In this work, the Ti/PbO2 anode materials were prepared from nitrate solutions in the presence of fatty alcohol polyoxyethylene ether AEO to study the effects of AEO on PbO2 deposition. The phase composition and microstructure of electrode material were characterized by XRD and SEM. The PbO2 electrodeposition mechanism and electrocrystallization behavior were investigated by cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA) and Scharifker-Hills (SH) mechanism. The results indicate that: The material is composed by β-PbO2 in this case and the growth orientation of the crystal face is changed by AEO; The growth model of PbO2 crystals is in good agreement with Generalized Electrochemical Aggregative Growth Mechanism; The AEO can improve the morphology of PbO2 plating, and makes the surface smoother without flaws; The PbO2 electrodeposition is diffusion-irreversible-controlled process in the presence of AEO; The deposition on substrate is promoted, nevertheless, the further deposition on PbO2 coating is restrained by AEO; The DPt at each of step potentials, which relates to diffusion coefficient, was improved by AEO revealed variation of solution nature; The electrocrystallization of PbO2 follows Scharifker-Hills(SH) progressive nucleation/growth mechanism with the oxygen evolution occurring simultaneously, and the AEO increased the number density of active sites but reduced the nucleation rate.

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As a new-type insoluble metallic oxide anode, lead dioxide (PbO2) is used for nonferrous metals extracting due to its excellent electrocatalytic activity, corrosion resistance and stability. Traditional leadsilver alloy anode for zinc metallurgy is going to be replaced by silver alloy anode for PbO2 because of its higher catalytic activity, corrosion resistance and stability. Traditional lead dioxide is used for nonferrous metals extracting due to its excellent electrochemical characteristics.

The AEOs are prepared by polymerizing polyethylene glycol with fatty alcohol. The m in general formula means degree of polymerization, and AEOs with different degree of polymerization show various surface properties.

The AEO with specific organic additive into electrolyte can make the PbO2 plating smoother. As a nonionic emulsifier, the development of fatty alcohol polyoxyethylene ether (AEOs, CnH2n+1O(CH2)mH) is very fast. The AEOs are prepared by polymerizing polyethylene glycol with fatty alcohol. The m in general formula means degree of polymerization, and AEOs with different degree of polymerization show various surface properties. The AEO with specific organic additive into electrolyte can make the PbO2 plating smoother.

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Figs. 2d, 2e, 2f. Visually, there is a prominent difference in the surface morphology between the different electrodes. As seen in Fig. 2a, there are some holes (Dia. 0.2 mm) and protrusion on the surface of the electrode in the absence of AEO. Unstable electrodeposition rate lead to the active sites distribute unevenly and then the protrusion formed, as well as the holes appeared due to adsorption of the bubbles which are caused by oxygen evolution in the process of the reaction. It could be seen in Fig. 2d that holes and protrusion were disappeared due to either the active sites distribute equally or the bubbles over-flow easily in the presence of AEO. High magnifying morphologies of the PbO2 in the presence of AEO are shown in Figs. 2e and 2f, and it is distinct that the crystalline grains are compact and concordant. The images of holes are presented clearly in Figs. 2b and 2c with higher magnification. The growth of the crystals was stopped, and a significant discovery is expounded by following description: There are many nanoclusters close to the crystals, and it can be explained by Generalized Electrochemical Aggregative Growth Mechanism,14 which considered that nanoclusters would incorporated as building blocks during the early stages of thin-film growth.

**Voltammetry analysis.**—Cyclic voltammetry curves in solution B with different sweep ranges (1.15 V, 1.20 V, 1.30 V, 1.45 V) are shown in Fig. 3. Both initial and final potential are 0 V. There are no oxidation and reduction peaks at stopping potential 1.15 V which indicates that no reactions occurred at this high potential. The anodic branch of the curve features an obvious current growth corresponding to the reactions of lead(II) oxidation at higher stopping potential 1.2 V, and there is a weak current wave at the negative branch of the curve which belongs to the reduction of lead dioxide. A distinct anodic current can be found at stopping potentials higher than 1.4 V, which signifies the appearance of the oxygen evolution. It should be noted that the anodic current starts to appear at the potential 1.16 V which can be identified as the deposition potential of the lead dioxide. There is no clear current peak at the anodic branch of the curve owing the oxygen evolution occurred at the similar reaction rate as the PbO2 electrodeposition. A current loop between 1.03 V to 1.23 V indicates that nucleating occurred on the surface of electrode.15 The equilibrium potential of the PbO2 electrodeposition, which should be equivalent with the low potential of the current loop,16 is 1.03 V in this case.
and then, the overpotential of nucleation for PbO$_2$ was calculated and given about 130 mV. A current peak caused by lead dioxide reduction can be observed at potential 0.55 V, and another cathodic peak at potential 0.3 V is confirmed to the reduction of dissolved oxygen.\(^{17}\)

Cyclic voltammetry curves on Pt in solution B with different stir rates are shown in Fig. 4a. The cathodic peaks growth along with the increase of stir rates while the stir rates slower than 100 r/mins. Early study proved that the peak area of PbO$_2$ reduction corresponds to the quantity of lead dioxide.\(^{18}\) Obviously, the quantity of lead dioxide was increased by stirring in this case due to the variation of active species concentration in diffusion layer caused by forced convection, which revealed a consequence of diffusion control. However, there is no longer changes when the stir rates higher than 100 r/mins owing the steady state was achieved close to the electrode surface in solution. Higher stir rate makes the diffusion of active species constant. It should be noted that concentration polarization cannot be eliminated by stirring.

Fig. 4b is linear sweep voltammetric (LSV) curves on Pt in solution B with different potential sweep rates. Obvious broken lines at 1.23 V, 1.26 V, 1.27 V, 1.29 V, 1.33 V and 1.39 V can be noticed in these curves. The current inflection points shift toward higher potentials demonstrating an irreversible electron transfer which was described by the Delahay equation.\(^{18,19}\) The relationship between current maximum and potential sweep rates was described by Randles-Sevcik equation.\(^{20}\) The current peak $I_p$ is proportional to the square root of sweep rates $\nu^1/2$. Although, this equation lose efficacy because of the indetectable current peak $I_p$ caused by oxygen evolution in this experiment, it is still certain that the electrodeposition process of PbO$_2$ is an irreversible process controlled by diffusion in the presence of AEO speculate from Figs. 4a and 4b.

Cyclic voltammetry curves were tested on Pt in solution A and solution B respectively for studying the effects of AEO on the mechanism of lead dioxide electrodeposition. As is shown in Fig. 5, the reduction peak (R$_1$) area of PbO$_2$ is greater in the presence of AEO, and it revealed that the lead dioxide electrodeposition on substrate was promoted by AEO. The current peak R$_2$ attributed to the reduction of dissolved oxygen is also increased by AEO. The above results can be analyzed by the following reasons: More hydroxyl radical OH$_{ads}$ chemisorbed on the electrode and reacted with Pb$^{2+}$ to form PbO$_2$, as well as the reduction of dissolved oxygen was enhanced due to the promotion of the oxygen evolution by more OH$_{ads}$ on substrate.

The mechanism of lead dioxide electrodeposition, for nitrate solutions, was explained by Velichenko\(^{21-25}\) which can be described by the following stages:

\[
H_2O \rightarrow OH_{ads} + H^+ + e^- \quad [1]
\]

\[
Pb^{2+} + OH_{ads} \rightarrow Pb(OH)_{2}^{2+} \quad [2]
\]
Nucleation/growth of PbO2 occurred in this case. The current occurred controlled by diffusion at step potential 1.30 V. Dissimilarly, the PbO2 electrocrystallization, the chronoamperometry curves on Pt in solution B contain due to the decreasing of electroactive species concentration, likely to correspond to the formation of intermediate product and electroactivity. The anodic peaks at potential 1.3 V are correlated to the nature of substrates, and caused the change of reaction potential and electroactivity. The active PbO2 formed in the first sweep changed the nature of substrates, and caused the change of the PbO2 formed on the substrate before. The active PbO2 formed in the first sweep changed the nature of substrates, and caused the change of reaction potential and electroactivity. The anodic peaks at potential 1.3 V are corresponding to the formation of intermediate product Pb(OH)2+ (stage 2), and Pb(OH)2+ transformed into PbO2 finally (stage 3). Stage 2 is the rate-determining step in this case, as the reaction rate of stage 3 is faster than that of stage 2 inferred from Fig. 6a and Fig. 6b. The anodic peaks at potential 1.13 V are decrescent, while, the anodic peaks at potential 1.35 V have no change almost in the presence of AEO (Fig. 6b). The reduction peaks increased since the second sweep tested in solution A, nevertheless have no change in solution B. The observed effects indicate that, in this experiment, the reaction rate of stage 2, as well as the further electrodiposition of PbO2 was limited by AEO.

**Chronoamperometry analysis.**—Nucleation/growth of PbO2 will occur on the substrates. Prior studies described two different models for nucleation and growth processes: The rate-determining step is identified as the incorporation of ions into the growing lattice (kinetic control); The limiting step is the mass transport from the solution to the growing nucleus (diffusion control).26 To study the PbO2 electrocrystallization, the chronoamperometry curves on Pt in solution B at step potential 1.25 V and 1.30 V are shown in Fig. 7 and nucleation/growth of PbO2 is occurred in this case. The current occurred abruptly due to the ohmic polarization between the working electrode and reference electrode in the initial period of electrode polarization, along with charging of the double electrical layer. Subsequently, the current reduced to a minimum value \(i_a\) and kept for some time \(t\) (induction period). The current value increased to a maximum value \(i_{\text{max}}\) after the induction period, which \(i_{\text{max}}\) kept attenuating markedly due to the decreasing of electroactive species concentration, likely to contain Pb(OH)2+. In the diffusion layer until a steady concentration. The steady state achieved finally and PbO2 electrodiposition was controlled by kinetics if the current value kept in maximum value \(i_{\text{max}}\) for long times.

Further study has been conducted to discuss the effects of AEO on PbO2 electrocrystallization controlled by diffusion. The chronoamperometry curves on Pt in solution A and solution B at different step potentials (1.30, 1.33, 1.35, 1.38 V and 1.40 V) are shown in Figs. 8a and 8b respectively. These curves show sufficient characteristic of three-dimension nucleation.27 The traces of current transients do not converge at long times into a single line, as it would be expected from diffusion-controlled growth of nuclei. Instead, the currents increased with the applied potential due to the oxygen evolution occurring simultaneously on the surfaces. Moreover, certain law, the \(i_{\text{max}}\) increased with the step potentials, is reflected.

Cottrell equation describe a electrochemical reaction controlled by diffusion from transient state to achieve steady state in constant step potentials analysis:28,29

\[
I = \frac{zFD_0v^{1/2}}{\pi^{1/2}v^{1/2}}
\]

Where \(I\) is current peak value; \(t\) is time correspond with \(I; z\) is electron transfer number; \(F\) is Faraday constant; \(c_0\) is concentration of the metal ion in the bulk of the solution; \(D_0\) is diffusion coefficient. \(D_0\) has been calculated by the data extracted from chronoamperometry curves (Fig. 8) with Cottrell equation and displayed in Table I. The change of

![Figure 6. Superposition charts of multiple cyclic voltammetry curves on Pt in (a): solution A (b): solution B.](image)

![Figure 7. Chronoamperometry curves on Pt in solution B at step potential 1.25 V and 1.30 V.](image)
Despite all this, the theoretical modes of metal and metal-oxide electrocrystallization cases are accordant with these two mechanisms: the progressive or instantaneous nucleation/growth mechanism. This mechanism has a certain applicability in many cases, even though not driven not only by concentration gradients but also by the electric potentials in this case. It should be noted that the ionic mass transport is increased by AEO, obtained from Table I announced the change of solution components caused by electrolysis is not conspicuous enough in general electrochemical systems. However, if the concentration of electroactive species is high, the solution nature, such as the viscosity, will changed mightily by electrolysis, and the migration disturbs the experiment result. In consequence the $D_0$ values increased with step potentials in this case. Despite all this, $D_0$ still can be used to discuss the influence of AEO on Pb$^{2+}$ diffusion behavior. The result, $D_0$ at each of step potentials increased by AEO, obtained from Table I announced the change of solution nature.

Electrocrystallization theory was presented and revised in early researches, and Scharifker-Hills (SH) mechanism is accredited to describe the nucleation in electrodeposition field. The electrocrystallization of metal and metal-oxide should obey three-dimensional instantaneous or progressive nucleation/growth mechanism. This mechanism has a certain applicability in many cases, even though not all of the electrocrystallization cases are accordant with these two theoretical modes absolutely. The equations deduced by Scharifker and Hills are displayed:

$$I = \frac{zF_{c_0}D_0}{(\pi D_0 t)^{1/2}} \left[1 - \exp\left[-aN_0(\pi D_0 t)^{1/2} \theta\right]\right]$$

Where $I$ is current density; $N_0$ is the number density of active sites; $A$ is the steady state nucleation rate constant; $t$ is time; Three-dimensional instantaneous or progressive nucleation/growth mechanism was inferred from 5 and 6 for a hemispherical nucleation/growth controlled by diffusion. Conveniently, Two theoretical nondimensional expressions are used in describing instantaneous and progressive nucleation:

$$\frac{I^2}{I_{m}^2} = \frac{1.9542}{t/t_m} \left[1 - \exp\left[-1.2564(t/t_m)\right]\right]^2$$

$$\frac{I^2}{I_{m}^2} = \frac{1.2254}{t/t_m} \left[1 - \exp\left[-2.3367(t/t_m)\right]\right]^2$$

Where $I_m$ is current peak value; $t_m$ is time correspond with $I_m$; Instantaneous nucleation is described by 7 and progressive nucleation in 8. Actual nondimensional curves were fitted based on chronoamperometry curves (Fig. 8) and compared with theoretical nondimensional curves on Fig. 9a and Fig. 9b. Evidently, PbO$_2$ electrocrystallization follows SH nucleation/growth mechanism controlled by diffusion whether in the presence of AEO or not. Actual nondimensional curves of PbO$_2$ electrocrystallization are highly close to progressive nucleation theoretical nondimensional curves when $\theta/t_m < 1$. Undoubtedly, PbO$_2$ electrocrystallization is complex in this case, and actual nondimensional curves are in disparity with the theoretical nondimensional curves when $\theta/t_m > 1$ due to the secondary reactions occurring simultaneously such as the oxygen evolution.

To study the effects of AEO on kinetic data such as the number density of active sites $N_0$ and the nucleation rate constant $A$ of PbO$_2$ with oxygen evolution occurring simultaneously on the surface, the research methods have been reference, and an equation has been applied to describe the potentiostatic current–time transients according to the previous literature:33

$$j(t) = \left(P_1^* + P_2t^{-1/2}\right) \times \left(1 - \exp\left[-P_2 \left(t - \frac{1}{P_2} \exp(-P_2t/\theta)\right)\right]\right)$$

with $P_1^* = \varepsilon_{eo} F k_{eo}(2\varepsilon_{eo} M/\pi p)^{1/2}$, $P_2 = N_0 \pi kD_1$, $k = (8\pi c_{eo}/p)^{1/2}$, $P_3 = A$ and $P_4 = 2FD_1^{1/2}c_{eo}/\pi^{1/2}$, where $\varepsilon_{eo}$, $F$ is the molar charge transferred during the oxygen evolution, $k_{eo}$ the rate constant of the oxygen evolution reaction, $\rho$ the density of the deposit and $M$ its molar mass.

Parameters and kinetic data are fitting nonlinearly by using origin 8 according to the Eq. 9 and showed in Table II. The $D$ values calculated from $P_4$ are in good agreement with that obtained from the Cottrell

Table 1. Kinetics data obtained from the chronoamperometry curves according to Eq. 4.

| Step potential/V | $I_m$ (A/cm$^2$) | $T_m$ (s) | $D_0$ (cm$^2$/s) |
|-----------------|------------------|----------|------------------|
| **Solution A**  |                  |          |                  |
| 1.30 V          | 0.00622          | 0.952    | 1.10 x 10$^{-8}$ |
| 1.33 V          | 0.00977          | 0.517    | 1.45 x 10$^{-8}$ |
| 1.35 V          | 0.01339          | 0.390    | 2.12 x 10$^{-8}$ |
| 1.38 V          | 0.01798          | 0.293    | 2.80 x 10$^{-8}$ |
| 1.40 V          | 0.02294          | 0.238    | 3.79 x 10$^{-8}$ |
| **Solution B**  |                  |          |                  |
| 1.30 V          | 0.00630          | 1.036    | 1.28 x 10$^{-8}$ |
| 1.33 V          | 0.00910          | 0.763    | 1.95 x 10$^{-8}$ |
| 1.35 V          | 0.01217          | 0.550    | 2.53 x 10$^{-8}$ |
| 1.38 V          | 0.01605          | 0.416    | 3.27 x 10$^{-8}$ |
| 1.40 V          | 0.01895          | 0.373    | 4.01 x 10$^{-8}$ |
The surface of PbO₂ plating is smoother and the flaw disappears in the presence of AEO, which indicates the change of the solution nature. The PbO₂ electrocrystallization follows Scharifker-Hills (SH) progressive nucleation/growth mechanism with the oxygen evolution occurring simultaneously, and the number density of active sites was increased with addition of the AEO, on the contrary, the nucleation rate was reduced.

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Table II. Fit parameters and kinetic data resulting from analysis of the chronoamperometry curves in Fig. 8 according to Eq. 9.

| Step potential/V | \( P_1^* \) (mA cm\(^{-2}\)) | \( P_2 \) (s\(^{-1}\)) | \( P_3 \) (s\(^{-1}\)) | \( P_4 \) (mA cm\(^2\) s\(^{1/2}\)) | \( A \) (s\(^{-1}\)) | \( N_0 \) (cm\(^{-2}\)) | \( D \) (cm\(^2\) s\(^{-1}\)) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Solution A      |                 |                 |                 |                 |                 |                 |                 |
| 1.30 V          | 0.19            | 3.12            | 14.67           | 6.66            | 14.67           | 1.31 \times 10^8 | 1.05 \times 10^{-8} |
| 1.33 V          | 2.78            | 6.25            | 15.88           | 8.02            | 15.88           | 1.82 \times 10^8 | 1.51 \times 10^{-8} |
| 1.35 V          | 3.78            | 12.55           | 16.69           | 9.71            | 16.69           | 2.50 \times 10^8 | 2.21 \times 10^{-8} |
| 1.38 V          | 6.90            | 21.77           | 17.44           | 10.60           | 17.44           | 3.51 \times 10^8 | 2.73 \times 10^{-8} |
| 1.40 V          | 9.39            | 35.95           | 18.66           | 12.78           | 18.66           | 4.13 \times 10^8 | 3.83 \times 10^{-8} |
| Solution B      |                 |                 |                 |                 |                 |                 |                 |
| 1.30 V          | 0.11            | 4.54            | 2.93            | 7.19            | 2.93            | 1.65 \times 10^8 | 1.21 \times 10^{-8} |
| 1.33 V          | 0.10            | 9.29            | 3.04            | 9.54            | 3.04            | 1.92 \times 10^8 | 2.13 \times 10^{-8} |
| 1.35 V          | 2.04            | 16.26           | 3.74            | 10.14           | 3.74            | 2.97 \times 10^8 | 2.41 \times 10^{-8} |
| 1.38 V          | 4.03            | 29.73           | 4.05            | 11.90           | 4.05            | 3.94 \times 10^8 | 3.32 \times 10^{-8} |
| 1.40 V          | 5.75            | 43.50           | 4.32            | 12.95           | 4.31            | 4.87 \times 10^8 | 3.93 \times 10^{-8} |
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