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A novel highly active nanostructured IrO₂/Ti anode for water oxidation

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ARTICLE INFO

Article history:

Received 4 February 2015

Received in revised form

4 April 2015

Accepted 14 April 2015

Available online 7 May 2015

Keywords:

IrO₂/Ti

Ti nanotube

Nanocomposite

Water splitting

ABSTRACT

IrO₂ is one of the most active water oxidant catalysis for the oxygen evolution anode owing to its chemical stability and outstanding catalytic activities, however iridium (Ir) is also one of the rarest metals in the world. In this report, a novel highly active nanostructured IrO₂/Ti anode for oxygen evolution reaction (OER) was fabricated by depositing IrO₂ nanoparticles onto Ti nanotube substrates. This nanostructured IrO₂/Ti anode exhibits comparable oxygen evolution catalytic activities as the traditional IrO₂/Ti dimensional stable anode with only 1% iridium consumption of the traditional method. This nanostructured IrO₂/Ti anode would be a promising candidate method for fabricating high effective IrO₂/Ti anode with low Ir consumption.

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Introduction

Hydrogen generated from solar energy is a promising renewable green energy. Lots of studies have focused on developing active water oxidization catalysts because water oxidation reaction is the rate-limiting step for overall water splitting [1–4]. The IrO₂ has been an ideal catalyst for water oxidation reaction due to its low overpotential and good corrosion resistance [5–11]. Dimensional stable anode (DSA) such as IrO₂/Ti is widely employed in industrial electrochemical process for water splitting [7,12–14]. DSA electrodes are typically titanium or tantalum substrates coated with electro-catalytic noble metal oxides such as IrO₂ to increase the performance and reduce the energy consumption. However, in the typical fabrication of IrO₂/Ti DSA anode, IrO₂ layer was coated on Ti

substrate by thermal decomposition of a large amount of Ir precursor such as IrCl₃ at high temperature.

The performance of IrO₂/Ti DSA largely depends on the geometric factors such as the active surface area and electronic factors such as electrocatalytic activities of different chemical composition [11]. The IrO₂ nanoparticles show a much higher electrocatalytic activity than the bulk ones due to the high active sites and high surface areas of IrO₂ nanoparticles. Embedding IrO₂ nanoparticles instead of bulk IrO₂ in IrO₂/Ti DSA electrode could improve the activity and reduce the usage of Ir precursor. However it is problematic to attach particles onto smooth Ti substrates for oxygen evolution [15]. A traditional method to increase the roughness is to etch Ti with hydrochloric acid or oxalic acid followed by spraying the IrCl₃ or IrBr₃ alcohol solution for thermal decomposition. Now it is a popular way to fabricate composite electrodes with

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<http://dx.doi.org/10.1016/j.ijhydene.2015.04.071>

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greater surface roughness than non-modified electrodes [16–18]. The Ti nanotubular membrane can be fabricated with controllable size and length by anodization [19]. Hence we adopted the anodization method as surface treatment to control the surface roughness of Ti. The highly active colloidal IrO₂ nanoparticles can be prepared by a facile solution chemistry method [9–11,20,21]. Here, we combined the Ti nanotube and IrO₂ nanoparticle to form a novel nanostructured IrO₂/Ti anode. The IrO₂ particles were first deposited onto the highly rough surface Ti nanotube substrate followed by the calcination/annealing procedures. Our novel nanostructured IrO₂/Ti anode exhibits high active for water oxidation reaction, which demonstrates our nanocomposite methods is promising for the design of highly active and low-cost dimensional stable anode for oxygen evolution.

Experimental and analysis method

The titanium foils (99.7% 0.25 mm thick) and IrCl₃·xH₂O (99.9% trace metals basis) are purchased from Sigma Aldrich. Before anodization, the foils are immersed in concentrated alkaline alcohol solution for 10 min to clean the surface followed by a deionized water rinse.

The Ti foils were anodized with Pt foils as a counter electrode at different potentials with different durations. The anodization is performed in electrolyte of 0.5 wt% NH₄F (98% + ACS reagent, Sigma Aldrich) ethylene glycol solution under room temperature. The as-anodized sample is ultrasonicated in isopropanol for 20–25 s. The iridium dioxide nanoparticles were synthesized as previous reported by first hydrolysis 100 mL of 2 mmol/L IrCl₃ aqueous at pH = 13 NaOH solution at 90 °C for 10 min. Then the pale solution was cooled down by ice bath and the solution was adjusted to pH = 1 with stirring overnight. The final dark blue IrO₂ nanoparticle solution was stored in refrigerator. The Ti foil with TiO₂ tubular membrane with ~1 cm² Ti foil is submerged in 2 mL IrO₂ solution for 90 min to absorb the IrO₂ nanoparticles. The consumption of iridium was measured by monitoring UV–Vis spectrum change of the IrO₂ nanoparticle solution. The absorbed sample was then annealed at 300–750 °C for 1 h.

A traditional IrO₂/Ti DSA anode was prepared by a reported traditional method [22]. In brief, the cleaned Ti foil is etched in boiling oxalic acid solution (10 wt%) for an hour. The foil was then washed in deionized water. While the foil was held at about 60–70 °C, 0.25 mL of IrCl₃ isopropanol solution (0.2 mol/L) was sprayed evenly on the surface of the foil with airbrush for several times finally reaching an Ir loading about 0.4 mmol/cm². The Ir deposited Ti foil was then thermally annealed in furnace at different temperatures for 1 h.

The morphology of the samples is characterized by NOVA NanoSEM 230 scanning electron microscope (SEM) and JOEL JEM-2010HT analytical transmission electron microscope (TEM) equipped with energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED). The electrochemical catalytic activities of each sample is tested in 1 mol L⁻¹ NaOH solution in a three-electrode configuration with Pt mesh counter using AgCl/Ag (3M NaCl) as reference electrode. The electrochemical behavior of the electrode is measured by linear sweep voltammetry (0–1.2 V, scan rate

25 mV/s) and cyclic voltammetry (0–0.5 V, scan rate 25 mV/s) on Gamry Reference 3000 electrochemical workstation.

Result and discussion

It is well known that the small nanoparticles would grow into large particles or even bulk material under high temperature thermal annealing. The high temperature annealing on Ti would form an insulating TiO₂ layer, which could block the electrical contact when the TiO₂ layer is too thick. An optimized annealing temperature is so important to obtain a nanostructure high active nanostructured IrO₂/Ti anode. Fig. 1 lists the OER current density of the same IrO₂/Ti anodes annealed at different temperature for 1 h. The 400–500 °C seems to be the best annealing temperature to obtain the highest OER current density. The 600 °C annealed sample shows lower OER activities, which may due to the increase of particles' sizes, and the 700 °C annealed sample almost exhibits no activity for OER reaction and the film turns to pale, which suggest there is a too thick TiO₂ layer formed. In contrast, the 300 °C annealed sample shows not bad activities for OER reaction, however this anode is unstable. Therefore, we selected the 400 °C as the annealing temperature for all the samples. For comparison, the thermal decomposition prepared DSA anode were also annealed at 400 °C.

The morphologies of the Ti foil, DSA IrO₂/Ti anode prepared by traditional thermal decomposition and our novel nanocomposite IrO₂/Ti anode annealed at 400 °C are illustrated in Fig. 2. The thermal decomposition treatment causes many irregular deep cracks on Ti foil surface with large black particles as shown in Fig. 2B while the initial Ti foils are smooth (Fig. 2A). The large black particles on the surface are expected to be bulk IrO₂ particles formed by the decomposition of IrCl₃ as confirmed by EDS, which is consisted with previous reported traditional DSA IrO₂/Ti anode [23]. In contrast, Fig. 2C shows our novel nanostructured IrO₂/Ti anode consists of distinctive nanotube arrays without obvious bulk IrO₂ particle or layer on the surface. The around 100 nm outer diameter of these nanotubes and their morphology are consistent with previous reported TiO₂ nanotube anodized at similar condition [19]. Fig. 2D shows the TEM images of our

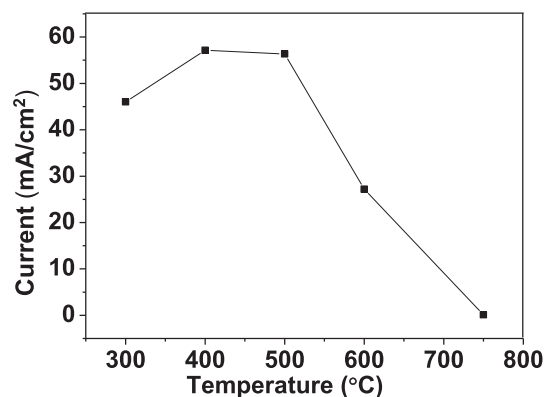


Fig. 1 – The annealing effect on our IrO₂/Ti anode's OER current density at 1 V vs Ag/AgCl.

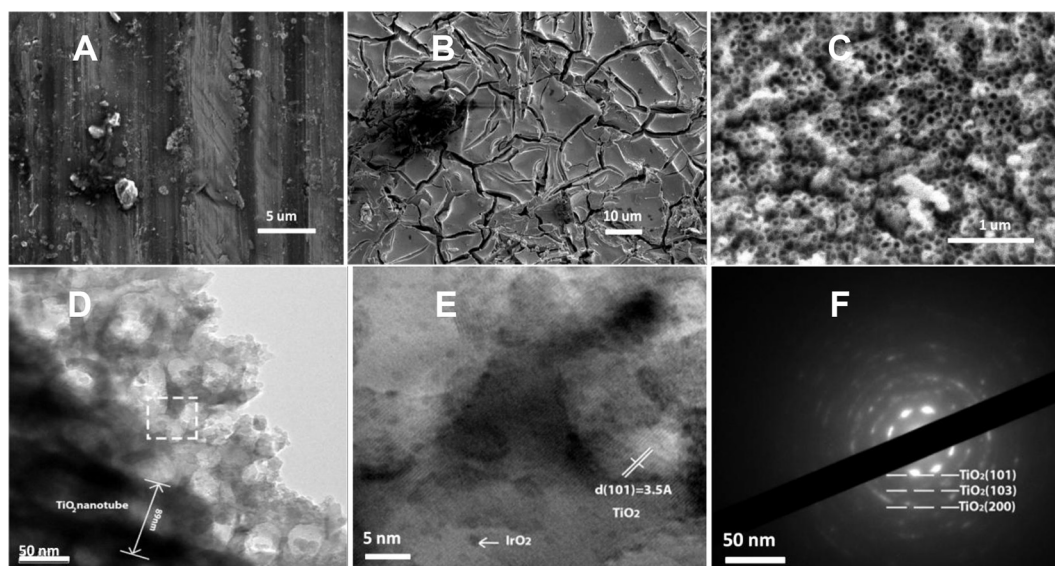


Fig. 2 – SEM image of (A) cleaned Ti foil substrate; (B) Ti/IrO₂ DSA by thermal decomposition method; (C) our novel nanocomposite Ti/IrO₂ anode; (D) TEM image (E) high resolution TEM images and (F) the SAED analysis of TiO₂ nanotube deposited with IrO₂ nanoparticles.

novel IrO₂/Ti anode. Fig. 2E and F shows that lots of small sized IrO₂ nanoparticles are found to deposit on the anatase TiO₂ nanocrystals. The TEM/EDS on the selected area suggested that there is Ir element in the selected area. These characterizations confirm that the titanium oxide nanotube is successfully constructed and IrO₂ particles are effectively deposited with the crystallized TiO₂ nanotube.

In order to improve the ability of IrO₂ nanoparticles absorption and thus to improve the performance of the

electrode, a straight forward way is to prepare a long Ti nanotube to absorb more IrO₂ nanoparticles. However, it is found that those long Ti nanotube fabricated IrO₂/Ti anodes are almost inactive because the long TiO₂ nanotubes may become an insulator barrier to block the electrical contact between the IrO₂ and Ti substrate. According to the previous study [19,24], the size including diameter and length of the anodized Ti can be tuned by anodization voltage and anodization duration. In order to optimize the performance of our

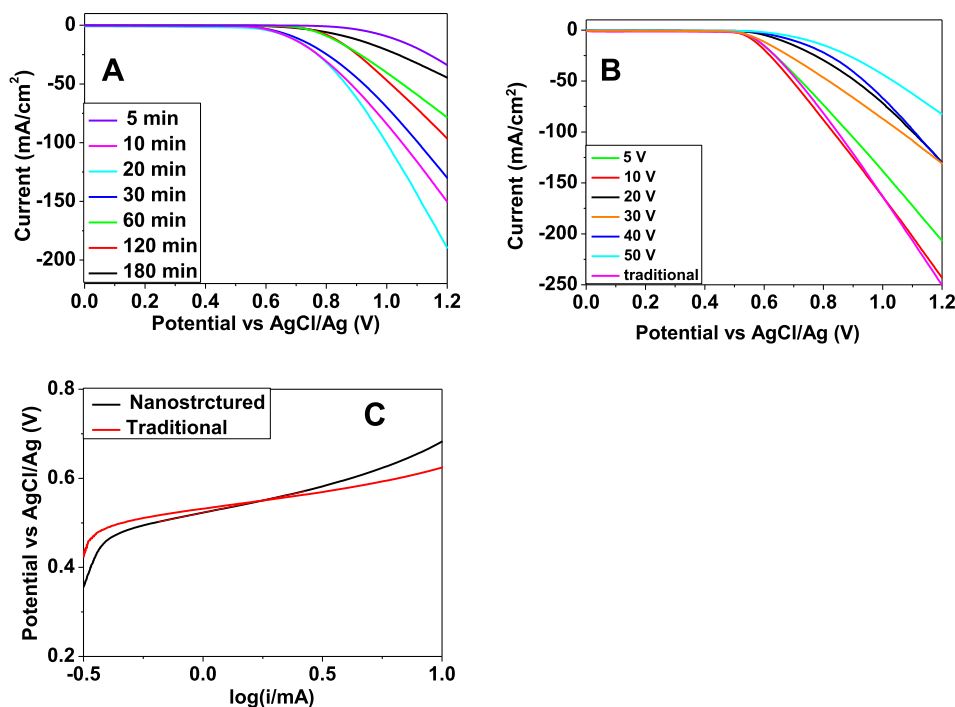


Fig. 3 – (A) Current density–voltage (*I*–*V*) curves of IrO₂/Ti anode using Ti nanotube anodized at 30 V for different duration; (B) Current density–voltage (*I*–*V*) curves of IrO₂/Ti anode using Ti nanotube anodized at different voltage for 20 min. (C) Tafel plots of nanostructured and traditional IrO₂/Ti and the thermalysis prepared IrO₂/Ti electrode.

IrO₂/Ti anodes, Ti nanotube substrates prepared from different anodization voltages and anodization durations were tested as candidates to evaluate the performance of our final nanostructured IrO₂/Ti anode for oxygen evolution reaction.

Since the length of the anodized Ti nanotube is mainly determined by the anodization time and anodization potential mainly affects the diameter of the anodized Ti nanotube, here we first figured out the optimized anodization time by anodized the Ti at 30 V for different durations. The Ti nanotubes were first soaking coated with IrO₂ nanoparticles and were then annealed at the optimized temperature 400 °C. The OER I–V curves of these nanostructured IrO₂/Ti anodes based on Ti nanotube anodized at 30 V for different durations are displayed in Fig. 3A. Our nanostructured IrO₂/Ti anodes OER current density first increases with anodization duration, which suggests that the longer tube could absorb more IrO₂ nanoparticles to achieve a higher IrO₂ nanoparticles deposition amount. Once the anodization duration is longer than 20 min, the nanostructured IrO₂/Ti anodes' OER currents decrease with the Ti tubes. It is evident that 20min is the best anodization duration to obtain the suitable Ti nanotube length. Therefore we set optimized anodization duration as 20 min for the different anodization potential trials. As shown in Fig. 3B, the OER I–V curves of these nanostructured IrO₂/Ti anodes based on Ti nanotubes anodized at different potential overall show the current density decrease with the anodization potential. It is well known that the diameter of Ti nanotube increases with the anodization potential. The Ti nanotube with smaller diameter is supposed to have higher surface area for IrO₂ deposition. In summary, the optimized condition for preparation of nanostructured IrO₂/Ti anodes is: anodization Ti substrate at 5–10 V for 20 min and then deposited with IrO₂ nanoparticles by soaked in solution, followed by annealing at 400–500 °C for 1h.

Here is the comparison of the Ir consumption between the traditional DSA anode and our nanostructured IrO₂/Ti anodes exhibiting the similar OER curve as shown in Fig. 3B. The concentration of iridium solution in the traditional method is 0.2 mol/L and for each layer, 0.25 mL of the solution is needed. The overall iridium consumption is 50 μmol/cm². In contrast to our nanostructured IrO₂/Ti anode fabrication, the Ir consumption is 0.6 μmol/cm² which is almost only 1% as the traditional one. Due to the much higher active site ratio in IrO₂ nanoparticles than the micrometer sized IrO₂, our nanostructured IrO₂/Ti anode is comparable to the traditional DSA electrode as demonstrated by the Tafel plots in Fig. 3C.

Conclusion

A novel method is successfully developed to decorate IrO₂ nanoparticles on TiO₂ nanotubes to fabricate a highly active anode for oxygen evolution. The optimal Ti nanotube's fabrication condition is to anodize at 10 V for 20 min, which leads to a more appropriate length and size of the nanotube to embrace more IrO₂ nanoparticles. The optimal annealing temperature to achieve a high active and stable nanostructure IrO₂/Ti anode is around 400–500 °C. Our nanocomposited IrO₂/

Ti anode exhibited a comparable OER activities with traditional DSA anode but with only ~1% Ir consumption.

Acknowledgement

This work is financial supported by Recruitment Program of Global Experts in China, the start-up funds from Shanghai Jiao Tong University and NSFC (Grant 51372151 and 21303103). Rui Shan thanks for the financial support from Junzheng Scholarship.

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