

## Preparation of Multiwall Carbon Nanotubes-supported High Loading Platinum for Vehicular PEMFC Application

Bing ZHANG<sup>1</sup>, Li Juan CHEN<sup>1\*</sup>, Kai Yong GE<sup>2</sup>, Yan Chuan GUO<sup>1</sup>, Bi Xian PENG<sup>1</sup>

<sup>1</sup>Technical Institute of Physics and Chemistry of CAS, Beijing 100101

<sup>2</sup>R&D Center, Beijing LN Power Sources Co., Ltd., Beijing 100094

**Abstract:** Multiwall carbon nanotube-supported Pt (Pt/MWNTs) catalysts with high dispersion and high loading of Pt were prepared by chemical reduction method and the loading of Pt got to 40 wt%. The average diameter of Pt nanoparticles on MWNTs was about 3.5 nm. When the hydrogen and air were used as reactant gases for PEMFC, Pt/MWNTs catalysts showed significantly higher performance than the Pt/XC-72 (carbon black) catalysts.

**Keywords:** Platinum nanoparticles, carbon nanotubes, PEMFC, catalytic activity.

Proton exchange membrane fuel cell (PEMFC) has been receiving much attention as a power source for both stationary and mobile applications, due to its many attractive features<sup>1</sup>. The performance of a membrane electrode assembly for PEMFC greatly depends on the activity and loading amount of the Pt/C catalyst<sup>2</sup>. The electrocatalytic activity of Pt nanoparticles for fuel cell is determined by various factors, which involve the size and dispersion of particles<sup>3</sup>, preparation method<sup>4-5</sup>, supporting materials and their surface conditions<sup>6</sup>. Among these factors, the morphology and nanostructure of supports are considered to be the main factors in obtaining high dispersions of nanoparticle catalyst. As compared to Vulcan XC-72 carbon black<sup>7-9</sup>, which is the most widely used support material for PEMFC and DMFC electrodes, carbon nanotube exhibit higher performance due to its unique structure. To prepare high-quality supported metal catalysts, one must be able to deposit dispersed metal particles, preferably with sizes in the nanometer range on carbon nanotubes. Because of the slow reaction rate of cathode oxygen reduction reaction<sup>10</sup>, high loading Pt-based catalyst is essential in order to accelerate the reaction and obtain high current density. On the other hand, the reduction of the mass-transport is essential when the air was used for cathode. When the thickness of the active layer in fuel cell electrodes is lowered, a high platinum loading must be combined with a high utilization coefficient of the catalyst. 40 wt% Pt/C or higher Pt loading catalyst are widely used for PEMFC and DMFC. Highly dispersed high loading metal nanoparticles on carbon black (Vulcan XC-72) have been achieved<sup>11</sup> and only less than 30 wt% Pt/MWNTs catalysts were prepared in the

---

\* E-mail: chenlijuan@mail.ipc.ac.cn

previous studies because high Pt loading on carbon nanotubes tend to aggregate<sup>12-16</sup>.

In this paper, we report the preparation of Pt/MWNTs with high loading and high dispersion of Pt. The Pt-based catalysts were also employed as cathode and anode catalysts for PEMFC to investigate their electrocatalytic activity.

The multiwall carbon nanotubes were prepared by chemical vapor deposition<sup>17</sup>. The Pt catalysts were supported on the carbon nanotubes with high loading of Pt by using a formaldehyde reduction method. Carbon nanotubes were functionalized in the mixture of concentrated vitriol and nitric acid. Surface oxidation of XC-72 was accomplished with 2.6 mol/L HNO<sub>3</sub> for 8 h at refluxing. Functionalized carbon nanotubes were taken in propan-2-ol and stirred first with ultrasonic treatment for 30 min and then mechanically stirred for 3 h. The hexachloroplatinic acid was added dropwise to the carbon ink with constant stirring. Na<sub>2</sub>CO<sub>3</sub> solution was added to adjust the pH to about 6 and the resulting heterogeneous mixture was allowed to stir for two hours at 80 °C under the flow of N<sub>2</sub> gas. Formaldehyde was added to the solution to reduce Pt at 80 °C for 3 h, and a flow of N<sub>2</sub> gas was also passed through the reaction system to isolate oxygen and prevent the production of byproducts. The resulting solution was filtered. The solid was washed with distilled water and then dried at 60 °C overnight. Pt/MWNTs catalysts with 40 wt% Pt loaded was obtained. For comparison, XC-72 was also employed as carrier to prepare Pt/XC-72 catalysts with the same Pt loading amount according to the above method.

The loading amount of Pt in Pt/MWNTs and Pt/XC-72 was determined by EDX spectrum. The microstructure of the Pt catalysts was characterized by transmission electron microscopy (TEM). Fuel cell performance was measured at 70 °C and 0.2 MPa by using reactant gas of H<sub>2</sub> and air.

**Figure 1** gives the EDX spectrum of Pt/MWNTs. The Pt loading amount of Pt/MWNTs composite was characterized to be 39.6 wt%. **Figure 2** shows a TEM micrograph of the Pt catalysts supported on the MWNTs and XC-72. Pt nanoparticles were homogeneously dispersed on the MWNTs and XC-72. Average size of Pt particle on MWNTs and XC-72 are 3.5 nm and 3.0 nm, relatively. **Figure 3** is the comparison of fuel cell performance using Pt/MWNTs and Pt/XC-72 as catalysts, relatively. The current density for Pt/MWNTs is larger than that of Pt/XC-72. Self-prepared Pt/XC-72 catalyst showed the poor electrocatalytic activity though the Pt nanoparticles were smaller on XC-72 than on MWNTs. We can conclude that Pt/MWNTs with 40 wt % Pt

**Figure 1** EDX spectrum of Pt / MWNTs

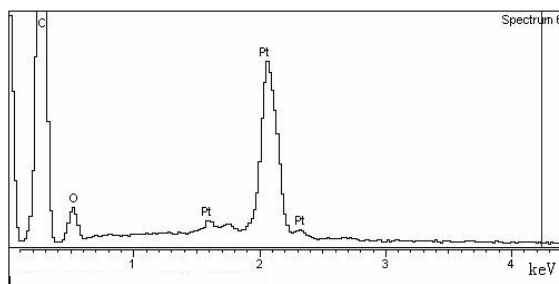


Figure 2 TEM micrographs of the Pt catalyst supported on MWNTs (a) and XC-72 (b)

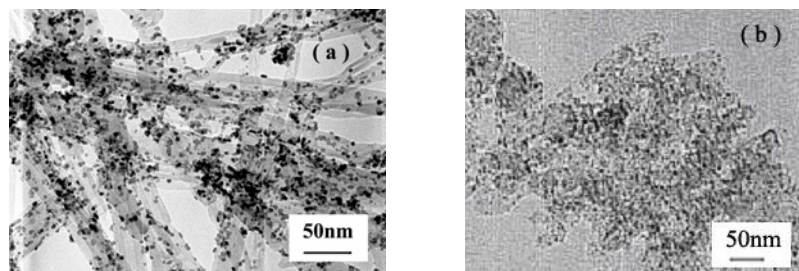
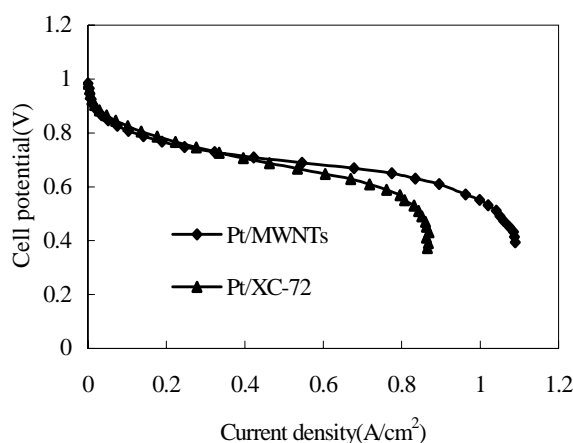


Figure 3 Comparison of single-cell polarization curves for the PEMFC in the presence of Pt/MWNTs, Pt/XC-72



40 wt %Pt in the catalyst; catalyst loading: 0.8 mg Pt/cm<sup>2</sup>. Electrolyte membrane: Nafion-115 membrane; operating temperature: 70 °C; pressure of hydrogen and oxygen: 0.2 MPa.

loading for PEMFC possess excellent electrocatalytic activity by using reactant gas of H<sub>2</sub> and air, and the capability of Pt/MWNTs is better than that of Pt/XC-72 by the same preparation methods greatly, which demonstrates carbon nanotubes are more suitable to be the support of Pt nanoparticles for PEMFC and high loading amount of Pt on carbon nanotubes could be obtained. MWNTs possess better crystallization, electrical conductivity and chemical stability and the average size of Pt nanoparticles approximate to the optimum size in our work, which attribute to the high performance of Pt/MWNTs. The most important thing is that more reactant gases could land on Pt nanoparticles easily, because the hollow cavity and graphitic layer's interspaces give more access to the gases than conventional support. The increase of reactant gases concentration result in the acceleration of reaction according to the theory of chemical balance, therefore, the power density of single cell was improved.

In summary, multiwall carbon nanotubes were used as support of Pt/C catalysts for PEMFC. Pt nanoparticles were homogeneously dispersed on the MWNTs without agglomeration though the loading of Pt got up to 40 wt%. The capability of Pt/MWNTs

is much better than that of Pt/XC-72 by the same preparation methods. Pt/MWNTs with high loading of Pt gained highly performance for PEMFC by using reactant gas of H<sub>2</sub> and air.

## References

1. R. Service, *Science*, **2002**, 296, 1222.
2. H. A. Gasteiger, J. E. Panels, S. G. Yan, *J. of Power Sources*, **2004**, 127, 162.
3. M. Peuckert, T. Yoneda, R. A. D. Betta, *J. Electrochem. Soc.*, **1986**, 133 (5), 944.
4. N. Rajalakshmi, H. Ryu, M.M. Shaijumon, S. Ramaprabhu, *J. Power Sources*, **2005**, 140(2), 250.
5. W. Chen, J. Zhao, J. Y. Lee, Z. Liu, *Mater. Chem. Phys.*, **2005**, 91(1), 124.
6. R. Yu, L. Chen, Q. Liu, *Chem. Mater.*, **1998**, 10, 718.
7. K. Amine, K. Yasuda, H. Takenaka, *Ann. Chim. Sci. Mat.*, **1998**, 23, 331.
8. J. Prabhuram, X. Wang, C. L. Hui, *J. Phys. Chem. B*, **2003**, 107, 11057.
9. E. G. Franco, E. Arico, M. Linardi, *Mater. Sci. Forum*, **2003**, 416-418, 4.
10. A.K. Shukla, M. Neergat, B. Parthasarathi, *J. Electroanal. Chem.*, **2001**, 504, 111.
11. B. L. Gratiot, H. Remita, G. Picq, *J. Catal.*, **1996**, 164, 36.
12. W. Li, C. Liang, W. Zhou, *Carbon*, **2004**, 42, 436.
13. W. Li, C. Liang, W. Zhou, *J. Phys. Chem. B*, **2003**, 107, 6292.
14. W. Li, C. Liang, J. Qiu, *Carbon*, **2002**, 40, 791.
15. Y. Xing, *J. Phys. Chem. B*, **2004**, 108, 19255.
16. T. Matsumoto, T. Komatsu, K. Arai, *Chem. Commun.*, **2004**, 840.
17. B. Zhang, Y. Guo, L. Chen, B. Peng, *Acta Chimica Sinica* (in Chinese), **2004**, 62, 2253.

Received 14 March, 2005