

Article

Study on the Performance and Corrosion Failure Process of Porous Titanium-Based Coated Electrodes

Jiamin Li ^{1,2}, Linhui Chang ^{1,2}, Buming Chen ^{1,2,3,*}, Hui Huang ^{1,2,3} and Zhongcheng Guo ^{1,2,3}¹ Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China² Research Center of Metallurgical Electrode Materials Engineering Technology, Kunming 650106, China³ Kunming Hendera Science and Technology Co., Ltd., Kunming 650106, China

* Correspondence: bumchen@kust.edu.cn

Abstract: Titanium-based coated electrodes are considered to be a substitute for Pb-based anodes because of their lower weights and lower energy consumption; however, their properties and service lives are affected by the matrix structure. Herein, the metal oxide coating was prepared via the thermal oxidation decomposition of a 5 μm -porous titanium plate. The scanning electron microscope (SEM) showed that the metal oxide coating on the porous titanium plate was strengthened in each layer that had pores. The inner coating of the particles are sized using nanometers, with a diameter of 22–64 nm and a compact structure. The electrochemical test results show that, compared with the flat titanium plate, the coating attached to the porous titanium plate has a better catalytic performance in the chlorine evolution reaction, (the chlorine evolution potential decreases by 121 mV), and the service life is increased by 3.78 times. Through a SEM, XRD, and EDS analysis of the coating composition after corrosion failure, the corrosion mechanism of the surface oxide coating was discussed.

Keywords: porous Ti sheet; micro-structure; Sn-Sb-Ru-Co oxide coating; catalytic performance; corrosion mechanism



Citation: Li, J.; Chang, L.; Chen, B.; Huang, H.; Guo, Z. Study on the Performance and Corrosion Failure Process of Porous Titanium-Based Coated Electrodes. *Lubricants* **2022**, *10*, 282. <https://doi.org/10.3390/lubricants10110282>

Received: 23 September 2022

Accepted: 24 October 2022

Published: 28 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Ti-based metal oxide coated electrodes have excellent chlorine/oxygen evolution activity and electrochemical stability in the electrolytic purification industry; however, more attention should be paid to their qualities which are not stable when used as industrial consumables [1]. Therefore, the current research focuses on improving the stability of electrode quality, in addition to the chlorine/oxygen evolution activity. The bond between the metal oxide coating and the titanium substrate has a great influence on the stability of the electrode [2]; therefore, before preparing the oxide coating, a series of pre-treatments must be carried out on the titanium substrate, such as grinding, sandblasting, alkaline cleaning and degreasing, etching, and so on [3–7]. Among them, sanding and sandblasting have similar effects, with the purpose of exposing a clean surface by removing the oxide film on the titanium surface. The surface is in a state of compressive stress after sandblasting, which is conducive to the adhesion of the coating on the substrate. Polishing enhances the surface roughness of the titanium substrate, which is beneficial to increasing the real surface area of the electrode and reducing the real current density, thereby improving the electrocatalytic performance of the electrode. During the pre-treatment process, as the last step, etching has a great influence on the combination used in the coating and the titanium substrate. The different etching parameters produce corrosion pits with different morphologies on the surface of the titanium substrate, and by filling these corrosion pits, the oxide coating can be tightly combined with the titanium matrix [2]. Among the causes of electrode failure, the most common and critical ones include the loss of active material in the coating and the passivation of the Ti matrix [8,9]. Both failure mechanisms are directly related to the bonding force between the coating and the titanium matrix. The roughening

of the titanium substrate surface physically improves the bonding force between the coating and the substrate, better preserves the active material, and slows down the passivation of the titanium substrate, thereby improving its conductivity and prolonging its service life.

At present, there are few studies on the influence of substrate surface roughness on electrode performance and life. By using different pretreatment methods for nickel substrates, and by testing the stability of $\text{Ti}_2\text{O}_3 + \text{Co}_3\text{O}_4$ anodes, Zinola et al. [10] found that the coating attached to the polished substrate surface is prone to peeling off during electrolysis and the potential rise time is only 80 h. The service life of the coating on the surface of the substrate polished by sandpaper was greatly increased, because the coating and the polished substrate were better combined. Hu et al. [11] found that the titanium substrate after sandblasting can effectively improve the electrochemical performance of the coating. In electrolysis experiments, the phenomenon involving the powdery peeling of the coating that is prepared on the substrate without sandblasting was observed. The roughening treatment of the titanium substrate, such as sandblasting, not only has no influence on the electrochemical performance of the electrode, but it also prolongs the electrode's service life because it improves the bonding force between the substrate and the coating [2]. It has been observed that the surface morphologies of the titanium substrate have an important influence on the performance of the anode. In recent years, 3D porous titanium has been used as a substrate material for electrodes, owing to its good electrical conductivity, high surface area, and corrosion resistance [12–15]. The results show that the boron-doped diamond electrode with a 3D porous titanium substrate (3D-Ti/BDD) has a high roughness, large porosity, and high surface area. Zhang [12] prepared a 3D porous Ti/Sn-Sb/PbO₂ material for the anode of lead–acid batteries using electrodeposition and found that it has a higher capacity than the traditional Ti/Sn-Sb/PbO₂ electrode.

Based on our previous research [9], in this paper, a thermal oxidation method was used to prepare a Sn-Sb-Ru-CoOx coating on porous titanium. The electrochemical behavior of the electrodes in the chloride electrolytic deposition system was studied. In addition, the possible corrosive behavior of the oxide coating is also discussed. The results provide a certain reference for industrial applications of coated porous electrodes.

2. Experimental

2.1. Materials

Ti sheets with a purity greater than 99.6%, and dimensions of 10 mm × 30 mm × 1 mm, were purchased from Baoji Hangtai Co., Ltd., Baoji, China. The coating solution was prepared by ultrasonically dissolving $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, SbCl_3 , RuCl_3 , and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (mole ratio of 6:1:1:0.8, Sn^{4+} was 0.018 mol) in a certain amount of 20 wt.% HCl and n-butanol. Electrochemical testing was performed in a mixed solution of 1 M NH_4Cl and 1.5 M HCl. All the chemical reagents were analytically pure, and the solvent was water of a high purity.

2.2. Experimental Methods

2.2.1. Pretreatment Process

In this experiment, the pretreatment was carried out on the two different titanium sheets, as shown in Table 1. Titanium sheets were immersed in a 10 wt.% NaOH solution at 70 °C for 30 min, and then it was washed with deionized water to remove excess grease. The cleaned titanium sheets were etched in a mixed acid solution ($V_{\text{HF}}: V_{\text{HNO}_3}: V_{\text{H}_2\text{O}} = 1:4:5$) for three minutes to remove the oxide layer, and then washed with deionized water. Then the titanium plates were etched in a 20 wt.% HCl solution at 90 °C for two hours to form a rough surface. Finally, the pretreated titanium substrates were stored in an ethanol solution at room temperature to prevent oxidation.

Table 1. Pretreatment method of the Ti sheet.

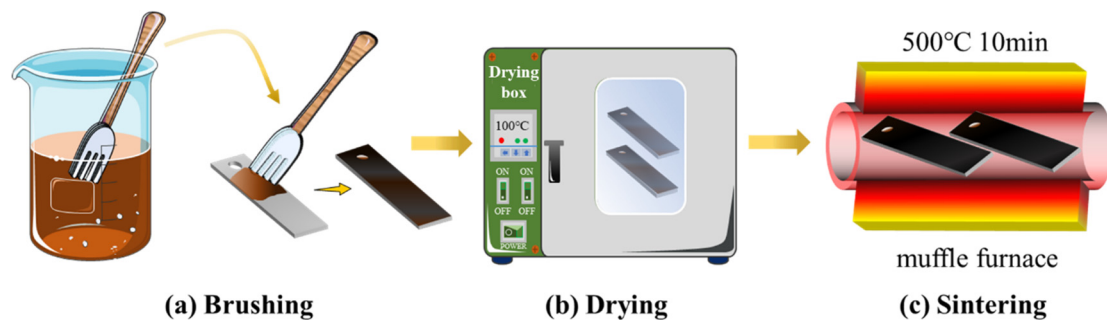
Name	I Alkaline Washing	II Mixed Acid (Room Temperature)	III Etching
Porous Ti	✓	×	×
Flat Ti	✓	✓	✓

Note: The porous titanium sheet will rapidly be corroded and dissolved in the second and third steps; therefore, in this paper, these processes were not performed.

2.2.2. Preparation of Metal Oxide Layer

A mixture of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, SbCl_3 , RuCl_3 , and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (mole ratio of 6:1:1:0.8) was dissolved, in a certain amount of 20 wt.% HCl and n-butanol, respectively. Next, the precursor solution was filtered with 1PS liquid phase separation filter paper to remove moisture. Then, the solution was ultrasonicated for five minutes and sealed for later use [2].

As shown in Figure 1, the pretreated titanium sheets were uniformly painted with the precursor solutions by using a brush. After drying at 120 °C for 5 min until the solvent evaporated, the sheets were heated in a muffle-furnace at 500 °C for 10 min. The abovementioned three steps were repeated 6 times, but the last cycle was heated for 1 h. After all of the abovementioned steps were completed, the Ti-sheets were air-cooled to room temperature [2]. The final effective oxide mass obtained on the porous titanium sheet is 75–80 g/m², whereas on the flat titanium sheet, it is only 13–14 g/m².

**Figure 1.** Schematic of the preparation process.

2.3. Characterization of Electrodes

The surface morphology of the anodic oxide layer was examined by SEM (SU8010, HITACHI, City, Tokyo, Japan). Moreover, the energy spectrometer was used to collect EDS information in the coating area. The phase compositions of the films were studied by using X-ray diffraction (XRD, D8Advance, Bruker, Germany) with Cu K α radiation.

An RST-5200 electrochemical workstation was used for all electrochemical tests. The working electrode was the prepared titanium-based coated anode with an effective area of 1 cm²; the reference electrode was the saturated calomel electrode (SCE); a Pt-sheet of 4 cm² was used as the auxiliary electrode. To ensure the consistency of the experimental results, all experiments were carried out in the same workstation. The corresponding potential range for Linear sweep voltammetry (LSV) test was 0.4–1.4 V, with a scanning rate of 10 mV/s; cyclic voltammetry (CV) testing was among 0.5–0.9 V, with a scanning rate of 1 mV/s; and the frequency interval of the electrochemical impedance spectroscopy (EIS) measurements ranged from 105 Hz to 10^{−1} Hz, with an AC amplitude at 5 mV. The applied anodic potential was 1.2 V (vs. SCE). The impedance data were converted to *Nyquist* data and fitted into the appropriate analog circuit.

The accelerated life test (ALT) of the coated anodes were evaluated by using a solution containing 10 wt.% H₂SO₄, at 40 °C, with 1070-Al (3 × 5 cm) acting as the cathode. The distance between the heteropolar electrodes was 2 cm, and the current density was 2 A/cm².

3. Results and Discussion

3.1. Surface Morphology of the Different Titanium Sheet

The surface microscopic morphology of the flat/porous titanium sheets after the above pretreatments were observed by SEM. Judging from the digital photos in Figure 2a,c, the flat titanium sheet is hemp gray, whereas the porous titanium sheet is silver-gray, thus indicating that the roughness is more visible. The SEM photograph of Figure 2b shows deep irregular depressions on the porous titanium sheet. From the enlarged view, it can be seen that the titanium matrix in these holes is alternately stacked in sheets, rather than simple single holes. The BET test shows that its specific surface area is $2.852 \times 10^{-2} \text{ m}^2/\text{g}$ (Figure S1). The corrosion pits with different sizes and depths appear on the acid-etched flat titanium sheet, and the inside is a honeycomb structure.

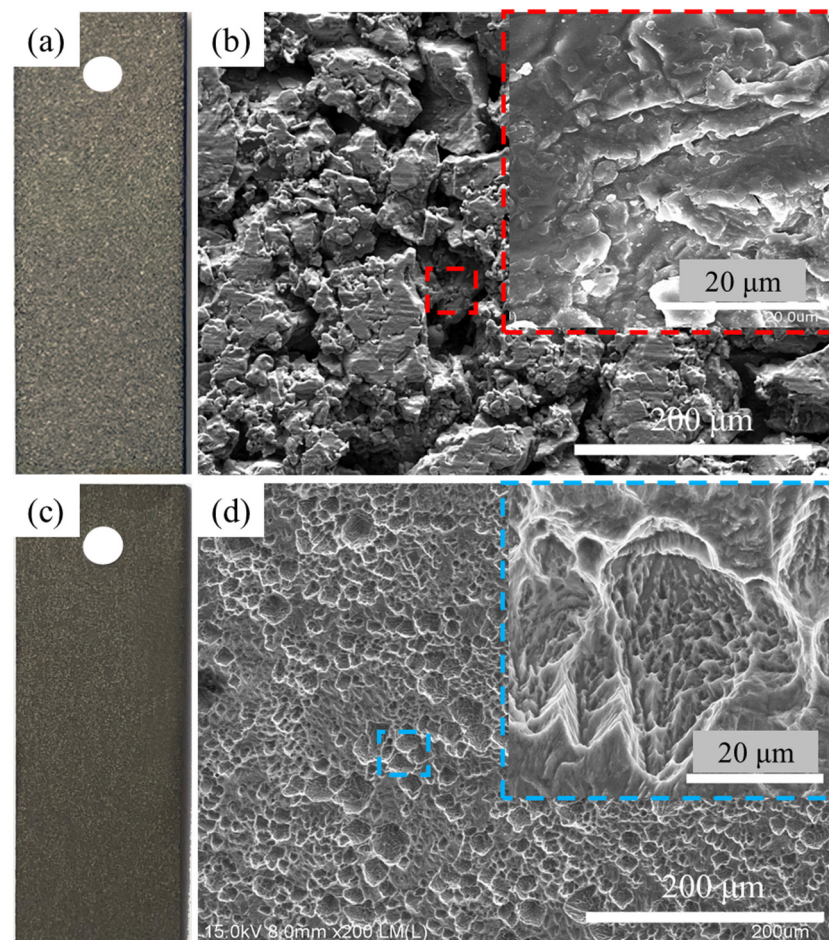


Figure 2. Digital photos and SEM photos of Ti surface before painting. (a,b) Porous Ti-Sheet; (c,d) Flat Ti-Sheet.

3.2. Phase Characterization of Coatings

The same Sn-Sb-Ru-CoOx metal oxide coating was prepared on the two pretreated titanium sheets, respectively, and their morphologies are shown in Figure 3. White granular crystals are distributed on the surface of the two kinds of titanium substrates, and the edges of the layered structure of the porous titanium sheet are wrapped by the crystals. From the enlarged view of “Area 1” in Figure 3a,b, it is evident that the crystals on the porous titanium sheet are clearer and more uniform. Judging from the SEM micrograph of the coating on “Area 2”, the coating formed inside the porous titanium sheet is sized using nanometers, with a particle size of 22–64 nm, and an average value of about 40 nm; however, the coating on the flat titanium sheet still had crack defects, therefore, the denseness of the

porous titanium sheet coating is significantly better than that of the flat titanium sheet. In addition, the pore structure greatly increases the specific surface area and the hydrophilicity of the substrate, which corresponds with the rapid penetration of the coating liquid during painting. The weight gain after sintering is 5–6 times the weight of the coating on the ordinary titanium sheet.

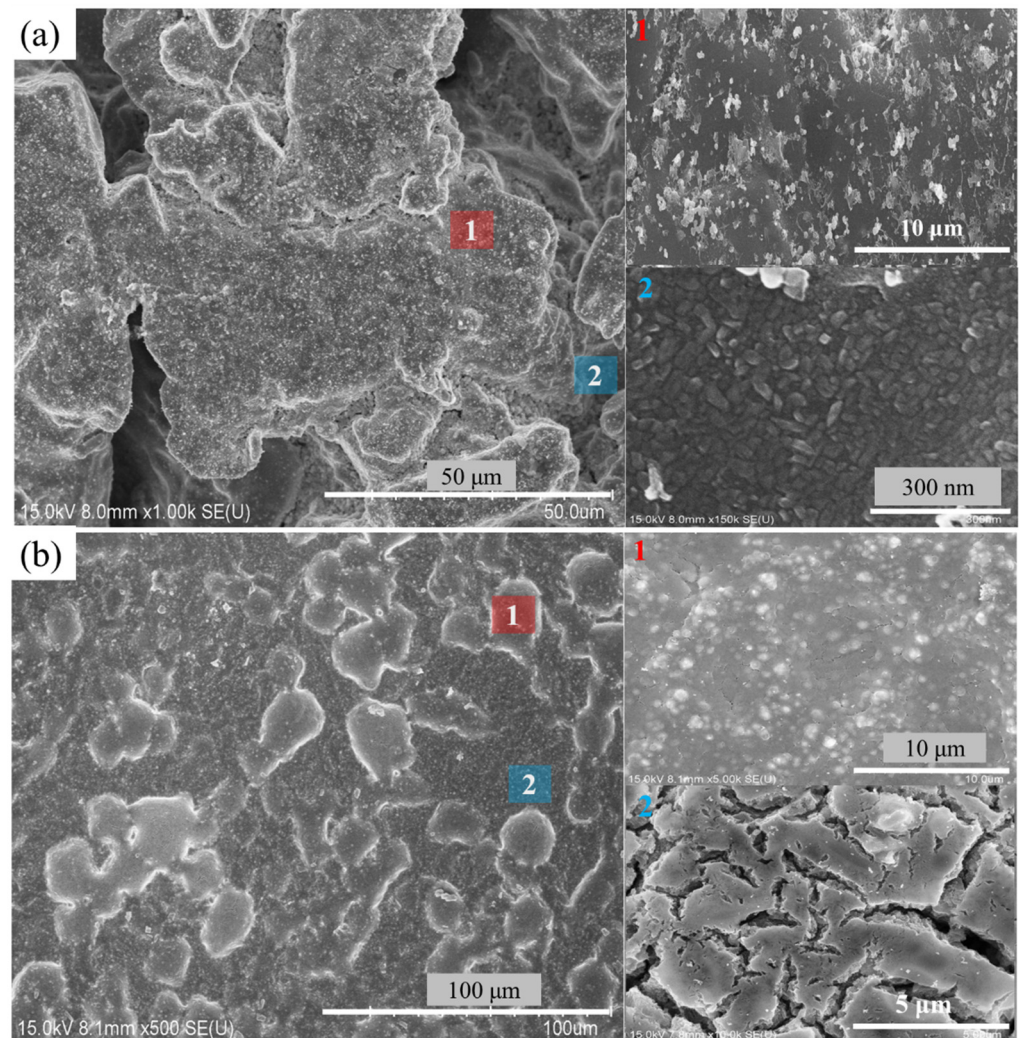


Figure 3. SEM of the Metal Oxide Coating on the Surface of (a) Porous Ti-Sheet and (b) Flat Ti-Sheet.

The different intensities of the XRD diffraction peaks of Ti (89-4893#), in Figure 4, on the same crystal plane are caused by the differences between the types of titanium flakes. The porous titanium sheet shows more grains of a certain orientation due to its loose structure; therefore, the intensity of the diffraction peaks, which correspond to the crystal plane, is very high. The diffraction peaks of RuO_2 (88-0286#) were detected in the two kinds of titanium coatings. The diffraction peaks of RuO_2 were relatively weak due to the very strong diffraction peaks of the porous titanium substrate; however, in this case, the intensity of the diffraction peak of RuO_2 is similar to that of the flat titanium sheet, and only the (222) crystal plane is detected in the porous titanium substrate coating. It can be determined that the RuO_2 content in the porous titanium substrate coating is higher than that of the flat titanium sheet. Sn mainly appears in the form of Ti/Sn mixed oxides, such as $(\text{Ti}_{0.6}\text{Sn}_{0.4})\text{O}_2$ (70-4406#); this is manifested in the strong diffraction peaks that are superimposed on the (002) crystal plane of the titanium matrix at approximately 38° and 82° (400) of the characteristic peaks of the crystal planes. It was indicated that Sn acts as an intermediate layer element that maintains a good chemical bond with the Ti substrate,

which further increases and improves the adhesion of the coating on the substrate as a whole, and it prolongs the electrode's service life. The individual oxide diffraction peaks of Co and Sb were not detected. The corresponding peaks of the mixed oxide, represented by CoSb_2O_6 (84-2602#), exist at around 28° and 63° . This causes the surface morphology of the coating to become a spherically stacked arrangement, which effectively releases the tension on the surface of the coating.

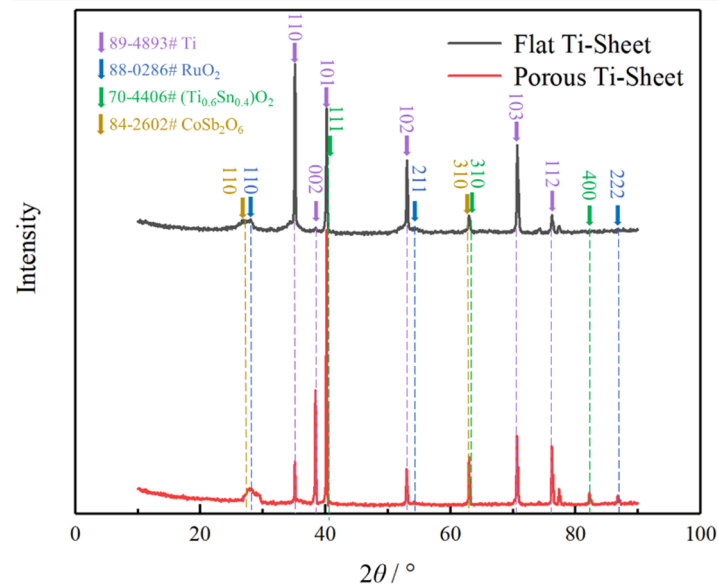


Figure 4. XRD of the Two Coated Ti-Sheets.

3.3. Electrochemical Catalytic Performance of Coated Electrodes

In Figure 5, the original EIS curves of the coatings on the two titanium substrates, and the curves after fitting using the equivalent model, are shown. Table 2 lists the parameters in the simulated circuit.

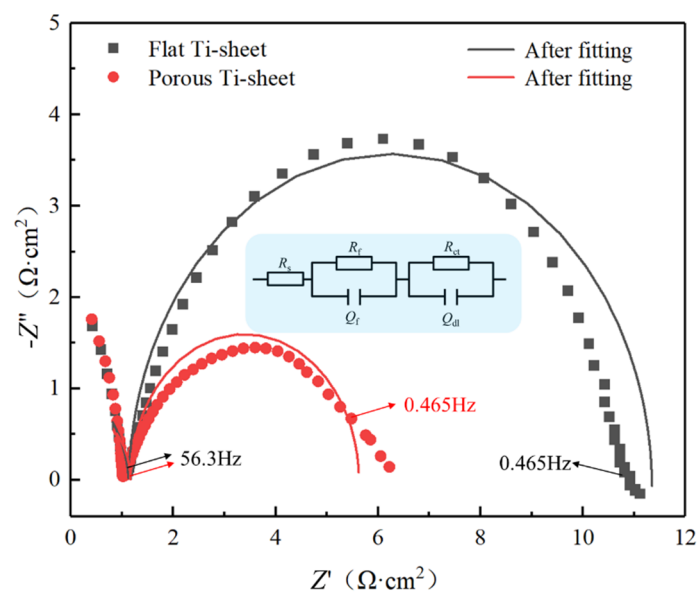


Figure 5. EIS equivalent model and its curve before and after fitting.

Table 2. Fitted data table of EIS.

No.	R_s ($\Omega \cdot \text{cm}^2$)	Q_f ($\mu\text{F} \cdot \text{cm}^{-2}$)	n_1	R_f ($\Omega \cdot \text{cm}^2$)	Q_{dl} ($\mu\text{F} \cdot \text{cm}^{-2}$)	Calculated Roughness Factor	n_2	R_{ct} ($\Omega \cdot \text{cm}^2$)
Flat	8.77×10^{-7}	0.763	1	2.226	1582	15.58	0.802	2.851
Porous	4.21×10^{-7}	1.022	1	1.594	84,080	3370.95	0.938	1.755

Among them: R_s denotes the solution resistance; Q_f describes the internal cracking of the coating; R_f is the resistance of the electrode itself; Q_{dl} is the number of active points on the surface of the electrode, and its value was directly proportional to the number of active points loaded on the electrode surface; R_{ct} represents the electrocatalytic activity of CER (chlorine evolution reaction) on the electrode, and its value is negatively correlated with the chlorine evolution activity of the electrode [16].

The impedance arc of the flat titanium sheet electrode is about 2.3 times higher than that of the porous titanium sheet electrode. The impedance arc shows that the electron transfer process on the surface of the porous titanium sheet coating is blocked less frequently during the reaction, and the number of electron transfers per unit of time is larger. Similarly, the Q_{dl} of the porous titanium flake coating is 50 times higher than that of the flat titanium flake coating, and the surface has unusually abundant active sites and better chlorine evolution performance. Ignoring the resistance of the copper wire connected to the test electrode, it was found that the impedance value of the porous titanium substrate electrode is smaller. This is due to the better bonding force between the active coating and the titanium substrate, and the tight bonding between the substrate and coating is, to a certain extent, reduced by interfacial resistance.

Q_{dl} is coupled with the charge transfer resistance, and the double layer capacitance, C_{dl} , can be evaluated using Formula (1):

$$Q_{dl} = (C_{dl})^n \left[(R_s)^{-1} + (R_{ct})^{-1} \right]^{(1-n)} \quad (1)$$

where n accounts for the deviation from ideal behavior. For perfect capacitors, $n = 1$. C_{dl} can be used as a relative measure of the surface area of the electrode [16].

Table 2 lists the C_{dl} and roughness factors (RF) of the anodes. The RF may be calculated using Formula (2):

$$RF = \frac{C_{dl}}{C^*} \quad (2)$$

where C^* , an assumed reference value for the capacitance, is proposed to be 20 Mf cm^{-2} for smooth Hg electrodes. The RF values that are normally observed in anodic oxide coatings frequently occur due to their characteristic morphology.

In the cyclic voltammetry curve, the capacitance area is usually defined as the electrochemically active surface area of the coated electrode in the chlorate electrolyte. Theoretically, the electrode with the lowest chlorine evolution potential should have more active sites and higher chlorine evolution activity. The capacitance area of the CV curve shown in Figure 6 is 1.018×10^{-4} (flat plate) and 1.707×10^{-3} (porous plate), respectively. Such high activity is mainly attributed to the layered superposition of its coatings. During the sintering process of the coating, when the experimental temperature is higher than the phase transition temperature, the chloride in the coating liquid is converted into oxides, which subsequently shrinks in the pores. The large area of contact between the coating and the substrate provides strong adhesion. During the cooling process of the second coating, when the temperature is lower than the phase transition temperature, the coating liquid will change and shrink into oxides. The corrosion pits of the metal oxide on the flat titanium sheet expand and squeeze each other; although, if it can improve the bonding force of the substrate, it will produce micro-cracks due to extrusion stress. There is enough space for oxide growth in the pores of the porous titanium sheet. Even if microcracks are formed, a

large area can be covered by the coating liquid. In fact, this enhances the bonding force between each layer of coating.

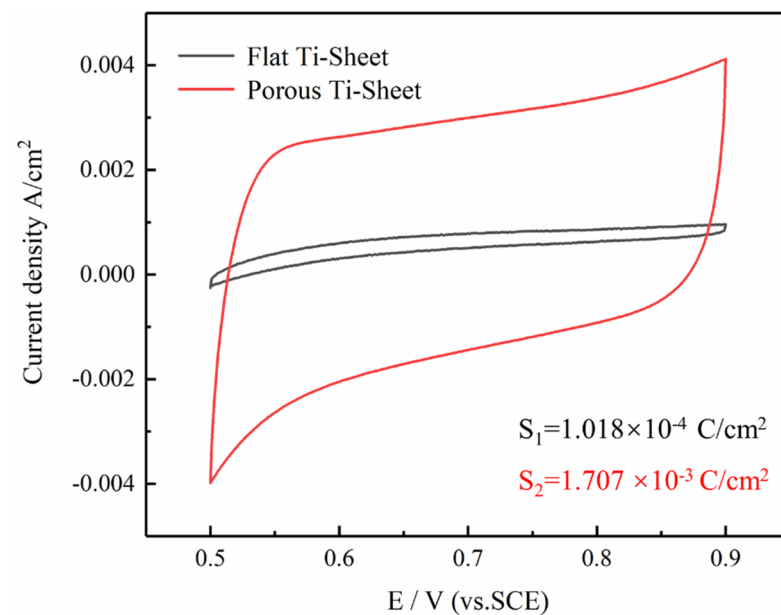


Figure 6. CV curves of different Ti-sheets.

As shown in Figure 7a, at a current density of 500 A/m², the chlorine evolution potentials of the prepared coated anodes are 1.296 V (flat plate) and 1.176 V (porous plate), respectively. Corresponding to the constant current polarization curve in Figure 6b, the working potentials of the two electrodes are very stable, with only slight fluctuations. When comparing the chlorine evolution potentials of these anodes, it is found that the potential of the porous titanium substrate is 121 mV lower than that of the flat titanium, which is a very large improvement. In the solution, the diffusion resistance of ions on the electrode surface is closely related to the distribution of active substances. In a sense, it profits from its porous characteristic, in that it is more hydrophilic. Moreover, the electric field distribution is more uniform on the surface with larger specific surface area; therefore, the large local ion concentration difference caused by tip discharge is effectively avoided. Thus, when porous titanium is used as the matrix, the diffusion resistance is smaller, which is conducive to the catalytic reaction.

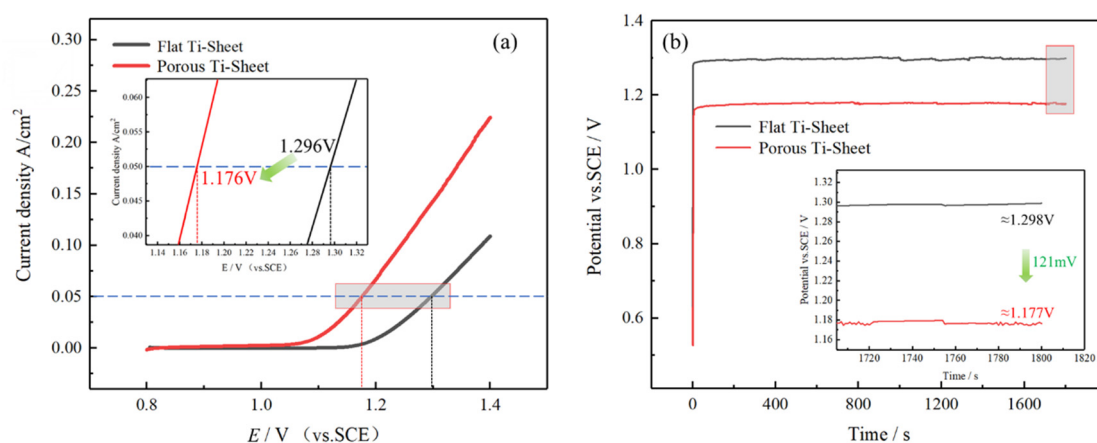


Figure 7. (a) Anodic polarization curves; and (b) constant current polarization at 500 A/m² of different Ti-sheets.

3.4. Accelerated Life Test and Corrosion Resistance of the Electrodes

The electrode potential is recorded regularly during the accelerated life test, as shown in Figure 8, and the potential change interval is shown in Table 3. In the initial phases, the electrode potential will rise briefly and then drop slightly for a period of time, which is called the activation phase. Then the electrode potential floats in a small range for a long time, and the chlorine evolution is stable. Before the electrode is about to fail, the potential of the flat titanium sheet rises rapidly in a short period time, which eventually leads to failure. Here, the difference is that the porous titanium substrate electrode has three plateau periods in the failure stage, at 6 V, 7.5 V, and 9 V, respectively. After the potential rises to this plateau, the electrode will work stably for a period of time. A rise in voltage indicates an increase in electrode resistance, which may be due to the formation of a non-conductive oxide; however, the remaining active sites can still meet the demand for oxygen evolution activity, and moreover, non-conductive oxides are not continuously generated, thus, the electrode voltage remains stable for a period time. When the dissolution of the active material and the exposure of the substrate gradually increases, the electrode voltage rises again. In this experiment, after the abovementioned process was repeated three times (platforms I, II, and III), the electrode finally failed. This also shows that the failure process of the electrode is divided into multiple stages. The lower electrode potential corresponds with a lower cell voltage in the actual production process, which is more efficient and it saves more energy.

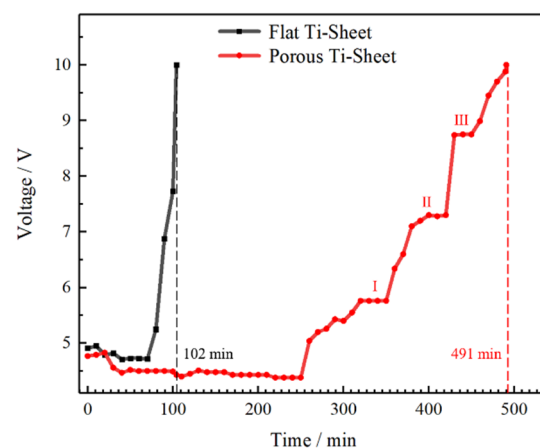


Figure 8. Potential change curve during the accelerated life experiment.

Table 3. Accelerated life test results of the electrodes.

Name	Initial Potential (V)	Stable Potential (V)	Test Results	Contrast Value
Porous Ti	4.77	4.30–4.50	491 min	+378.85%
Flat Ti	4.91	4.70–4.75	102 min	100%

SEM and EDS analysis were performed on the failed electrodes. Figure 9e is a digital photo of the disassembled electrode. Compared with the closed surface, the color of the working surface changed from dark gray to light gray, which is almost similar to its state before painting and sintering, thus indicating that the coating in this area has been dissolved and separated. It is consistent with the results of the morphology characteristics that are shown in Figure 9a–d, as a result of using SEM. A significant number of the white granular RuO_2 crystals in the coating are lost, thus exposing the coating–substrate bonding surface. Furthermore, the bonding surface also becomes blurred due to the corrosion of corrosive ions. We also found that the boundary between the closed domain and the working domain is not an established as closed straight line, which may be related to the surface tension of

the solution. The fine pores in the matrix show the migration path of the solution, which produces capillary action, and causes the solution to diffuse upward in the matrix.

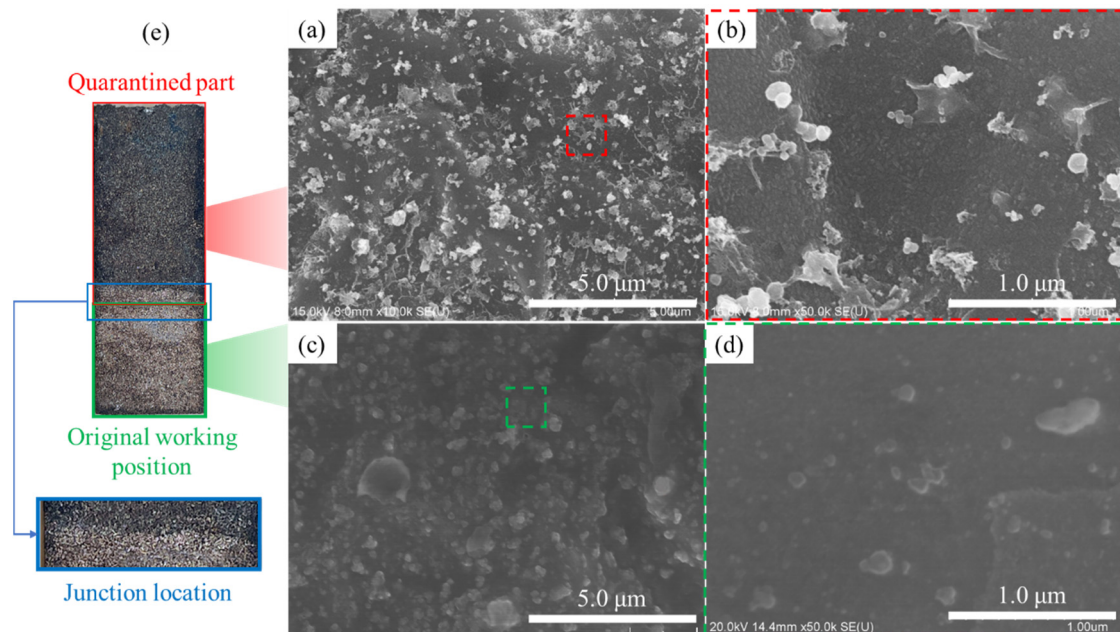
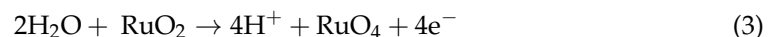
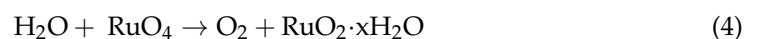


Figure 9. Digital photos and SEM after corroding the coating on porous Ti-sheets. (a,b) Unworking area; (c,d) working area; (e) digital photos of failed electrodes.

The coating element composition of the electrode surface layer, a deeper layer, and an even deeper layer, after the accelerated corrosion failure, was detected by EDS. As shown in Figure 10a, it was found that the surface area is almost composed of Ti and O, and only 0.307 wt.% of Ru remains. This implies that the surface coating was almost dissolved, and a part of the Ti substrate was exposed before it became oxide. The element S was detected due to the residual SO_4^{2-} in the sulfuric acid system. The reaction initially occurred on the surface of the electrode, and the active material in the coating was slowly drained under the action of the applied voltage. According to thermodynamic calculations [17], RuO_2 will be oxidized to RuO_4 when the polar potential is higher than 1.157 V (40 °C, vs. SCE):



Subsequently, RuO_4 will further decompose:



The porous titanium sheet has a larger specific surface area than the flat titanium sheet, which provides more bonding sites and at the same time enhances the bonding force between the substrate and the coating. Meanwhile, the coating is flake-like with repeated superimposed and strengthened effects. It is because of this kind of electrode surface, with a large specific surface area, under the same apparent current density, that its actual current density is lower, and thus, the corrosion rate of RuO_2 as a result of its surface coating is relatively low. Furthermore, it produces better electrochemical activity. With the prolongation of the electrolysis time, the active material on the surface layer is continuously decomposed and is moved away, and the remaining active sites on the surface of the flat titanium sheet are not enough to maintain the full activity of the chlorine evolution; thus, the electrode becomes invalid.

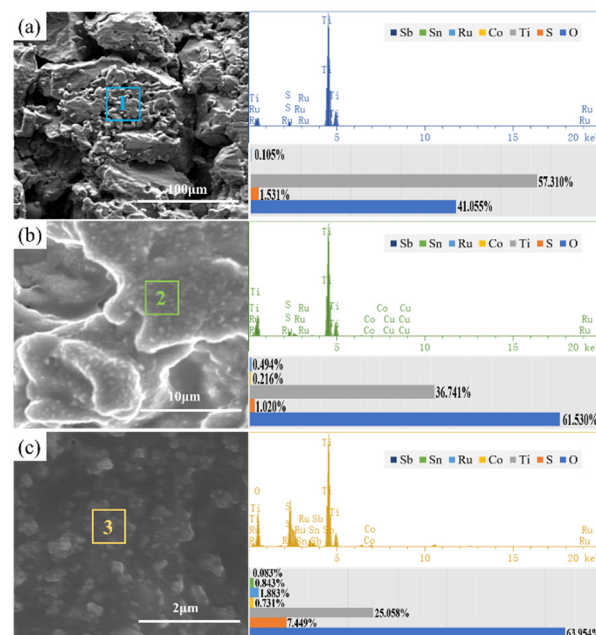


Figure 10. SEM and EDS of failed coatings on porous Ti-sheets. (a) Outermost; (b) deeper; (c) innermost.

The dissolution of the coating inside the porous structure is slightly better than that of the surface. The content of Ti is about 20 wt.% less than that of the surface layer, and the proportion of O is increased by 20 wt.%. There is also about 1.537 wt.% Ru and a trace amount of Co. This shows that the oxygen evolution process mainly occurs at this interface. It is known that Sn and Sb are the intermediate layer elements that form compounds with the Ti matrix to enhance the bonding force [18]; however, the Sn and Sb components in the coating solution were not detected, which indicates that the coating peels off after being corroded [19]. When the electrode is working in the solution, the electrolyte will penetrate into the tortoise crack due to the siphoning effect, and O₂ will continue to be precipitated when the oxygen evolution reaction occurs [20]. The precipitated gas will then produce tensile stress on both sides of the crack, and the resulting updraft will also have a scouring effect on the active coating and cause the coating to peel off [21]. Due to the long-term operation of the electrochemical reaction, the bubbles experienced repeated generation, growth, and rupture processes; this meant that both sides of the crack and the coating surface were subjected to periodic impacts. When the peeling of the active coating reaches a certain limit, the coated electrode slowly loses its activity and becomes ineffective [22,23]. The advantages of the porous titanium sheet are as follows: firstly, because the coating layer is repeatedly superimposed during the sintering and oxidation process, the early peeling does not have a great impact on the electrode performance; secondly, the combination of the coating and the porous substrate is stronger than that of the flat titanium sheet, which further delays the failure of the coating, as a result of the peeling.

The amount of Sn, Sb, and Ti in the intermediate layer that could be detected in the deeper part of the porous sheet was also reduced compared with the shallow detection point, and the amount of Ru rose to 6.781 wt.%, thus indicating that the coating in the deeper part has not been destroyed. There were more S elements, thus indicating that corrosion occurred previously. The nano-particle-like coating inside the porous titanium sheet can effectively resist being filled by ions in the solution, and it had a certain blocking effect on the infiltration damage of corrosive ions and media, thus making the infiltration path tortuous, and prompting the corrosion speed to be reduced; this will extend the service life of the electrode. It is difficult to change from initial electronic conductivity to ionic conductivity, thus avoiding the change of the conductive mechanism of the coating and the resulted increase of potential; however, due to the dissolution of the active material in the

outer layer, the Ti matrix in the deeper part was exposed and oxidized to non-conductive Ti oxide, therefore, the test cell voltage reached 10 V, and the electrode was considered to have failed. In the accelerated life test, this still greatly prolonged the life of the electrode to 8h 11min, before the electrode failed.

Combined with the test results, we propose the failure mechanism of the coating on the porous titanium sheet (Figure 11): the dissolution of the active material in the outer layer, the corrosion and peeling from the middle bonding layer, and the exposure of the Ti matrix and the formation of oxides. The penetration corrosion of SO_4^{2-} ions and H^+ ions, as well as the continuous precipitation and oxidation effect of O_2 , are the main causes of corrosion.

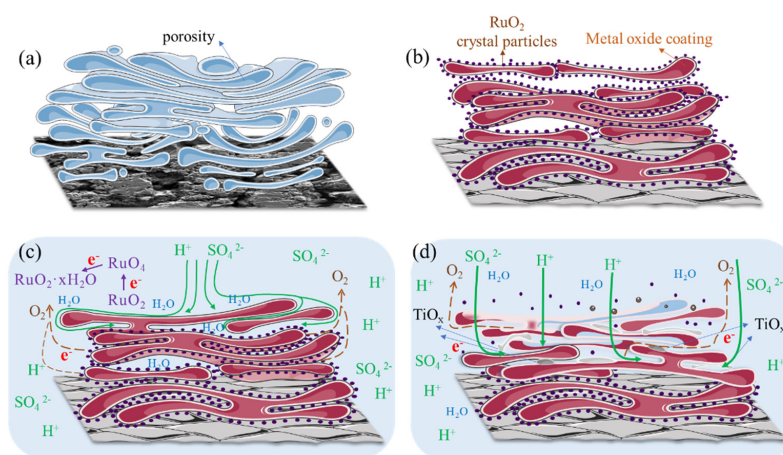


Figure 11. Diagram of coating formation and corrosion process on porous Ti sheet. (a) Original; (b) coating state; (c) early stage of corrosion; and (d) before expiration.

4. Conclusions

We studied the effects of the porous titanium matrix on the performance of coated electrodes. The Sn-Sb-Ru-CoOx metal oxide coating on the porous titanium plate was successfully prepared using a simple thermal decomposition method. Moreover, the corrosion failure process of oxide coating was revealed.

1. Due to its special structure, the porous titanium sheet contains as five times more active material than the flat titanium sheet. The coatings are laminated and strengthened in the form of sheets, and the bonding force between the substrate and the coating is stronger.
2. The chlorine evolution potential of the coating on the porous titanium sheet is 121 mV lower than that of the flat titanium sheet, which greatly improves the electrode performance and accelerates the service life by 3.79 times.
3. The corrosion process of the coating on the porous titanium sheet is divided into three stages, which is “Dissolve-Peel-Oxidize obstruct”. The final failure is caused by a combination of the abovementioned reasons.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/lubricants10110282/s1>, Figure S1: BET analysis of porous Ti-sheet.

Author Contributions: Investigation, Conceptualization, data curation, formal analysis and writing original draft, J.L.; investigation, conceptualization and data curation, L.C.; investigation, conceptualization, validation, writing-review & editing and supervision, B.C.; resources, funding acquisition, validation and supervision, H.H. and Z.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by the National Natural Science Foundation of China (No. 51564029 and 51874154), the Technology Innovation Talents Project of Yunnan Province (No.2019HB111), and

Analysis and Testing Foundation of Kunming University of Science and Technology (2020M20192202035 and 2020M20192202099).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Kariman, A.; Marshall, A.T. Improving the Stability of DSA Electrodes by the Addition of TiO₂ Nanoparticles. *J. Electrochem. Soc.* **2019**, *166*, E248–E251. [\[CrossRef\]](#)
- Chang, L.H.; Chen, B.M.; Qiao, H.H.; Huang, H.; Guo, Z.C.; He, Y.P.; Xu, R.D.; Xie, X.H. Study of the Effects of Pretreatment Processing on the Properties of Metal Oxide Coatings on Ti-Based Sheet. *J. Electrochem. Soc.* **2021**, *168*, 033501. [\[CrossRef\]](#)
- Nam, K.W.; Lee, E.S.; Kim, J.H.; Shin, K.H.; Kim, K.H. Effect of Etching Ti Substrate on a Catalytic Oxide Electrode. *J. Electrochem. Soc.* **2005**, *148*, B111–B115.
- Dan, J.; Chen, K. Analysis of factors affecting electrode surface morphology and electrical properties. *Chloral Kali Ind.* **2000**, *3*, 11–15.
- Yan, Z.; Zhao, Y.; Zhang, Z.; Li, G.; Li, H.; Wang, J.; Feng, Z.; Tang, M.; Yuan, X.; Zhang, R. A study on the performance of IrO₂–Ta₂O₅ coated anodes with surface treated Ti substrates. *Electrochim. Acta* **2015**, *157*, 345–350. [\[CrossRef\]](#)
- Wang, S.C.; Wang, T.; Yan, W.; Chen, B.M.; Huang, H.; He, Y.P.; Guo, Z.C.; Xu, R.D. Effect of Hydrochloric Acid with Different Concentrations on the Activity and Lifetime of Titanium Based Sn–Sb–Ru Oxide Coating Electrodes. *Mater. Prot.* **2019**, *52*, 59–63.
- Wang, T.; Chen, B.M.; Zhang, Z.; Jin, L.; Zhang, X.; Guo, Z.C.; Xu, R.D. Influences of Pre-Treatment Processes on Properties of Titanium Based PbO₂ Electrode. *Mater. Prot.* **2018**, *51*, 68–73.
- Xu, L.K.; Scantlebury, J.D. A study on the deactivation of an IrO₂–Ta₂O₅ coated titanium anode. *Corros. Sci.* **2003**, *45*, 2729–2740. [\[CrossRef\]](#)
- Xie, X.H.; Chang, L.H.; Chen, B.M.; Li, J.M.; Huang, H.; Guo, Z.C.; He, Y.P. Effects of coating precursor states on performance of titanium-based metal oxide coating anode for Mn electrowinning. *Electrochim. Acta* **2022**, *400*, 139459. [\[CrossRef\]](#)
- Zinola, C.F.; Arvia, A.J. A semiempirical quantum chemistry approach to possible structures and energies of hydrogen atoms adsorbed on Pt (100) and Pt (111) clusters at a simulated Pt/aqueous electrochemical interface. *Electrochim. Acta* **1996**, *41*, 2267–2273. [\[CrossRef\]](#)
- Hu, J.M.; Men, H.M.; Zhang, J.Q.; Cao, C.N. Effect of preparation conditions on the properties of Ti based IrO₂ + Ta₂O₅ anodes. *Acta Metall. Sin.* **2002**, *38*, 69–73.
- Zhang, W.; Lin, H.; Kong, H.; Lu, H.; Yang, Z.; Liu, T. Preparation and characterization of lead dioxide electrode with three-dimensional porous titanium substrate for electrochemical energy storage. *Electrochim. Acta* **2014**, *139*, 209–216. [\[CrossRef\]](#)
- Rolison, D.R.; Long, J.W.; Lytle, J.C.; Fischer, A.E.; Lubers, A.M. Multifunctional 3D nanoarchitectures for energy storage and conversion. *Chem. Soc. Rev.* **2009**, *38*, 226–252. [\[CrossRef\]](#) [\[PubMed\]](#)
- Wang, Y.L.; Zhao, Y.Q.; Xu, C.L. May 3D nickel foam electrode be the promising choice for supercapacitors. *J. Solid State Electrochem.* **2012**, *16*, 829–834. [\[CrossRef\]](#)
- Sun, J.R.; Lu, H.Y.; Lin, H.B.; Huang, W.M.; Li, H.D.; Lu J.Cui, T. Boron doped diamond electrodes based on porous Ti substrates. *Mater. Lett.* **2012**, *83*, 112–114. [\[CrossRef\]](#)
- Yang, H.T.; Liu, H.R.; Guo, Z.C.; Chen, B.M.; Zhang, Y.C.; Huang, H.; Li, X.L.; Fu, R.C.; Xu, R.D. Electrochemical behavior of rolled Pb–0.8%Ag anodes. *Hydrometallurgy* **2013**, *140*, 144–150. [\[CrossRef\]](#)
- Luo, S.L.; Guo, H.J.; Wang, Z.X.; Li, X.H.; Wang, J.X.; Yan, J.C. The Electrochemical Performance and Reaction Mechanism of Coated Titanium Anodes for Manganese Electrowinning. *J. Electrochem. Soc.* **2019**, *166*, E502–E511. [\[CrossRef\]](#)
- Chen, X.; Chen, G. Stable Ti/RuO₂–Sb₂O₅–SnO₂ electrodes for O₂ evolution. *Electrochim. Acta* **2005**, *20*, 4155–4159. [\[CrossRef\]](#)
- Chen, B.M.; Wang, S.C.; Liu, J.H.; Dong, C.; He, Y.P.; Yan, W.K.; Guo, Z.C.; Xu, R.D.; Yang, H.T. Corrosion resistance mechanism of a novel porous Ti/Sn–Sb–RuOx/β–PbO₂ anode for zinc electrowinning. *Corros. Sci.* **2018**, *136*, 144. [\[CrossRef\]](#)
- Mazhari, A.H.; Jafarzadeh, K.; Mirali, S.M. An investigation of the effect of RuO₂ on the deactivation and corrosion mechanism of a Ti/IrO₂ + Ta₂O₅ coating in an OER application. *J. Electrochem. Chem.* **2016**, *777*, 66–74.
- Xu, W.; Haarberg, G.M.; Seland, F.; Sunde, S.; Ratvik Petter, A.; Susanne, H.; John, G.; Asa, A.; Erik, Z.; Akre, T. The durability of the thermally decomposed IrO₂–Ta₂O₅ coated titanium anode in a sulfate solution. *Corros. Sci.* **2019**, *150*, 76–90. [\[CrossRef\]](#)
- Moradi, F.; Dehghanian, C. Addition of IrO₂ to RuO₂ + TiO₂ coated anodes and its effect on electrochemical performance of anodes in acid media. *Prog. Nat. Sci. Mater. Int.* **2014**, *24*, 134–141. [\[CrossRef\]](#)
- Silva, L.M.D.; Faria, L.; Boodts, J. Electrochemical impedance spectroscopic (EIS) investigation of the deactivation mechanism, surface and electrocatalytic properties of Ti/RuO₂(x)+Co₃O₄(1–x) electrodes. *J. Electroanal. Chem.* **2002**, *532*, 141–150. [\[CrossRef\]](#)