— **Communication** —

Carbon Nanotube and Carbon Black Supported Platinum Nanocomposites as Oxygen Reduction Electrocatalysts for Polymer Electrolyte Fuel Cells

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Pt supported on a binary support of multi-walled carbon nanotube (CNT) and carbon black (CB) with different ratio of CNT and CB (Pt/CNT-CB) has been prepared by reducing H_2PtCl_6 with ethylene glycol. Pt/CNT-CB (CNT/CB = 50/50, 80/20), Pt/CB and Pt/CNT have been used as electrocatalysts for cathode in polymer electrolyte fuel cells (PEFC). In the low current density region, the cathode with a CNT/CB ratio of 50/50 shows the best performance as compared to CNT based catalyst. Whereas in the high current density region, the cathode with a CNT/CB ratio of 80/20 exhibits the best performance.

Key Words : Carbon Nanotubes, Carbon Black, Binary Support, Fuel Cell

1 Introduction

Since its discovery,[1] carbon nanotubes (CNT) have attracted much attention due to its unique electrical, mechanical and morphological properties. For polymer electrolyte fuel cells (PEFCs), CNT has been studied as a novel catalyst supporting material.[2-15] It was reported that the performance of the fuel cells with CNT support is higher than with carbon black (CB) support.[2-5] In addition the graphitic nature of CNTs provides better corrosion resistance in the acidic environment of PEFC. This is important from durability point of view, since support (CB) corrosion is one of the important factors for the aggregation of Pt particles during the PEFC operation which leads to the loss of electrochemically active surface area of Pt and hence the performance over a period of time. One reason for the higher performance for Pt supported CNT electrode based cathode in PEFCs is that CNTs have higher electrical conductivity than CB,[2] and the other is that CNT supported catalyst leads to better mass transport in the catalyst layer.[4] The facile mass transport is due to the unique tubular morphology of CNT. On the other hand CB supported catalyst, due to its fine particulate morphology, tends to form a dense catalyst layer, while for CNT, the catalyst layer is open because of its fibrous structure. Thus from the point of view of structure openness as well as the electrical conductivity, CNT is a better catalyst support.

Another important factor to consider for better fuel cell performance is the thickness of the catalyst layer.[16,17] Usually a thinner catalyst layer is desirable in that it shortens the distance that the protons, electrons and gas molecules have to traverse. In this aspect, CB is advantageous as the catalyst support due to the dense structure of the catalyst layer.

A binary support of CNT and CB may be able to combine the advantages of each individual support while at the same time avoid their shortcomings. However, few studies related to binary support have been published and to date there is no report on the fuel cell performance with the use of a binary catalyst support.[18,19] In this work, we prepared membrane electrode assemblies (MEAs) with cathode catalyst on a CNT-CB binary support and investigated their PEFC performance.

2 Experimental

Carbon black (CB, Vulcan XC-72) and multi-walled carbon nanotube (CNT) were purchased from Cabot Corporation and Material & Electrochemical Research Corporation, respectively. To achieve uniform Pt deposition on the outer wall of the nanotube, the surface of CNT was oxidized under reflux condition in a mixture of 2.0 M H_2SO_4 and 3.7 M HNO_3 for 4 h at 110℃. Pt deposition was conducted using H_2PtCl_6 as a precursor and ethylene glycol as a reducing regent. The oxidized CNT was mixed with CB and H_2PtCl_6 in ethylene glycol. The weight ratio of CNT/CB in the ethylene glycol solution was 50/50 or 80/20. After adjusting the pH of the solution to above 13 with 1 M NaOH in ethylene glycol, the mixture was held at 140℃ for 3 h under N_2 atmosphere to reduce Pt. Since the deposited Pt nanoparticles were stabilized by oxalate anion, which is an intermediate originated from ethylene glycol, the Pt particles were well dispersed in the reaction bath.[13] Then pH was adjusted to 3 with 1 M HCl aqueous solution. By this pro-

cedure, stabilizers (oxalate anions) were protonated and desorbed from Pt surface. At this moment, Pt nanoparticles could deposit on the support. After filtration, washing with de-ionized water (80℃) and then drying at 90℃ under vacuum overnight, the catalyst with binary support (Pt/CNT-CB) was obtained with a Pt loading of 30 wt%. Catalysts with single support (Pt/CNT and Pt/CB) were prepared by the same procedure as in the case of binary support except for that only one support was used.

In the MEA, both cathode and anode consist of carbon paper backing layer with 10 wt% Teflon, gas diffusion layer and catalyst layer. The diffusion layer was prepared by brush-painting a paste containing 5 wt% Teflon suspension, carbon black and ethanol on a Teflon-treated carbon paper (Toray), followed by annealing at 240℃ for 30 min then 340℃ for 30 min. Carbon loading in the diffusion layer was 4 mg/cm^2. The catalyst layer was prepared on diffusion layer by spraying a paste containing catalyst, Nafion solution and ethanol onto the diffusion layer, followed by drying. Nafion percent (= Nafion weight divided by the sum of Nafion weight and catalyst weight) in the catalyst layer was 20%. A Nafion solution (5 wt%) was finally sprayed on the catalyst layer (1.0 mg-Nafion/cm^2) to form a thin Nafion layer. For anode, Pt/CB was used as the catalyst. Pt loadings of cathode and anode were 0.25 mg/cm^2 and 0.20 mg/cm^2, respectively. The MEA was obtained by hot pressing the cathode, Nafion 112 membrane and the anode with a pressure of 140 atm at 140℃ for 1 min. Before use in the MEA, Nafion 112 membranes were washed by consecutive boiling treatments in 3% H_2O_2 solution, in pure water, in 0.5 M H_2SO_4 solution, and in pure water.

Fuel cell performance was measured in an Arbin Instruments test station. The tests were performed using a cell temperature of 70℃, oxygen gas temperature of 70℃ and hydrogen gas temperature of 80℃. The gas pressures were 35 psig. The gas flow rates were 0.2 slm (standard liter per minute). Both oxygen and hydrogen gases were humidified by passing through humidifiers filled with de-ionized water at 70℃ and 80℃, respectively.

The catalysts were characterized by transmission electron microscopy (TEM) using a Philips TECNI12 microscope, and X-ray diffraction (XRD) analysis using a Bruker AXS D8 Advance diffractometer with Cu Kα radiation ($\lambda_{K\alpha l}$ = 1.5418 Å).

3 Results and Discussion

Figure 1 shows the TEM images of Pt/CNT-CB with a CNT/CB ratio of 80/20. Pt nanoparticles are deposited homogeneously on both CNT (Fig. 1a) and CB (Fig. 1b) with narrow particle size distribution. The images are the same as those on single support of CNT and CB.[2,3,12,13]

XRD patterns of Pt/CNT-CB (80/20) were shown in Fig. 2. The diffraction peaks at 26.5°, 42.4°, 54.7° and 77.4° can be ascribed to the (002), (100), (004) and (110) reflections of carbon with the hexagonal graphite struc-
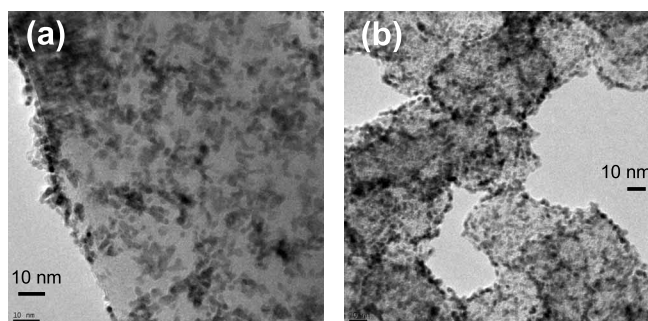

Fig. 1 TEM images of Pt on (a) CNT and (b) CB in the binary catalyst support with the CNT/CB ratio of 80/20.
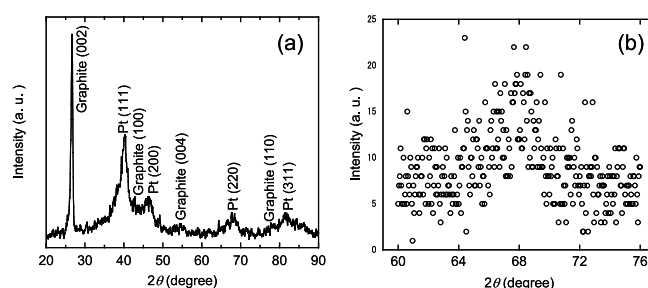

Fig. 2 (a) Powder XRD pattern of Pt/CNT-CB with CNT/CB = 80/20. (b) Magnified Pt (220) diffraction peak of Pt/CNT-CB with CNT/CB = 80/20.

ture (Fig. 2a).[2] If the support is composed of CB only, the sharp (002) peak cannot be observed. The binary support has a hexagonal graphite structure with a sharp (002) diffraction peak, which is originated from CNT, indicating that CNT has graphite structure as shown in Fig. 6 in ref. 2 even after Pt deposition. The Pt diffraction peaks at 39.7° (111), 46.2° (200), 67.4° (220), and 81.2° (311) show that Pt particles are present in the face-centered cubic structure. Because Pt (220) peak is isolated from the graphite diffraction peaks (Fig. 2b), the mean Pt particle size can be calculated from this peak using Scherrer's equation.

$$L = \frac{0.9\lambda_{K\alpha l}}{B_{(2\theta)} \cos\theta_{max}} \tag{1}$$

L is the mean Pt particle size, $\lambda_{K\alpha l}$ is the X-ray wave length (1.5418 Å), θ_{max} is the angle at maximum height in (220) peak and $B_{(2\theta)}$ is the half peak width of (220) peak in radians. The calculated mean Pt particle size is 2.74 nm. The mean Pt particle size of the other three Pt/CNT-CB catalysts are 2.35 nm (0:100), 2.11 nm (50:50), 2.63 nm (100:0), respectively (XRD patterns are not shown). Since this study is designed to focus on the effects of the support, it is highly desirable to have similar Pt particle size on the supports used. From the XRD and TEM results, all of the four catalysts have similar mean Pt particle size (from 2.2 to 2.7 nm), and thus the Pt particle size may not play a major role on the MEA performance.

The fuel cell polarization curves are shown in Fig. 3. Since the effects of catalyst layer structural openness and thickness on cell performance are closely correlated
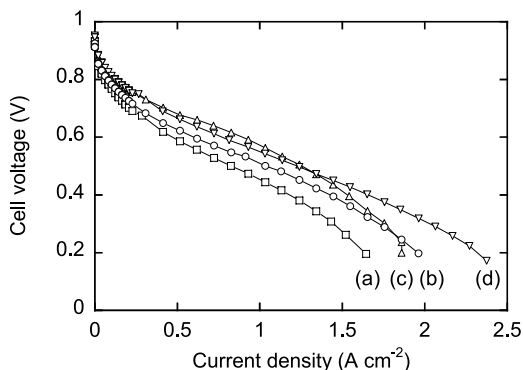
Fig. 3 Cell performance of MEA with (a) Pt-CB, (b) Pt-CNT, (c) Pt/CNT-CB with a CNT/CB ratio of 50/50 and (d) Pt/CNT-CB with a CNT/CB ratio of 80/20.
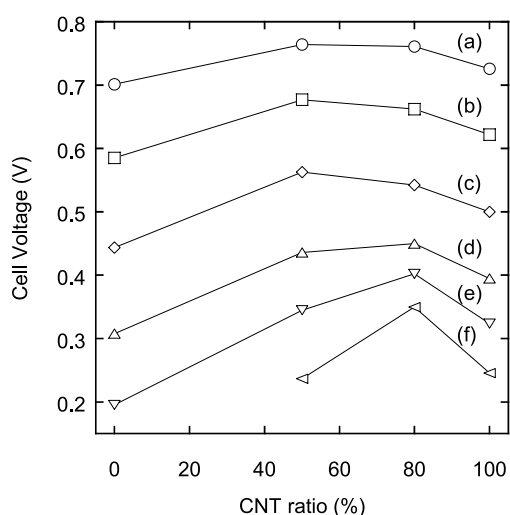

Fig. 4 Plots of cell voltage as a function of CNT ratio in the catalyst support at the current density of (a) 0.20 A/cm^2, (b) 0.50 A/cm^2, (c) 1.00 A/cm^2, (d) 1.40 A/cm^2, (e) 1.65 A/cm^2, and (f) 1.86 A/cm^2.

with the current density, the data in Fig. 3 are re-plotted in Fig. 4. Over all of the current ranges tested, the MEA with Pt/CNT exhibits higher performance than with Pt/CB, possibly due to the unique morphology and higher electrical conductivity of CNT.[2,3,12] Also over the whole current density ranges, the Pt/CNT-CB based MEAs show higher performance than with Pt/CNT and with Pt/CB suggesting that it is better to use a binary support. It is interesting to note that in the low to medium current density range, the CNT/CB 50/50 support performs the best, but at the high current region, the highest performance shits to the CNT/CB 80/20 support. It is known that as the current density increases, the mass transport of the reactants, protons within the catalyst layer becomes the limiting factor for the performance. As discussed previously, while CNT based catalyst layer provides mass transfer benefit due to the tubular morphology of CNTs, the thickness of the catalyst layer is higher for CNT based catalyst layer as compared to CB based catalyst layer. This contrasting trend suggests that there should be an optimum performance

with the combination of the CNT and CB supports which explains highest performance for the CNT/CB 80/20 support. This result is consistent with the hypothesis of this study in that as current density increases, the mass transport needs are increased and thus a more open electrocatalyst layer is preferred, which is provided by the binary support with more CNTs. These findings show that it is advantageous to use a binary support of CNT and CB, and furthermore, the cell performance can be optimized by adjusting the ratio of CNT/CB in the catalyst support. In addition, the approach demonstrated here suggests that using a mixed support could be a new design strategy for improved cell performance that has so far not been adequately explored.

Conclusion

The mixture of CNT and CB was used as a binary Pt support. Pt nano-particles were deposited homogeneously on both CNT and CB by chemical reduction of H_2PtCl_6 using ethylene glycol as a reducing agent. An MEA with binary catalyst support (Pt-CNT/CB) exhibited higher performance than with single supports (Pt-CNT or Pt-CB). In the middle current region, MEA with support having the CNT/CB ratio of 50/50 showed the best performance whereas in higher current region MEA with CNT/CB = 80/20 showed the best. By choosing appropriate CNT ratio, cell performance can be optimized.

Acknowledgement

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