

Electrochemical deposition of Pt nanoparticles on CNTs for fuel cell electrode

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(Received 23 May 2007 • accepted 1 August 2007)

Abstract—In order to increase the performance of fuel cell electrode, carbon nanotubes (CNTs) were used as support instead of conventional carbon black, and the Pt catalyst was synthesized by using electrochemical deposition (ECD) method which has recently been adopted as a synthetic tool of metal nanoparticles. CNTs used in this paper were grown directly on carbon paper by chemical vapor deposition (CVD) of acetylene. Highly dispersed and nano-sized Pt particles were electrochemically deposited on CNTs surface, which would simplify the manufacturing process of membrane-electrode-assembly (MEA). Pt particles on CNTs were investigated by SEM and TEM. The particle size of Pt is less than 2 nm, which is relatively small compared to that of conventional wet impregnated catalyst (2-8 nm). CO chemisorption results show that the amounts of catalytic sites are about three times larger in Pt/CNT prepared by ECD than those in conventional wet-impregnated one. The mass activity of the former catalyst for oxygen reduction is more than three times higher compared to that of the latter one.

Key words: Carbon Nanotubes (CNTs), Pt, Fuel Cell, Electrochemical Deposition (ECD), Chemical Vapor Deposition (CVD)

INTRODUCTION

Carbon nanotubes (CNTs) have received much attention for their application as catalyst support due to their interesting properties such as nanometer size, large surface area, electronic conductivity and resistibility to acid/base media [1,2]. Recently, some studies have been presented on the application of CNTs as support of Pt catalyst for fuel cell electrode [3-5]. In the conventional manufacturing process of membrane-electrode-assembly (MEA), the catalytic sites on Pt/C (or Pt/CNT) catalyst are often blocked during the pasting procedure of the catalysts on the electrode. Thus, a few studies have been presented on the direct growth of CNTs on carbon paper for fuel cell electrode application [6]. Directly growing CNTs on the electrode is effective not only for electrochemical and catalytic performance but also for the durability of the electrode.

So far, most of Pt/C catalysts for fuel cell electrodes have been synthesized by wet-impregnation which often leads to the agglomeration of Pt particles. For the enhancement of catalytic activity and the cost efficiency of fuel cell electrodes, the size of Pt particles must be reduced. For this purpose, a new synthetic method for Pt nanoparticles has to be developed. Electrochemical deposition (ECD) has recently been adopted as a catalyst preparation method due to its peculiar advantages: high purity of deposits, simple process for deposition, and easy control of metal loading [7].

The objective of this study was to enhance the performance of fuel cell electrode by following two techniques: i) direct growth of CNTs on carbon paper by chemical vapor deposition (CVD) of acetylene, and (ii) deposition of Pt nanoparticles on CNT/carbon paper electrode by ECD method. The surface of Pt/CNT was character-

ized by SEM and TEM. The chemisorbed amounts of CO and the mass activity of Pt/CNT catalysts were also measured and compared with those of wet-impregnated ones.

EXPERIMENTAL

CNTs used in this study were grown directly on carbon paper (Toray, TGP-H-090, 30 mm×30 mm×260 μm) by CVD method in a quartz tube reactor. For the enhancement of surface wettability, carbon paper was cycled in the range of -0.25 V-1.00 V at a sweep rate of 50 mV s⁻¹ in 0.1 M H₂SO₄ solution for 40 cycles. Then, Ni particles for CNT growth were deposited on carbon paper by ultrasonic treatment in 0.5 mol Ni(NO₃)₂ solution for 5 min. CNTs were grown on the pretreated carbon paper by CVD of acetylene at 700 °C for 1 h in a quartz tube reactor. After the CNTs synthesis, the CNT/carbon paper was treated in a 0.1 M HCl solution for 24 h for the removal of Ni particles and then in a mixed acid of 0.1 M H₂SO₄ and 30 wt% HNO₃ solution for the increase of wettability and the electrochemical activity of CNTs. ECD was carried out by potential-step deposition method, where the potential was varied from 0.25 V to 1.5 V (versus SCE) with a pulse with 0.001 s in the bath solution (1 mM H₂PtCl₆+0.5 M H₂SO₄). Pt/CNT was also prepared by wet impregnation for the comparison of catalytic activity with electrochemically prepared catalyst. CNTs used in this process were CM-95 (Iljin nanotech), and H₂PtCl₆·6H₂O (99.9%, Strem) dissolved in deionized water was used as Pt-precursor.

Pt content of each catalyst was measured by inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin-Elmer). The surface of catalysts was investigated by SEM (Hitachi, S-4700) and HR-TEM (JEOL JEM). The amounts of CO chemisorbed selectively on Pt catalytic sites were measured by Autochem 2910 (Micromeritics). Mass activity, defined as the current per unit mass of Pt contained in the electrode for oxygen reduction reaction (ORR), was determined at 0.9 V by using a reversible hydrogen electrode

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[‡]This paper was presented at the 11th Korea-Japan Symposium on Catalysis held at Seoul, Korea, May 21-24, 2007.

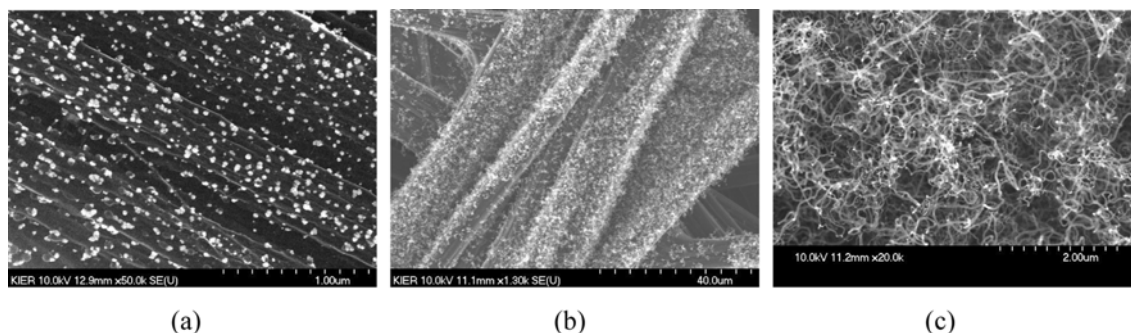


Fig. 1. SEM images for ECD process; (a) Ni particles on carbon paper, (b) and (c) CNTs grown on carbon paper.

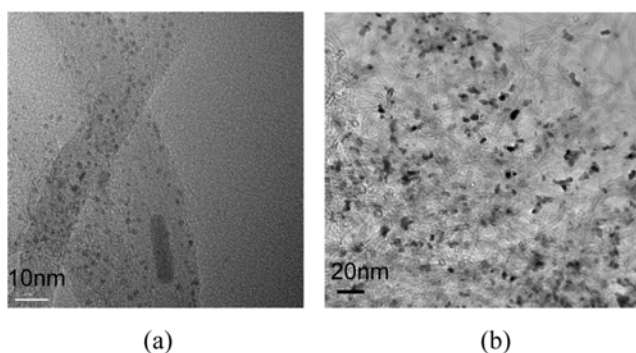


Fig. 2. TEM images of Pt/CNT catalysts prepared by (a) ECD and (b) wet impregnation.

Table 1. Pt amounts in Pt/CNT and in Pt/CNT/carbon paper

	Pt amount (wt%)		Pt amount (mg/cm ²)
Pt(ECD)*/CNT	9.7	Pt(ECD)*/CNT/carbon paper	0.2
Pt(IMP)**/CNT	9.9	Pt(IMP)**/CNT/carbon paper	0.2

*Pt catalyst prepared by ECD technique.

**Pt catalyst prepared by wet impregnation.

(RHE) as reference in 0.5 M H₂SO₄ solution at 60 °C.

RESULTS AND DISCUSSION

For the effective performance of Pt/CNT electrode, CNTs need to be highly dispersed and homogeneous in shape and size on carbon paper. Therefore, carbon paper was electrochemically treated in H₂SO₄ solution for the increase of surface wettability. Then Ni particles were deposited by ultrasonic treatment in Ni precursor solution for 5 min. The SEM image in Fig. 1(a) indicates highly dispersed Ni particles on carbon paper, which are mostly present in 5–20 nm of diameter. CNTs were grown on carbon paper by CVD of acetylene in a quartz tube reactor at 700 °C for 1 h, and the results are shown in Fig. 1(b) and (c). Fig. 1(b) shows the CNTs grown on carbon paper. Pt particles were electrochemically deposited on CNT/carbon paper (Fig. 1(c)) and their particle size below 2 nm and the high dispersion were observed by TEM as shown in Fig. 2(a).

Pt/CNT catalysts were synthesized by ECD and wet impregnation, respectively. The amounts of Pt in Pt/CNT and Pt/CNT/car-

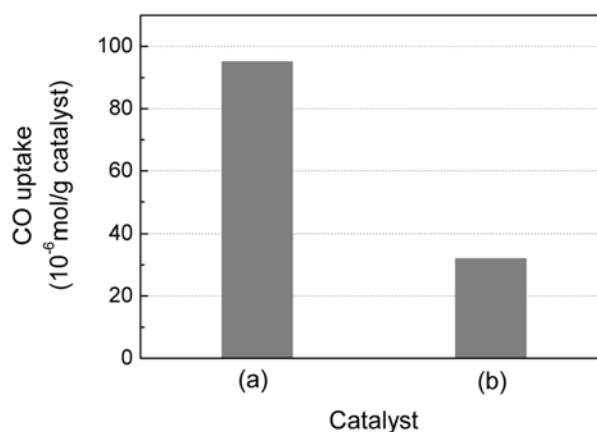


Fig. 3. CO uptake of Pt/CNT catalyst prepared by (a) ECD and (b) wet impregnation.

bon paper were measured by ICP-OES and the results are presented in Table 1. Both catalysts show similar Pt loading, where the Pt loadings are 9.7 wt% in the case of ECD and 9.9 wt% in the case of wet-impregnation. It is noteworthy that the size of Pt particles is much smaller on the former catalyst (<2 nm) than on the latter one (2–8 nm). Also, the former catalyst shows smaller size and higher dispersion of Pt particles, which can be confirmed by Fig. 2. Compared to the wet impregnated catalyst, the catalyst prepared by ECD shows higher dispersion of Pt particles and a narrow distribution of Pt particle size. It is noteworthy that the size of Pt particles is much smaller on the former catalyst (<2 nm) than on the latter one (2–8 nm).

In the CO chemisorption results (Fig. 3), the amount of adsorbed CO on Pt/CNT prepared by ECD is about 3 times larger than those on wet impregnated one. This result indicates that the amounts of catalytic sites is much more in the former catalyst than in the latter one, which is due to the reduction of particle size. This result can be confirmed by TEM results in Fig. 2. That is, the former catalyst contains larger amount of highly dispersed Pt nano particles than the latter one. Accordingly, the former has larger amount of catalytic sites than the latter. In the case of Fig. 2(b), on the contrary, Pt particles are often agglomerated to form bigger particles which leads to a little amount of catalytic sites.

Similar trends are observed in mass activity as shown in Fig. 4. The mass activity of Pt/CNT prepared by ECD is more than 3 times higher compared to that of the wet-impregnated catalyst. This re-

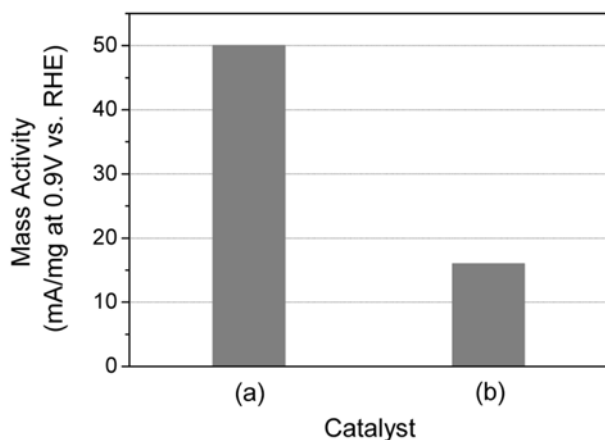


Fig. 4. Mass activity of Pt/CNT catalyst prepared by (a) ECD and (b) wet impregnation. The activity for oxygen reduction was measured at 0.9 V vs. RHE in 0.5 M H₂SO₄ aqueous solution at 60 °C.

sult can be explained with the effect of particle size and the dispersion of Pt particles. Comparing the CO chemisorption results with the mass activity data, it is worth noting that the activity of the wet-impregnated Pt particles exhibited in Fig. 4(b) is slightly less than that expected from the results of CO uptake in Fig. 3(b). In general, catalytic activity is enhanced by reducing the particle size, which is caused by the increased amounts of catalytic sites and the strong metal support interaction. Thus, it is considered that all the Pt particles of the wet-impregnated catalysts are not the same in mass activity and the small Pt particles would be more active than the larger ones [8].

CONCLUSIONS

ECD is a useful technique for the preparation of nano-sized and

highly dispersed Pt catalyst. In SEM and TEM results, Pt particles synthesized by ECD are much smaller (<2 nm) than those prepared by wet impregnation (2-8 nm). The amount of adsorbed CO on the former catalyst is about 3 times larger than the latter one. Moreover, the mass activity is more than 3 times higher in the case of the former than the latter. These results are caused by the reduction of Pt particle size and the enhancement of metal dispersion. Consequently, the performance of fuel cell electrode can be significantly enhanced by directly growing CNTs on carbon paper and then synthesizing Pt nanoparticles on them by ECD technique. Future work would involve performance and resistance tests of MEA composed of Pt/CNT/carbon paper electrode.

REFERENCES

1. A. K. M. Fazle Kibria, Y. H. Mo, M. H. Yun, M. J. Kim and K. S. Nahm, *Korean J. Chem. Eng.*, **18**, 208 (2001).
2. M. Shajahan, Y. H. Mo and K. S. Nahm, *Korean J. Chem. Eng.*, **20**, 566 (2003).
3. Y. Mu, H. Liang, J. Hu, L. Jiang and L. Wan, *J. Phys. Chem. B*, **109**, 22212 (2005).
4. W. Li, X. Wang, Z. Chen, M. Waje and Y. Yan, *J. Phys. Chem. B*, **110**, 15353 (2006).
5. Z. Liu, X. Lin, J. Y. Lee, W. Zhang, M. Han and L. M. Gan, *Langmuir*, **18**, 4054 (2002).
6. J. M. Planeix, N. Coustel, B. Coq, V. Brotons, P. S. Kumbhar, R. Dutartre, P. Geneste, P. Bernier and P. M. Ajayan, *J. Am. Chem. Soc.*, **116**, 7935 (1994).
7. Z. He, J. Chen, D. Liu, H. Tang, W. Deng and Y. Kuang, *Mater. Chem. Phys.*, **85**, 396 (2004).
8. A. Guha, W. Lu, T. A. Zawodzinski Jr. and D. A. Schiraldi, *Carbon*, **45**, 1506 (2007).