Nano-structured Carbon Support for Pt/C Anode Catalyst in Direct Methanol Fuel Cell

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Abstract   Platinum catalysts for the DMFC (Direct Methanol Fuel Cell) were impregnated on several carbon supports and their catalytic activities were evaluated with cyclic voltammograms of methanol electro-oxidation. To increase the activities of the Pt/C catalyst, carbon supports with high electric conductivity such as mesoporous carbon, carbon nanofiber, and carbon nanotube were employed. The Pt/e-CNF (etched carbon nanofiber) catalyst showed higher maximum current density of 70 mA cm^{-2} and lower on-set voltage of 0.54 V vs. NHE than the Pt/Vulcan XC-72 in methanol oxidation. Although the carbon named by CNT (carbon nanotube) series turned out to have larger BET surface area than the carbon named by CNF (carbon nanofiber) series, the Pt catalysts supported on the CNT series were less active than those on the CNF series due to their lower electric conductivity and lower availability of pores for Pt loading. Considering that the BET surface area and electric conductivity of the e-CNF were similar to those of the Vulcan XC-72, smaller Pt particle size of the Pt/e-CNF catalyst and stronger metal-support interaction were believed to be the main reason for its higher catalytic activity.

Keywords : Direct methanol fuel cell, Platinum, Carbon, Methanol electro-oxidation

1. Introduction

The direct methanol fuel cell (DMFC) has been highlighted as an alternative energy source for mobile electric devices[1]. Unlike other types of fuel cell, the DMFC needs no fuel processor to reform hydrocarbon fuels, making DMFC advantageous for application in small and portable devices. Unfortunately, however, currently developed DMFCs have low power density problem due to insufficient activity of the anode catalyst. To operate the DMFC with better performance, one of the most urgent technologies to develop is preparing the highly active anode catalyst for electro-oxidation of methanol, the fuel, and, accordingly, many studies have been carried out[2-4]. To date, Pt-based alloys are known to be the most active catalysts for this oxidation reaction. Therefore, major researches have endeavored to develop bimetallic and even ternary metallic catalysts with Pt as a main catalytic material.

As another route to enhance catalytic performance, there have been several attempts to improve catalyst support. In general, a promising support material should have large surface area for metal dispersion, strong structural stability, and high electric conductivity. So far the most confident support for Pt-based catalysts is carbon, especially nano-structured carbon[5-6].

In this paper, we synthesized four different types of nano-structured carbons to upgrade their use as support for Pt-based catalyst. Effect of microstructure of the prepared carbons on surface area and electric conductivity were elucidated.

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2. Experimental

2.1. Catalyst preparation

The 20 wt% Pt catalysts for the anode of the DMFC were impregnated by the conventional impregnation method on the synthesized carbon nanotubes (CNT) and carbon nanofibers (CNF)[7]. The carbon nanotubes and the carbon nanofibers were prepared with CO/H_2 mixture and labeled e-CNT and e-CNF for the etched carbon nanotube and etched carbon nanofibers, respectively. $H_2PtCl_6 \cdot 6H_2O$ (Acros, ACS reagent) was used as a Pt precursor. The metal precursor was dissolved in deionized water (5.4×10^{-8} S cm^{-1}), and impregnated on carbon support and then dried, milled, and thermally treated in the reducing atmosphere of 5 vol% H_2/N_2 gas stream.

2.2. Catalyst evaluation

The activities of the newly prepared catalysts were evaluated with the maximum current density of electro-oxidation of methanol in the half cell test. The half cell employed was a three-electrode cell system. One molar concentration of methanol was used as fuel. The catalyst was loaded with Nafion binder onto a graphite rod (Gamry Instruments, 935-00003) for a working electrode. A Pt mesh electrode (Princeton Applied Research, 219810) and a saturated calomel electrode (Princeton Applied Research, K0077) were used as a counter electrode and a reference electrode, respectively. All the potential employed in this paper were recorded with respect to a normal hydrogen electrode (NHE). The activity test was carried out in a 0.5 M H_2SO_4 aqueous solution after nitrogen purging for removal of dissolved oxygen in the water. Cyclic voltammogram was recorded with a potentiostat (Gamry Instruments, PC4/750) at the constant temperature of 40°C in a water-jacket reactor.

2.4. Characterization

The BET surface area and the pore size distribu-

tion were determined by N_2 adsorption using a porosimetry analyzer (Micromeritics, ASAP 2010). Electric conductivity was measured using four-point probing system (Keithley, 2400). Electron microscopic images were obtained using a TEM (JEOL, JEM-2000EXII) at 200 kV voltage.

3. Results and discussion

Platinum catalysts impregnated on several carbon supports were prepared and their catalytic activities were measured by cyclic voltammograms of methanol electro-oxidation. The carbon supports employed in this study include mesoporous carbon, carbon nanotube and carbon nanofiber. The platinum on a commercial carbon, Vulcan XC-72, was used as a reference catalyst. The mesoporous carbon was prepared by carbonization at 850°C by following the recipe described elsewhere[8]. Although the prepared mesoporous carbon turned out to have extremely large surface area of 1,940 m^2 g^{-1}, the platinum on the mesoporous carbon showed no activity in methanol electro-oxidation. It was due to the very low electric conductivity of the mesoporous carbon, two orders lower than that of Vulcan XC-72. Despite its large surface area which indicates that catalytically active Pt metal can be well-dispersed, low conductivity seemed deteriorate its use as a support. In fact, the electro-oxidation reaction on platinum metal produces electron that must be transferred to current collector through carbon support. Therefore, not only the intra-electric conductivity of the material but also the inter-electric conductivity, the contact electric conductivity, between carbon particles is important for a good support. As an effort to increase electric conductivity of the mesoporous carbon, the carbonization temperature was increased from 850°C to 1,050°C. It is well known that up to 1,300°C, increasing carbonization temperature usually results in increased electric conductivity by increasing graphitization and concentration of positive hole[9]. The resulting carbon material had less

Table 1. Characteristics of the prepared carbon supports and platinum crystallite sizes on the supports measured by X-ray diffractometer

Support	CNT	e-CNT*	CNF	e-CNF*	Vulcan XC-72
Electric conductivity (S cm⁻¹)	0.28	0.17	8.3	6.5	5.4
BET surface area (m² g⁻¹)	212	510	95	218	225
Pt crystallite size (nm)	9.2	8.5	7.4	7.2	8.4

*e-CNT and e-CNF represent the etched CNT and the etched CNF, respectively, as illustrated in experimental section.

surface area (1,400 m² g⁻¹) and one order higher electric conductivity (2×10^{-1} S cm⁻¹). Although we were successful in increasing electric conductivity of the mesoporous carbon by applying higher carbonization temperature, the overall performance measured by maximum current density of the catalyst was not as good as that of the Pt/Vulcan XC-72.

In order to increase the electric conductivity of carbon support more, CNT and CNF materials were synthesized. The physical properties of those carbon materials and the crystallite size of Pt supported on those carbons measured by XRD are summarized in Table 1. The electric conductivities of the carbon nanofibers were greater than that of Vulcan XC-72, while those of carbon nanotubes were an order lower. When the carbon nanotube and the carbon nanofiber were etched with acid, the BET surface areas increased more than 2 times. The maximum current density and the on-set voltage of the Pt/C catalysts are compared in Fig. 1. The Pt/e-CNF (etched carbon nanofiber) catalyst showed the highest maximum current density of 70 mA cm⁻² and the lowest on-set voltage of 0.54 V vs. NHE, far better than the Pt catalyst on Vulcan XC-72, the reference catalyst. While the surface area and electric conductivity of the e-CNF are similar to those of Vulcan XC-72, the supported Pt crystallite on e-CNF is approximately 14% smaller than the Pt on Vulcan XC-72. This corresponds to approximately 17% increase in metal dispersion. Higher metal dispersion usually means better usage of loaded metal for catalysis. In addition, stronger Pt-support interaction by surface modification with acid is believed to result in better catalytic performance as men-
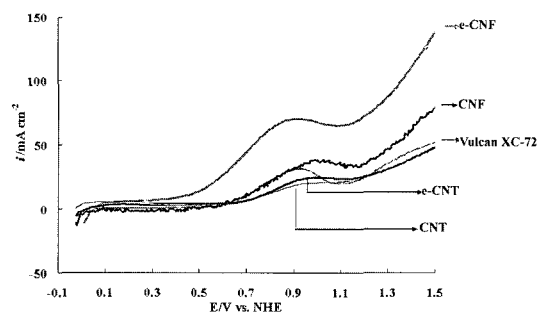

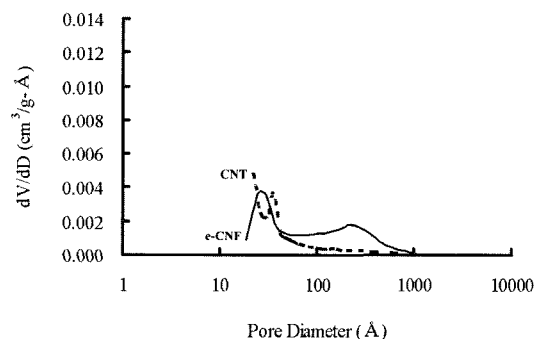**Fig. 1. Catalytic activities of the Pt catalysts supported on various carbon supports.**

Fig. 2. Pore size distributions of the CNT and the e-CNF.

ioned by Baker et al.[10] These two seem to be a reason for the far better performance of the Pt/e-CNF than that of Pt/Vulcan XC-72. We are currently investigating the relationship between surface modification with acid and catalytic performance. Despite larger surface areas of CNT materials, whether etched or not, the Pt catalysts supported on CNT materials were not as active as the reference catalyst due to their lower electric conductivities and lower availability of pores as discussed below.

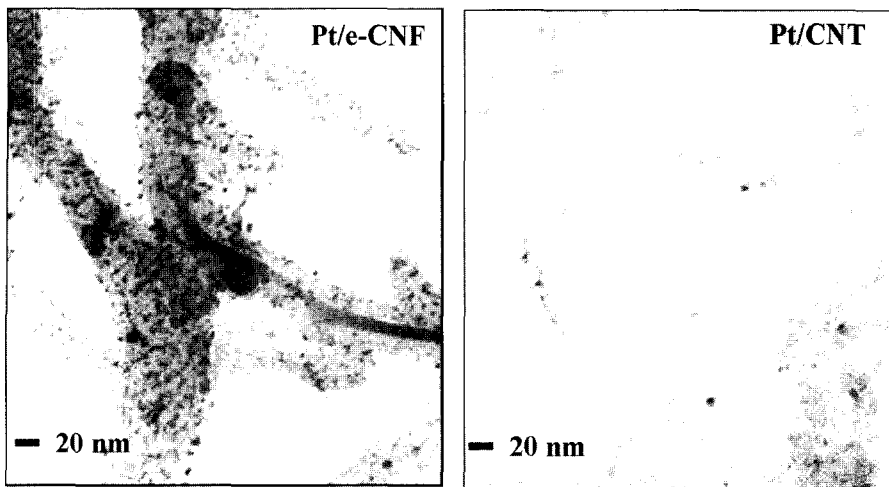Pore size distributions (PSD) of CNT and e-CNF

Fig. 3. TEM images of the Pt/e-CNF catalyst and the Pt/CNT catalyst.

were illustrated in Fig. 2. Those carbons were selected for comparison because of their similar BET surface areas. While the e-CNF is a mesoporous carbon with a considerable fraction of large pores greater than 10 nm, the CNT is a microporous carbon with a negligible fraction of large pores. Considering Pt crystallite sizes of 7.2~9.2 nm, microporous carbons such as the CNT series should provide less effective surface area for supporting Pt particles. This should result in the formation of bigger Pt particles when 20 wt% of Pt was loaded on the support. Although the CNT had a similar BET surface area compared to the e-CNF, the surface availability of CNT for Pt loading should be far worse than that of the e-CNF. This can be evidenced by TEM images in Fig. 3. The dispersion of Pt particles loaded on e-CNF was much better than that of Pt particles loaded on the CNT.

4. Summary

Based on the methanol electro-oxidation study for DMFC application, the Pt/e-CNF anode catalyst showed the highest catalytic activity among the supported Pt catalysts on several carbon materials. Its maximum current density and on-set voltage vs. NHE

were 70 mA cm^{-2} and 0.54 V, respectively, far better than those of the Pt/Vulcan XC-72. Considering the similar BET surface area and electric conductivity of the e-CNF compared with those of the Vulcan XC-72, smaller Pt particle size of the Pt/e-CNF catalyst and stronger metal-support interaction seem to be the principal reason for its higher catalytic activity.

Because of the low contact electric conductivities of the mesoporous carbons and the carbon nanotube materials, giving larger surface area did not contribute to better catalytic performance when platinum was loaded.

Acknowledgements

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