Simple synthesis of Pt/TiO₂ nanotube arrays with high activity and stability

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1. Introduction

TiO₂ is a widely used material with a variety of potential applications including photocatalysis, photovoltaics, water splitting, and gas sensors.[1] It has been considered as one of the most studied compounds in materials science due to good physical and chemical properties and high stability in acidic and alkaline solutions. Furthermore, TiO₂ could improve the oxygen reduction activity of Pt catalysts by facilitating mechanisms, such as reactant surface diffusion and oxygen spillover in fuel cells.[2-5] TiO₂ is also very attractive as a promising candidate of carbon support.[6] At present, the oriented nano-structured electrode with low Pt loading and high electrochemical surface area has attracted much attention.[7] Besides the oriented organic whiskers, other ordered materials such as carbon nanotube, metal oxide arrays may play a similar role in fuel cells. In comparison with other forms of nonstructured TiO₂ materials, TiO₂ nanotubes (TNTs) arrays show the unique ordered and vertically oriented tubular structure.[8] These properties recommend consideration of TNTs as an alternative catalyst support of ordered electrode in fuel cells.

Recently, various methods have been reported for the preparation of Pt/TNTs electrodes including microwave-assisted solvothermal method,[9] layer-by-layer self-assembly method,[10] photo irradiation method,[11,12], and physical methods[13-15]. Some researches focus on the application of TNTs in fuel cells. The sputtering technique may be an option for Pt deposition onto the interior of TiO₂ nanotubes, but it is costly.[13] Photo irradiation method was introduced to decorate TNTs with uniform Pt nanoparticles. The resulting hybrid nanotube arrays showed an excellent catalytic activity for methanol electrooxidation.[11]. Besides, the Cu[16] and Ni[17] were both used as precursors for Pt deposition on the TNTs. However, only a few researches focus on the durability of the electrodes[12,13,17]. As there may be weak interaction effect between the Pt catalysts and the TNTs support, the fabricated electrodes have poor stability compared to the TNTs. On the other hand, hydrogen treatment is considered as one of the effective ways for the catalysts stability enhancement.[18] In this work, Pt catalysts were supported onto the TNTs with hydrogen treatment. The effects of the reduction atmospheres and temperatures for Pt catalysts preparation were investigated. The electrochemical performance and durability of the prepared electrodes were tested in half-cell system.

2. Experimental

2.1. Preparation of Pt/TiO₂ nanotube arrays

Prior to the anodization, Ti sheets were ultrasonically cleaned with acetone followed by deionized water rinse. The TNTs were prepared by electrochemical anodization of a Ti sheet (99.7%, pur-
ity) in glycol aqueous solution containing 0.5 wt.% NH4F at 50 V for 3 h at room temperature [17].

The Pt precursor (17 mM H2PtCl6 ethanol solution) was dropped onto the ordered TNTs, the ethanol was then removed in a vacuum system at 80 °C. Finally, the samples were treated in H2 at 350 °C, 450 °C for 1 h respectively. The ultrahigh purity (>99.99%) hydrogen gas and H2/Ar (5 vol.% H2) were used as the annealing atmosphere, respectively. The gas flow rate is 30 ml min⁻¹. Thermal treatment was implemented in a tube furnace. The TNTs without Pt precursor were also annealed in high purity H2 and H2/Ar at 350 °C, 450 °C for 1 h respectively, as the samples for comparison.

2.2. Materials characterizations

The morphology and microstructure of the samples were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800) and Transmission electron microscopy (TEM, JEM2010-HR, 120 kV). The phase and the composition of the samples were investigated by X-ray diffraction (XRD, Bruker, D8 ADVANCE) with Cu Kα radiation (λ = 1.5418 Å) and X-ray Photoelectron Spectroscopy (XPS, Thermo Scientific ESCALab250 Xi spectrometer) with Al Kα in twin anode. For the XPS spectra, the binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference. The metal loading of electrodes was measured by the inductively coupled plasma atomic emission spectrometry (ICP-AES) on Leeman Plasma-Spec-I equipment.

2.3. Electrochemical measurements

The conductivity of the electrodes was tested using four-point probe measuring system (Suzhou Jingge Electronic Co., China). The as-prepared electrodes were characterized by cyclic voltammetry (CV) in a conventional three-electrode system using the as-prepared samples as the working electrode, saturated calomel electrode (sat. SCE) as the reference electrode and a Pt foil as the counter electrode, at 50 mV s⁻¹ in 0.5 M H2SO4 solution saturated with N2.

The electrochemical surface area (ECSA) was calculated based on the following relation:

\[
\text{ECSA} = \frac{Q_H}{m \times q_H} \tag{1}
\]

where \(Q_H\) is the charge for hydrogen desorption, \(m\) is the Pt metal loading, and \(q_H\) is the charge required for desorbing a monolayer of hydrogen on Pt surface.

To carry out the Accelerated Durability Test (ADT) [19], the electrodos were repeatedly cycled between 0 and 1.2 V vs. RHE. The electrochemical stability and performance of the electrodes were also examined using a modified Accelerated Stress Test (AST) protocol [20]. According to the AST protocol, the stability of the catalysts was tested by holding the cell potential at 1.6 V vs. RHE. The CV curves were measured after potential holding experiments for 1, 20, 50, and 100 h. For comparison, the CV curve of the commercial JM 20 wt.% Pt/C was also examined on a thin film rotating disk (RDE). The total Pt loading of Pt/C catalyst was 0.040 mg cm⁻².

3. Results and discussion

The growth mechanism of the TNTs is deduced as follows [21]. Under a high applied potential and the presence of water molecules in the electrolyte, Ti was oxidized to form a thin barrier oxide layer of TiO2 as follows:

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4e + 4\text{H}^+ \text{ (field assisted)} \tag{2}
\]

\[
\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2 \text{ (field assisted)} \tag{3}
\]

Then the presence of the fluoride ion, F⁻, and the high applied potential led to substance dissolution of TiO2 through the formation of TiF6²⁻, resulting in nanotube formation:

\[
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O} \text{ (field and chemical dissolution)} \tag{4}
\]

The nanotube growth is determined by the equilibrium between anodic oxidation and chemical dissolution. The anodic oxidation rate is determined by the anodic potential, while the chemical dissolution rate is determined by the electrolyte acidity and F⁻ concentration.

The TNTs were prepared in glycol aqueous solution containing 0.5 wt.% NH4F at 50 V for 3 h. In Fig. 1, it is clear that TNTs have a uniform diameter and thickness of 125 nm and 12 nm, respectively.

Fig. 1a–d exhibit the images of the Pt supported TNTs electrodes by H2 reduction. The content of H2 in reduction atmosphere may have little effect on the diameter of Pt catalysts. In Fig. 1a and c, the reduced Pt particles show large diameter at 350 °C for 1 h either in high purity H2 (350-Pt–H–TNTs) or in H2/Ar (350-Pt–5H–Ar–TNTs). From the TEM image of the 350-Pt–H–TNTs electrode in Fig. 2a, the average diameter of Pt particles is about 90 nm. When the temperature increased to 450 °C, smaller Pt nanoparticles were supported onto the TNTs for both in purity H2 (450-Pt–H–TNTs) and in H2/Ar (450-Pt–5H–Ar–TNTs). From the TEM image of the 450-Pt–H–TNTs electrode in Fig. 2b, a number of Pt particles with the diameter of about 10 nm are located inside the tubes, indicating the direct reduction method in this work realizes the well dispersion of Pt particles in TNTs. When the reduction temperature is higher than 360 °C, the H2PtCl6 was decomposed to HCl gas and PtCl4; the PtCl4 was then decomposed to Cl2 and PtCl6 at 370 °C. The decomposition of H2PtCl6 together with the reduction at H2 atmosphere decreases in Pt nanoparticles for the 450-Pt–H–TNTs and 450-Pt–5H–Ar–TNTs electrodes. The loading of Pt detected by AES-ICP in the electrodes is about 0.067 mg cm⁻².

The TNTs without Pt precursors were also annealed at the different atmospheres. The XRD analysis found that all the samples exhibited anatase phase (JCPDF # 21-1272) after annealed (Fig. 3a). The peak intensity of the samples annealed in pure H2 atmosphere is stronger than that in H2/Ar. No phase change was observed for TNTs with or without Pt precursors when the TNTs were annealed. In Fig. 3b, the Pt (1 1 1), Pt (2 0 0) and Pt (2 2 0) crystal faces are detected at 39.78°, 46.29°, and 67.51° for both 450-Pt–H–TNTs and 450-Pt–5H–Ar–TNTs electrodes.

XPS analysis in Fig. 4a demonstrates the Ti existence (Ti 2p 3/2 peak at ~459.4 eV) both in the 350-H–Ar–TNTs and 450-H–Ar–TNTs electrodes. The peak has little shift of the Pt catalysts supported 350-Pt–5H–Ar–TNTs electrode (Fig. 4b). Although the electrodes annealed at different atmospheres have similar catalyst diameter, the Ti 2p peak of the sample annealed in high purity H2 shows a negative shift. In comparison with the 350-Pt–5H–Ar–TNTs electrode, the Ti 2p peak at ~459.1 eV of 350-Pt–H–TNTs electrode is lower. In Fig. 4d, the Ti 2p3/2 peak shifts ~0.3 eV for the 350-Pt–H–TNTs and 450-Pt–H–TNTs electrodes compared to 350-Pt–H–TNTs. The lower energy peak may be related to the strong metal-support interaction (SMSI) effect between Pt catalysts and TNTs [3,6,15,22]. The SMSI effect is associated with electron transfer from the support to the metal. For the 350-Pt–H–TNTs and 450-Pt–H–TNTs electrodes treated at high purity hydrogen atmosphere, the partly reduced Ti(IV) at the interface between the TiO2 and Pt catalyst leads to negative shift of Ti 2p peak [3].
The electrical conductivity of the samples was examined by four-point probe measuring system. The apparent conductivity of Non-annealed TNTs is about 0.034 mS cm$^{-1}$, while there is slightly increase for the 350-Pt–H–TNTs (0.069 mS cm$^{-1}$). When the reduction temperature rose to 450 °C, the apparent conductivity of 450-Pt–H–TNTs was increased to 0.092 mS cm$^{-1}$. The effect of the annealed atmosphere was not observed during the conductivity test. To evaluate electrochemical property of the as-prepared samples, CV curves were obtained in 0.5 M H$_2$SO$_4$ solution at 50 mV s$^{-1}$. In Fig. 5a, all of the annealed TNTs deliver an obvious electrical double-layer capacitive behavior, which indicates that no electrochemical reaction occur at this potential region. The increased electrical double-layer capacitive can be attributed to the increased oxygen vacancy states that are known to be electron donors for TiO$_2$. The 350-H–TNTs sample has larger double-layer capacity than the 350-5H–Ar–TNTs and 350-5H–Ar–TNTs, indicating more oxygen vacancies appeared during the high purity H$_2$ annealing. Fig. 5b exhibits the electrochemical performance of the electrodes annealed at H$_2$/Ar after 500 potential cycles between 0 and 1.2 V vs.RHE. The electrodes show slight activity in 0.5 M H$_2$SO$_4$.

On the other hand, there was little electrochemical activity for both 350-Pt–H–TNTs and 450-Pt–H–TNTs electrodes at the initial potential cycle. CV testing plays an important role in the activation of catalysts. The performance of the electrodes was enhanced gradually along with the increase of cycles. This phenomenon was
attributed to surface roughening and contaminants removal [23]. After 50 potential cycles, the ECSA of the 350-Pt–H–TNTs and 450-Pt–H–TNTs are 23.5 and 18.3 m$^2$ g$^{-1}$, respectively. In the Fig. 6a–c, it is obvious that the 350-Pt–H–TNTs and 450-Pt–H–TNTs have a positive shift in the oxide-reduction peaks (∼70 and 80 mV respectively) relative to the Pt/C catalysts. It can be attributed to the spillover transfer of the primary oxide (M–OH) onto the TNTs support [2–5]. It is indicated that the TNTs could facilitate the oxygen reduction activity of Pt catalysts by the fast desorption of OH from the TNT surfaces.

The ECSA of 350-Pt–H–TNTs increased by 13% after 200 cycles, and then gradually decreased by 26% after 2000 cycles during ADT at 0–1.2 V vs. RHE compared to the one after 50 cycles. While the reduction of ECSA for commercial JM 20% Pt/C is 68% after 800 cycles (Fig. 6a and c). Furthermore, there is little decrease for 450-Pt–H–TNTs even after 2000 cycles. The ECSA of 450-Pt–H–TNTs after 2000 cycles is about 2.3-fold than the initial one. However, the reduction of surface oxide decreases after potential cycling (Fig. 6b). The smaller decrease in ECSA during ADT may be attributed to the stability of the SMSI between Pt and TNTs support talked above [2,24,25]. It has been reported that the TiO$_2$ can anchor Pt particles by interacting with Pt to inhibit Pt migration and agglomeration. The smaller Pt nanoparticles for the 450-Pt–H–TNTs anchored tightly in the TNTs may have higher resistance for the Pt migration and agglomeration than the 90 nm Pt particles of the 350-Pt–H–TNTs.
The electrochemical stability and performance of the 450-Pt–H–TNTs electrode were also examined using a modified AST protocol. The electrocatalysts were tested by holding potential at 1.6 V vs. RHE. Fig. 7a and b show CV curves for the 450-Pt–H–TNTs electrode after the potential was held at 1.6 V for 0–100 h. In the case of the 450-Pt–H–TNTs electrode, the electrochemical performance still increased even after a corrosion time ($T_c$) of 100 h. While the Pt/C electrocatalyst significantly decreased due to carbon corrosion, subsequent detachment and agglomeration of catalyst particles at high potential reported by Dou et al. [20]. The procedure of AST may also have the same effect on the electrode by surface roughening and contaminants removal just like in ADT. It indicated that the 450-Pt–H–TNTs electrode in this work with excellent electrochemical property would be a promising catalysts support in fuel cells.
4. Conclusions

In this work, we demonstrated a simple method for preparing Pt/TNTs electrodes. The effect of the reduction atmospheres and temperatures on Pt catalysts preparation was investigated. The catalyst particles on electrodes annealed at 350°C were larger than those at 450°C. The well-dispersed Pt catalysts with the diameter of 10 nm onto the ordered TNTs support were formed when annealed at 450°C for 1 h. The reduction atmosphere had little impact on the catalysts diameter, however, the electrodes annealed at H$_2$/Ar showed only a weak electro-activity. On the contrary, both of the 350-Pt–H–TNTs and 450-Pt–H–TNTs electrodes exhibited favorable electrochemical performance and excellent durability. The ECSA of 350-Pt–H–TNTs electrode decreased by 26% after 2000 potential cycles which was much better than the commercial JM 20% Pt/C (reduced by 68% after only 800 cycles). There was no decrease for the 450-Pt–H–TNTs electrode after even 2000 cycles. Furthermore, the electrochemical performance of 450-Pt–H–TNTs electrode is still stable after holding at 1.6 V for 100 h. The study gave convincing evidence on the feasibility of using the electrodes derived from the Pt supported TNTs prepared by the simple high purity H$_2$ reduction strategy for the applications in fuel cells and other energy devices.

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