Rare Metal Materials and Engineering
Volume 51, Issue 7, July 2022
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Feng Qing, Wang Kuaishe, Yan Ailing, et al. Effect of Acid Etching on Lifetime of IrO_2-Ta_2O_5/Ti Anodes[J]. Rare Metal Materials and Engineering, 2022, 51(07): 2387-2392.

ARTICLE

Effect of Acid Etching on Lifetime of IrO_2-Ta_2O_5/Ti Anodes

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Abstract: The effect of surface etching by $H_2C_2O_4$ and H_2SO_4 on Ti substrates on the electrochemical properties and surface morphologies of titanium oxide anode was investigated through different etching methods. The scanning electron microscope, X-ray diffraction, and X-ray photoelectron spectroscopy were used to analyze the specimen structure. The electrocatalytic activity and the electrochemical stability of the specimens were also evaluated by the electrochemical workstation and accelerated lifetime tests, respectively. Results show that the dual acid etching can achieve denser and more homogeneous surface with better catalytic stability. In addition, the influence mechanism of pretreatment on the lifetime of Ti anodes was discussed. The catalytic activity and stability of IrO_2-Ta_2O_5/Ti anodes are strongly dependent on the sequence of acid etching and the surface structure of anodes, and thereby the relationship between the pretreatment methods and the anode performance is established. The dual acid etching can achieve a Ti surface with moderate roughness, therefore improving the coating adhesion. The titanium hydride formed through the dual acid-treatment is transformed into the rutile with barely changed surface morphology, which is conducive to the electrons transport. Therefore, the coating adhesion is enhanced and the accelerated lifetime is prolonged.

Key words: acid etching; accelerated lifetime; IrO_2-Ta_2O_5/Ti anodes

In the production of copper foil for lithium-ion battery, reducing the electrolytic cell voltage and power consumption is important to decrease the production cost. The oxygen evolution reaction (OER) occurs on the anode of electrolytic cell, and the over-potential of OER is the main cause of the high cell voltage. Compared with other anodes, such as PbO_2 and graphite, the titanium anodes of size-stability type with precious metal coating show better performance[1-3]. These dimensionally stable anodes (DSAs) have better properties in electrocatalytic activity and service life than the traditional anodes do, such as graphite and lead alloys. Among them, the IrTa-coated Ti-based anode (IrO_2-Ta_2O_5/Ti) has been rapidly developed in the past decades due to its high stability and extreme durability under aggressive operation conditions. However, due to the high current density required for electrolysis of copper foil, the IrO_2-Ta_2O_5/Ti anode is easily in contact with the oxygen, leading to the oxidation of Ti matrix and the abnormal failure of anode[4,5]. It is found that Ti substrate is usually oxidized during heating, and thus a TiO_2 film layer with poor conductive is formed on the Ti substrate surface, which results in high cell voltage and short service life[6]. Based on these results, the coating process of the precious metal anode needs to be further improved to reduce the possibility of abnormal anode failure and to prolong the service life of the anode.

As reported in Ref.[7-10], the surface layer structures of Ti substrates etched by hot HCl, HF, and boiling oxalic acid solutions are modified to achieve better adhesion between the substrate and IrO_2-Ta_2O_5 coating layer. The relative content of TiH_2 on the Ti surface is independently determined by X-ray diffraction (XRD) [11-14]. The surface analysis of the etched anodes shows that TiH_2 on the surface of Ti substrate is conductive to the improvement of electrocatalytic activity of the anodes.

Therefore, in this research, the Ti substrate was firstly treated by oxalic acid and sulfuric acid etching in order to reduce or even eliminate the negative effect of TiO_2 film layer which is generated during the heating process. After that, the

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Received date: March 06, 2022
Foundation item: National Key Research and Development Program of China (2021YFB3400800)

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IrO_2-Ta_2O_5-coated anodes were prepared by thermal decomposition method. Furthermore, the morphology, phase component, and electrochemical properties of these anodes were examined to distinguish the influence of the pretreated Ti substrate on the IrO_2-Ta_2O_5-coated anodes.

1 Experiment

The Ti sheet (TA1) was purchased from Xi'an Baotai Co., Ltd, and it was cut by laser cutting into the specimens with dimension of 60 mm×80 mm×1 mm. The coating solution was obtained by mixing H_2IrCl_6, Ta_2Cl_5, and HCl in *n*-butanol solution. The electrochemical test was performed in 0.5 mol/L H_2SO_4. The accelerated lifetime test was conducted in 1 mol/L H_2SO_4. All the chemical reagents were at analytical grade without further purification.

In order to remove the oxide layer and to obtain a larger surface area of the Ti flakes, all the Ti flakes were sandblasted. Ti sheets were ultrasonically cleaned with deionized water. Then the plates were etched in 10wt% H_2SO_4, 10wt% $H_2C_2O_4$, or 10wt% HCl solution at 90 °C for 2 h to form a rough surface. Finally, the pretreated Ti substrate was placed in ethanol solution at room temperature to prevent oxidation.

The metal oxide coating was prepared by conventional pyrolysis method. The mixed solution of H_2IrCl_6 and Ta_2Cl_5 was diluted by the *n*-butanol solution with the molar ratio of 7: 3. After stirring for 30 min, the precursor was obtained. Then, the pretreated Ti sheets were painted with the precursor solution through a brush. After drying at 60 °C for 3 min, the solvent evaporated. Then the plates were heated in a muffle furnace at 500 °C for 15 min. The painting process was repeated for 15 times, and the heating duration was 1 h for the final painting process. These Ti sheets were air-cooled to room temperature for further use in electrochemical test.

The CS2350H electrochemical workstation was used for electrochemical tests. The working electrode was the coated anode with active area of 1.4 cm^2. The reference electrode was the saturated calomel electrode (SCE), and the Pt-sheet of 4 cm^2 was used as the auxiliary electrode. To ensure the consistency of experiment results, all electrochemical tests were conducted on the same workstation under the same test conditions.

2 Results and Discussion

2.1 Morphology characterization

After polishing by 1500# sandpaper, the Ti sheets without oxide scale were obtained. Then the pretreatment of acid etching was conducted immediately. These Ti sheets were etched by different acid solutions for different durations, as shown in Table 1.

Table 1 Pretreatment parameters of different Ti specimens

Specimen	Pretreatment
TA1	10wt% $H_2C_2O_4$/2 h
TA2	10wt% H_2SO_4/2 h
TA3	10wt% H_2SO_4/1 h+10wt% $H_2C_2O_4$/1 h
TA4	10wt% $H_2C_2O_4$/1 h+10wt% H_2SO_4/1 h
TA5	20wt% HCl/2 h

With increasing the reaction temperature, small gas bubbles are formed on the surface of Ti substrate during the acid-etching process. When the Ti substrate is treated by the oxalic acid, the yellow-brown titanium oxalate is generated, and the solution color is gradually darkened with prolonging the reaction. In contrast, the sulfuric acid reacts violently with Ti, and the solution gradually becomes dark purple with the reaction proceeding. The Ti sheet surface after acid etching is grayish white. The surface morphologies of the etched Ti sheets were analyzed by scanning electron microscope (SEM), as shown in Fig. 1b~1f. The surface morphology of the Ti sheet before etching is shown in Fig. 1a. The Ti sheet surface etched by oxalic acid is scattered with corrosion pits of different sizes, and there are jagged structures in the pits, as shown in Fig. 1b. As shown in Fig. 1c, the corrosion pits on Ti sheet surface treated by sulfuric acid are round with different sizes. The depth of these pits is greater than that of the pits caused by oxalic acid, which is consistent with the higher surface roughness caused by the sulfuric acid treatment[15,16]. The morphologies of TA3 and TA4 specimens show scale-like corrosion structure and circular corrosion pits. It can be seen that the surface morphology of TA3 specimen consists of three-dimensional honeycomb structures with uniform corrosion depth, and no deep corrosion pits appear. This phenomenon is similar to that of TA5 specimen, as shown in Fig. 1f. It is generally believed that the corrosion of Ti sheet by hydrochloric acid is shallow[13], due to the formation of chlorine gas in the reaction of hydrochloric acid with Ti matrix, resulting in the new dense oxide film on the Ti surface at the beginning of reaction. As a result, the deposition of H_2 and H^+ on the Ti matrix surface is hindered. It is well-known that the hydrogen produced during the reaction can be absorbed by Ti substrate because of its strong hydrogen absorption ability in the initial stage of acid etching. With the hydrogen adsorption amount increasing, TiH_2 with various crystal phases is precipitated at the grain boundary[17], where the crack likely occurs due to the phase transformation stress between the brittle titanium hydride and the matrix. The TiH_2 formed through dual acid-treatment is transformed into the rutile without obvious changes of the surface morphology, which is beneficial to the electrons transport. This phenomenon leads to the more violent hydrogen-absorbing corrosion along the crack and then the formation of more corrosion pits. In these corrosion pits, some of the hydrogen ions are used as depolarizing agent to reduce to hydrogen, and the others produce the unstable black-gray titanium hydride. Due to the corrosion pit and corrosion crack, Ti^{4+} accumulates in the corrosion pit and reacts with water to form dense oxide passivation film[18]. When the hydrogen reduction process is hindered, the hydrogen ions spill out from the corrosion pits, and thereby more titanium hydride is formed outside the corrosion pit, which gradually increases the corrosion area and finally forms the ichthyoid pattern.

The valence states of the elements on the Ti substrate surfaces etched by different solutions were studied by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 2a, the high-resolution spectra of TA3 specimen show a typical fluctuation curve of titanium. The peaks at 453.8 and 458.6 eV correspond to the spin orbital peaks of Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively. The peak at 458.8 eV corresponds to Ti^{4+}, which is consistent with the characteristic peak of TiO_2. This result indicates that Ti exists mainly in the form of TiO_2. Meanwhile, the peak of Ti $2p_{3/2}$ can be divided into a high binding energy peak (456.0 eV) and a low binding energy peak (453.8 eV), which correspond to Ti^{2+} and Ti^0, respectively[19]. The appearance of Ti^{2+} characteristic peaks indicates the existence of TiH_2 compound on the Ti surface, which is consistent with the results in Ref.[19,20]. The peak at 464.3 eV is considered as a satellite peak of one of these peaks. The XPS spectra of Ti sheets etched by different acid solutions are shown in Fig. 2b. It is clear that the XPS spectrum of TA3 specimen is similar to that of TA1 specimen, suggesting that Ti^0, Ti^{2+}, and Ti^{4+} exist on both the TA1 and TA3 specimen surfaces. Meanwhile, the TA2 and TA4 specimens show smaller peaks of Ti^0 and Ti^{2+}, compared with those of TA3 specimen, indicating that there is less TiH_2 phase on the surface of the Ti sheets[19]. In addition, the trend of electron loss can be observed from the spectrum of TA2 specimen.

2.2 Coating characterization

The phase composition and crystal structure of the IrO_2-Ta_2O_5 coating on Ti substrate were investigated by XRD, as shown in Fig. 3. The spectra of coatings on different Ti substrates are in good agreement with those of IrO_2 (PDF #86-0330) and Ti (PDF #44-1294). The sintering temperature of the anodes is 500 °C, which is far below the crystallization temperature (800 °C) of Ta_2O_5. Therefore, the characteristic peaks of Ta_2O_5 cannot be observed. Meanwhile, due to the thin coating thickness, the diffraction peaks of Ti substrate appear. The obvious characteristic peaks of IrO_2 in all the specimens indicate that the synthesized material is well crystallized and

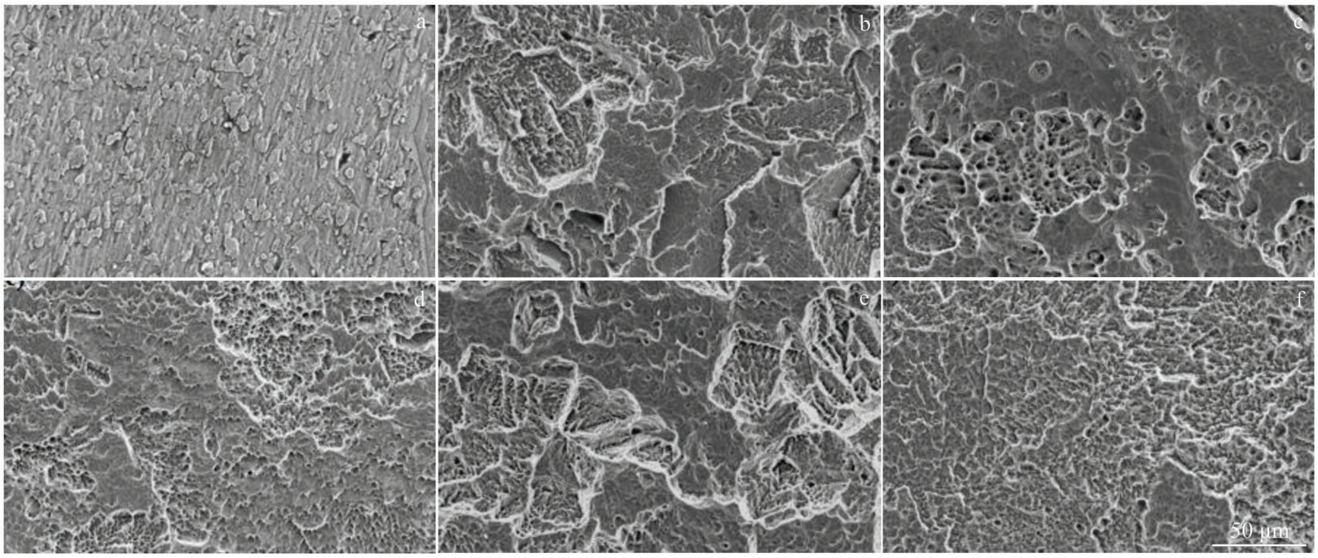

Fig.1 SEM morphologies of Ti sheets after different pretreatments: (a) after polishing; (b) TA1; (c) TA2; (d) TA3; (e) TA4; (f) TA5

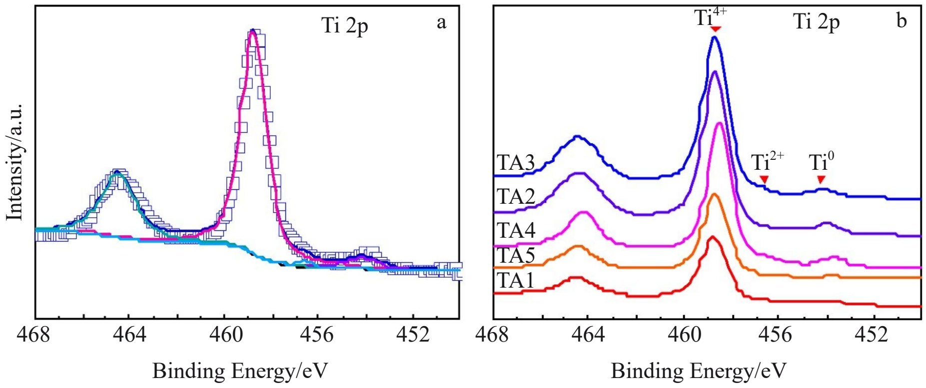

Fig.2 XPS spectra of TA3 specimen (a) and Ti sheets after different pretreatments (b)

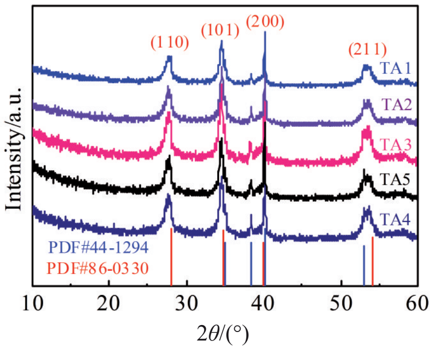

Fig.3 XRD patterns of IrO_2-Ta_2O_5/Ti specimens processed by different pretreatments

has a pure phase. On the contrary, the diffraction peaks of tantalum oxide at the (200) and (211) crystal planes are weak, suggesting the existence of amorphous tantalum oxide phase.

2.3 Electrochemical performance

The electrochemical properties of the specimens were tested in 0.5 mol/L H_2SO_4 solution. Fig. 4a shows the linear sweep voltammetry (LSV) curves of the specimens prepared by different pretreatments. Fig. 4b shows the overpotential of all the specimens at current density of 50 mA·cm^{-2}. It can be seen that the overpotential of TA1 specimen is 320 mV, which is higher than that of TA4 (258 mV), TA3 (278 mV), TA5 (287 mV), and TA2 (250 mV) specimens. The Tafel plots in Fig.4c show the similar slopes of all specimens in the range of 90~95 mV/dec. In this research, there is no significant change due to the same IrO_2-Ta_2O_5 coating on different Ti substrates. However, it should be considered that the Tafel slope can also exhibit the small contribution of the difference in specific surface areas. Fig.4d shows the change in current density with the variation of scanning rate. It is well-known that the electrochemical active surface area (ECSA) of an electrocatalyst can be represented by a double layer capacitance ($2C_{dl}$). The calculated ECSA of TA3 specimen is 74.3 mF·cm^{-2}, which is much larger than that of TA1 specimen (61.5 mF·cm^{-2}). The ECSA of TA5 specimen is 71.7 mF·cm^{-2}, which is similar to that of TA3 specimen. This phenomenon infers that the pretreatment increases the active area of Ti anode, and the high ECSA value guarantees the high catalytic activity of TA3 specimen[20]. The integral area of the cyclic voltammetry (CV) curves is another important factor to evaluate the catalytic effective area. According to CV curves of all the specimens, TA1 specimen shows the smallest catalytic active area (Fig. 4e), which can be attributed to the shallow etching pits caused by oxalic acid, and therefore results in less loading of IrO_2-Ta_2O_5 coating on the surface of Ti substrate. As shown in Fig.4f, the impedance spectra of the specimens can represent the kinetic effects of the reactions during the catalytic reaction. The fitting model of electrochemical impedance spectrum (EIS) is also shown in Fig. 4f, where R_S denotes the solution resistance, Q describes the internal cracking of the coating, and R_{ct} represents the

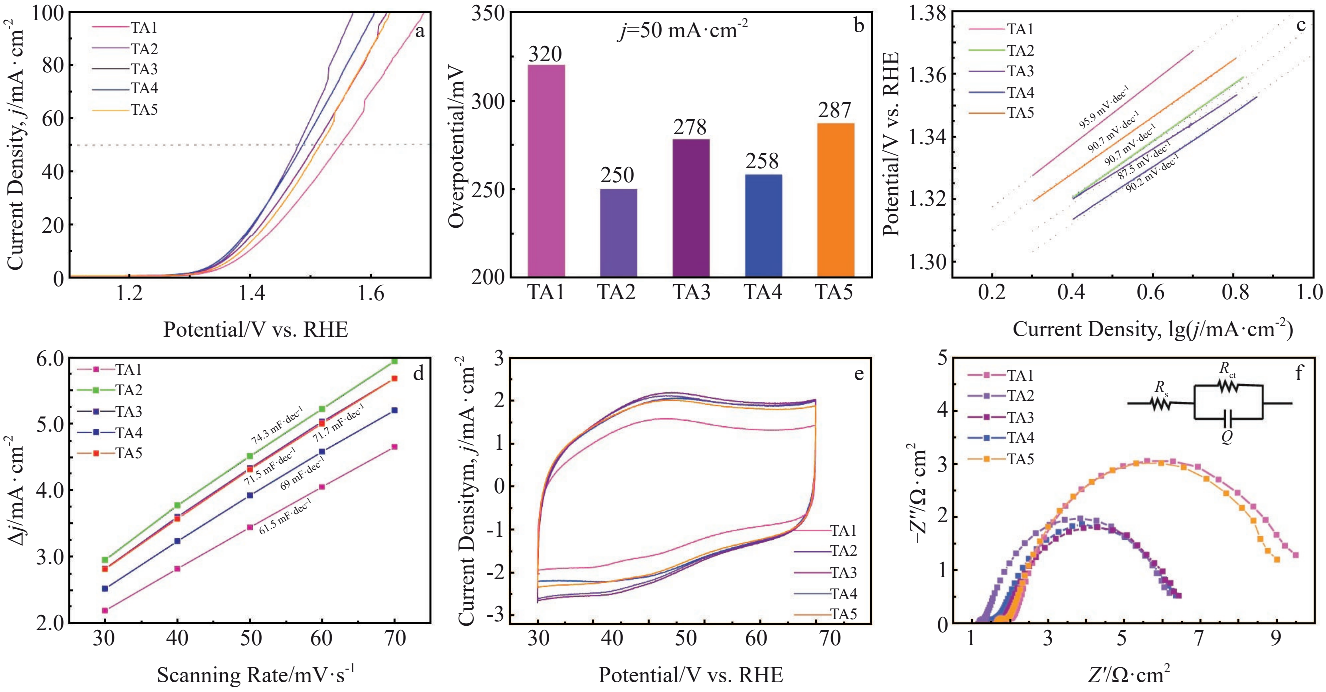

Fig.4 OER electrocatalytic performance including LSV curves (a), overpotential (b), Tafel plots (c), ECSA plots (d), cyclic voltametric curves (e), and Nyquist plots (f) of IrO_2-Ta_2O_5/Ti specimens processed by different pretreatments (RHE represent the reversible hydrogen electrode)

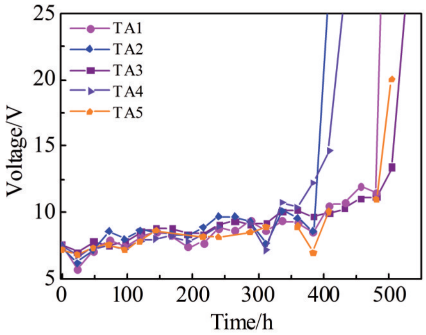

Fig.5 Accelerated lifetime results of IrO_2-Ta_2O_5/Ti anodes processed by different pretreatments

electrocatalytic activity of oxidation evolution of the electrode. The value of R_{ct} is negatively correlated with the chlorine evolution activity of the electrode. As shown in Fig.4f, TA2, TA3, and TA4 specimens all exhibit lower charge transfer resistance R_{ct}, compared with that of TA1 specimen, which is consistent with their better catalytic activity. This may be ascribed to the better adhesion between the coating layer and the Ti substrate for TA2~TA4 specimens, and more active sites in these anodes.

2.4 Accelerated lifetime

The service life was investigated through the acceleration life test for shorter experiment period. The H_2SO_4 solution of 10wt% was used. The solution was heated to 40 °C through water bath heating, the current density was 4 $A \cdot cm^{-2}$, and Ti plate was used as the cathode plate. It can be seen form Fig.5 that the TA3 specimen exhibits the best stability and the longest service life among all these specimens. Although the catalytic activity of TA5 specimen is not the best, its lifetime is relatively long under harsh conditions. However, the TA2 and TA4 specimens show shorter service life. The difference in these properties is related to the TiH_2 phase on the surface of Ti substrate after pretreatment[10]. The TiH_2 existence increases the binding force between the substrate and the oxide layer, and decreases the resistance between the substrate and the coating layer. In brief, the acid etching and heat treatment jointly improve the coating adhesion and accelerated lifetime.

3 Conclusions

1) The IrO_2-Ta_2O_5/Ti anode treated by sulfuric acid followed by oxalic acid shows the best electrocatalytic activity and the longest service life. The anodes with etched surface of uniform honeycomb structures have higher catalytic activity for oxygen reduction.

2) The sulfuric acid etching shows the more obvious corrosion effect on Ti sheets than the oxalic acid etching or hydrochloric acid etching does.

3) More TiH_2 can be observed on the surface of Ti sheet treated by oxalic acid, thereby improving the bonding force between the substrate and oxide coating. The TiH_2 formed through dual acid-treatment is transformed into the rutile without obvious changes of the surface morphology, which is beneficial to the electrons transport. The acid etching and heat treatment jointly improve the coating adhesion and accelerated lifetime.

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酸刻蚀处理对IrO_2-Ta_2O_5/Ti阳极寿命的影响

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摘　要：通过改变腐蚀方法，研究了使用$H_2C_2O_4$和H_2SO_4进行钛基体表面刻蚀对金属氧化物钛阳极电化学性能和表面形貌的影响。采用扫描电子显微镜、X射线衍射仪和光电子能谱等测试方法对样品进行了结构分析。然后利用电化学工作站测试了样品的电催化活性，利用加速寿命测试研究了样品的电化学稳定性。结果表明，通过$H_2C_2O_4$和H_2SO_4分步腐蚀可以获得更加均匀致密的表面形貌和更好的催化稳定性。在此基础上，进一步研究了预处理对钛阳极寿命的影响原因。IrO_2-Ta_2O_5/Ti阳极的催化活性和稳定性与酸刻蚀处理的先后顺序及表面结构密切相关，并建立了预处理方法与阳极性能之间的关系。分步腐蚀使钛表面具有合适的粗糙度，因而提升了涂层附着力。在热分解过程中，经分步腐蚀形成的氢化钛在不改变表面形貌的情况下转变为金红石结构的氧化钛，有利于电子输运，从而增强涂层附着力并延长加速寿命。

关键词：酸刻蚀；强化寿命；IrO_2-Ta_2O_5/Ti阳极

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