

- [5] Jun S, Jo SH, Ryoo R, Kruk M, Jaroniec M, Liu Z, et al. Synthesis of new nanoporous carbon with hexagonally ordered mesostructure. *J Am Chem Soc* 2000;122:10712–5.
- [6] Kim SS, Pinnavaia TJ. A low cost route to hexagonal mesostructured carbon molecular sieves. *Chem Commun* 2001:2418–9.
- [7] Lee J, Yoon S, Oh SM, Shin S, Hyeon T. Development of a new mesoporous carbon using an HMS aluminosilicate template. *Adv Mater* 2000;12:359–63.
- [8] Lee J, Joo SH, Ryoo R. Synthesis of mesoporous silicas of controlled pore wall thickness and their replication to ordered nanoporous carbons with various pore diameters. *J Am Chem Soc* 2002;124:1156–7.
- [9] Prouzet E, Pinnavaia TJ. Assembly of mesoporous molecular sieves containing wormhole motifs. *Angew Chem Int Ed* 1997;36:516–8.
- [10] Boissiere C, Larbot A, Lee A, Kooyman P, Prouzet E. A new synthesis of mesoporous MSU-X silica controlled by a two-step pathway. *Chem Mater* 2000;12:2902–13.
- [11] Fuertes AB, Nevskaja DM. Control of mesoporous structure of carbons synthesised using a mesostructured silica template. *Micropor Mesopor Mater* 2003;62:177–90.
- [12] Kruk M, Jaroniec M, Sayari A. Application of large pore MCM-41 molecular sieve to improve pore size analysis using nitrogen adsorption measurements. *Langmuir* 1997;13:6267–73.

Homogeneous and controllable Pt particles deposited on multi-wall carbon nanotubes as cathode catalyst for direct methanol fuel cells

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Direct methanol fuel cells (DMFCs) are attracting much attention for their potential as clean and mobile power sources for the future [1–5]. However, a serious problem for polymer electrolyte fuel cells, including DMFCs, is the low reaction rate of the cathode oxygen reduction reaction (ORR), for which one potentially effective solution is using a novel carbon material as electrocatalyst support that help improve or increase mass activity of the catalyst (Pt) in ORR. In this regard, several novel carbon materials have been tested, including carbon tubule membranes prepared by template methods [6], highly ordered nanoporous arrays of carbon [7] and graphite nanofibers [8–10]. Previous studies have shown that multi-wall carbon nanotubes (MWNTs) exhibit better performance in DMFCs as compared to carbon black (XC-72) [11,12] under identical conditions both for catalyst preparation and for cell performance test. It is well known that the particle size and the distribution of Pt-based catalysts are key factors that determine their ORR activity and cell performance for DMFCs. It was reported that tractable noble metal nanoparticles could be obtained by using a

polyol synthesis method [13–16]. In previous work [11,12], the performances in DMFCs of different Pt catalysts supported on different carbon materials (XC-72 and MWNTs) were compared, and it was found that ORR and DMFC performances were enhanced when MWNTs-supported Pt catalysts were used as cathodic electrocatalysts. The cathodic electrocatalysts from the formaldehyde reduction method and the polyol synthesis method were also investigated and compared with each other. This previous work also revealed that the ratio of water to ethylene glycol (EG) had an impact on Pt particle size. However, some questions related to this phenomenon were not clear and needed to be answered in greater detail. In the present study, we used a modified polyol synthesis method to prepare MWNTs supported Pt catalysts, and found that the particle size can be controlled by simply adjusting the ratio of water to EG in the preparation process. In the meantime, the relationship between the performance of direct methanol single cells and the mean particle size of Pt catalysts was also explored and established.

The MWNTs used in this work were produced from high purity graphite by the classical arc-discharge method. The MWNTs with hollow tubular structure and highly graphitic multi-layer walls were mostly from 4 to 60 nm in diameter. The MWNTs were purified and surface oxidized following a procedure described in Ref.

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[12]. The BET surface area of MWNTs after purification is about 42 m²/g, as determined by N₂ physisorption at 77 K. In order to control the size of Pt particles, different EG solutions with varying content of deionized water (DI water, 0%, 5%, 40% and 70%) were used. The roles of EG in solution include reducing Pt hydroxide to Pt metal and stabilizing Pt metal colloidal. Generally, the absence of water favors metal formation while its presence favors oxide or hydroxyacetate formation. Therefore, the presence of a small amount of water in EG solution may buffer the formation rate of the metal particle, and result in the size of the metal particles to be controlled at a specific value [13]. Typical preparation processes for MWNTs-supported Pt catalysts (denoted as Pt/MWNTs) are as follows: 500 mg of surface oxidized MWNTs were suspended in 50 ml EG solution (with different DI water content) and stirred with an ultrasonic treatment for 10 min, then mechanically stirred for 4 h, during which 7.5 ml of hexachloro-platinic acid (7.4 mg Pt/ml EG, 10 wt.% Pt) was added to the solution dropwise by an eyedropper. The pH of the solution was adjusted to above 13. The pH value of the initial Pt hydroxide colloidal solution is very important for obtaining stable Pt particles in glycol. If the pH value was lower than ~12, instead of a metallic colloidal solution, a precipitate would be obtained during the subsequent heating process. The solution was heated in an oil bath at 140 °C to reduce Pt completely. Refluxing conditions were used in order to maintain water contents in the EG–water system. A flow of argon was passed through the reaction system to eliminate oxygen and to remove organic by-products. After filtration, washing and drying, the Pt/MWNTs samples were obtained and designated a, b, c, d samples. The filtrates for all Pt/MWNTs were analyzed by NaBH₄ reduction and no Pt was detected. The mass of all the MWNTs supported Pt samples increased by ~11 ± 1 wt.% in comparison to that of the MWNTs supports, which means the Pt metal loading is about 10 wt.% for all Pt/MWNTs samples. The EDX analysis confirmed that the Pt metal loading for Pt/MWNTs-b was 10.70 wt.%.

The Pt/MWNTs samples were characterized by recording their X-ray diffraction (XRD) patterns shown in Fig. 1. The 20–85° 2θ angular regions were explored with a scan rate of 5°/min, the Pt (220) peak (64–72°) was scanned at 1°/min with a resolution of 0.02° in order to obtain the size of Pt particles by Scherrer formula [17]. As the DI water content increases, the Pt peaks become sharper, indicating a bigger Pt particle size. The average particle size is 2.0 nm for catalyst a, 2.5 nm for catalyst b, 4.0 nm for catalyst c and 4.5 nm for catalyst d, respectively. The TEM images for Pt/MWNTs a, b, c and d samples are shown in Fig. 2. The average size of Pt particles on the catalysts was also obtained by directly measuring over 200 particles from bright-field TEM micrographs. The mean size of Pt particle for a, b,

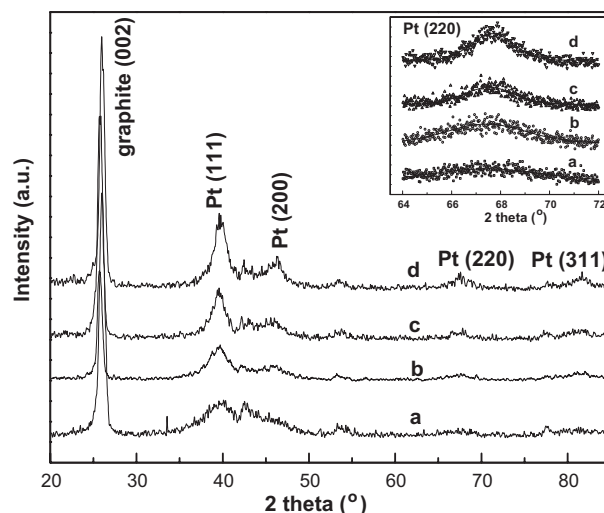


Fig. 1. Powder XRD patterns of Pt/MWNTs sample a, b, c, and d, which were prepared by EG method, 0%, 5%, 40% and 70% DI water in EG solution, respectively. Detailed Pt (220) peaks are on the top right.

c, d catalysts is 2.2, 2.6, 4.3, 4.9 nm, respectively, which is in good agreement with the results from XRD. These results show that the fine and homogeneous Pt particles deposited on MWNTs can be obtained when less DI water was used. With the increase of DI water content, Pt particles aggregate and the particle size distribution becomes wider. The size distribution of Pt particles for catalysts a, b, c and d is 1–4, 2–5, 2–8 and 2–12 nm, respectively. Detailed preparation procedures, such as sequence of DI water addition, pH value, and refluxing condition may all play a role to determine the Pt particle size and size distribution of catalysts [13,16]. However, following the optimum preparation conditions we reported, with the increasing DI water content in the synthesis system, the average particle size increases and the particle size distribution becomes wider, implying these could be controlled to some extent by simply adjusting the water content in the EG solvent. A 2.0 M H₂SO₄–4.0 M HNO₃ (1:1) solution was applied to the purified MWNTs to create some surface functional groups, such as carboxyl, hydroxyl and carbonyl groups [18]. The oxidized MWNTs can be dispersed stably in EG better than in DI water, suggesting a denser EG solution is superior. In our case, the particle size of Pt does not grow when the DI water content is below 5 vol.%. Further, it was observed from TEM micrographs (Fig. 2) that, in the case of sample a, less Pt particles deposited on MWNTs in comparison to sample b (5 vol.% DI water). The functional groups on MWNTs and more homogeneous dispersion of surface oxidized MWNTs in a 95% EG may be responsible for this effect. In this case, Pt hydroxide colloidal solution is formed under the initial reaction conditions. Pt hydroxide colloid may interact with surface functional groups of

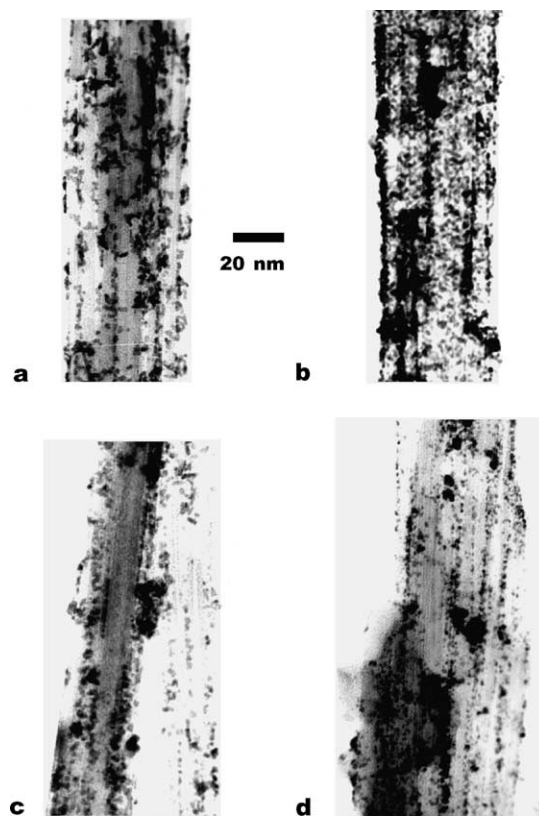


Fig. 2. Transmission electron microscopy images of Pt/MWNTs sample a, b, c, and d, which were prepared by EG method, 0%, 5%, 40% and 70% DI water in EG solution, respectively. Reprinted in part, with permission from The Journal of Physical Chemistry B, 107, 6292–6299, 2003, American Chemical Society.

MWNTs, then deposit on MWNTs. The surface functional groups were also found critical for loading Pt onto SWNTs [19].

The electrochemical performance of these Pt/MWNTs samples was tested under the same operation conditions illustrated in Fig. 3. The details about membrane treatment, electrode preparation, MEA fabrication and DMFC single cell test conditions can be found elsewhere [12]. Because the Pt mass per electrode area is 1.0 mg/cm^2 , the mass activity at 0.6 V for these Pt/MWNTs catalysts is 7.0 mA/mgPt for sample a, 14.8 mA/mgPt for sample b, 4.4 mA/mgPt for sample c and 3.0 mA/mgPt for sample d. At a current density of 0.3 A/cm^2 , the cell potentials for these catalysts are 0.270 V for a, 0.309 V for b, 0.189 V for c and 0.150 V for d. The cell performance with catalyst b is a bit higher than that of catalyst a, and obviously it is superior to other single cells with catalyst c and d in DMFC tests. Catalysts c and d have bigger particle sizes, thus a loss of surface area as compared to catalyst b. Catalyst a has the smallest Pt particle size (2.0 nm) but a lower ORR activity than catalyst b. It was reported [20,21] that the ORR exhibits a maximum in catalyst mass activity at a particle size of about $2.0\text{--}5.0 \text{ nm}$ for Pt deposited on

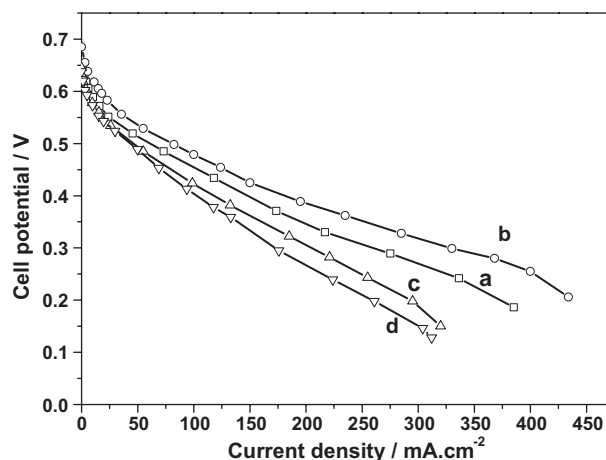


Fig. 3. Comparison of single cell polarization curves for the DMFC in presence of Pt/MWNTs (a, b, c, d) cathode catalysts (1.0 mgPt/cm^2); anode: Pt–Ru/C (20 wt.%Pt, 10 wt.%Ru, Johnson Matthey Corp.; catalyst loading: 2.0 mgPt-Ru/cm^2); electrolyte membrane: Nafion-115® (Dupont) membranes; operation temperature: $90 \text{ }^\circ\text{C}$; methanol concentration: $1.0 \text{ M CH}_3\text{OH}$; flow rate: 1.0 ml/min , oxygen pressure: 0.2 MPa .

carbon black supports (12.5 A/g for Pt particles with an average size of 2.0 nm ; 14.0 A/g for Pt particles with an average size of $3.0\text{--}5.0 \text{ nm}$ at 0.9 V vs. SHE). This is presumably because the (1 1 1) and (1 0 0) Pt surfaces are more electro-catalytically active than Pt atoms located on higher Miller index planes. The specific activity increases gradually with an increase in Pt particle size and closely follows the trend observed between surface fraction of (1 1 1) and (1 0 0) Pt surfaces and the particle size. Obviously, there is a maximum in the fraction of (1 1 1) and (1 0 0) surfaces on Pt particles of cubo-octahedral geometry in this particle size range [22]. Maillard et al. [23] investigated the effect of particle size of Pt/C on the tolerance of ORR electrocatalysts to methanol competition using a rotating disk electrode. They found that the mass activity increased continuously with a decrease in particle size from 4.6 to 2.3 nm , while in methanol-free electrolyte the mass activity was roughly independent of particle size, when the particle size was smaller than 3.6 nm . In our case, catalyst b exhibits higher ORR activity and superior cell performance as compared to other Pt/MWNTs catalysts in DMFC tests, implying that there exists an optimum Pt particle size in Pt/MWNTs cathodic catalysts for DMFC, which may also be determined by the compromise between specific activity and surface area of Pt particles [22]. Narrow particle size distribution of Pt/MWNTs catalysts a and b may also play an important role in the improvement of ORR activity. For these two catalysts, the Pt particle size distribution is narrow and very few big particles are found.

In summary, MWNTs-supported homogeneous Pt particles, controlled simply by adjusting the ratio of

water to EG in the preparation process, show an optimum ORR activity when employed as cathode catalysts in DMFCs. This preparation strategy may be of great potential in supporting noble metal and/or multi-component electrocatalysts on carbon materials, such as Ru, Rh, Pt–Ru, Pt–Fe, Pt–Sn systems.

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References

- [1] Hamnett A. Mechanism and electrocatalysis in the direct methanol fuel cell. *Catal Today* 1997;38:445–8.
- [2] McNicol BD, Rand DAJ, Williams KR. Direct methanol–air fuel cells for road transportation. *J Power Sources* 1999;83: 15–31.
- [3] Wasmus S, Kuver A. Methanol oxidation and direct methanol fuel cells: a selective review. *J Electroanal Chem* 1999;45:19–31.
- [4] Arico AS, Srinivasan S, Antonucci V. DMFCs: from fundamental aspects to technology development. *Fuel Cells* 2001;2:1–29.
- [5] Ren XM, Zelenay P, Thomas A, Davey J, Gottesfeld S. Recent advances in direct methanol fuel cells at Los Alamos National Laboratory. *J Power Sources* 2000;86:111–6.
- [6] Che GL, Lakshmi BB, Fisher ER, Martin R. Carbon nanotubule membranes for electrochemical energy storage and production. *Nature* 1998;393:346–9.
- [7] Joo SH, Choi SJ, Oh I, Kwak J, Liu Z, Terasaki O, et al. Ordered nanoporous arrays of carbon supporting high dispersion of platinum nanoparticles. *Nature* 2001;412:169–73.
- [8] Bessel CA, Laubernds K, Rodriguez NM, Baker RTK. Graphite nanofibers as an electrode for fuel cell applications. *J Phys Chem B* 2001;105:1115–8.
- [9] Steigerwalt ES, Deluga GA, Cliffler DE, Lukehart CM. A Pt–Ru/Graphitic carbon nanofiber nanocomposite exhibiting high relative performance as a direct-methanol fuel cell anode catalyst. *J Phys Chem B* 2001;105:8097–101.
- [10] Steigerwalt ES, Deluga GA, Lukehart CM. Pt–Ru/carbon fiber nanocomposites: synthesis, characterization, and performance as anode catalysts of direct methanol fuel cells. A search for exceptional performance. *J Phys Chem B* 2002;106: 760–6.
- [11] Li WZ, Liang CH, Qiu JS, Zhou WJ, Han HM, Wei ZB, et al. Carbon nanotubes as support for cathode catalyst of a direct methanol fuel cell. *Carbon* 2002;40:791–4.
- [12] Li WZ, Liang CH, Zhou WJ, Qiu JS, Li HQ, Sun GQ, et al. Preparation and characterization of multi-walled carbon nanotube-supported platinum cathode catalysts of direct methanol fuel cells. *J Phys Chem B* 2003;107:6292–9.
- [13] Wang Y, Ren JW, Deng K, Gui LL, Tang YQ. Preparation of tractable platinum, rhodium, and ruthenium nanoclusters with small particle size in organic media. *Chem Mater* 2000;12:1622–7.
- [14] Toshima N, Wang Y. Preparation and catalysis of novel colloidal dispersions of copper/noble metal bimetallic clusters. *Langmuir* 1994;10:4574–80.
- [15] Yan XP, Liu HF, Liew Y. Size control of polymer-stabilized ruthenium nanoparticles by polyol reduction. *J Mater Chem* 2001;6:3387–92.
- [16] Zhou ZH, Wang SL, Zhou WJ, Wang GX, Jiang LH, Li WZ, et al. Novel synthesis of highly active Pt/C cathode electrocatalyst for direct methanol fuel cell. *Chem Commun* 2003:394–5.
- [17] Radmilovic V, Gasteiger HA, Ross Jr PN. Structure and chemical composition of a supported Pt–Ru electrocatalyst for methanol oxidation. *J Catal* 1995;154:98–106.
- [18] Yu RQ, Chen LW, Liu QP, Lin JY, Tan KL, Ng SC, et al. Platinum deposition on carbon nanotubes via chemical modification. *Chem Mater* 1998;10:718–22.
- [19] Lordi V, Yao N, Wei J. Method for supporting platinum on single walled carbon nanotubes for a selective hydrogenation catalyst. *Chem Mater* 2001;13:733–7.
- [20] Mukerjee SJ. Particle size and structural effects in platinum electrocatalysis. *Appl Electrochem* 1990;120:537–48.
- [21] Kinoshita K. Particle size effects for oxygen reduction on highly dispersed platinum in acid electrolytes. *J Electrochem Soc* 1990;137:845–9.
- [22] Giordano N, Passalacqua PL, Arico AS, Antonucci M, Vivaldi M, Kinoshita K. Analysis of platinum in particle size and oxygen reduction in phosphoric acid. *Electrochim Acta* 1991;36: 1979–84.
- [23] Maillard F, Martin M, Gloaguen F, Leger J-M. Oxygen electro-reduction on carbon-supported platinum catalysts. Particle-size effect on the tolerance to methanol competition. *Electrochim Acta* 2002;47:3431–40.