

Graphene-Modified IrO₂-Ta₂O₅ Coated Titanium Anodes for the Application of Impressed Current Cathodic Protection

Yonglei Xin*

State Key Laboratory for Marine Corrosion and Protection, Luoyang Ship Material Research Institute (LSMRI), Qingdao 266237, China

*E-mail: xinyi@sunrui.net

Received: 7 July 2021 / Accepted: 18 August 2021 / Published: 10 September 2021

IrO₂-Ta₂O₅ coated titanium anodes with different graphene contents (Ti/IrO₂-Ta₂O₅-G) were prepared by the thermal decomposition method. The microstructure and the composition were analyzed using the field-emission scanning electron microscope and the energy dispersive spectrometer, and the electrochemical properties were investigated by electrochemical tests including cyclic voltammetry, anode polarization and electrochemical impedance spectroscopy. Results show that The Ti/IrO₂-Ta₂O₅-G anode with 0.4g·L⁻¹ graphene content presents the best electrochemical performance. As compared with the traditional Ti/IrO₂-Ta₂O₅ anode, Ti/IrO₂-Ta₂O₅-G anodes display the rugged morphology with tiny cracks which can provide more active centers, increase the electrochemically active surface area and thus enhance the electrocatalytic activity for the oxygen evolution process.

Keywords: IrO₂-Ta₂O₅; graphene; titanium anode; electrocatalytic capability.

1. INTRODUCTION

Titanium-based metal oxide anode has good electrochemical activity, low wear rate and long life as well as light weight and excellent plasticity. Because of its high cost performance and adaptability, it is widely used as the oxygen or chlorine evolution electrode in the fields including chlor-alkali industry, electroplating, wastewater treatment, cathodic protection and organic electrosynthesis and so on[1]. The IrO₂-Ta₂O₅ coated titanium anode is considered to be an oxide anode with high stability which has long life under oxygen evolving conditions. In particular, it is suitable for the electrolytic industry with poor working conditions, the high-speed electro-galvanized steel plate production lines using sulfuric acid as electrolyte and the impressed current cathodic protection engineering under high current density [2-3]. Accordingly, the titanium anode material is expected to have the low oxygen overpotential, the large electrochemically active surface area, the long service life under high current density and the sufficient

resilience to mechanical and chemical effects of oxygen deposition on the surface of anode [4-5]. With the continuous expansion of application fields and the increasingly complication of service environment for Ti/IrO₂-Ta₂O₅ anode, the development of new-type titanium anode material has been attracting the focus from material researchers.

Recently, various carbon nanomaterials have been used as the dopants to improve the catalytic ability and the stability of titanium-based metal oxide anodes, and excellent results have been obtained [6-11]. Whereinto, graphene is a new type of two-dimensional carbon nanomaterial with the single flake structure composed of carbon atoms. Compared with carbon nanotubes and buckminsterfullerene, it has larger specific surface area (2630 m²·g⁻¹) and higher chemical stability [12]. It is not only one of the thinnest known materials, but also quite hard and strong. As simple substance, it delivers electron faster than every known conductor at the room temperature. With its excellent electrical, mechanical, and thermal properties, graphene has been widely concerned in the material research area.

In this paper, IrO₂-Ta₂O₅ coated titanium anodes with different graphene contents (Ti/IrO₂-Ta₂O₅-G) were prepared using the conventional thermal decomposition method, and the electrochemical performance and the stability were studied and compared.

2. EXPERIMENTAL

In this experiment, the TA2 titanium plate (15 cm × 14 cm × 0.1 cm) was utilized as substrate. Prior to use, titanium plates were firstly sandblasted, then degreased in lye for 1 h and etched in 10% oxalic acid for 2 h, and finally dried after rinsed in distilled water. A certain amount of graphene was dispersed in normal butanol mixed with a small amount of hydrochloric acid by ultrasonic vibration for 20 min. The painting solution with a nominal composition of Ir:Ta = 70:30 in mole was obtained by dissolving H₂IrCl₆·6H₂O and TaCl₅ in the above solution. The surface of titanium plate after pretreatment was uniformly coated with painting solution, and then dried at 120 °C for 10 min followed by sintered at 500 °C for 10 min. The painting process was repeated after cooled until the desired coating thickness was attained. Finally, the titanium plate was sintered for 1 h at 500 °C. The preparation of Ti/IrO₂-Ta₂O₅ anode for comparison is similar to Ti/IrO₂-Ta₂O₅-G anode.

The Ultra 55 field emission scanning electron microscope (FESEM) was used to observe the morphology of anodes, and the surface composition was analyzed by the energy dispersive spectrometer (EDS).

Electrochemical measurements were carried out in a three-electrode electrolytic cell, taking platinum-niobium electrode as an auxiliary electrode and saturated calomel electrode (SCE) as a reference electrode. The electrochemical workstation type was Parstat 2273, and the test area of the working electrode was 1 cm². The test was performed in 1 mol·L⁻¹ H₂SO₄ solution at (25±0.5) °C. Electrodes were immersed in the electrolyte for 2 h before test. Cyclic voltammetry (CV) measurements were performed with 20 cycles between 0.16 and 1.16 V with a scanning rate of 20 mV·s⁻¹. Electrochemical impedance measurements were performed at 1.35 V DC bias with a frequency range from 100 kHz to 10 mHz, and the signal amplitude was 10 mV. Polarization curve measurements were performed between 0.2 and 1.8 V with a scanning rate of 0.33 mV·s⁻¹. Experimental data was processed

by using softwares Origin 8.0, C-View and ZsimpWin 3.21. Voltammetric charge (Q) was obtained by integrating the last cyclic voltammogram according to the following formula:

$$Q = \frac{\int_{V_a}^{V_b} i dV}{S} \quad (1)$$

Where Q is the voltammetric charge, V_a and V_b are the upper and lower bounds for potential scanning limits, respectively, and S is the scanning rate.

3. RESULTS AND DISCUSSION

The morphology of graphene is shown in Figure 1. The graphene was made by chemical exfoliation method [13]. Its powders typically present single-layer nanosheets (single layer ratio >80%) which have a lateral size of 0.5-5 μm , an average surface area of 700-800 $\text{m}^2 \cdot \text{g}^{-1}$, an oxygen content of 7.0-7.5 at% and a conductivity of 500-700 $\text{s} \cdot \text{m}^{-1}$. Figure 2 shows the FESEM images of Ti/IrO₂-Ta₂O₅ electrodes (Figure 2-a) and Ti/IrO₂-Ta₂O₅-G electrodes (Figure 2-b). Because the surface morphologies of Ti/IrO₂-Ta₂O₅-G with different graphene contents are similar, here just list the surface morphology of Ti/IrO₂-Ta₂O₅-G with the graphene content of 0.4 $\text{g} \cdot \text{L}^{-1}$. From Figure 2, the anode surface is composed of dense area and crack area, and the crack area displays dried-mud cracks. The difference of thermal expansion coefficient between the metal substrate and the metal oxide coating results in the mechanical stress and the thermal stress when the sample is cooled [14]. The interaction between mechanical stress and thermal stress results into this kind of crack. Lots of cracks can provide more active centers for oxygen evolution reaction and increase electrochemically active surface area. But the surface of Ti/IrO₂-Ta₂O₅ anode is relatively smooth while that of Ti/IrO₂-Ta₂O₅-G anode presents honeycomb. The uneven surface of anode increases the surface roughness, the number of active sites, thereby potentially improving the electro-catalytic activity of Ti/IrO₂-Ta₂O₅-G anode. Differing from continuous, deep and large cracks of Ti/IrO₂-Ta₂O₅ anode, the cracks of Ti/IrO₂-Ta₂O₅-G anode are incontinuous, thin and small. This kind of cracks can resist the contact between titanium substrate and oxygen as well as corrosive electrolyte, thereby improving the stability of the anode.

The compositions of Ti/IrO₂-Ta₂O₅-G anodes with different graphene contents examined by EDS were listed in Table 1. Compared with Ti/IrO₂-Ta₂O₅ anode, Ti/IrO₂-Ta₂O₅-G anodes have higher Ir content, which can be taken as IrO₂ crystallites. It is indicated that more IrO₂ crystallites are separated out because of the addition of graphene, consequently improving active center for oxygen evolution reaction on the coating surface [15]. With the amount of graphene increasing, the content of Ir element on the anode surface increases. The content of Ir element on the anode surface most obviously increases with the graphene content of 0.4 $\text{g} \cdot \text{L}^{-1}$, and decreases with the graphene content of 0.5 $\text{g} \cdot \text{L}^{-1}$. A certain amount of graphene benefits the surface segregation of IrO₂ and the composition distribution tends to be uniform when the amount exceeds a certain value. Meanwhile, the content of Ti element of Ti/IrO₂-Ta₂O₅-G anode is less than that of Ti/IrO₂-Ta₂O₅ anode, which suggests that the higher coating coverage area of Ti/IrO₂-Ta₂O₅-G anode reduces the exposure of Ti substrate and benefits the stability of anode.

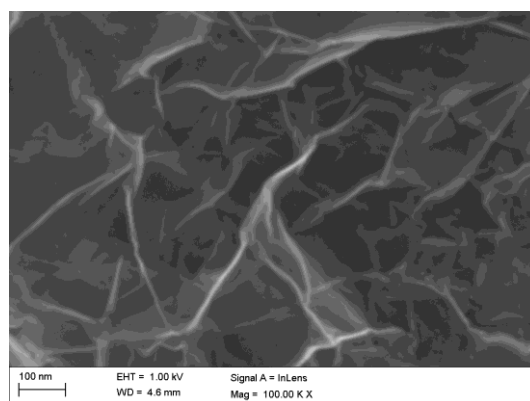


Figure 1. FESEM image of graphene prepared by the chemical exfoliation method.

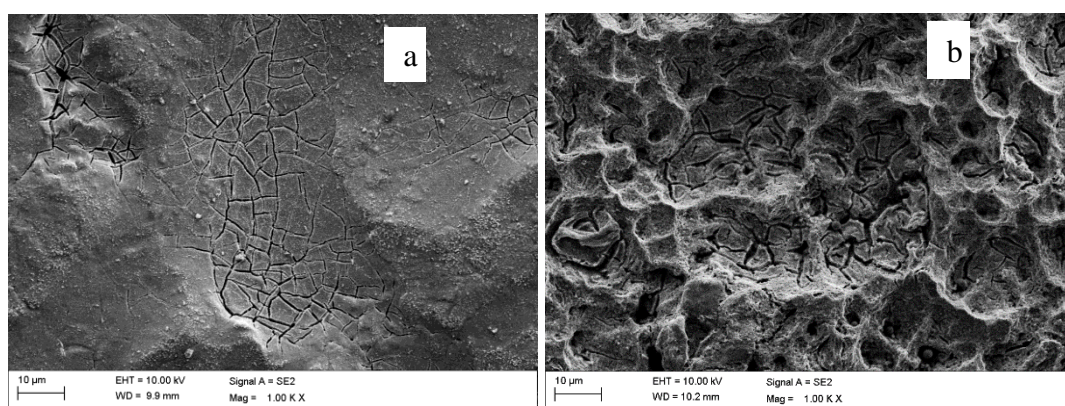


Figure 2. Surface morphologies of (a) Ti/IrO₂-Ta₂O₅ and (b) Ti/IrO₂-Ta₂O₅-G anodes. The graphene content of Ti/IrO₂-Ta₂O₅-G is 0.4 g·L⁻¹.

Table 1. Surface composition of Ti/IrO₂-Ta₂O₅-G anodes with different graphene contents.

Graphene contents/ g·L ⁻¹	0	0.1	0.2	0.3	0.4	0.5
A _O /%	68.49	68.61	68.53	68.61	68.06	68.49
A _{Ta} /%	5.72	5.42	5.40	5.47	5.61	5.91
A _{Ir} /%	11.97	15.26	15.27	15.38	15.64	15.21
A _{Ti} /%	13.82	10.71	10.80	10.54	10.69	10.39

Figure 3 shows the cyclic voltammograms of Ti/IrO₂-Ta₂O₅-G anodes with different graphene contents. There are obvious redox peaks around the potential of 0.7 V for all anodes, which can be related to the reversible Ir³⁺/Ir⁴⁺ redox transition in 1 mol·L⁻¹ H₂SO₄ solution. From the shape of cyclic voltammograms, the repeatability of Ti/IrO₂-Ta₂O₅-G anode is better than that of Ti/IrO₂-Ta₂O₅ anode, indicating the good reversibility of Ir³⁺/Ir⁴⁺ redox for the graphene-modified anode.

The integration area of cyclic voltammograms is often used to represent specific capacitance for the supercapacitor composite material which is consist of graphene[16]. For IrO₂-Ta₂O₅ anodes, the

voltammetric charge Q is in direct proportion to the amount of active centers on the coating surface [17-19], so the voltammetric charge Q is employed to represent the amount of active centers. Figure 4 gives the voltammetric charge of Ti/IrO₂-Ta₂O₅-G anodes with different graphene contents. It can be seen that the graphene content has a significant impact on the voltammetric charges of metal oxide anodes. Firstly, the voltammetric charge increases with the rise of the graphene content, and reach the maximum value with the graphene content of 0.4 g·L⁻¹. It can be considered that voltammetric charge Q is not only related to the active component but also the coating structure of anodes. On one hand, the active component Ir increases with the rise of the graphene content, consequently improving active points on the anode surface. On the other hand, the active area of anode increases with the change of surface morphology. But voltammetric charge Q declines when the graphene content turns to 0.5 g·L⁻¹. The relative amount of active component Ir decreases with the further increase of graphene content, therefore, the voltammetric charge of metal oxide anode declines. So it is very important to select appropriate graphene contents for electrocatalytic activity of anodes.

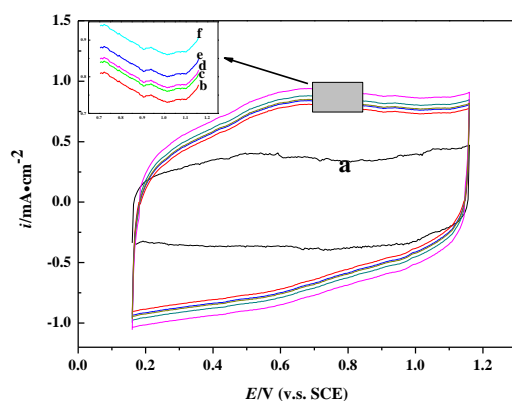


Figure 3. Cyclic voltammograms of Ti/IrO₂-Ta₂O₅-G anodes with different graphene contents: (a) 0 g·L⁻¹, (b) 0.1 g·L⁻¹, (c) 0.2 g·L⁻¹, (d) 0.3 g·L⁻¹, (e) 0.4 g·L⁻¹, and (f) 0.5 g·L⁻¹. The scanning rate is 20 mV s⁻¹ and the electrolyte solution is 1 mol·L⁻¹ H₂SO₄ solution.

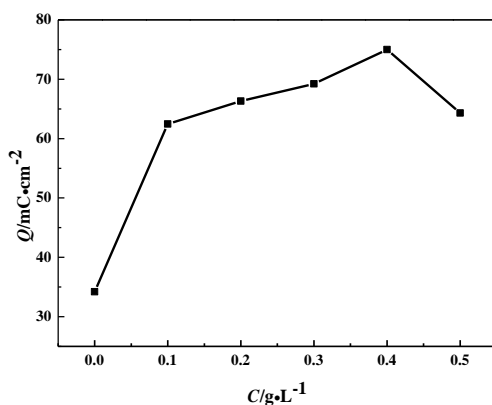


Figure 4. Voltammetric charge variations of Ti/IrO₂-Ta₂O₅-G anodes with the graphene content.

The polarization curve for the oxygen evolution reaction is an important method to evaluate the electrocatalytic activity of IrO₂-Ta₂O₅ anodes. Polarization curves of Ti/IrO₂-Ta₂O₅-G anodes with different graphene contents are shown in Figure 5. It shows that all potentiodynamic polarization curves have a wide range of Tafel area with the addition of graphene. The Tafel equation indicates semilogarithm relation between overpotential $\Delta\phi$ and electric current density i :

$$\Delta\phi = a + b \lg i \quad (2)$$

In the course of anodic polarization,

$$a = -2.3 \frac{RT}{\beta n F} \lg i_0 \quad (3)$$

$$b = 2.3 \frac{RT}{\beta n F} \quad (4)$$

Where R is the universal gas constant, T is the absolute temperature, β is the transfer coefficient, n is the electron number in electrode reaction, F is the faraday constant and i_0 is the exchange current density.

Tafel slopes b and a can be got through fitting the polarization curve and then the anodic exchange current density can be got (shown in Table 2) from plugging a and b into formula (3) and (4). During the electrode dynamic process, the exchange current density is one of the most important parameters for evaluating the electrocatalytic activity of electrode, and the electrocatalytic activity of electrode is in direct proportion to the exchange current density. As can be seen from Table 2, the values of exchange current densities of anodes increase with the addition of graphene and can tower above two orders of magnitudes compared to that one without graphene, therefore, Ti/IrO₂-Ta₂O₅-G anodes have higher electrocatalytic activity than Ti/IrO₂-Ta₂O₅ anodes and this is in accordance with the analytical result of cyclic voltammograms.

Table 2. Fitted values of polarization curves of different anodes.

graphene contents/g·L ⁻¹	0	0.1	0.2	0.3	0.4	0.5
a / V	2.014	1.618	1.615	1.609	1.605	1.717
b / V	0.293	0.312	0.325	0.324	0.347	0.294
$i_0 / A \cdot cm^{-2}$	1.337×10^{-7}	6.518×10^{-6}	1.073×10^{-5}	1.081×10^{-5}	2.369×10^{-5}	1.445×10^{-6}

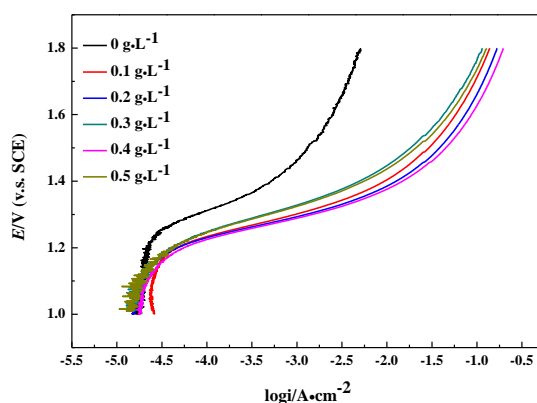


Figure 5. Polarization curves of Ti/IrO₂-Ta₂O₅-G anodes with different graphene contents. The scanning rate is 0.33 mV·s⁻¹ and the electrolyte solution is 1 mol·L⁻¹ H₂SO₄ solution.

Electrochemical impedance spectroscopy can be used to obtain the information from the interface between oxide layer and electrolyte and therefore it earns widespread application for studying the electrochemical property of metal oxide anode [20]. Figure 6 shows the Nyquist plots of Ti/IrO₂-Ta₂O₅-G anodes tested in 1 mol·L⁻¹ H₂SO₄ solution. Seen from the plots, the profiles of all anodes are very similar and display a semicircle which represents the capacitive reactance arc. Compared with that of Ti/IrO₂-Ta₂O₅ anode, the radius of capacitive reactance arc of Ti/IrO₂-Ta₂O₅-G anodes are significantly less, suggesting the improvement of anode activity. The equivalent electrical circuit model $R_s(Q_{dl}R_{ct})(Q_fR_f)$ is often used to analyze the EIS data of IrO₂-Ta₂O₅ anodes. Whereinto, R_s , R_f and R_{ct} are the solution resistance, the coating resistance and the charge transfer resistance for oxygen evolution reaction, respectively; the constant phase angle elements Q_{dl} and Q_f are used to represent the double layer capacitance and the coating capacitance, respectively [21-23].

$Q_{dl}R_{ct}$ represents the impedance between coating and electrolyte solution, and Q_{dl} reflects the changing rule of double layer capacitance. The value of Q_{dl} is related to the number of electrochemically active points on the coating surface, and in general, the increasing value of Q_{dl} indicates the porosity improvement of coating [24]. Figure 8 gives the change of Q_{dl} and R_{ct} with the graphene content. The Q_{dl} of Ti/IrO₂-Ta₂O₅-G anodes are apparently higher than Ti/IrO₂-Ta₂O₅ anode, indicating that the addition of graphene can enlarge the number of electrochemically active points, which is consistent with the result of surface morphologies of Ti/IrO₂-Ta₂O₅-G anodes. The value of Q_{dl} firstly increases and then decreases with the rise of graphene content, and reaches the maximum with the graphene content of 0.4 g·L⁻¹, which is consistent with the results of cyclic voltammograms and polarization curves. R_{ct} also represents the electrocatalytic activity of IrO₂-Ta₂O₅ coated titanium anodes for oxygen evolution, and the larger R_{ct} is, the lower electrocatalytic activity is for oxygen evolution. From Figure 6, the value of R_{ct} decreases rapidly after adding graphene, being connected with the increasing electrochemically active points, which means that the adding of graphene is conducive to oxygen evolution.

(Q_fR_f) can be a substitute for the coating impedance, and meanwhile Q_f reflects the active points on coating internal surface (the surface of cracks and crystal boundary) and the quantity of pore structure. Figure 7 demonstrates the variations of Q_f and R_f with the graphene content. Anodes with graphene exhibit higher Q_f values than the anodes without graphene, suggesting adding graphene can increase the amount of the active points on the coating internal surface, and improve the porosity in the internal surface. The value of Q_f firstly increases and then decreases with the rise of graphene content, and reaches the maximum value with the graphene content of 0.4 g·L⁻¹. R_f reflects the coating resistance. From Figure 8, the value of R_f decreases rapidly after adding graphene, indicating that adding graphene can significantly reduce the resistance of coating, which could be because of the excellent electron transfer property of graphene, in the meantime R_f decreases to some extent but not obviously, indicating that the graphene content does not much affect R_f .

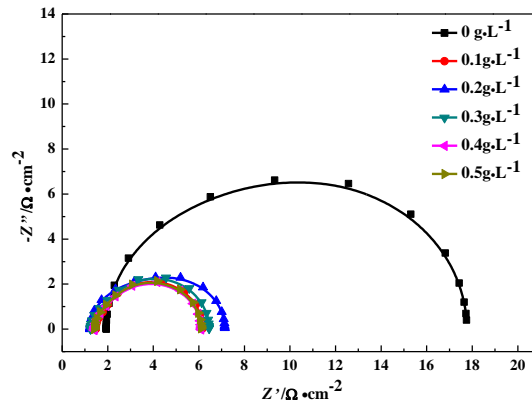


Figure 6. Nyquist plots of Ti/IrO₂-Ta₂O₅-G anodes with different graphene contents. The test potential is 1.35 V DC bias with a frequency range from 100 kHz to 10 mHz, and the signal amplitude was 10 mV.

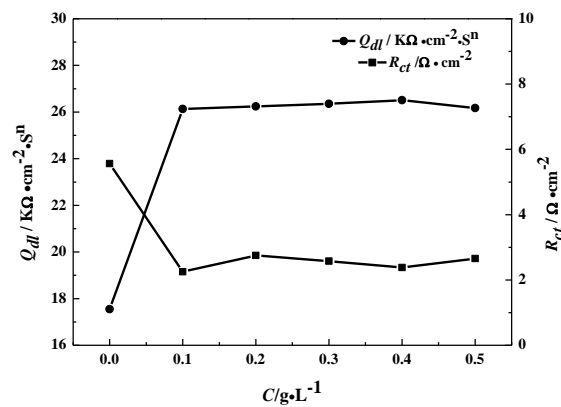


Figure 7. Variations of Q_{dl} and R_{ct} with graphene contents for Ti/IrO₂-Ta₂O₅ anodes.

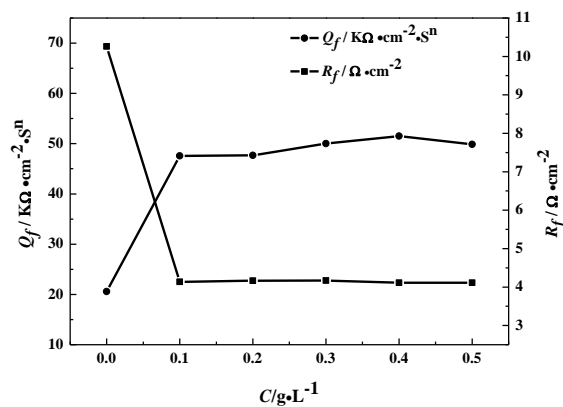


Figure 8. Variations of Q_f and R_f with graphene contents for Ti/IrO₂-Ta₂O₅ anodes.

4. CONCLUSIONS

Ti/IrO₂-Ta₂O₅-G anodes with different graphene contents were prepared by the thermal decomposition method. This kind of anode has following features that the rugged surface morphology with tiny and discrete cracks offers amounts of active centers for oxygen evolution reaction. Ti/IrO₂-Ta₂O₅-G anodes have higher electrocatalytic activity for oxygen evolution and larger electrochemically active surface area comparing with Ti/IrO₂-Ta₂O₅. And Ti/IrO₂-Ta₂O₅-G anode with the graphene content of 0.4 g·L⁻¹ presents the best electrochemical performance.

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