Effect of $K_2Cr_2O_7$ on preparation and properties of Ti/Sn–Sb–RuO$_x$/α-PbO$_2$ for zinc electrowinning

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Abstract
In this study, a Ti/Sn–Sb–RuO$_x$/α-PbO$_2$ electrode was prepared by continuous extrusion coating technique. The surface microstructure of α-PbO$_2$ coating was examined by scanning electron microscopy (SEM). The electrocatalytic characteristics of the electrode were explored by anodic polarization curves, linear sweep voltammetry curve, electrochemical impedance spectroscopy (EIS). It was found that the addition of potassium dichromate ($K_2Cr_2O_7$) to the alkaline lead plating solution can significantly inhibit the cathode deposition of lead, which can stabilize the lead ions in the plating solution, prevent the solution from decomposing red Pb$_3$O$_4$, and increase α-PbO$_2$ deposition rate; when the amount of $K_2Cr_2O_7$ added is 2%, the prepared Ti/Sn–Sb–RuO$_x$/α-PbO$_2$ electrode has the best performance, and the oxygen evolution potential of the electrode is 1.5962 V (500 A m$^{-2}$), the charge transfer resistance Rt is 28.81 Ω·cm$^2$.

1. Introduction

In recent years, there has been a growing interest in zinc electrowinning. The titanium-based lead dioxide electrode material is a stable anode (DSA), which has the advantages of good electrical conductivity, high catalytic activity, small mass, stable structure, corrosion resistance and low preparation cost [1–4]. As the consumption of high-grade zinc concentrate in zinc hydrometallurgy continues to increase, the demand for anode materials in complex zinc concentrate production will become higher and higher in the future. Because the chlorine and fluorine contained in the zinc concentrate are relatively high, and the chlorine and fluorine elements in the existing production process cannot be effectively removed, chlorine and fluorine will form chlorine and fluoride ions in the electrolyte during the electrolysis process [5–7]. Severe exceeds the normal value and chemically reacts with the lead alloy anode to form lead chloride and lead fluoride crystals, thus greatly damaging the service life of the lead alloy anode [8–10]. Lead-based anodes have gradually failed to meet the needs of electroplating zinc production. So it is a meaningful reality to study the application of lead dioxide in zinc hydrometallurgy.

PbO$_2$ is classified into α type and β type according to the crystal type. α-PbO$_2$ is orthorhombic, the size structure of the crystal grain is small, and the binding force is strong, but the conductivity is poor and the stability is relatively good [11, 12]. β-PbO$_2$ is a tetragonal system with relatively large grain size, most of which is porous. Its resistivity is 96 μΩ cm, which is generally obtained from acid lead plating bath [13, 14]. In the process of preparing the intermediate layer α-PbO$_2$ of the PbO$_2$ electrode. Since the cathode reaction (Pb$^{2+} + 2e = Pb$) can consume Pb$^{2+}$ in the solution, the concentration of divalent lead ions in the plating solution is rapidly lowered, which is very disadvantageous for preparing the α-PbO$_2$ plating layer [15]. PbO is usually added to the plating solution to solve the problem of main Pb$^{2+}$ in the cathode consumption, but this increases the production cost of the PbO$_2$ electrode.

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In order to solve this problem, this study attempts to add potassium dichromate (K$_2$Cr$_2$O$_7$). The main function is to change the cathodic reaction in the electroplating process to achieve a stable concentration of Pb$^{2+}$ in the plating solution [16, 17]. Because the Cr$^{6+}$ in the plating solution changes in the valence state at the cathode.

In this study, a Ti/Sn–Sb–RuO$_x$/α–PbO$_2$ electrode was prepared by continuous extrusion coating technique. The surface microstructure of α–PbO$_2$ coating was examined by scanning electron microscopy. The electrocatalytic characteristics of the electrode were explored by anodic polarization curves, cyclic voltammetry, electrochemical impedance spectroscopy and Tafel curves.

### 2. Experimental

#### 2.1. Preparation of the Ti/Sn–Sb–RuO$_x$/α–PbO$_2$

**2.1.1. Electrode pretreatment**

The titanium piece was dehydrated in a sodium hydroxide solution at 70 °C for 30 min, was washed in deionized water for 2 min, and the oxidized layer was removed by mixing the acid with HF: HNO$_3$: H$_2$O at a volume ratio of 1: 4: 5 for 5 min. Etching was carried out with 20% hydrochloric acid at 90 °C for 2 h and was washed in deionized water for 2 min.

**2.1.2. Preparation of Sn–Sb–RuO$_x$ bottom layer**

The Sn–Sb–RuO$_x$ bottom layer was prepared by thermal decomposition. The SnCl$_4$, 5H$_2$O, SbCl$_3$, and RuCl$_3$·3H$_2$O materials were dissolved in a mixed solvent at a molar ratio of 6 : 1 : 2, and then placed in a rotary evaporator under a pressure of 0.06 MPa to control a certain temperature. The coating liquid was obtained by rotary evaporation for 1 h to completely dissolve the chloride. Brush the coating solution evenly on the acid-etched titanium plate with a brush, put it in an oven at 120 °C for 5 min, taked out the air and cool it to room temperature, then put it into a muffle furnace at 500 °C for high temperature and calcination for 10 min. The brushing, drying and calcining were repeated 10 times, and the last time was fired in a muffle furnace for 1 h. The average mass of the Sn–Sb–RuO$_x$ bottom layer is about 1.5 mg cm$^{-2}$.

**2.1.3. Preparation of α–PbO$_2$ coating**

According to the table 1, the plating solution of α–PbO$_2$ was set. The current density of electrodeposition was 3 mA·cm$^{-2}$, the electrodeposition time was controlled at 1 h, and the electrodeposition temperature was kept at 40 °C. After the solution was set, it was added before starting the plating [18]. Different amounts of K$_2$Cr$_2$O$_7$ was added to the plating solution were to be used after being dissolved.

**2.2. Measurements**

The prepared electrode was used as the anode, the titanium mesh was used as the cathode, and the electrolyte was placed in the electrolyte. The electrolyte composition and test conditions for the enhanced life test are 150 g l$^{-1}$ H$_2$SO$_4$ solution, and the current density of the accelerated life test was maintained at 1 A cm$^{-2}$.

A XL30 ESEM (Philips, Holland) scanning electron microscope was used to observe the microscopic surface morphology of the α–PbO$_2$ coating. An electrochemical workstation (CS350, Corrtest, China) with the three electrode system was used during the measurements of the chronoelectric potential, cyclic voltammetry, anodic polarization curve, electrochemical impedance spectroscopy (EIS) and galvanostatic electrolysis in a synthetic electrolyte with 50 g l$^{-1}$ Zn$^{2+}$ and 150 g l$^{-1}$ H$_2$SO$_4$ at 35 °C. The anodic polarization curve test has a potential interval of 0.9 to 1.9 V and a scan rate of 5 mV s$^{-1}$. The linear sweep voltammetry (LSV) curve test has a potential interval of 0 to 0.6 V and is tested at a scanning speed of 5 mV s$^{-1}$.

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**Table 1.** The plating solution composition and electroplating conditions for preparation of α–PbO$_2$ coating.

| Bath composition | Electroplate conditions |
|------------------|-------------------------|
| PbO             | 22.32 g · l$^{-1}$     |
| NaOH            | 140 g · l$^{-1}$       |
| Current density | 3 mA · cm$^{-2}$       |
| Temperature     | 40 °C                   |
| Time            | 1 h                     |

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3. Results and discussions

3.1. Surface morphology
The surface morphology of the α-PbO₂ coating of the Ti/Sn–Sb–RuOₓ/α-PbO₂ electrode prepared by adding different concentrations of K₂Cr₂O₇ is shown in figure 1. It can be seen that the needle-like structure of α-PbO₂ appears in all the four graphs. The α-PbO₂ coating prepared without adding K₂Cr₂O₇ is shown in figure 1(a). Although α-PbO₂ is deposited, the deposition effect is not good and agglomeration occurs, which may result in uneven coating surface. From the figures 1(b)–(d), as the concentration of K₂Cr₂O₇ increases, the agglomeration phenomenon disappears. The concentration of K₂Cr₂O₇ is more higher, the size of the deposited α-PbO₂ particles is more uniform, which may enhance the adhesion to the surface-active β-PbO₂ coating and may also increase the oxygen evolution electrocatalytic activity of the electrode.

3.2. Polarization curves
Figure 2 shows the anodic polarization curve of leaching lead dioxide in the plating solution when depositing the α-PbO₂ layer. It can be seen from the figure 2 that a change of the initial potential of the anodic deposition of lead dioxide occurs after the addition of different concentrations of K₂Cr₂O₇. As adding 1.5% and 2% K₂Cr₂O₇ into the plating solution, the initial potential is about 0.23 V. The initial deposition potential of lead dioxide in the plating solution without K₂Cr₂O₇ is about 0.38 V. The deposition of lead dioxide with the addition of K₂Cr₂O₇ has a small resistance and a lower deposition potential.

Figure 3 shows the cathodic reaction during the deposition process. The potential of PbO reduced to Pb in an alkaline environment is 0.58 V [19]. The potential of the reduced lead ion is different due to the influence of other ions in the plating solution. It can be seen from the reduction peak in figure 3 that the peak of reduced lead ions becomes smaller and smaller as the concentration of K₂Cr₂O₇ increases, indicating that the addition of K₂Cr₂O₇ can significantly inhibit cathode deposition of lead. The lead ions in the plating solution are kept stable,
3.3. Oxygen evolution catalytic activity

It can be seen from figure 4 that under the current density of 500 A m$^{-2}$, the oxygen evolution potential of the prepared electrode decreases with the increase of K$_2$Cr$_2$O$_7$ concentration. The prepared α-PbO$_2$ layer is more even and flat after the addition of K$_2$Cr$_2$O$_7$. So that the oxygen evolution electrocatalytic activity of the electrode is improved. The oxygen evolution potential of the electrode prepared by adding 2% K$_2$Cr$_2$O$_7$ at a current density of 500 A m$^{-2}$ is 1.5962 V. The oxygen evolution potential of the electrode prepared by adding 1.5% K$_2$Cr$_2$O$_7$ at a current density of 500 A m$^{-2}$ is 1.6073 V. The oxygen evolution potential of the electrode prepared by adding 1% K$_2$Cr$_2$O$_7$ is 1.6577 V. The oxygen evolution potential of the electrode prepared by adding 2% K$_2$Cr$_2$O$_7$ is 0.0615 V lower than that of the electrode prepared without adding K$_2$Cr$_2$O$_7$. The addition of K$_2$Cr$_2$O$_7$ can increase the electrocatalytic activity of the electrode because the oxygen evolution potential of the electrode has been reduced [20].

The AC impedance fitting map is shown in figure 5. The values of Rs, Rt and C after fitting analysis by ZsimDemo software are shown in table 2. Rs is the resistance of the solution between the working electrode and the reference electrode, Rt is the transfer resistance of electric charge, and C is the capacitance of the electrode surface [21]. The larger the Rt is, the larger the charge transfer resistance is, and the more difficult the oxygen
The evolution reaction on the electrode surface is. It can also be seen from the AC impedance diagrams and parameters of the graphs and tables that the charge transfer resistance $R_t$ of the electrochemical reaction prepared by adding 2% K$_2$Cr$_2$O$_7$ is smaller than that of other K$_2$Cr$_2$O$_7$ additions. It indicates that the oxygen evolution reaction is the easiest. The $R_t$ prepared by adding 1.5% K$_2$Cr$_2$O$_7$ is similar to the value by adding 2% K$_2$Cr$_2$O$_7$. The addition of K$_2$Cr$_2$O$_7$ results in better deposition of the surface coating and increases the active surface area.

According to the anodic polarization curve and the AC impedance value, the oxygen evolution overpotential can be obtained by calculation, and the oxygen evolution activity can be determined by comparing the oxygen evolution reaction activity with the electrode surface.

### Figure 4
Anodic polarization curves of $\alpha$-PbO$_2$ coatings prepared from different concentrations of K$_2$Cr$_2$O$_7$.

### Figure 5
The EIS of $\alpha$-PbO$_2$ coatings prepared from different concentrations of K$_2$Cr$_2$O$_7$.

### Table 2
Equivalent circuit parameters of $\alpha$-PbO$_2$ coatings prepared from different concentrations of K$_2$Cr$_2$O$_7$.

| Concentration of K$_2$Cr$_2$O$_7$ | $R_s$ (Ω cm$^{-2}$) | $R_t$ (Ω cm$^{-2}$) | $C$ (μF cm$^{-2}$) |
|----------------------------------|----------------------|----------------------|---------------------|
| 0%                              | 0.9037               | 53.12                | 4013               |
| 1%                              | 0.8095               | 38.84                | 9987               |
| 1.5%                            | 0.6444               | 31.56                | 1088               |
| 2%                              | 1.0388               | 28.81                | 5210               |

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evolution overpotential. In the study of the oxygen evolution overpotential of the electrode, the oxygen evolution overpotential ($\eta$) of the electrode is calculated by the formula \[ \eta = E + 0.640 - 1.242 - iR_s \] (1) \[22, 23\].

Where $E$ represents the oxygen evolution potential relative to the reference electrode (MSE) measured by the anodic polarization curve; 1.242 V is equilibrium potential and is used in the measurement system (50 g l$^{-1}$ Zn$^{2+}$; 150 g l$^{-1}$ H$_2$SO$_4$; 35 °C). The oxygen evolution equilibrium potential calculated by the Nernst equation; 0.640 is the potential of the MSE relative to the standard hydrogen electrode; $i$ is the measured current density at the relative potential; $R_s$ is electrolyte resistance between the reference electrode and the working electrode.

The anodic polarization curve processed by the formula (1) is converted into the Tafel curve form ($\eta$-lg$i$), and then linearly fitted by the Origin software can obtain $a$, $b$ values as shown in figure 6 and table 3. The oxygen evolution overpotential and $a$ and $b$ values of the electrodes at current densities of 500 A cm$^{-2}$ and 1000 A cm$^{-2}$ are calculated by the formula \[24\] and are listed in table 3. The overpotential $\eta$ and the current density $i$ have a logarithmic relationship of the equation (2):

\[ \eta = a + b \log i \] (2)

Where $\eta$ and $i$ represent the overpotential of oxygen evolution and the Faradaic current, respectively. Meanwhile, $a$ and $b$ are Tafel parameters.

It can be seen from table 3 that under the conditions of 500 A m$^{-2}$ and 1000 A m$^{-2}$, the oxygen evolution overpotential is the lowest electrode prepared by adding 2% K$_2$Cr$_2$O$_7$, and the oxygen evolution reaction is more likely to occur. The electrode electrocatalytic performance can be expressed by the electrode process kinetic parameters. The smaller the $a$ value is, the smaller the cell voltage is. From the data in the table 3, the $a$ value of the electrode prepared by adding 1% K$_2$Cr$_2$O$_7$ is similar with the $a$ value of the electrode prepared without adding K$_2$Cr$_2$O$_7$, and is slightly higher than that of the electrode prepared without adding adding. While the $a$ value of the electrode prepared by adding 1.5% and 2% K$_2$Cr$_2$O$_7$ decreases greatly. It means that when the amount of potassium dichromate added is above 1% (mass fraction), the cell voltage of the electrode is lowered. From the value of $b$ in table 3, it can be concluded that when the amount of K$_2$Cr$_2$O$_7$ added is 1%, the $b$ value of the
prepared electrode does not decrease but rises; and the b value of the electrode prepared by adding 1.5% and 2% obvious decreases. It also indicates that the addition of K$_2$Cr$_2$O$_7$ should be above 1%, which will have an effect on the electrocatalytic activity of the electrode.

4. Conclusions

The addition of K$_2$Cr$_2$O$_7$ has a significant effect on the morphology of α-PbO$_2$ coating, which can change the grain size more uniform. The oxygen evolution potential of the electrode prepared by adding 2% K$_2$Cr$_2$O$_7$ is 0.0615 V lower than that of the electrode prepared without adding K$_2$Cr$_2$O$_7$. The charge transfer resistance $R_t$ of the electrochemical reaction prepared by adding 2% K$_2$Cr$_2$O$_7$ is 28.81 $\Omega \cdot \text{cm}^2$. The oxygen evolution overpotential is the lowest electrode prepared by adding 2% K$_2$Cr$_2$O$_7$, and is 0.8989 V. When the addition amount reaches 2%, the prepared electrode has the best oxygen evolution electrocatalytic performance and maximum electrochemical active surface area.

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