can be seen that the value changes of R1 (electrolyte resistance) and n are not obvious from Table 3. It indicates that the adsorption type of the reactive ions was like the pure capacitance adsorption, and the dispersion effect was inconspicuous.^{22,23} Moreover, with the

Table 3. Electrochemical Parameters of Equivalent Circuit Elements for TF/ β -PbO₂ Prepared at Different Current Densities

J (mA·cm ⁻²)	R1 (Ω·cm ⁻²)	R2 (Ω·cm ⁻²)	CPE1 (Ω ⁻¹ ·cm ⁻²)	n (Ω ⁻¹ ·cm ⁻² ·s ^{n})
60	0.945	20.905	0.661	0.796
80	1.128	21.935	0.679	0.814
100	0.926	20.034	0.642	0.812
120	1.172	20.011	0.611	0.838
140	1.105	19.932	0.605	0.855

increase of current density, R2 (charge-transfer resistance) of the oxygen evolution reaction decreased, which indicates that the internal spread resistance of TF/ β -PbO₂ electrodes gradually decreased. This result was consistent with the decrease of the overpotential for the oxygen evolution reaction. The results show that the optimum electrode exhibited superior anticorrosion performance.

Figure 7 shows the corresponding Tafel polarization curve. All curves were obtained in solution containing 1 mol/L

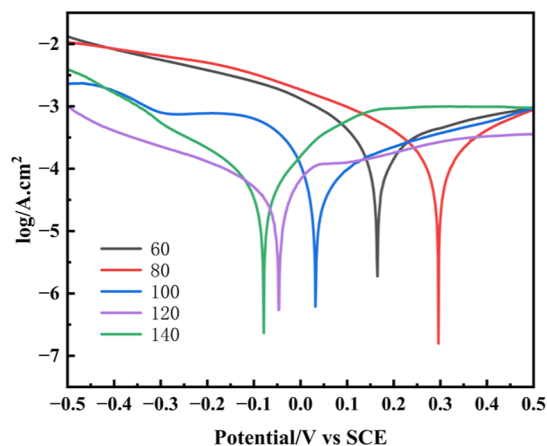


Figure 7. Tafel polarization curves of TF/ β -PbO₂ prepared under different current densities.

H₂SO₄ at room temperature at a scan rate of 10 mV·s⁻¹. It can be seen that a current density of 80 mA·cm⁻² significantly accelerates the corrosion current density of the electrode, leading to the increase of the corrosion potential of the electrode, which indicates that the electrode has better corrosion resistance characteristics under this condition. It was further verified that the anode material electrode prepared with a current density of 80 mA·cm⁻² showed better corrosion resistance. The results show that the optimum electrode exhibited superior anticorrosion performance.

3.5. XRD Patterns of TF/ β -PbO₂. Electrodeposition of metal oxides generally are three states: matrix epitaxial growth, disordered orientation, and preferred orientation.²⁴ For polycrystalline coatings formed by electrocrystallization, the growth rate of different crystal faces is different, and the growth direction of the grain will be preferentially developed under the same current direction. Thus, it may result in a preferred orientation of crystallization, that is, a texture is formed on the coating.²⁵ Figure 8 shows the XRD patterns of TF/ β -PbO₂ prepared at different current densities. Compared with the data of the standard powder diffraction card (76-0564), the crystalline grains of β -PbO₂ show that the obvious preferred orientations were (200), (301), and (310) crystal faces. Meanwhile, with the current density increased to 80 mA·cm⁻², the thickness of PbO₂ coating increased, new crystal faces (101) and (220) appeared in the XRD pattern and the preferred orientation of the (101), (211), and (301) crystal faces of the coating became more obvious. Moreover, the obviously preferred orientation of the coating gradually changed to (301) and (310) crystal faces when the current density increased to 100, 120, and 140 mA·cm⁻², respectively. This indicates that the increase of current density will affect the preferred orientation of the crystal. When the current density reached 100 mA·cm⁻², the preferred orientation of the crystal

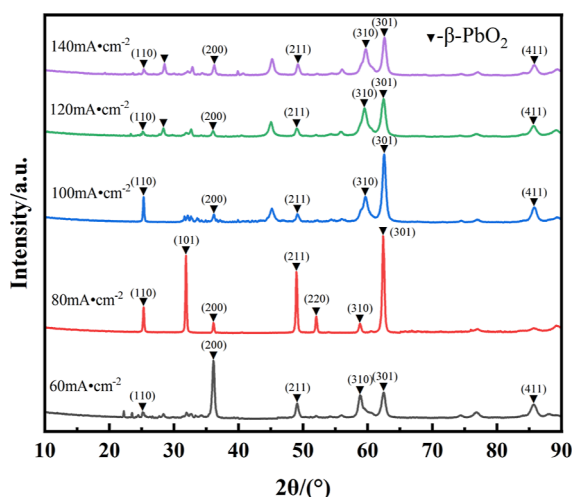


Figure 8. XRD patterns of TF/ β -PbO₂ anodes prepared under different current densities.

did not change. However, the preferred orientation of β -PbO₂ crystal was obvious using a current density of 80 mA·cm⁻². Figure S2 shows the XRD patterns of different β -PbO₂ electrode materials after corrosion. From the figure, it can be seen that PbSO₄ may be generated on the surface of the coating, which needs to be further demonstrated by SEM.

3.6. Surface Morphology of Different PbO₂ Coatings.

Current density is one of the most important factors to determine the surface morphology of the coating. The crystal morphology characteristics are different under different deposition conditions. Porous PbO₂ coating can be obtained without any additives in electrodeposition. Figure 9 shows the SEM images of different PbO₂ coatings obtained by electrodeposition with current densities of 60, 80, 100, 120, and 140 mA·cm⁻² for 2 h in MSA solutions with an additive of CTAB.

The surface morphology of β -PbO₂ grains obtained by electrodeposition with a current density of 60 mA·cm⁻² was not smooth enough, and the whole surface was not flat and dense. In contrast, β -PbO₂ grains were smoother and denser with a typical pyramid structure when the current density reached 80 mA·cm⁻², and their grains were interconnected, interwoven, grew up, and distributed evenly. However, with the further increase of current density, the size of β -PbO₂ grains in the electrode surface gradually decreased, the number of grains increased, and the growth of grains was uneven. They led to the decrease of the area density of β -PbO₂, which easily led to the electrolyte dipping into the electrode substrate and was not conducive to the growth of β -PbO₂ grains. Thus, it may result in the failure and falling of the coating.

Figure S3 shows the SEM images of the electrode coating after corrosion of the β -PbO₂ electrode material, which is not very different from the surface topography of the electrode without corrosion. The surface structure is still β -PbO₂, which further proves that the electrode material prepared has good corrosion resistance.

4. CONCLUSIONS

- (1) TF/ β -PbO₂ were prepared by electrodeposition in MSA solutions. The variable current density experiments indicated that the optimum current density was 80 mA·cm⁻². Under this condition, the current efficiency

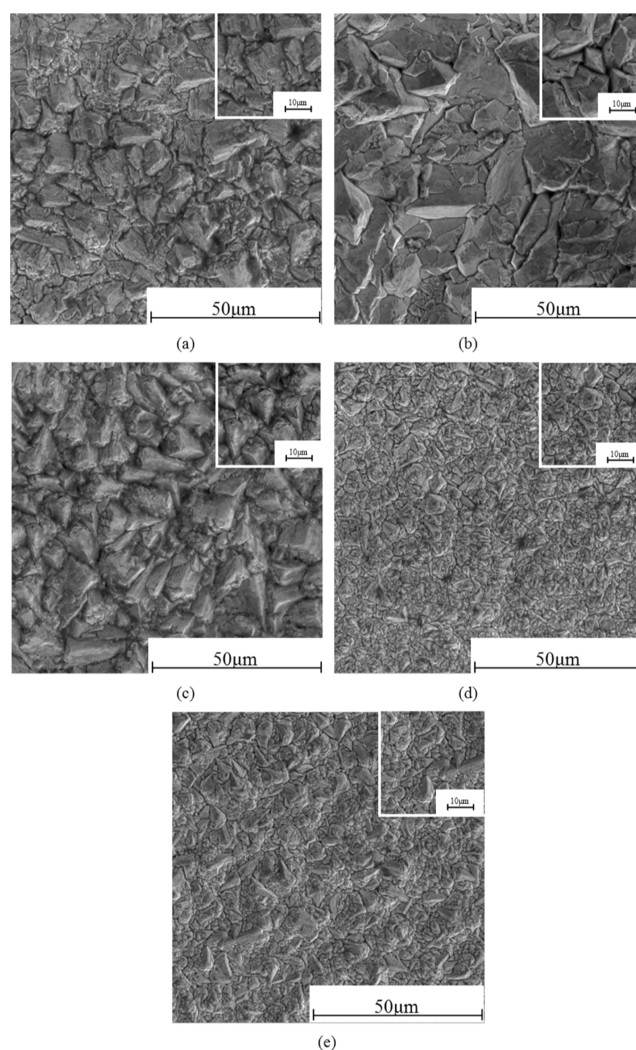


Figure 9. SEM images of TF/ β -PbO₂ prepared under different current densities (a) $J = 60$ mA·cm⁻², (b) $J = 80$ mA·cm⁻², (c) $J = 100$ mA·cm⁻², (d) $J = 120$ mA·cm⁻², and (e) $J = 140$ mA·cm⁻².

was 89.7% and the deposition rate was 5.36 v/ μ m·min⁻¹, respectively.

- (2) The results of the CV curve and anodic polarization curve show that the optimum TF/ β -PbO₂ have high electrocatalytic activity. The smaller anodic peak potential, larger anode voltammetry charge, and higher exchange current density were 2.135 V, 3.564 $\times 10^{-2}$ C, and 8.284 $\times 10^{-6}$ A·cm⁻², respectively.
- (3) The results of EIS and Bode plot indicated that the optimum TF/ β -PbO₂ had a superior anticorrosion performance. Meanwhile, the Tafel polarization curve further verifies this conclusion.
- (4) The results of XRD and SEM show that the β -PbO₂ phases had an orientation preference with bonded, uniform grains, and a good anticorrosion performance in the optimum TF/ β -PbO₂.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c07879>.

Phase plot of Bode of TF/ β -PbO₂ anodes prepared under different current densities and, XRD patterns and SEM images of TF/ β -PbO₂ prepared after corrosion (PDF)

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Notes

The authors declare no competing financial interest. Data will be made available on request.

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