Materials Research Express

PAPER

Study on the effect of tin and antimony oxide interlayer on the performance of titanium-based manganese dioxide anode

Bo-Yan Du1,*∗, San-Fan Wang1,2 and Sheng-San Yu1,2

1 School of Environmental and Municipal Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu, 730070 People’s Republic of China
2 Engineering Research Center of Comprehensive Utilization of Water Resources in Cold and Arid Regions, Ministry of Education, Lanzhou Jiaotong University, 730070 People’s Republic of China
* Author to whom any correspondence should be addressed.
E-mail: dby19960206@foxmail.com and sfwang1612@163.com

Keywords: Ti/Sn+Sn/Sb/MnO2, the anode, the middle layer, load, calcination temperature, the oxygen evolution performance

Abstract

Tin-antimony interlayer and manganese dioxide active catalytic coating were prepared on titanium plate by coating and thermal decomposition. The load of interlayer and calcination temperature were selected as the influencing factors for univariate experiment. The seen morphology of the electrode was explored by SEM. The electrocatalytic performance and oxygen evolution mechanism were analyzed by testing the cyclic voltammetry curve, oxygen evolution polarization curve and AC impedance graph, the optimal preparation conditions of the Ti-MnO2 anode interlayer were obtained.

1. Introduction

DSA (Dimension Stable Anode) electrode, also known as shape Stable Anode, is the one coated with metal oxide coating on the substrate by the thermal decomposition method, sol-gel method and electroplating methods. The base material is usually titanium with high mechanical strength and good chemical stability, and the coating materials are mainly platinum group metal oxides with high catalytic (RuO2, IrO2, PbO2, PtO2, etc). The common DSA electrode coating is usually composed of two or more metal oxides to form a multicomponent metal oxide coating. It can not only improve the stability of the electrode, but also help to inhibit the occurrence of side reactions of electrolysis [1, 2]. It has good electrochemical, low consumption rate and long life, light in weight, easy to be processed into the needed shape, with high-cost performance and adaptability. And it is widely used as an oxygen evolution or chlorine evolution electrode in the fields of chlor-alkali industry, electroplating, wastewater treatment, cathodic protection and organic synthesis [3, 4]. The main advantages of DSA electrodes over conventional electrodes in electrocatalysis are as follows: (1) High electrocatalytic and selective catalytic capacity; (2) low energy consumption, low slot voltage and energy saving in electrolysis; (3) good electrochemical stability, no secondary pollution to the electrolyte [5].

Currently the international research on anodes focuses on titanium as the substrate and noble metal oxides as the electrodes with active layers. Noble metal oxides, here, mainly refer to oxides of iridium, platinum and ruthenium. However, considering the high cost of noble metals, small output and limited reserves, the development of non-noble metal oxide anodes is of more practical significance [6]. Non-noble metal oxide electrodes mainly include titanium-based manganese dioxide, titanium-based lead dioxide, titanium-based tin dioxide, titanium-based cobalt oxide, and carbon-based oxides [7]. Manganese dioxide has always been used as an active material for batteries. After the 1970s, titanium-based manganese dioxide electrodes became one of the main anode materials. The main types of manganese dioxide are α-MnO2, β-MnO2 and γ-MnO2. Among them, electrodeposition mainly obtains γ-MnO2 resistant to anodic polarization, and thermal decomposition method mainly obtains high catalytic activity α-MnO2 and β-MnO2 [8]. The electrolysis method can obtain high-purity metal manganese, and the electrolysis conditions are reasonably controlled. While manganese is prepared by the electrolysis method, powdered manganese dioxide can also be obtained [9]. The demand for electrolytic manganese dioxide, which is an important source of manganese for battery cathode materials, is increasing.

© 2021 The Author(s). Published by IOP Publishing Ltd
Anode design and preparation is the core content of electrochemical deposition method. The voltage, electric energy consumption and current efficiency of the electrolytic cell are closely related to the anode material and its preparation method [10]. In this article, a kind of non-noble metal plate was prepared as anode plate for manganese electrolysis, so that anode slime can be directly applied to the preparation of lithium manganate. The manganese dioxide coating was prepared by the thermal decomposition method on the surface of titanium plate, and the interlayer of Sn and Sb was added between the substrate and the coating under different conditions. The role of the interlayer is to increase the bonding force between the titanium substrate and the active coating, prevent the spalling of the coating, avoid the passivation of the titanium substrate, and improve the service life of the oxide anode [11]. Finally, Ti/Sn-Sb/MnO2 was obtained. The seen morphology of the electrodes was investigated by SEM. The electrochemical properties of them were analyzed and evaluated by measuring the oxygen evolution polarization curve, cyclic voltage curve, AC impedance spectroscopy, and determined the optimum preparation conditions for the interlayers.

2. Experiment

2.1. Experimental reagents, instruments and related software
Experimental reagents: NaOH, acetone, oxalic acid, SnCl4, SbCl3, n-butanol, HCl, 50% Mn(NO3)2 solution, H2SO4, K2SO4, KCl, etc were all analytically pure.

Experimental instruments: Ti plate, 200–300 Mesh metallographic sandpaper, platinum electrode, saturated calomel reference electrode, digital display constant temperature water bath, ultrasonic cleaner, electric heating blast drying oven, box-type resistance furnace, electronic analytical balance, electrochemical workstation, GeminiSEM500 field emission scanning electron microscope.

Related software: Nova1.10, Origin2018.

2.2. Preparation of Ti/Sn-Sb/MnO2 plate
The preparation of Ti/Sn-Sb/MnO2 polar plates includes pretreatment of titanium substrate, preparation of Sn-Sb interlayer and MnO2 coating by thermal decomposition method.

(1) Pretreatment of titanium substrate
Titanium substrate is pretreated by cutting, grinding, pickling and alkaline washing. Then it is cut to 50 mm*10 mm*1 mm and polished with sandpaper (200–300 mesh) to show silver-white metallic gloss. The purpose is to remove passivated Titanium oxide on the surface of Titanium substrate. Rinse it with distilled water and place it in an alkaline washing solution Medium alkaline, washing for 1 h (80 °C). The alkaline washing solution is a mixture of NaOH and acetone. (The volume ratio is 1:1 and the mass fraction of NaOH solution is 20%). The purpose is to remove the grease adhering to the surface of the Titanium substrate. Then rinse again with distilled water and place it in a pickling solution to slightly boil for 2 h. The pickling solution is oxalic acid solution (mass fraction is 10%), in order to increase the roughness of the titanium substrate and improve the adhesion between the substrate and the coating. Finally, it is washed with distilled water and stored in an oxalic acid solution (mass fraction 2%) in a light-shielded storage.

(2) Preparation of Sn-Sb interlayer
Dissolve SnCl4 and SbCl3 in n-butanol, add a small amount of concentrated HCl to hydrolyze (the ratio of Sn and Sb substances is 10:1) to prepare the interlayer solution, and evenly coat the prepared interlayer solution on the pretreatment. The finished titanium substrate is dried in an oven (120 °C, 10 min), and then thermally decomposed in a muffle furnace (300 °C–500 °C, 10 min, the last time is 1 h).

(3) Preparation of MnO2 active layer
After the interlayer preparation was completed, the substrates were soaked in 50% Mn(NO3)2 solution for 3–15 s, first placed in an oven for drying (120 °C, 10 min), and then placed in a muffle furnace for thermal decomposition (400 °C–500 °C, 10 min).

(4) Single factor experiment
Based on previous studies, the range of variables in the experimental scheme was determined, and a large number of single-factor variable experiments were carried out by selecting the load amount of the interlayer and the calcination temperature as the influencing factors.

In this experiment, the electrodes were prepared under the conditions of 6, 7, 8, 9 and 10 g m⁻² of the load of the interlayer to explore the influence of the load of the interlayer on the performance of Ti/Sn-Sb/MnO2 electrode.
The calcination temperature was controlled by adjusting the muffle furnace temperature. Electrodes, in this experiment, were prepared under the conditions of 300 °C, 350 °C, 400 °C, 450 °C and 500 °C respectively, to explore the effect of the calcination temperature of thermal decomposition of the middle-position layer on the performance of Ti/Sn-Sb/MnO₂ electrodes.

2.3. Structure and morphology testing
The seen morphology of the coating was characterized by field emission scanning electron microscope (SEM).

2.4. Electrochemical test
The electrochemical properties of 10 self-made electrodes were tested by electrochemical workstation using a three-electrode system. The counter electrode is a platinum electrode, the working electrode is a homemade Ti/Sn-Sb/MnO₂ electrode, and the reference electrode is a saturated calomel electrode (SCE). The size of the counter electrode is 2 cm × 2 cm, and the size of the working electrode is 5 cm × 1 cm. Use 0.5 mol l⁻¹ H₂SO₄ solution as the solution system, and control the test environment temperature to (25 ± 1) °C. The cyclic voltammetry curve (CV) potential scan range is −1.2–1.5 V (versus SCE, the same below), and the scanning rate is 20 mV s⁻¹. The potential scanning range of the oxygen evolution polarization curve is 0–2 V, and the scanning rate is 10 mV s⁻¹. The test potential of the AC impedance map is 1.35 V, the frequency range is 10 mHz–100 KHz, and the impedance map is fitted with Nova software.

3. Analysis

3.1. The influence of the load of the interlayer on the electrochemical performance of the anode
The calcination temperature of the interlayer was 300 °C, while the coating times of the active layer was 10 times, and the calcination temperature of the active layer was 400 °C. The Ti/Sn-Sb/MnO₂ electrode was prepared under different interlayer load (6 g m⁻², 7 g m⁻², 8 g m⁻², 9 g m⁻², 10 g m⁻²). SEM, cyclic voltammetry curve, oxygen evolution polarization curve and AC impedance spectroscopy were used to analyze the effect of the load on the seen morphology and electrocatalytic performance of the electrode.

3.1.1. Seen morphology analysis
In figure 1, a–e shows the SEM diagram of Ti/Sn-Sb/MnO₂ electrodes prepared at 6 g m⁻², 7 g m⁻², 8 g m⁻², 9 g m⁻² and 10 g m⁻² respectively. It can be seen that there are cracks with different sizes and distributions on the surface of each coating. The proper number, size and distribution of cracks can increase the active surface area and improve the electrocatalytic performance. But the excessive number and size of cracks will instead aggravate the electrolyte penetration and oxygen impact, accelerate the process of electrode passivation and deactivation, and have a negative impact on the electrode stability and life [12].

When the load of the interlayer is in the range of 6–8 g m⁻², with the increase of the load, the cracking degree of the coating decreases. The cracks become shallow and narrow until they disappear. The distribution of them
becomes more and more uniform. The reason is that when the load of the interlayer is too low, the distribution of tin and antimony oxide coatings is uneven, which weakens the adhesion between the active layer of MnO2 and the substrate, resulting in excessive cracking on the electrode surface.

When the load capacity of the interlayer is 8 g m\(^{-2}\), the number of cracks is very few and the electrode surface is relatively compact. The dense surface structure of the coating can prevent oxygen from entering the coating, which is beneficial to slow down the passivation of the titanium substrate and improve the stability of the electrode.

When the load of the interlayer exceeds 8 g m\(^{-2}\) and keeps increasing, the surface of the coating begins to show sagging, broken and loose structures. When it reaches 10 g m\(^{-2}\), the cracks on the surface of the coating reach the maximum size and there are a lot of pits. The cause of that most probably is when the load is too large, the adhesion of the coating becomes worse, and it is more likely to fall off. Although the surface of the electrode is very rough, the loose structure makes the coating difficult to resist external interference, which reduces the stability and service life of the electrode.

3.1.2. Analysis of cyclic voltammetry

Figure 2 shows the cyclic voltammetry curves of Ti/ Sn-Sb/ MnO2 anodes prepared under different loadings of the interlayer when the scanning speed is 20 mV s\(^{-1}\) (loads are respectively 6 g m\(^{-2}\), 7g m\(^{-2}\), 8 g m\(^{-2}\), 9 g m\(^{-2}\), 10 g m\(^{-2}\)), it can be seen that the symmetry of each curve is poor, indicating that the reversibility of each electrode is low, and the curves of 6 g m\(^{-2}\), 8 g m\(^{-2}\), 9 g m\(^{-2}\) and 10 g m\(^{-2}\) are similar. The results show that the stability and capacitance performance of each electrode are good under 6 g m\(^{-2}\), 8 g m\(^{-2}\), 9 g m\(^{-2}\) and 10 g m\(^{2}\).

By graphically integrating the whole regularly repeating voltammetry curve of the last test of each CV curve in figure 2, the unit mass integral voltametric charge capacity (\(Q^*\)) of the anode can be obtained. The calculation formula is:

\[
Q^* = \int_{\Psi_1}^{\Psi_2} \frac{j \mathrm{d}E}{\nu}
\]  

(3.1)

In the above formula, \(Q^*\)-volt-ampere charge capacity (mC cm\(^{-2}\)), \(j\)-current density (mA cm\(^{-2}\)), \(\Psi_2\)-scan lower limit potential (V), \(\Psi_1\)-scan upper limit potential(V), \(\nu\)-potential scan rate (mV s\(^{-1}\)).

The change curve of \(Q^*\) with the load of the interlayer is shown in figure 3. \(Q^*\) is related to the electrochemically active surface area. If the conductive material in the coating is the same, \(Q^*\) can also indicate the number of electrochemically active sites and the degree of catalyst dispersion. The larger the \(Q^*\), the more active sites, and the more uniform the catalyst dispersion, the electrode shows higher electrocatalytic activity [13, 14].

\(Q^*\) increases at first and then decreases with the increase of the load of the interlayer. When the load of the interlayer is 8 g cm\(^{-2}\), the \(Q^*\) is the largest and the seen electrocatalytic activity is the highest. This may be
attributed to the fact that when the load capacity of the interlayer is 8 g cm$^{-2}$, the cracks on the coating surface are narrow and shallow. The number of cracks is small and the distribution is very uniform. The electrode surface roughness, the number of active surface area and active point sites is the largest, the catalyst dispersion is the most uniform, and therefore $Q^*$ is the largest. When the load capacity of the interlayer is greater than 8 g cm$^{-2}$, the interlayer is too thick and dense, which affects the adhesion of the active layer on the electrode surface. The active surface area and the number of active point sites decrease, and $Q^*$ decreases accordingly, which is basically consistent with the SEM image analysis results.

3.1.3. Analysis of oxygen evolution polarization curve

Figure 4 shows the oxygen evolution polarization curves of Ti/Sn-Sb/MnO$_2$ anodes prepared under different loads of the interlayer when the scanning speed is 10 mV s$^{-1}$ (loads are respectively 6 g m$^{-2}$, 7 g m$^{-2}$, 8 g m$^{-2}$, 9 g m$^{-2}$, 10 g m$^{-2}$). There are two methods for analyzing the electrocatalytic activity of electrodes through the oxygen evolution polarization curve:

1. Compare the potential at the inflection point or the slope of the curve after the inflection point. The smaller the inflection point potential or the greater the slope of the curve after the inflection point, it indicates that under the same potential, the larger the oxidation current value and exchange current density, the smaller
the overpotential for oxygen evolution reaction, the easier the oxygen evolution reaction occurs, and the more electrocatalytic activity of the electrode.

2) Compare the polarization potential at the same current density or the current density at the same polarization potential. When the polarization potential is the same, the higher the current density is, the faster the oxygen evolution reaction rate and the higher the electrocatalytic activity of the electrodes. When the current density is the same, the lower the polarization potential and the larger the negative potential shift, indicating that the higher the exchange current density is, the more electron transfer and the faster the electron transfer speed is. The easier the oxygen evolution reaction occurs, the faster the rate of oxygen evolution reaction and the better the electrocatalytic activity. Both methods are widely used in the literature at home and abroad [15, 16].

Figure 5 shows the polarization potential of each electrode in figure 4 at the same current density. Through the above second analysis method, it can be seen that the polarization potential decreases at first and then increases with the increase of the load of the interlayer, and reach the minimum when the load of the interlayer is 8 g cm$^{-2}$, and the seen electrocatalytic activity is getting higher. Meanwhile, the analysis results of CV curve and oxygen precipitation polarization curve were basically consistent, indicating that the loading level of the interlayer had a great influence on the active surface area and the number of active sites, and the active surface area, the number of active sites and the electrocatalytic activity of the electrode reached the highest when the loading level of the interlayer was 8 g cm$^{-2}$ [17].

3.1.4. AC impedance atlas analysis

The porous structure of the electrode surface was explored by AC impedance spectroscopy. Figure 6 shows the complex impedance plane diagrams of Ti/Sn-Sb/MnO$_2$ anodes with different interlayer loads in H$_2$SO$_4$ solution under 1.35 V conditions [18]. Each curve presents a relatively regular semicircle at low frequencies, corresponding to the oxygen evolution reaction on the outer surface of the coating. And another small circle at high frequencies, corresponds to the physical response of the inner surface of the coating and the Ti/oxide interface. It has been observed that the electrode has high-frequency inductance behavior. This phenomenon was once believed to be caused by the test equipment, but recent studies have pointed out that the high-frequency inductance is related to the porous characteristics of the electrode surface.

Use the equivalent circuit LRs (RfCf) (RctCdl) shown in figure 7 to fit the impedance data [19–22]. Among them, R$_s$, R$_f$, R$_t$, represent the uncompensated resistance, the solution resistance between the working electrode and the reference electrode, and the charge transfer resistance between the ‘internal’ /’external’ active surfaces of the electrode. And C$_f$, C$_dl$ respectively represent the electric double-layer capacitance between the ‘internal’ active surface/electrolyte interface of the electrode and the electric double-layer capacitance between the ‘outer’ active surface/electrolyte interface of the electrode. L represents inductance.

Through fitting, it can be seen that the shapes of the curves are similar, indicating that increasing the load of the interlayer does not change the oxygen evolution reaction mechanism. $X^2 < 10^{-3}$ indicates that the fitting
The effect is good, and it is reasonable to use this equivalent circuit for fitting. Considering the influence of electrode surface inhomogeneity, constant phase element CPE is used instead of pure capacitance element, and its impedance $c$ is calculated by the following formula:

$$C_{dl} = Y_0^{1/n}(1/R_{ct} + R_{dl})^{(n-1)/n}$$

(3.2)

$Y_0$ is the CPE constant, and $n$ is the CPE power. $C_{dl}$ is directly proportional to the number of active sites on the coating surface, hence, the surface area of the electric double layer at the solid/solution interface of the Cdl reaction is often used.

$R_{ct}$ is the Faraday charge transfer resistance. It is generally believed that $R_{ct}$ is proportional to the product of active point and site activity, which can reflect the difficulty of charge transfer on the anode surface. In order to explore the true electrocatalytic activity of the electrode, the total electrode activity $1/R_{ct}$ is divided by the number of active points $Q^*$ to normalize the $R_{ct}$ value. Figure 8 shows the influence curve of load capacity in the interlayer on $1/(R_{ct}Q^*)$ value. It indicates that when the load capacity of the interlayer is 6 g m$^{-2}$, the $1/(R_{ct}Q^*)$ value is the largest, and the true electrocatalytic activity is the highest. And when the load of the interlayer is 8 g m$^{-2}$, the value of $1/(R_{ct}Q^*)$ is larger. It is because the dense and uniform tin-antimony oxide interlayer reduces the contact resistance between Ti matrix and MnO$_2$ layer that reduces the resistance polarization and improving the catalytic performance of the electrodes. When the load capacity of the interlayer is 10 g m$^{-1}$, $1/(R_{ct}Q^*)$ value is the lowest, and the true electrocatalytic activity is the lowest. It may be due to the depression and porosity of the coating surface, which has a negative impact on the test results.

### 3.1.5. Summary

The load of the interlayer is in the range of 6–10 g m$^{-2}$. The Changing load of the interlayer has a significant impact on the electrode performance. And the optimal load of the interlayer is 8 g m$^{-2}$.

The results of SEM analysis show that with the increase of loading, the cracking degree of the coating decreases, the cracks become shallow and narrow until they disappear, and the distribution of cracks is more and more uniform, and the coating tends to be dense, but when the load is too high, the electrode structure become depressed, crushed and loosened.
The results of CV curve and oxygen evolution polarization curve indicate that the seen electrocatalytic activity of the electrode is the highest when the interlayer load is around 8 g m\(^{-2}\).

However, the analysis results of ac impedance spectroscopy show that the true electrocatalytic effect is the highest when the loading capacity of the interlayer was 6 g m\(^{-2}\).

The true electrocatalytic effect reaches the highest when the load of the interlayer is 6 g m\(^{-2}\). But it can be inferred by SEM analysis that the tin and antimony oxide coating is too thin under this condition, and does not completely cover the substrate. It leads to the decrease of the adhesion between the active catalytic coating on the electrode surface and the substrate, resulting in too many and too deep cracks on the electrode surface, which will speed up the passivation of the titanium substrate and the shedding of the coating, and badly affect the stability as well as service life of the electrode. However, when the load of the interlayer is too high, the surface structure of the electrode is getting depressed, broken and loosened, which will also adversely affect the stability and service life of the electrode\[24\]. When the interlayer load tends to 8 g m\(^{-2}\), The active surface of the electrodes is tightly bound to the titanium substrate. The crack degree on the surface of the electrodes decreases, the crack distribution becomes more and more uniform, and the active coating becomes compact and evenly covers the surface of the titanium substrate. This makes it difficult for the electrolyte to penetrate into the surface of the titanium substrate and prevents the diffusion of the active titanium oxide matrix precipitated during the electrolysis process. Thus, the ability of coated anode to resist solution erosion during electrolysis is improved, and the formation of TiO\(_2\) oxide film on the insulating layer is delayed, thus prolong the service life of the electrode considerably. Therefore, it is considered that the optimum interlayer load of Ti/Sn-Sb/MnO\(_2\) anode is 8 g m\(^{-2}\).

3.2. The influence of the calcination temperature of the interlayer on the electrochemical performance of the anode

Ti/Sn-Sb/MnO\(_2\) electrodes were prepared at different middle-position layer calcination temperatures (300 °C, 350 °C, 400 °C, 450 °C, 500 °C) by controlling the middle-position layer coating times to be 10 times and the active layer coating times to be 15 times. SEM, cyclic voltammetry curve, oxygen evolution polarization curve and AC impedance spectroscopy were used to analyze the effect of calcination temperature on the seen morphology and electrocatalytic performance of the electrode.

3.2.1. Seen morphology analysis

In figure 9, a-e show the SEM images (×3000) of Ti/Sn-Sb/MnO\(_2\) anodes prepared at the calcination temperatures of 300 °C, 350 °C, 400 °C, 450 °C and 500 °C respectively. It can be seen that the surfaces of each electrode are composed of flat areas and mud cracks, and their morphs are significantly different.

At 300 °C and 350 °C, the surface of the coating appears broken and concave in, and there are a lot of pores and mud cracks in the concave area. As the calcination temperature of the interlayer increases, the electrode surface tends to be loose and uniform. At 400 °C, the number and size of cracks on the electrode surface decreased, because with the increase of temperature, the grains of tin and antimony oxide in the interlayer began to precipitate, and the grains gathered together, and their number and size increased. When the temperature
reaches 500 °C, the electrode surface is the most flat, and the precipitation of tin and antimony oxide grains may reach a critical value. The reason for that is the increase of calcination temperature promotes the oxidation of tin and antimony and the formation of solid solution, but when the amount of tin and antimony oxides is greater than the capacity of solid solution, the oxides begin to segregate. Grain segregation of tin and antimony oxides destroys the crystal structure of the surface of the interlayer, resulting in reduced adhesion between the substrate and the active coating, thus reducing the electrocatalytic activity of the electrode [25, 26].

3.2.2. Analysis of cyclic voltammetry

Figure 10 represents the cyclic voltammetry curves of Ti/Sn-Sb/MnO₂ anodes prepared at different calcination temperatures (300 °C, 350 °C, 400 °C, 450 °C and 500 °C respectively) at a scanning speed of 20 mV s⁻¹. Poor symmetry of the curves indicates that the electrode is not reversible. Similar shapes and similar contours indicate that the stability and capacitance performance of the electrodes are good, which is beneficial to the electrode storage. CV curve has the largest contour and the largest active surface area at 500 °C.
It is generally believed that the electrocatalytic reaction of oxide electrodes closely depends on the support and active sites of the catalytic reaction. Integrate the CV curve to obtain the curve of the volt-ampere charge Q* with the calcination temperature of the interlayer (figure 11). Q* is closely related to the electrochemically active surface area of the coating surface and can be used to reflect the level of electrocatalytic activity [27]. With the increase of the calcination temperature, Q* shows a wave-like rise, reaching a maximum at 500 °C and significantly greater than other temperatures, indicating that the coating’s active surface area and the number of active sites reach the maximum at 500 °C. It is speculated that the possible reasons are: (1) the calcination temperature affects the crack size and uniform distribution of the interlayer, which has an impact on the active surface area; (2) the influence of the precipitation of Sn and Sb oxide crystals on the active surface area.

The above speculation is caused by the fact that the microstructure, composition, structure and other properties of the coating are affected by the thermal oxidation process such as calcination temperature and time, and the composition and structure of the coating often determine the electrocatalytic activity and stability of the oxide anode. The electrocatalytic activity of metal oxide anodes increases with the increase of sintering temperature, but it decreases sharply when the sintering temperature increases to a certain extent, which indicates that there is a critical value for sintering temperature [28].

3.2.3. Analysis of oxygen evolution polarization curve

Figure 12 demonstrates the oxygen evolution polarization curves of Ti/Sn-Sb/MnO2 anodes prepared at 300 °C, 350 °C, 400 °C, 450 °C, and 500 °C, respectively. And the inflection point potential of each curve in figure 12 is shown in figure 13. It can be seen that as the calcination temperature of the interlayer increases, the potential at the inflection point decreases stepwise and reaches a minimum at 500 °C. This indicates that the seen activity of the oxygen evolution reaction continues to increase with the rise of temperature, reaching the maximum at 500 °C, which is also consistent with the results of CV curve analysis.

3.2.4. AC impedance atlas analysis

EIS can reflect the electrochemical structure and catalytic activity between the DSA anode substrate/interface. It is often used to study the electric double layer charging process and oxygen evolution reaction on the coating surface. Figure 14 is a complex plan view of AC impedance spectra of Ti/Sn-Sb/MnO2 anodes prepared at different calcination temperatures of the interlayer (calcination temperatures are 300 °C, 350 °C, 400 °C, 450 °C, 500, respectively).

The equivalent circuit LR, (RL, (RL, Cdl) is used to fit the impedance data. The results are very close to the experiment (X2 < 10^-3), indicating that the circuit fitting is reasonable. The effect of electrode roughness and asymmetry is reduced by using constant potential element CPE instead of pure resistance element [29, 30].

It is generally believed that Rct is proportional to the product of the active potential and site activity. Some researchers attempted to standardize Rct values by dividing total electrode activity 1/Rct by the activity number Q*, so as to obtain the real electrocatalytic activity information (as shown in figure 15). The value of 1/(RctQ*) is the largest at 350 C. Secondly, at 500 C, 1/(RctQ*) value is higher. At other calcining temperatures, the 1/(RctQ*)
values do not differ much. It is shown that single site activity and true electrocatalytic activity are the highest at 350 °C.

3.2.5. Summary
When the calcination temperature is 300 °C–500 °C, the seen morphology, coating composition, electrocatalytic activity, stability and oxygen evolution reaction mechanism of the electrode are significantly affected by changing the calcination temperature. The optimal calcination temperature is 500 °C.

The results of SEM image analysis show that the number of cracks and pores on the surface of the coating decreases obviously with the calcination temperature of the interlayer, and the coating tends to be compact and uniform.

The CV curve, oxygen evolution polarization curve shows that as the calcination temperature of the interlayer increases, the electrocatalytic activity and true electrocatalytic activity of each electrode shows an upward trend. The active surface area, number of active sites, and apparent electrocatalytic activity of the coating reach the maximum at 500 °C. This may be due to: (1) The calcination temperature affects the crack size and uniform distribution of the interlayer, which affects the active surface area. (2) The degree of precipitation of Sn and Sb oxide crystals affects the tightness of the active layer and the titanium substrate. The results of AC impedance graph indicate that the true electrocatalytic effect reached the highest at 350 °C, but referring to SEM
images, the electrode surface structure was depressed, broken and loose, which resulted in a small number of active points of the coating and affected the test results, and adversely affected the stability and service life of the electrode\cite{31,32}. Therefore, after comprehensive analysis, 500 °C is the best calcination temperature of the interlayer.

Since the calcination temperature level in this experiment was as high as 500 °C, the electrochemical performance of Ti/Sn-Sb/MnO₂ anode at a higher calcination temperature could not be carefully studied. However, it is speculated through experiments and data of other researches that when the calcination temperature of the interlayer is further increased, the active surface area, the number of active sites, and the apparent electrocatalytic activity of the electrode will likely decline. For example, Zhong Xianghua’s study proved that in the process of preparing RuO₂30%-TiO₂70% anode, the electrochemical performance and stability of the electrode prepared altered with the change of temperature. The electrode prepared at 500 °C had better catalytic activity, while the electrode prepared above 700 °C had worse electrocatalytic activity and stability\cite{33}. This is because the surface of each coating of the electrode presents the characteristics of mud cracks. As the temperature increases, the interlayer of each electrode surface tends to be loose, well-distributed and rough, and the oxide crystals of Sn and Sb begin to precipitate and aggregate with each other, which will lead to tighter bonding between the catalytic coating and the titanium substrate. When the temperature continues to rise until a critical value is exceeded, the number of crystal grains decreases, the size increases, and the cracks on

![Figure 14. Complex plane diagrams of impedance of Ti/Sn-Sb/MnO₂ anodes at different interlayer sintering temperatures.](image1)

![Figure 15. The influence of the interlayer sintering temperature on the impedance complex plane graph 1/(R⁰Q*) value.](image2)
the coating surface increase, affecting the binding ability of the active layer to the titanium substrate, thereby affecting the electrodes performance. In the meanwhile, if the calcination temperature is too high, the coating structure will be too loose, and the partial coating may fall off, which will shorten the service life of the electrode.

4. Conclusion

In this study, the optimal preparation conditions of titanium Sn-Sb/MnO₂ anode interlayer were investigated. The seen morphology, electrocatalytic performance and oxygen evolution mechanism of the electrode were analyzed and tested by SEM image, cyclic voltammetry curve, oxygen evolution polarization curve and AC impedance graph.

(1) Preparation conditions: Titanium-based Sn-Sb/MnO₂ anode was prepared by using thermal decomposition method. The amount ratio of tin and antimony substance in the coating solution of the interlayer was controlled to 10:1, and the load of the interlayer to 6 g m⁻², 7 g m⁻², 8 g m⁻², 9 g m⁻², 10 g m⁻². The calcination temperature of the interlayer was 300 °C, 350 °C, 400 °C, 450 °C, 500 °C. The influence of the load of the interlayer and the calcination temperature on the electrocatalytic performance of the Ti/Sn-Sb/MnO₂ electrode was explored, and the optimal preparation conditions were obtained.

(2) The following conclusions are drawn through experiments and data analysis:

(3)①The optimal load of the interlayer is 8 g m⁻². It is due to the fact that when the load of the interlayer tends to 8 g m⁻², the active surface of the electrode and the titanium substrate gradually become tighter. The cracks on the surface of the electrodes decrease, narrow and shallow until they disappear. What’s more, the cracks are more and more evenly distributed, and the active coating becomes dense.

②The best calcination temperature of the interlayer is 500 °C. The causes are as follows: (1) The calcination temperature affects the crack size and uniform distribution of the interlayer, thereby affecting the active surface area. (2) The degree of precipitation of Sn and Sb oxide crystals influences the tightness of the binding between the active layer and the titanium substrate.

Acknowledgments

In the process of writing and publishing this paper, I have received a lot of help and care. I hereby express my sincere thanks to them.

First of all, I would like to express my gratitude to Professor Wang Sanfan. Thanks for his careful guidance and help from the topic selection of the paper, the formulation of the experimental scheme, the conduct of the experiment to the writing and revision of the paper. And thank the National Natural Science Foundation of China (51804150) for financial support.

Secondly, I would like to thank Associate Professor Li lezhao. When I encountered a bottleneck in my experiment, she always put forward valuable opinions and pointed to the problem, which made me open up and find a solution quickly.

At the same time, I would like to thank Zhao Hongjing, Yu Shengsan, Zhou Jian and other teachers and students for their patient help when I encounter problems in my experiment.

Last but not the least, I am grateful to Associate Professor Fu Yongjun, from the School of Foreign Languages of Lanzhou Jiaotong University. She provided great help in polishing the thesis.

Thanks to all those who have contributed to the writing of the paper.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Bo-Yan Du @ https://orcid.org/0000-0002-2410-3974

References

[1] Kong D S et al 2009 Advances and Some Problems in Electrocatalysis of DSA Electrodes Progress in Chemistry 21 1107–17
[2] Chi M C et al 2021 Research progress on preparation and application of DSA electrode Applied Chemical Industry 50 498–503
[3] Niu J F et al 2013 A high activity of Ti/SnO2-Sb electrode in the electrochemical degradation of 2,4-dichlorophenol in aqueous solution J. Environ. Sci. 25 1424–30
[4] Li J Y et al 1982 Application of Titanium anode instead of Platinum electrode in silver electrolysis Chinese Journal of Rare Metals 06 67–71
[5] Foti G et al 1998 Characterization of DSA type electrodes prepared by rapid thermal decomposition of the metal precursor Electrochim. Acta 44 813–8
[6] Wen Y Q et al 2017 Preparation and Properties of Composite Coating Modified Titanium Anode for Electrolytic Manganese Dioxide China Surf. Eng. 30 85–91
[7] Tang C B et al 2020 Research progress of non-precious metal oxide coated anodes for electrocatalytic degradation of organic pollutants in water Journal of Materials Engineering 48 62–72
[8] Lu Y X et al 2018 Progress in development and application of manganese dioxide electrode materials Electroplating and Finishing 37 1108–15
[9] Yang W C et al 2014 Preparation of Titanium-substrate Modified Ti / SnO2 / MnO2 Anode Plate for Electrolytic Manganese Metal and Its Performance Study Mining and Metallurgical Engineering 34 90–6
[10] Jin S M 2018 Oxidation Water Treatment and Electrochemical Catalysis Technology Chemical Engineering Design Communications 44 130
[11] Huang Y T and Peng Q 2006 Progress in the Study of the Ti-based Metal Oxide Anodes Total Corrosion Control 20 10–2
[12] Zhu F L et al 2010 Effect of Calcining Temperature on properties of Europium Doped Ti/ SnO2-Sb Electrode Journal of The Chinese Rare Earth Society 28 709–15
[13] Makgae M E et al 2005 Preparation and surface characterization of Ti/SnO2-RuO2-IrO2 thin films as electrode material for the oxidation of phenol Materials Chemistry Physics 92 559–64
[14] Ning H L et al 2016 Properties of IrO2-Ta2O5 Coated Titanium Anodes Modified with Graphene Rare Met. Mater. Eng. 45 946–51
[15] Audichon T et al 2015 Effect of Adding CeO2 to RuO2-IrO2 Mixed Nanocatalysts: activity towards the oxygen evolution reaction and stability in acidic media Chem electrochem 2 1128–37
[16] Li R P et al 2019 Effects of current density on preparation and performance of Al/α-PbO2–CeO2–TiO2 composites Mater. Res. Express 6 075802
[17] Yang H T et al 2014 Effects of current density on preparation and performance of Al/conductive coating/α - PbO2 – CeO2 – TiO2/β-PbO2 – MnO2 – WC– ZrO2 composite electrode materials Transactions of Nonferrous Metals Society of China 24 3394–404
[18] Li Y J et al 1997 A mixture design approach to thermally prepared Ir–Pt–Au ternary electrodes for oxygen reduction in alkaline solution J. Appl. Electrochem 27 227–34
[19] Cao C N and Zhang J Q 2002 Introduction to Electrochemical Impedance Spectroscopy (Beijing: Science Press)
[20] Kerner Z and Pajkossy T 2000 On the origin of capacitance dispersion of rough electrodes Electrochim. Acta 46 207–11
[21] Wen T C and Hu C C 1992 Hydrogen and oxygen evolutions on Ru–Ir binary oxides Journal of the Electrochemical Society 139 2158–63
[22] Hou Y Y et al 2006 Effect of calcination temperature on electrocatalytic activities of Ti/ IrO2 electrodes in methanol aqueous solutions Electrochim. Acta 51 6258–67
[23] Piela B, Piela P and Wrona P K 2002 Oxidation of nitrite on solid electrodes: II. Determination of the reaction mechanism on surfaces covered by an oxide layer J. Electroanal. Chem. 149 357–66
[24] Zhang C, Liu J H and Chen B M 2019 Effect of Ce(NO3)3 on the electrochemical properties of Ti/PhO2–TiO2–Ce(NO3)3 electrode for zinc electrowinning, Appl. Phys. A, 125 1–7
[25] Cao F F, Yang Z D and Pei R J 2002 Adjusting of Particles Segregation During Paste Sintering Ferro-Alloys 06 19–20
[26] Zhang H, Zhu S R and Luo P 1992 The Segregation of Mn In Hydride Electrodes Chinese Journal of Applied Chemistry 9 123–6
[27] Xu J et al 2012 The electrocatalytic properties of an IrO2/SnO2 catalyst using SnO2 as a support and an assisting reagent for the oxygen evolution reaction Electrochim. Acta 59 105–12
[28] Geng G W 2014 Preparation and Performance of Catalytic Electrode for Chlorine and Oxygen Evolution(J) (Zhengzhou: Zhengzhou University)
[29] Spataru N, Helloco J G and Durand R 1996 A study of RuO2 as an electrocatalyst for hydrogen evolution in alkaline solution Journal of Applied Electrochemistry 26 397–402
[30] Lasaia A and Rami A 1990 Kinetics of hydrogen evolution on nickel electrodes, J. Electroanal. Chem. Interfacial Electrochem. 294 123–41
[31] Liao Y L, Liu G C and Zhao Y 2008 Preparation and properties of the oxygen evolution anode with an interlayer containing tin and antimony Electroplating and Finishing 27 51–4
[32] Zhu C F, Gao H and Xie R 2011 Effect of Ti – Antimony Oxide Intermediate Layer on the Performance of Titanium -Based Anodizing MnO2 Electrode Materials Protection 44 17–9
[33] Zhong H X, Tang D and Shao Y Q 2008 Effect of thermal oxidation for titanium substrates on the structures and properties of a titanium anode Heat Treat. Met. 33 146–9