PtRuP nanoparticles supported on mesoporous carbon thin film as highly active anode materials for direct methanol fuel cell[☆]

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ABSTRACT

PtRu nanocatalyst supported on mesoporous carbon thin film (TFC) with incorporation of the non-metallic phosphorus is explored as an anodic catalytic material for direct methanol fuel cell (DMFC). The catalyst 20 wt.% $PtRuP_{0.1}$/TFC gives a very high current density in the electrochemical oxidation of methanol, which is much enhanced than that of the PtRu/TFC without P loading and two times higher compared to a commercial PtRu/XC-72 catalyst. XPS and EXAFS analysis of the catalysts show that phosphorus helps to reduce the size of PtRu nanoalloy by acting as a surface protecting agent to the nanoparticles and it does not alter the electronic structure of PtRu. The PtRuP nanocatalyst with a particle size of 3 nm was found to have the best reactivity and catalytic stability.

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1. Introduction

Anodic catalytic material for direct methanol fuel cell (DMFC) has been receiving increasing attention in its detailed nanostructure [1–3]. One needs to have precise manipulation in structure and composition of the electrocatalyst in order to achieve substantial improvement in its performance. In most of the new developments, one mainly worked on Pt-based nanoparticles supported on conductive porous carbon which is in turn deposited on the electrode. There are many factors affecting the performance of the anode: (1) pore structure of the carbon materials to facilitate good transport of electrons and fuel molecules, (2) the second and other elements in alloying with Pt to avoid CO poisoning, (3) the size of the metal nanoparticle, and (4) the surface composition of the Pt-based alloy nanoparticles. It is necessary to combine and optimize all the above factors to achieve good performance of the anodic material for DMFC.

For the carbon support materials in anode, ordered mesoporous carbon (OMC) has the advantages of high surface area, tunable pore size, interconnected pore network, and tailorable surface properties [4]. Various designing features for electrode materials have been emphasized in recent reports [5–8]. Recently, we have presented a novel OMC of CMK-3 type thin film of high surface area to increase dispersion of metal nanocatalysts and with very short perpendicular (to electrode) nanochannels to facilitate the transport of reactants and products [9]. The thin film morphology simultaneously improved its electric contact with electrode surface and the mass transport of the reactants in and out of the short channels where metal nanoparticles are confined.

The Pt-based bimetallic catalyst (often with Ru) is considered the best strategy to give catalytic synergy in enhancing both reactivity and stability for electrooxidation of methanol. However, the bifunctionality can be lost from the electrochemical dissolution of the less noble component of the alloy [10]. For long-term operation of the anodic material in acidic medium of DMFC, the second metal is gradually lost and accompanied by extensive aggregation and CO poisoning on Pt. This decreases the efficiency of catalytic current density of the nanosized particles. Liang et al. studied the stabilization of PtRu by gold and found that the dissolution of Ru can be reduced substantially [11]. Wang et al. incorporated nickel in the PtRu bimetallic nanoparticle and obtained much enhanced catalytic performance and CO tolerance [12]. The third incorporated transition metal elements include RhNi [13], Ir [14] and Co [15,16]. Their effects are most probably in altering the electronic structure of Pt-based nanoparticle in effecting catalytic synergy.

The other approach to have PtRu alloy with high activity and well-preserved bifunctionality is to decrease the size of the bimetallic PtRu nanoparticle [17–19]. For example, nanosized PtRu particles were synthesized by colloid method using ethylene glycol as the stabilizer [20,21]. However, before carrying out the catalysis reaction, the stabilizer needs to be removed and it often leads to sintering in the process. In another approach, the addition of a non-metallic element, such as N, S or P, for the dispersion

of Pt-based nanoparticle has been found to be effective [22–25]. The element phosphorus is found to reduce the size of Pt particle notably better by generating Pt–P and Ru–P interactions in a stable way [22]. It has been shown that the growth of PtRu is suppressed by the incorporation of P. However, the perturbation on the electronic structure of PtRu by phosphorus is not clear. Detailed microscopic understanding of the effect of P on the catalytic nanoparticle is still lacking. Herein, we report a PtRu nanocatalyst supported on mesoporous carbon thin film with the incorporation of phosphorus. The catalyst system gave superior electrocatalytic activity compared to the one without P loading. With detailed EXAFS and XPS analysis, we can understand the electronic structure and composition of the P-modified bimetallic PtRu nanoparticle. The best bifunctional synergy and catalytic stability for the electrooxidation of methanol is found with a PtRuP alloy size of 3 nm. Together with the special nanostructure of the carbon thin film support of perpendicular nanochannel, the PtRuP/meso-C catalyst system is found to give very high electrocatalytic activity for DMFC.

2. Experimental

2.1. Preparation of TFC carbon and supported PtRuP catalyst

In the first step, ordered mesoporous carbon thin film with perpendicular channels (TFC) was synthesized according to our previously reported method [9]. Repeated loading of sucrose, dehydration by concentrated sulfuric acid, and complete carbonization at 900 °C were performed. The silica content was then dissolved with 10 wt.% hydrogen fluoride solution to recover the TFC carbon product.

The bimetallic PtRu with the non-metallic additive of phosphorus was synthesized and deposited on carbon support using a wet-chemical reduction method. 0.1 g of TFC material was added to a solution containing desired amount of 0.01 M H_2PtCl_6 (Acrôs), 0.01 M $RuCl_3$ (Aldrich), and 0.01 M NaH_2PO_2 (Acrôs). The mixture was stirred for 0.5 h, and an excess of 0.1 M $NaBH_{4(aq)}$ solution was added into the mixture drop by drop. After stirring for another hour, the solid suspension was recovered by centrifugation, washing with water twice, and drying in air at 60 °C. The product was denoted as PtRu/TFC or $PtRuP_X$/TFC (with nominal P content of X = 0.05, 0.1, and 0.2).

2.2. Electrochemical activity tests

The electrochemical activity measurements were carried out by cyclic voltammetry (CV) using an Autolab PGSTAT 30 potentiostat equipped with a rotatory disk electrode (RDE) [26]. A conventional three-compartment electrochemical cell consisting of glassy carbon (GC) electrode with an area of 0.196 cm^2 as the working electrode, Pt as the counter electrode, and reference hydrogen electrode (RHE) as the reference electrode was used. The GC electrode was polished to a mirror finish with a 0.05 μm alumina suspension before each experiment. The catalyst ink was prepared by adding 5 mg of the catalyst in 2.5 ml water and ultrasonically dispersed for 0.5 h. Then, 20 μL of suspension was pipetted onto the top surface of a GC electrode, followed by drying at 60 °C for 1 h in air. A metal loading at 0.04 mg/cm^2 on the working electrode was obtained. After the electrode was cooled down to room temperature, 20 μL of 1 wt.% Nafion® solution was pipetted onto the ink surface. CV study of methanol oxidation was measured in 0.5 M H_2SO_4 and 1.0 M CH_3OH solution at 60 °C with a scan rate of 10 mV/s and working electrode rotating at 1600 rpm. The electrochemical activity was characterized by the steady-state current density at 0.5 V.

2.3. Structure and elemental characterization

The powder XRD patterns were collected on a PANalytical X'Pert PRO instrument operating at 45 kV and 40 mA with Cu Kα (λ = 1.5406 Å) radiation. Nitrogen adsorption characterizations were conducted at −196 °C on a Micromeritics ASAP 2010 apparatus. The specific surface area of the sample was calculated according to the Brunauer–Emmett–Teller (BET) method, and the Barrett–Joyner–Halenda (BJH) method for estimating pore size distribution. TEM images were obtained using a Hitachi H-7100 instrument with an operating voltage of 75 kV SEM images were taken with a JSM-6700F microscope (JEOL) operating at 10 kV. Elemental analysis was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Jarrel-Ash ICAP 9000 instrument. XPS measurements were performed with a Thermo VG Scientific, ESCALAB 250 equipped with an Al Kα radiation source (1486.6 eV) under a residual pressure of ∼1 × 10^{-9} Torr. For analysis, the spectra were deconvoluted by a least-squares procedure to a product of Gaussian–Lorentzian functions after background subtraction using XPSPEAK software.

X-ray absorption spectra (XAS) were recorded at beamline 01C1 of the National Synchrotron Radiation Research Center (NSRRC) of Taiwan. The electron storage ring is operated at 1.5 GeV and 300 mA. A double Si(1 1 1) crystal monochromator was employed for energy selection with a resolution $\Delta E/E$ better than 1×10^{-4} at Pt L$_{III}$-edge and Ru K-edge. All the experiments were conducted in a stainless steel cell with Krypton film cap in two sides for beam path to avoid exposure of air. Before each measurement, the sample was reduced with 10% H_2 for 0.5 h to remove the surface oxygen. All spectra were recorded at room temperature in a transmission mode, and with the double-crystal monochromator detuned to eliminate the effect of higher harmonics in the X-ray beam. A standard compound (Pt foil or Ru powder) was measured simultaneously so that energy calibration could be performed scan by scan. Raw XAS data were analyzed following standard procedures.

The EXAFS function was obtained by subtracting the post-edge background from the overall absorption and normalized with respect to the edge jump step. The normalized $\chi(E)$ was transformed from energy space to k-space with $\chi(k)$ multiplied by k^3 to compensate for EXAFS oscillations in the high-k region. Subsequently, k^3-weighted $\chi(k)$ data in k-space ranging from 3.0 to 14.3 Å^{-1} for the Pt L$_{III}$-edge and from 3.5 to 12.9 Å^{-1} for the Ru K-edge were Fourier transformed to r-space. A nonlinear least-squares curve fitting was carried out with regard to the data in r-space ranging from 1.60 to 3.10 Å for Pt and from 1.69 to 3.10 Å for Ru. Reference phase and amplitude for the Pt–Pt and Ru–Ru coordination shells were each obtained from a Pt foil and a Ru powder. All the computations were implemented in the UWXAFS software package with the backscattering amplitude and phase shift for the atom pairs being calculated using FEFF 7 code [27].

3. Results and discussion

3.1. Synthesis and characterization of carbon-supported nanocatalysts

By impregnating carbon supports with platinum, ruthenium, and phosphorus sources and reducing chemically with sodium borohydride, PtRuP nanoparticles are homogeneously dispersed onto the external and internal surfaces of mesoporous carbon thin film. Fig. 1 shows the XRD patterns of 20 wt.% PtRuP/TFCs with different nominal ratios of phosphorus. All of the samples give similar diffraction profiles of face-centered cubic (fcc) structure of Pt crystallites, with the (2 2 0) diffraction peaks shifting from about 67.5° to 68.0°, corresponding to a decrease in the lattice constant due