

Pt/WO₃/C nanocomposite with parallel WO₃ nanorods as cathode catalyst for proton exchange membrane fuel cells

Meiling Dou^{a,b}, Ming Hou^{b*}, Zhilin Li^{a*}, Feng Wang^a, Dong Liang^b, Zhigang Shao^b, Baolian Yi^b

a. State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China;

b. Fuel Cell System and Engineering Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

[Manuscript received August 7, 2014; revised September 27, 2014]

Abstract

Pt/WO₃/C nanocomposites with parallel WO₃ nanorods were synthesized and applied as the cathode catalyst for proton exchange membrane fuel cells (PEMFCs). Electrochemical results and single cell tests show that an enhanced activity for the oxygen reduction reaction (ORR) is obtained for the Pt/WO₃/C catalyst compared with Pt/C. The higher catalytic activity might be ascribed to the improved Pt dispersion with smaller particle sizes. The Pt/WO₃/C catalyst also exhibits a good electrochemical stability under potential cycling. Thus, the Pt/WO₃/C catalyst can be used as a potential PEMFC cathode catalyst.

Key words

tungsten oxides; Pt nanoparticles; catalyst; proton exchange membrane fuel cells

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are ideal future power sources due to their high efficiency, zero emission, low-temperature operation, and fast response [1]. Although much progress has been made in the past decade, there are still some critical issues that need to be overcome to make PEMFCs more competitive, which include the sluggish kinetics of the oxygen reduction reaction (ORR), the high expense, and relatively low durability of the state-of-the-art Pt/C catalyst. Consequently, more robust catalysts with enhanced activity, such as Pt nanowire catalyst [2], Pt based alloy catalysts (e.g. PtSn [3]), Pt core shell catalysts (e.g. Pt/Cu [4]), and metal oxide (e.g. SnO₂ [5], TiO₂ [6], SiO₂ [7]) decorated Pt/C, have been studied as potential alternatives for PEMFCs. Among them, metal oxide decorated Pt/C catalysts attracted increasing attention due to the excellent electrochemical stability of metal oxides in oxidative and acidic environments. Jiang et al. [6] demonstrated that the microcapsule Pt/MWCNTs-TiO₂ catalyst has higher activity and stability than Pt/MWCNTs, due to more uniform dispersion and smaller size of Pt nanoparticles. Zhu et al. [7] prepared SiO₂/Pt/C catalyst with higher durability than Pt/C, of which

the covered silica layers were beneficial for reducing the Pt aggregation and dissolution as well as increasing the corrosion resistance of supports.

Tungsten trioxide (WO₃) with a variety of special electrochemical properties has been proposed as promising electrocatalyst material [8–12]. WO₃ has the advantages of being resistant to CO poisoning and the hydrogen ad/desorption via the formation of hydrogen tungsten bronze [13–16]. Several studies have reported that Pt/WO₃/C and Pd/WO₃/C catalysts show a high activity towards the electrooxidation of ethanol [17], methanol [9,18], formic acid [19,20], and hydrogen [8,11,12]. Ye et al. [18] deposited Pt (average particle size of 3 nm) and WO₃ (average particle size of 10 nm) nanoparticles on carbon support, and the as-prepared Pt/WO₃/C catalyst exhibited higher activity for methanol electro-oxidation due to the improved distribution of Pt nanoparticles. Cui et al. [9] showed that the improvement in catalytic activity of methanol oxidation for Pt/WO₃/C catalyst is probably attributed to the hydrogen spillover effect and the uniform distribution of Pt and WO₃ particles. However, to the best of our knowledge, little attention has been focused on the application of nano-architected WO₃, such as nanorods, as the catalyst promoter for PEMFCs.

* Corresponding authors. Tel: +86-411-84379051; Fax: +86-411-84379185; E-mail: houming@dicp.ac.cn (M. Hou); Tel: +86-10-64411301; Fax: +86-10-64411301; E-mail: lizl@mail.buct.edu.cn (Z. L. Li)

This work was financially supported by the National Natural Science Foundation of China (No. 51125007) and the National Basic Research Program (No. 2012CB215500).

Previously, our group prepared a type of WO_3 nanocluster with parallel nanorods and used it as the anode catalyst support for PEMFCs [21]. The WO_3 nanocluster demonstrated a good stability under high potentials (1.6 V). However, due to the limited surface area (less than $50 \text{ m}^2/\text{g}$) and relatively low electronic conductivity, bare WO_3 nanocluster is not suitable to be used as the cathode catalyst support.

In this work, we present a WO_3 nanocluster composited Pt/C, and used it as the ORR catalyst for PEMFCs. Results show that the addition of WO_3 nanocluster improves the catalytic activity and also renders the catalyst a higher resistance to potential cycling.

2. Experimental

2.1. Material preparation

The WO_3 nanocluster was prepared using SBA-15 as the hard template and silicotungstic acid as the tungsten source, as described in our previous work [21]. The WO_3/C hybrid material was prepared by mixing 25 mg WO_3 nanocluster with 175 mg XC-72 carbon (Cabot Corp.) in ethanol under vigorous stirring followed by the solvent evaporation under vacuum at 80°C . The Pt/ WO_3/C composite catalyst was prepared via the polyol method. Typically, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ with 12.58 mg Pt was first dissolved in 30 mL of ethylene glycol (EG), and 2 mol/L NaOH/EG solution was added dropwisely to adjust the pH to 12. The mixture was then heated for 1 min in a microwave oven (100 W) to promote the reduction of Pt^{4+} ions to Pt nanoparticles. The Pt colloidal thus obtained was dropped to 50 mg WO_3/C suspended in 10 mL ethanol. The resultant was vigorously stirred for 4 h and the pH was then adjusted to 1 by 2 mol/L HNO_3 to ensure the sedimentation. After centrifuged, washed with water, and dried in an 80°C vacuum oven, the Pt/ WO_3/C catalyst was obtained. For comparison, the Pt/C catalyst with the same Pt loading (20 wt%) was also prepared.

2.2. Material characterizations

Physical properties of the prepared samples were characterized by X-ray diffraction (XRD), X-ray photoemission spectroscopy (XPS), and transmission electron microscopy (TEM). XRD analysis was performed using a Philips X'pert Pro X-ray diffractometer equipped with a Cu K_α source operating at 40 kV and 30 mA. The XPS spectra were obtained on an ESCALAB250XI spectrometer and the binding energies were calibrated according to the C 1s peak (284.6 eV). TEM images were taken using a JEOLJEM-2000EX microscope operated at an accelerating voltage of 120 kV.

2.3. Electrochemical measurements

All electrochemical measurements were conducted at room temperature using a CHI730 electrochemical station.

The Pt sheet and saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. All the potentials were given in reference to normal hydrogen electrode (NHE). Catalyst coated glassy carbon (GC) rotating disk electrode (RDE, with a diameter of 4 mm) was used as the working electrode. 5 mg catalyst and 50 μL Nafion[®] solution (5 wt%, Alfa Aesar) were homogeneously dispersed in 4 mL ethanol by sonicating for at least 1 h. Then 10 μL of the mixture was transferred onto the RDE. The solvent was allowed to evaporate at ambient conditions. Cyclic voltammetry (CV) measurements were taken in 0.5 mol/L H_2SO_4 solution pre-deaerated by high purity N_2 . The potential sweep range was 0 to 1.2 V and the scan rate was 50 mV/s. The ORR activity was measured using linear sweep voltammetry (LSV) in O_2 saturated 0.5 mol/L H_2SO_4 . The rotation rate was 1600 rpm and the potential was swept from 1.0 to 0.2 V at 5 mV/s.

2.4. Single cell test

The home-made electrode (Johnson Matthey 40 wt% Pt/C catalyst, Pt loading of $0.4 \text{ mg}/\text{cm}^2$) was used as the anode. The cathode electrode was prepared by ultrasonically blending the Pt/ WO_3/C catalyst with the Nafion[®] solution (5 wt%, Alfa Aesar) in ethanol for 2 h, and then sprayed onto the prefabricated gas diffusion layer (Torry carbon paper, 7 wt% poly-tetrafluoroethylene). The loading of Pt was $0.2 \text{ mg}/\text{cm}^2$ and the dry Nafion[®] loading was $0.64 \text{ mg}/\text{cm}^2$ for the cathode. Similarly, a Pt/C cathode with the same Pt loading was also prepared. The membrane electrode assembly (MEA) were prepared by hot-pressing the anode, the Nafion[®]212 membrane (DuPont), and the cathode at 140°C for 1 min. Single cell tests were performed with 5 cm^2 active area at 60°C using fully humidified reactants (flow rates were 20/100 mL/min for H_2/O_2). The operating pressures were kept at 0.05 MPa for both electrodes.

3. Results and discussion

3.1. Structural characteristics

Figure 1 displays the XRD patterns of WO_3 nanoclusters, Pt/C, and Pt/ WO_3/C catalysts. All the diffractions of WO_3 nanoclusters correspond to the characteristics of single crystalline monoclinic WO_3 , indicating a well-crystallinity. Pt/C and Pt/ WO_3/C catalysts both show the Pt(111) reflection located at around 39.9° , and compared with Pt/C there is no obvious shift for Pt/ WO_3/C . Therefore, the addition of WO_3 did not change the crystalline structure of Pt. The diffraction peak observed at around 25° for Pt/ WO_3/C catalyst is related to the merging of the carbon (002) reflection and the WO_3 (020) reflection. Figure 2 shows the Pt 4f XPS spectrum of the Pt/ WO_3/C catalyst. The Pt 4f excitation includes Pt $4f_{5/2}$ and Pt $4f_{7/2}$ peaks located at 75.1 eV and 71.7 eV, respectively. It can be seen that the Pt 4f feature of Pt/ WO_3/C shows no apparent bonding energy shift compared with Pt/C. This effect indicates that the introduction of WO_3 did not induce an ob-

Download English Version:

<https://daneshyari.com/en/article/63827>

Download Persian Version:

<https://daneshyari.com/article/63827>

[Daneshyari.com](https://daneshyari.com)