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Short Communication

Pt/IrO_2/CNT anode catalyst with high performance for direct methanol fuel cells

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ABSTRACT

Carbon nanotube immobilized IrO_2 (IrO_2/CNT) was prepared by a simple oxidation method with hydrogen peroxide as an oxidant and used as an improved catalyst support to load active Pt to prepare Pt/IrO_2/CNT anode catalyst for direct methanol fuel cell. Electrochemical measurement revealed that Pt/IrO_2/CNT exhibits much higher activity for methanol oxidation and better CO tolerance than Pt/CNT. The anodic peak current of methanol oxidation on Pt/IrO_2/CNT (873.1A g_{Pt}^{-1}) is 2.6 times that of Pt/CNT catalyst (335.7A g_{Pt}^{-1}). The enhanced performance of Pt/IrO_2/CNT is attributed to the fact that IrO_2 improves the dispersion of Pt nanoparticles, and lowers the charge transfer resistance in methanol electrooxidation.

1. Introduction

Polymer electrolyte membrane fuel cells have been investigated extensively in recent years because of their use of sustainable fuels and high energy-conversion efficiency [1–3]. However, the poor methanol oxidation activity at the anode and high cost of noble metal catalysts are the major challenges for the practical development of direct methanol fuel cells (DMFCs) [4]. Adding a second or a third metal, such as Ru, Sn, Co and so on, to Pt-based catalyst is a well-known method to improve the methanol oxidation performance [5–7]. Although PtRu-based catalyst is the most efficient and widely studied one [8], it has insufficient stability in acidic media [9]. It has been reported that the addition of Ir to the catalyst can significantly enhance its stability against dissolution in an acidic medium [10,11] and improve the activity for methanol and ethanol electrooxidations [10,12]. However, all these researches are focused on Ir metal and there is little attention focused on IrO_2 for methanol electrooxidation.

IrO_2 exhibits metal-like conductivity and has been used in the industry for electrical, magnetic, and electrochemical purposes [13,14]. Kong [15] supported Pt on porous IrO_2 to obtain Pt/porous-IrO_2 composite as bifunctional oxygen electrocatalyst with high oxygen evolution reaction activity and high oxygen reduction reaction activity. In this paper, we use a simple oxidation method with hydrogen peroxide as an oxidant to load IrO_2 onto CNT to obtain IrO_2/CNT and then use the IrO_2/CNT as support to prepare Pt/IrO_2/CNT by ethylene glycol reduction method. The structure of Pt/IrO_2/CNT catalyst and the role of IrO_2 in methanol electrooxidation were investigated. Compared with Pt/CNT, Pt/IrO_2/CNT exhibits much higher activity for methanol oxidation and better CO tolerance.

2. Experimental

2.1. Preparation of Pt/IrO_2/CNTs

IrO_2/CNT was synthesized by a simple oxidation method with hydrogen peroxide as an oxidant. Prior to synthesis, CNT was treated with the method detailed in our previous paper [5]. Pretreated CNT and iridium chloride hydrate were dispersed in deionized water with ultrasonication for 1 h. Then a proper amount of H_2O_2 (30% V/V) was added dropwise at room temperature. The solution mixture was refluxed at 80 °C for 4 h under constant stirring. After cooling down to room temperature, the precipitates were collected by filtering and then dried at 110 °C overnight to obtain IrO_2/CNT.

Pt/IrO_2/CNT was synthesized by a glycol ethylene reduction method detailed in our previous work [5]. For comparison, Pt/CNT catalyst with the same Pt loading as that of Pt/IrO_2/CNT was also prepared with the same method just with CNT as support. According to the electron probe microanalysis (EPMA) results, the Pt content in both Pt/IrO_2/CNT and Pt/CNT is about 15 wt.% and the IrO_2 content in Pt/IrO_2/CNT is about 3.6 wt.%.

2.2. Characterization of the catalysts

Electron probe microanalysis (EPMA-16000, Shimadzu) was used to analyze the content of Pt and IrO_2 in the catalysts. The morphology of the catalyst was characterized by transmission electron microscopy (TEM, JEOL, JEM2010) operating at 200 kV. Structural characterization of the catalyst was carried out by X-ray diffraction (XRD, D/max2 IIIA

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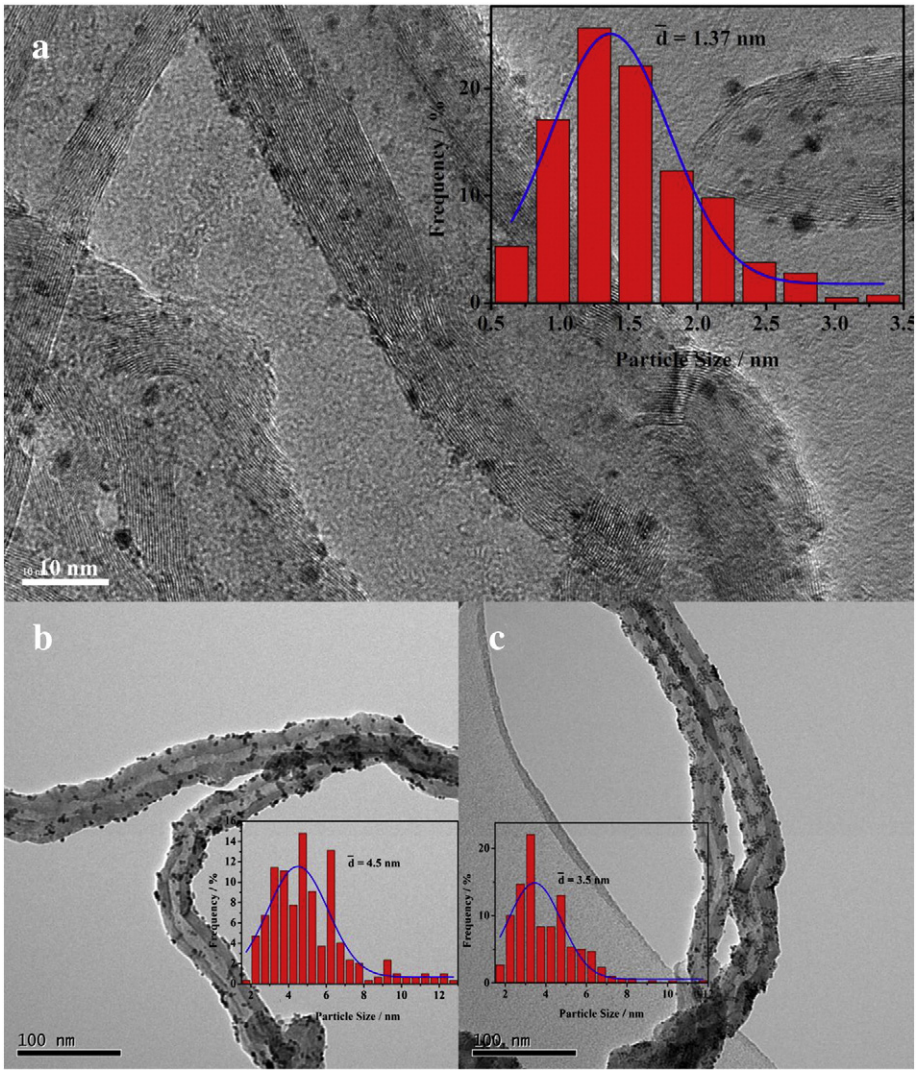

Fig. 1. TEM images of IrO_2/CNT (a), Pt/CNT (b) and Pt/IrO_2/CNT (c).

spectrometer). The chemical valences of Pt and Ir in the prepared catalyst were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos, Axis Ultra DLD). The spectra were corrected by using the C 1s binding energy of 284.6 eV as reference.

2.3. Electrochemical characterization

All electro-catalytic performances in this work were evaluated with a computer-controlled Autolab PGSTAT30 electrochemical analyzer (Eco Chemie B. V., Utrecht, Netherlands). The catalyst modified glassy carbon electrode was used as working electrode, and the preparation of the working electrode was described in our previous paper in detail [5,16]. Ag/AgCl electrode saturated with KCl and Pt electrode was used as reference electrode and counter electrode, respectively. Cyclic voltammetry measurements (CV) were carried out in 0.5 M H_2SO_4 solution and 0.5 M H_2SO_4 with 1.0 M CH_3OH solution with 0.1 V s^{-1} scan rate from −0.1 V to 0.9 V. The CO oxidation ability was tested through CO-stripping experiment in 0.5 M H_2SO_4 electrolyte and the CV curves were recorded from −0.245 V to 0.9 V with the sweep rate of 0.1 V s^{-1}. Electrochemical impedance spectra (EIS)

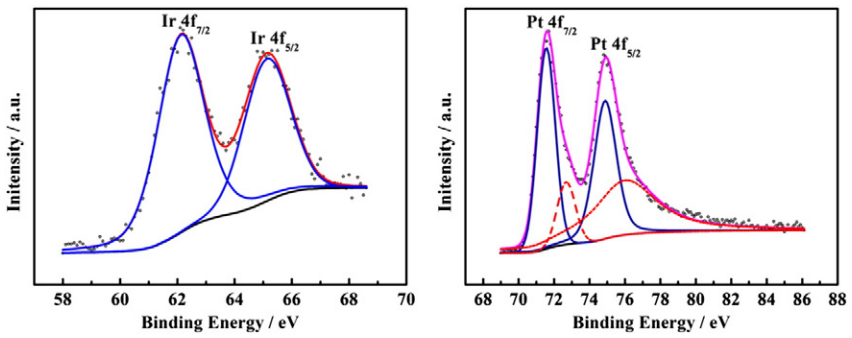

Fig. 2. XPS spectra of Ir 4f and Pt 4f for Pt/IrO_2/CNT.