

NANOSTRUCTURED CARBONS AND THEIR HIERARCHICAL ASSEMBLY: NOVEL METAL CATALYST SUPPORTS FOR FUEL CELLS

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Abstract

The catalyst supports have a significant influence on the performance of metal catalysts using in low temperature fuel cells. Recently, there are increasing interests in the study of nanostructured carbon materials as catalyst supports. Our report will be divided into two parts. In the first part, through X-ray diffraction, analytical electron microscopy and electrochemical analysis, we try to establish a relationship between nanostructures of carbon supports and the electrochemical properties of supported metal catalysts (such as intrinsic catalytic activity, utilized efficiency and mass transport). In the second part, hierarchically assembled carbon nanostructures are demonstrated as novel catalyst supports. Carbon nanotubes, carbon nanosheets etc. are grown directly on various carbon substrate materials (carbon blacks, carbon spheres and carbon fibers etc.) to form hierarchical structures. The great benefit of such hierarchical structures is to combine the advantages of carbon nanostructures (good conductivity, large surface area, etc.) and carbon substrate materials (mesopores and macropores can provide fast mass transport) on a multiscaled space, thus maximally improve the fuel cell performance.

Key words: Carbon nanotubes; Catalyst support; Electrochemical properties

Introduction

Platinum and platinum based alloy nanoparticles supported on carbon materials have been found that there are important applications in polymer electrolyte membrane fuel cells (PEMFCs), either for the electrocatalysis of methanol oxidation reaction (MOR) in the anode or for the electrocatalysis of oxygen reduction reaction (ORR) in the cathode. The high cost of the noble metals and their unsatisfied performance has become the main challenge towards the commercialization of PEMFCs. As a result, many studies have been devoted to the exploration of new catalyst systems, such as Pt based binary (Yang, H. 2004) or ternary alloy (Liang, Y.M. 2006) or even no Pt systems (Ganesan, R. 2005; Yang, X.G. 2005), in order to low down the use of the noble Pt (in another word, to increase the utilized efficiency of Pt) and maintain or even increase their catalytic performance. On the same time, there has been a great deal of publications demonstrated that, the carbon supports have great impact on the

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performance of the metal catalysts. Various carbon nanostructures, such as carbon nanotubes (Kongkanand, A. 2006; Li, W.Z. 2003), carbon nanofibers (Bessel, C.A. 2001; Chai, G.S. 2005; Guo, J.S. 2006) and carbon nanohorns (Yoshitake, T. 2002), have been used as catalysts support and they all have shown much more improved performance and higher Pt utilization efficiency in PEMFC.

There is much difference between supported catalysts and unsupported catalysts. During the past two decades, a great deal of researches have dealt with a specific phenomenon occurring in supported catalytic materials: the metal support interaction (MSI), which do not occur in unsupported catalysts. The origin of the MSI has been widely discussed and two major factors were considered. The first one involves the electronic interactions between metal phase and the support materials. The other one is from a geometric origin: upon certain conditions, metal particles would be covered by a layer of the supports, thus blocking the chemisorption active centers at the metal surface (Bernal, S. 2003). In this study, we will investigate the existence of the MSI in the Pt catalysts supported on carbon nanotubes, and its influence on their electrocatalytic performance.

For powdered carbon supported catalysts, the conventional ink-process is often applied to their integration into the gas diffusion electrode (e.g. carbon paper) in the membrane electrode assemblies (MEA), which is the core unit of fuel cells. To be effectively utilized, the Pt catalyst must have simultaneous access to the reactants, the electron-conducting medium, and the proton-conducting medium. Good proton-conducting medium is achieved by adding Nafion (Dow) in the catalyst ink. However, the great drawback of the ink-process is that the carbon supports may be isolated from the electrode by the Nafion, thus blocking the electron-conducting path. Recently, much effort has been attempted to overcome this difficulty. For example, carbon nanotubes as catalyst supports were grown directly on the carbon paper electrode to form a hierarchical structure, which ensure direct electronic contact between them (Hou, H.Q. 2004; Sun, X. 2004; Waje, M.M. 2005; Wang, C. 2004). In this paper, we will demonstrate a new kind of hierarchical structure, which consists of carbon nanosheets grown on carbon paper, to be used as the catalyst support.

Experimental

Preparation of carbon supported catalysts

Powdered carbon nanotubes were used as catalyst support in this study. Before the deposition of Pt catalyst, carbon nanotubes were ultrasonically pre-oxidized in 30wt % peroxide aqueous solution for 2 hours. Ethylene glycol (EG) reduction method (Bock, C. 2004) was adopted to prepare Pt catalyst supported on carbon nanotubes (Pt CNT). Briefly, 50 mg oxidized carbon nanotubes were added to 50 mL ethylene glycol, and dispersed with stirring and ultra-sonicated for 15 min. Then 370 μ l H_2PtCl_6 solution in ethylene glycol (33.6 mg Pt/mL) was added by droplet to the mixture. To control the size distributions of Pt catalysts, the pH value of the solution was adjusted by adding NaOH solution in EG. The whole solution was heated at 120 $^{\circ}C$ for 2 hr with magnetic stirring on a hot plate. After the reaction was completed, the pH value of the mixture was adjusted to below 1.0 by adding HCl aqueous solution. The mixture was magnetically stirred for further 12 hr, then vacuum filtered, washed by large amount of DI water and dried for use. Three kinds of Pt catalysts with different particle sizes supported on carbon nanotubes were prepared by adjusting the pH value of the reaction solution to be 11.8, 10.6 and 9.8. They were noted as PtCNT 1, PtCNT 2 and PtCNT 3, respectively.

Carbon nanosheets grown directly on carbon paper (CNSCP) were received from Dr. Xin Zhao in William Marry University. Electrodepositing of Pt nanoparticles onto CNSCP was operated on

Solartron 1280C Electrochemical Workstation. Pt foil was used as counter electrode and saturated calomel electrode (SCE) was the reference electrode. CNSCP was used directly as the working electrode, and immersed in 5 mM H_2PtCl_6 and 0.05 M HCl aqueous solution under magnetically stirring. The deposition mode was potentiostatic, A short potential pulse from 0.8 V (1 s, vs. SCE) to 0V (0.2 s, vs. SCE) was applied on the working electrode to reduce the PtCl_6^{2-} into Pt, and 200 cycles were performed.

Characterization of carbon supported catalysts

Inductively coupled plasma-mass spectrometry (ICP-MS) was performed on Thermo X-Series II to confirm the actual metal content in the powdered catalysts.

Transmission electron microscope (TEM) images were obtained on JEOL 2100F field emission transmission electron microscope operated at 200 KV. To prepare samples for TEM study, a small amount of catalysts was suspended in ethanol using an ultrasonic bath. Then a drop of such suspensions was dropped onto a Cu 200-mesh grid with holey carbon film and dried in the air.

The surface morphologies of CNSCP and Pt CNSCP were observed on a field emission scanning electron microscope (FESEM) Hitachi S5200.

Electrochemical measurement

Three-electrode reactor was employed with a Pt wire as a counter electrode and Hg/Hg₂SO₄ electrode (0.64V vs. SHE) as a reference electrode. All the potentials referred below were referenced to Hg/Hg₂SO₄ electrode. The working electrodes were divided into two kinds. For nanostructured carbon powder samples, glassy carbon electrode (GCE) with diameter 3 mm was used for the preparation of working electrode. The GCE was polished by 0.5 μm alumina paste, then ultrasonically washed by de-ionized water and dried for use. 1.00 mg as-prepared Pt/CNT catalyst was dispersed in 1.00 mL mixed solution of 75 vol% isopropanol aqueous solution and 5 wt% Nafion solution in ethanol (1:1% volume ratio), and ultra-sonicated for 10 min to form a uniform catalyst ink. Then 5 μl portion of the ink was piped onto 3 mm diameter glassy carbon electrode and dried at 45 °C to form a thin layer. For carbon nanosheets grown on carbon paper, they were cut into an area of 0.5 cm×0.5 cm and used directly as working electrode.

The working electrodes were immersed in 0.5 M H₂SO₄ with or without 1.0 M CH₃OH aqueous solution for electrochemical measurement. High purity nitrogen gas was conducted through the solutions to exhaust oxygen. Cyclic voltammogram measurement was performed on Solartron 1280C electrochemical workstation from -0.66 V to 0.54 V at a scanning rate of 20 mV/s at room temperature.

Results and discussions

Powdered carbon nanotubes as catalyst support

The actual weight percentages of Pt in the catalysts were determined by ICP-MS to be 11.1%, 20.9% and 20.1% for Pt/CNT1, Pt/CNT2 and Pt/CNT3, respectively. Figure 1 shows typical TEM images of the Pt catalysts supported on carbon nanotubes. It illustrates clearly that the spatial distribution of the metal particles on the carbon support is uniform and in a narrow particles size distribution. The histogram of the particle size distribution was acquired based on analysis of several different catalyst regions and quantifications of the sizes of around 100 particles (not shown here). A mean particle diameter of 1.6 nm, 3.2 nm and 4.2 nm was suggested for Pt/CNT1, Pt/CNT2, and

Pt/CNT3, respectively.

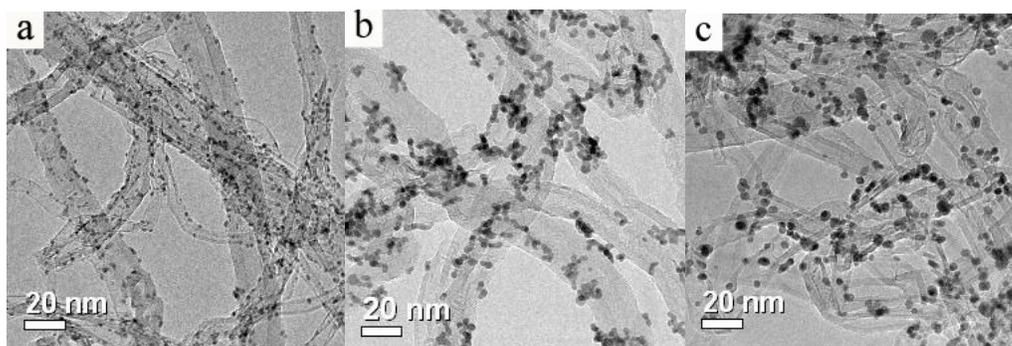


Figure 1. TEM images of the catalysts Pt/CNT1 (a), Pt/CNT2 (b) and Pt/CNT3 (c)

In order to explore the detailed nanostructure of the supported Pt catalysts, high resolution TEM was carried out. Long time electron beam irradiation was avoided because it may induce specimen damage and contaminations. Figure 2b shows a typical HRTEM image of Pt/CNT2 with the Pt particle size about 3 nm. It was found that there were carbon species on the surface of Pt catalysts and showed a single layered structure, as indicated by the black arrow. The phase contrast of the carbon layer was quite similar to that found on the surface of the oxidized carbon nanotubes (shown by white arrow), which suggested that it could have similar structure to the latter and really comes from the carbon support.

Moreover, the extent of the MSI seems to be different for Pt catalysts with different sizes. When the size of Pt catalysts decreases to be quite small, i.e. 1.6 nm in this paper, most of them tended to be severely covered by a carbon layer as indicated by the arrow in Figure 2a, where shows a double layered carbon covered on the small Pt nanoparticles. Due to interfere of the carbon layer and weak signals originated from such tiny Pt particle, the phase contrast of Pt nanoparticles appears quite obscure, and shows no characteristics of lattice fringes. In contrary, when the size increased to larger, i.e. in Pt/CNT3, the extent of being covered by a carbon layer was more slightly and the surface of some Pt nanoparticles showed quite clean (Figure 2c), as indicated by the arrow. The phase contrast of Pt nanoparticles also became much clearer, and lattice fringes corresponding to Pt (111) could be identified.

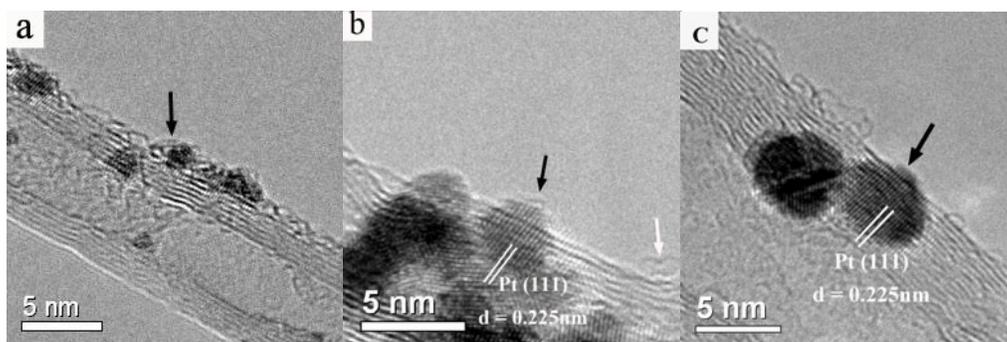


Figure 2. HRTEM images of Pt/CNT1 (a), Pt/CNT2 (b) and Pt/CNT3 (c)

The electrochemical properties of the three kinds of catalysts were investigated. Figure 3 shows the CV plots of catalysts Pt/CNT1, Pt/CNT2 and Pt/CNT3 in 0.5 M H₂SO₄ aqueous solution. Due to within the potential window for deposition of hydrogen on the surface of Pt, well defined hydrogen adsorption and desorption peaks can be seen between -0.64 V and -0.3 V in the CV curves for all of the three catalysts. The electrochemically active surface area (ECSA), i.e. the surface area contributing to the electrochemical reactions, of the Pt catalysts can be estimated from the charges associated with hydrogen adsorption or desorption (Xing, Y.C. 2004; Yang, R.Z. 2005). On the other hand, the real surface area of Pt catalysts can be calculated with the average particle diameter, supposing that Pt particles are spherical.

As the Pt nanoparticles in Pt/CNT1 has a half weight percent but a half average particle diameter of Pt nanoparticles in Pt/CNT2, the real surface area of Pt nanoparticles for both should be more or less the same. However, the ECSA of Pt nanoparticles in Pt/CNT1 was found much smaller to that of Pt/CNT2, suggesting that much more Pt nanoparticles in Pt/CNT1 were inactive. This is quite consistent with the HRTEM study, that is, the surface of Pt nanoparticles in Pt/CNT1 was much more seriously covered by a carbon layer, thus blocking the adsorption and desorption of hydrogen. The ECSA of Pt nanoparticles in Pt/CNT3 was also smaller than that in Pt/CNT2, which is due to the larger average particle diameter and lower real surface area. Therefore, too small particle size for Pt catalysts (below 2 nm) may not bring significant improved electrocatalytic performance, and slightly larger particle size (about 3 nm in here) may be more proper.

It is worthy to note that similar phenomenon was also found in Pt catalyst supported on carbon nanofibers (not shown here), which illustrates that the MSI may be generally exist in carbon supported Pt catalysts for fuel cells. The carbon layer distributed over the surface of Pt catalysts may be an important reason for their low utilized efficiency in fuel cells.

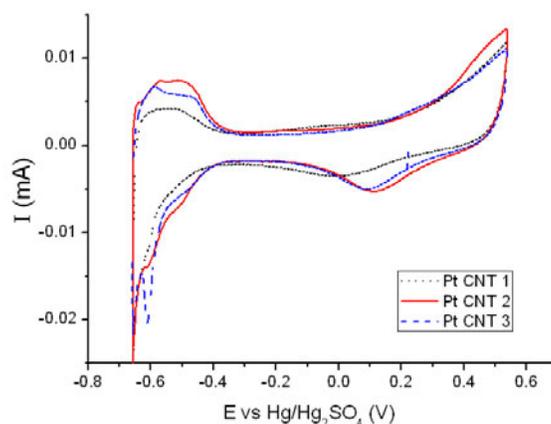


Figure 3. Cyclic voltammograms of the catalysts of Pt/CNT1, Pt/CNT2 and Pt/CNT3 in 0.5M H₂SO₄

Carbon nanosheets grown directly on carbon paper as catalyst supports

Carbon nanosheet was an ultrathin sheet-like carbon nanostructure, and has been effectively synthesized with CH₄ diluted in H₂ by an inductively coupled radio-frequency plasma enhanced chemical vapor deposition (Wang, J.J. 2004). It can be formed on various kinds of substrates, including

metals, semiconductors and insulators, without the use of catalysts. In this study, carbon nanosheets were deposited on carbon paper which consisted of graphite carbon fibers and used as the gas diffusion electrode for PEMFCs. The as-prepared carbon nanosheets on carbon paper were used as Pt catalyst support directly. In another word, the carbon catalyst support and the gas diffusion electrode were integrated into one unit, which is quite beneficial to the electron-conducting process during electrocatalysis.

Pt nanoparticles supported on CNSCP (denoted as Pt/CNSCP) were prepared through electrochemical deposition. For comparison, Pt nanoparticles were also electrodeposited on carbon paper (denoted as Pt/CP) under the same condition. Figure 4a and 4b show typical SEM images of Pt/CP and Pt/CNSCP, respectively. The average particle size of the electrodeposited Pt particles was about 20~50 nm for both of the two kinds of support, and the coverage density of the Pt particles was quite low compared to that on powdered carbon support. The electrodeposition conditions need further optimized.

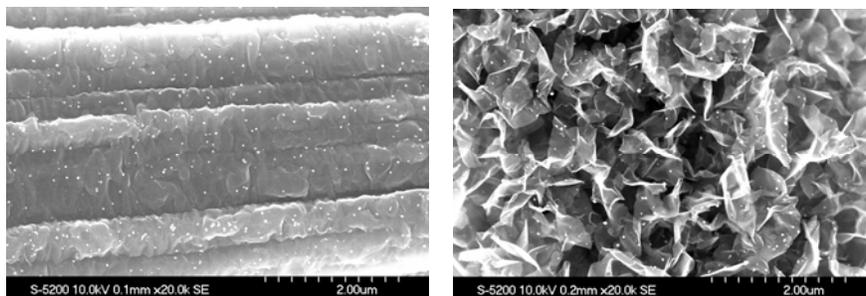


Figure 4. SEM images of Pt nanoparticles electrodeposited on carbon paper (a) and on carbon nanosheets grown on carbon paper (b)

The electrocatalytic performance towards MOR for the prepared Pt/CP and Pt/CNSCP were investigated. Figure 5 shows the cyclic voltammograms (CV) plots in 0.5 M H_2SO_4 with 1.0 M CH_3OH aqueous solution. No obvious MOR peaks were found in the CV curve for Pt CP, which may arise from the weak signal of the low amount Pt particles loaded on CP. However, there are obvious MOR peaks in the CV for Pt/CNSCP. This can be contributed to the increased electrode surface area by the deposition of CNS, thus increasing the loading amount of Pt during electrodeposition. The electrodeposited Pt nanoparticles can be ensured to be electrically contact with the electrode due to the nature of the electrodeposition method, thus can maximally increase the utilization efficiency of Pt. Meanwhile, the carbon nanosheets grown on carbon paper show an open pore structure, which is beneficial for the mass transport of the reactions.

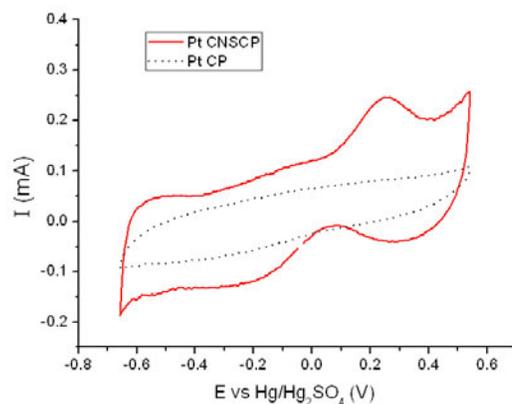


Figure 5. Cyclic voltammograms of Pt/CP and Pt/CNSCP in 0.5 M H₂SO₄ with 1.0 M CH₃OH aqueous solution

Conclusions

Pt catalysts with different size distributions supported on carbon nanotubes have been prepared. Through HRTEM study, we found that the surface of Pt catalysts was covered by a carbon layer, which illustrated a strong metal support interaction, and may be an important reason for the low utilized efficiency of Pt in fuel cells. Moreover, the smaller the particle size of Pt catalysts is, the stronger the interaction is. As a result, too small particle size of Pt catalysts supported on carbon nanotubes may not bring in obviously improved electrocatalytic performance. This phenomenon was also found in other carbon supports such as carbon nanofibers.

Carbon nanosheets were grown directly on carbon paper and to be used both as catalyst support and gas diffusion electrode for fuel cells. Electrodeposition was adopted to support Pt catalysts. The growth of carbon nanosheets on carbon paper increases the surface area of the latter (thus it can support more Pt catalysts) and will make the electronic-conducting path easily in fuel cells at the same time.

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