A Study on the Performance of IrOx Electrodes Prepared by Double-titanium Cyclic Voltametric Electrodeposition Mode

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Abstract. The electrodes were fabricated in double-titanium cyclic voltametric electrodeposition system, corresponding to the anode and cathode of the system. For further study the practicality of this mode, the performance of the resulting electrodes was investigated. Through a series of physical and electrochemical characterization, it is concluded that the IrOx electrode corresponding to the anode of the system has a flat and uniform deposit layer, and shows better electrolytic durability (its actual working life is more than 3072 h), while the cathode electrode has better performance in electrocatalytic activity.

1 Introduction

Iridium-coated titanium anodes have the advantages of low oxygen evolution potential, high current density carrying capacity (>100A dm^{-2}), excellent catalytic activity, and electrical durability [1-3]. Since their inventation, they have been widely used in water electrolysis, cathodic protection, electroplating, non-ferrous metal extraction, water treatment, etching solution recovery and other fields. In 1973, Bianchi obtained the patent right of IrO_2/Ta_2O_5 coated electrode[4]. Since then, the core position of thermal decomposition method for preparing iridium-tantalum-coated titanium electrode has been established. Recently, many creative fabrication methods of IrO_2 electrodes, such as chemical bath deposition [5], sputtering deposition [6, 7], pulsed laser deposition [8], chemical bath deposition [9] and electrodeposition [10-12], etc have been investigated.

With the continuous expansion of the market demand for DSA (Dimensionally Stable Anode) and the country's emphasis on the upgrading of the industrial system, the traditional thermal decomposition method can no longer meet the requirements of industrial production and conform to the industrial development of the times. Although the new method such as sol-gel, chemical bath, and sputtering deposition, etc. can provide Nano-scale coatings and thin iridium oxide film, but due to its complex equipment and strict process requirements, it is incompatible with the preparation of iridium-coated titanium electrodes, cannot be used for the preparation of large-scale iridium-based coated titanium electrodes in the actual industrial system, seems no operability. Due to its mild preparation conditions, high degree of mechanization, and strong operability, electrodeposition method is very suitable for the preparation of iridium-coated titanium electrodes in the actual industrial system. Relevant studies [13-15] have shown that the iridium oxide titanium electrode prepared by the electrodeposition method has better electrocatalytic activity than that prepared by the traditional thermal decomposition method, it shows relatively simple preparation process and controllable parameters, having research value and development potential.

In recent years, iridium oxide electrodeposition technology is mainly used to prepare pH transmission micro-sensing electrodes, polymer membrane electrodes and DSA anodes. In most cases, these electrodes are mainly prepared by potentiostatic, galvanostatic and cyclic voltammetry electrodeposition techniques. The author's research group mainly has done research on the electrodeposition preparation technology of DSA anode. When using cyclic voltametric electrodeposition technology to prepare the electrode, it was found that when iridium oxide was electrodeposited on the anode, a black layer of iridium compound material was also generated on the cathode. Based on this, a double-titanium cyclic voltametric electrodeposition mode was proposed, and the physical characterization and electrochemical properties of the obtained anode, and cathode electrodes were studied. It is expected to reduce unnecessary waste of iridium elements while ensuring the performance of the electrodes, thereby improving the electrodeposition efficiency of iridium.

2 Materials and Methods

To prepare the electrodeposition solution, 0.1mM iridium chloride ($IrCl_3$) was dissolved in 250mL deionized water (DI water) and mixed for 10min under magnetic stirring. Then, 0.5mM oxalic acid ($(COOH)_2 \cdot 2H_2O$) were added, and the resulting solution was mixed for 10min (the molo ratio of $IrCl_3$ and $H_2C_2O_4$ is 1:5). After the solution pH was adjusted to 10.0~10.5 by the addition of anhydrous potassium

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carbonate (K_2CO_3), a light green solution was obtained. Finally, the electrodeposition solution was kept at 40℃ in thermostatic water bath for 4 days to allow stabilization, achieving a dark blue stable solution.

The anodic electrodeposition process was completed in a three-electrode system in which a saturated calomel electrode (SCE) was used as the reference electrode. Industrially pure titanium (grade TA2) with oxalic acid etching treatment (effective deposition area: 1.0 cm^{-2}) was used as the counter and working electrodes, respectively. Cyclic voltametric electrodeposition technology was adopted to prepare the IrOx film. Fig 1 shows a typical production process executed. After the electrodeposited anode and cathode were prepared, the IrOx coatings were completely converted into metal oxides through a thermal decomposition process: heating at 450℃ for 1h in a muffle furnace.

The morphologies of deposits on anode and cathode were observed by SCE (scanning electron microscopy) with the magnification of 10k, and was investigated by EDS (Energy Dispersive Spectthe component element type and contentrometer). Furthermore, X-ray diffraction (XRD) was utilized to analyze the microstructure of IrO_X films. Electrochemical characterization was performed in a three-electrode system by an electrochemical workstation (CS310H, CorrTest Ltd.). Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed in a 0.5 M H_2SO_4 solution with a potential scan rate of 20 mV s^{-1} and 1 mVs^{-1}, respectively. Electrochemical impedance spectroscopy (EIS) was determined at 1.35V (vs. SCE) with an amplitude of 5mV, and the frequency of that from 0.01Hz to 10kHz. An accelerated life test (ALT) on these electrodeposited IrOx/Ti electrodes was carried out in an electrochemical cell with Pt cathode, referring to previous studies, the potential-time curve was monitored at an applied current density of 0.25 A cm^{-2}. These tests were run until the potential increased up to 10V.

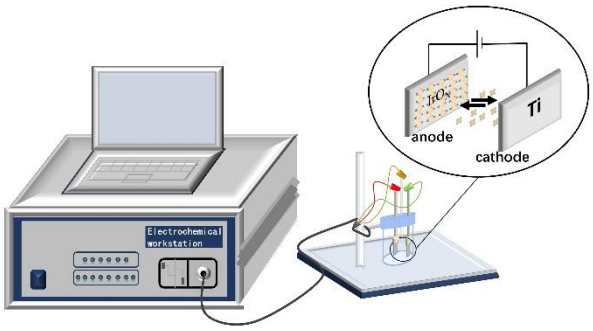

Fig. 1. Schematic diagram of preparing IrOx electrode by double-titanium cyclic voltametric electrodeposition mode.

3 Results and Discussion

Cyclic voltametric electrodeposition technology is mainly used to prepare iridium oxide electrodes based on the substate of Pt, CP (carbon paper). In this study, the iridium oxide electrode was fabricated by this method where both the anode and the cathode were based on titanium. The deposition bath is a complicated iridium complex based on oxalate. Scheme 1,2 shows the typical reaction on anode[16], but the related reaction on cathode is uncleared.

$$[Ir(C_2O_4)(OH)_4]^{3-} \rightarrow [Ir(C_2O_4)(OH)_4]^{2-} + e- \quad (1)$$

$$[Ir(C_2O_4)(OH)_4]^{2-} \rightarrow IrO_2 + 2H_2O + 2CO_2 + e^- \quad (2)$$

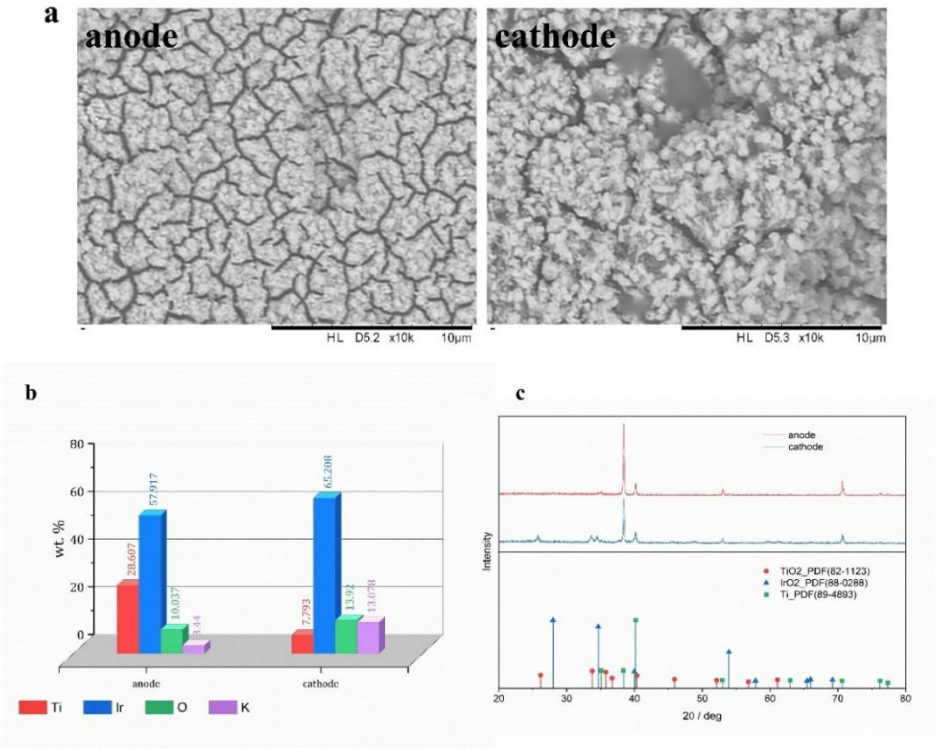

Fig. 2. (a) SEM images, (b) EDS results, and (c) XRD patterns of IrO_X electrodes corresponding to the anode and cathode of the cyclic voltametric electrodeposition system.

3.1 Physical characterization

The resulting physical characterization of the IrO_X electrodes corresponding to the anode and cathode prepared by the cyclic voltametric electrodeposition technology are shown in Fig. 2. The morphologies of the deposits based on the anode is varied from that of the cathode, the former is film-like, smooth and flat, while the latter is pile-like, rough and uneven, and both cracks generating. The component element type and content of the deposits was summarized in Fig. 2b. In addition to the main Ir and O elements, there are Ti elements and a small amount of K elements. The presence of K indeed suggest that the redox deposition reaction occurs with the salt adsorption. Compared to the anode, the Ir content is lower than that of the cathode, indicating that the electrodeposition of Iridium on the cathode is much more efficient, resulting in higher coverage of the titanium substrate. obviously, two typical crystalline microstructures can be observed in the anode and cathode samples (Fig. 2c), no rutile IrO_2 is found, probably IrO_X deposits is too thin to be characterized. The deposits of cathode are more complicated, with pronounced TiO_2 crystallization, which suggests that the IrO_X deposits are not tightly bonded to the substrate, resulting in the generation of TiO_2 during the thermal decomposition.

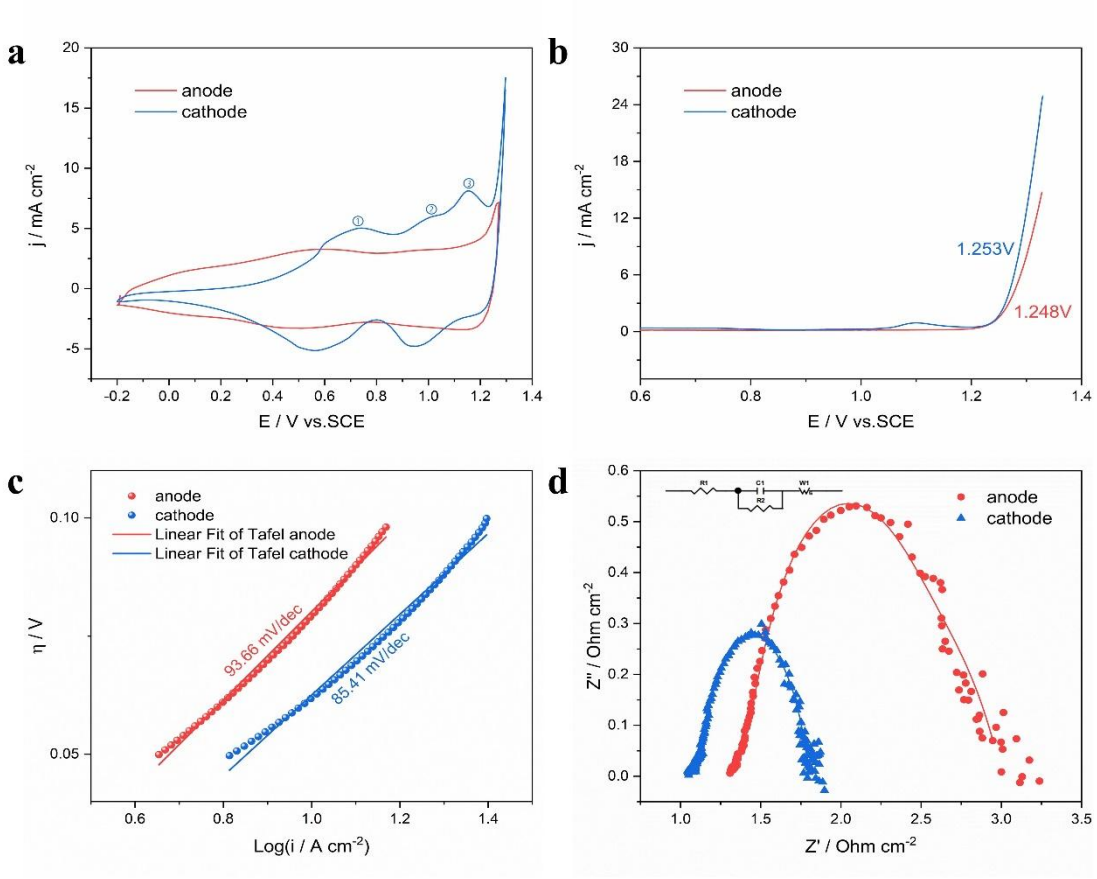

Fig. 3. (a) Cyclic voltammograms, (b) polarization curves, (c) Tafel curves, and (d) Bode diagrams of IrO_X electrodes corresponding to the anode and cathode of the cyclic voltametric electrodeposition system.

Table 1. the fitting result of EIS plots with electrical equivalent circuit.

	anode	cathode
R1	1.299	1.051
C1	0.131	0.245
R2	0.725	0.272
W1-R	0.975	0.475
W1-T	2.257	0.331
W1-P	0.315	0.398

3.2 Electrochemical characterization

The voltammetry behaviour was summarized in Fig. 3. Obviously, the cyclic voltammograms (shown in Fig. 3a) of these IrOx/Ti electrodes (derived from anode and cathode electrodeposited by the cyclic voltametric technique) are very different from each other. These curves are obtained by cycling the potential in the range between -0.2 and 1.3V. the CV curve of the anode sample is similar with that of the TDIROF (an IrO2 electrode prepared by thermal decomposition of a precursor), showing an axial symmetry (around the potential axis). However, the CV curve of the cathode sample shows more complexity. Three anodic peaks appear at 0.70V(region ① in Fig. 3a), 1.0V(region ② in Fig. 3a), 1.15V(region ③ in Fig. 3a). the reversible peak ① (reported as pre-peak) is the first to appear followed by the reversible peaks ② and ③ before oxygen evolution. According to previous reports[17], the surface reaction related to redox couples② and ③ is correspond to the Ir(Ⅲ)/Ir(Ⅳ) and Ir(Ⅳ)/Ir(Ⅴ)redox, which are believed to be the following:

At 1.0V, peak ② on Fig. 3a:

$$Ir(OH)_3 \leftrightharpoons IrO(OH)_2 + H^+ + e- \quad (3)$$

At 1.15V, peak ③ on Fig. 3a:

$$IrO(OH)_2 \leftrightharpoons IrO_2(OH) + H^+ + e- \quad (4)$$

The polarization curves of the IrOx deposits based on anode and cathode samples were measured to compare its electrocatalytic characters. In Fig. 3b, before the onset of oxygen evolution, there is a clear Ir(Ⅳ)/Ir(Ⅴ)redox for the cathode sample, corresponding to ③ peak (Fig. 3a). The oxygen evolution overpotential (obtained by linear fitting of the potential over the oxygen evolution section) of the cathode sample is larger than that of the anode sample, indicating that the anode sample is more practical because of the lower energy consumption. As shown in Fig. 3c, the Tafel plots for the polarization curves provided a straight line for each sample and the Tafel slops (lines shown in Fig. 3c) are calculated. The value of the cathode sample is smaller (85.41mV/dec <93.66 mV/dec), which means the cathode sample shows better electrocatalytic performance. This might be result of the rough deposits on cathode, providing more active area.

Intuitively, the electrochemical impedance spectroscope of the anode and cathode sample was roughly similar in Bode diagrams (Fig. 3d), which means that they have the same circuit model[R1(C1-R2) Ws]. The circuit was utilized to acquire the data obtained from the analysis of EIS spectra, presented in Table 1. The value of R1 reflects the difficulty of charge transfer between electrode and electrolyte. Therefore, the large the R1 value, the more difficult it is for the redox reaction occur on the electrode surface, at the same time, means better corrosion resistance. The R2 value represent the charge transfer situation between IrOx deposits and titanium substrates, larger R2 means larger charge transfer resistance, indicating a better adhesion of deposits for the titanium substrate. Where, C is capacitance, has a positive relationship with the active surface area. In summary, the anode sample has larger R1, R2, and smaller C, so its shows worse electrocatalytic activity but better electrolytic durability compared to the cathode sample. This is consistent with previous analysis of voltammetry behaviour such as LSV. Ws consists of three parts: Ws-R, T, P. Thereinto, Ws-R is relevant to the corrosion resistance of IrOx deposits. the larger the value, the more complete and uniform the deposits is, and the less likely it is to be damaged.

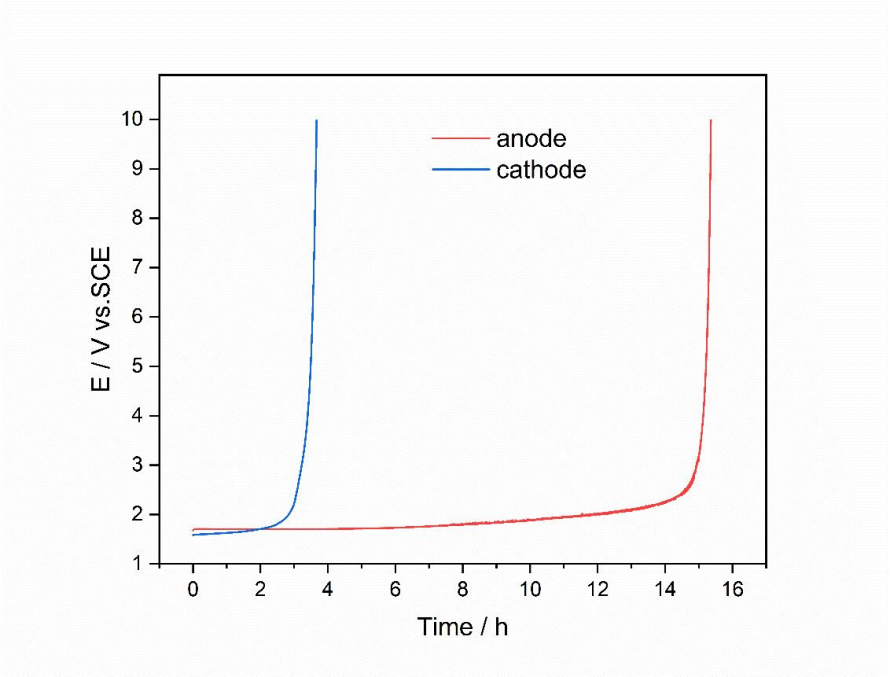

Fig. 4. Accelerate life of IrO_X electrodes corresponding to the anode and cathode of the cyclic voltametric electrodeposition system.

3.3 Accelerate life test

For DSA, the actual working life is longer due to the working condition at low current density and weak acid-base strength. So, its lifetime is expressed in terms of accelerate life time, which is measured in strong acid solution at high current density and temperature. The accelerate life time of the samples are shown in Fig. 4. The result shows that the initial potential of the anode sample is higher than that of the cathode, but its accelerate life time is longer (15.82h, more than the value estimated in the literature for 4.16h [18]). Furthermore, the SEM of the anode and cathode sample measured by the accelerate life test for 2h were investigated. The IrOx deposits on the anode sample appears unchanged, while the IrOx film on the cathode sample is visibly damaged, showing spilt blocks-like, implying a worse working life for the cathode sample. This confirms above physical characterization and electrochemical performance analysis for these two electrodes. According to the Hideo Tamura experience formula, the accelerate lifetime is 200-300 times of the actual service lifetime, concluding that the actual working life of the anode and cathode sample is at least 732h and 3072h, respectively, indicating that the IrOx electrode corresponding to the anode of the cyclic voltametric electrodeposition system has value in practical fields such as wastewater treatment, electrodeposition industry.

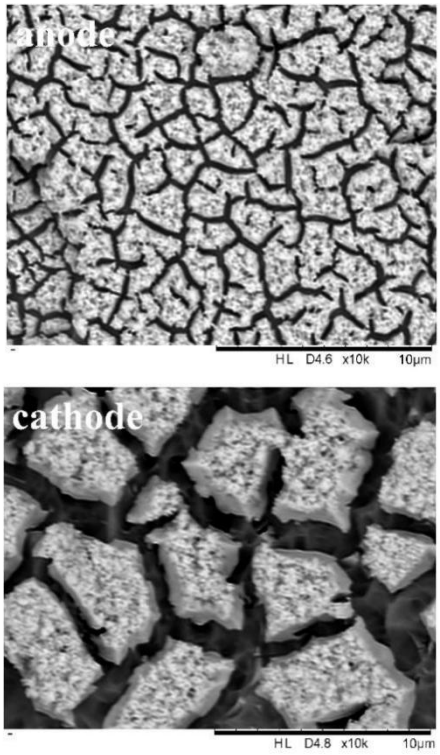

Fig. 5. SEM of the IrOx films on anode and cathode after electrodeposited in 0.5 M H_2SO_4 at 0.25 A cm^{-2} for 2h.

4 Conclusion

The physical characterization and electrocatalytic activity of the IrO_X electrodes corresponding to the anode and cathode of the cyclic voltametric electrodeposition system are compared. The cathode has better electrocatalytic activity, but worse lifetime, no practical value. This may be ameliorated by pretreating the cathode titanium substrate, such as anodizing, hydrogen heat treatment to enhance the adhesion of the deposited IrO_x coating to the substrate. The anode IrO_X electrode exhibits superiority in electrolytic durability, and its actual working lifetime (at least 3072h) indicates that it can be used in practical fields such as water electrolysis and wastewater treatment, etc. Besides, it provides a good idea for pre-coating a layer of iridium oxide film on the titanium substrate because of its perfect wrapping. Therefore, the successful preparation of these two electrodes shows that the double-titanium cyclic voltametric electrodeposition mode has certain research value and development potential.

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