

Short communication

# Effects of chemical treatment of carbon supports on electrochemical behaviors for platinum catalysts of fuel cells

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## Abstract

Carbon-supported metal nanoclusters were prepared by chemical method of Pt precursor reduction onto chemically treated carbon blacks (CBs). The size and the loading level of Pt metal clusters were dependent on surface characteristics of CBs. Base-treated CBs-supported Pt showed the smallest particle size of 2.65 nm and the highest loading level of 97% among the chemical-treated CBs-supported Pt catalysts. The electroactivity of the catalysts had been enhanced when the CBs supports were treated by basic or neutral agents, while the electroactivity had been decayed for the acid-treated CBs-supported Pt.

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## 1. Introduction

Many types of fuel cells are attracting much attention as clean power sources for mobile devices or electric vehicles and on-site power generation systems due to their high-energy conversion efficiency and low emission of pollutants [1–4]. Generally, platinum (Pt) or platinum alloy-based nanoclusters, which are impregnated on carbon supports, are the best electrocatalysts for anodic and cathodic reaction of direct methanol fuel cells (DMFCs). These catalyst materials are very expensive, and thus there is a need to minimize the catalyst loading, without sacrificing electro-catalytic activity. One way to maximize catalyst utilization is to enhance the external Pt specific surface area per unit mass of Pt. The most efficient way to achieve this goal is to reduce the size of the Pt clusters.

Among a variety of routes for a synthesis of nanocluster electrocatalysts, the colloidal methods [5,6] have the advantage to produce small and homogeneously distributed carbon-supported metal nanoclusters. Still, the search for alternative routes to produce carbon-supported metal nanoclusters is a critical theme in these research areas. It is reported that the particle size and the loading level of Pt-based catalysts are key factors that determine

their electrochemical activity and cell performance for DMFCs [4,7,8].

For support materials of catalysts, carbon blacks (CBs) are generally used due to a good electronic conductivity and a high specific surface area. However, the effect of surface characteristics of carbon materials on the preparation and electrochemistry of catalysts have not fully studied to our best knowledge. In the present study, the size and the loading level of metal particles have been investigated by modifying the carbon supports of the platinum catalysts. The objective of this study is to investigate the influences of chemical modification of carbon supports on the preparation and electrochemical behaviors of carbon-supported platinum catalysts.

## 2. Experimental

### 2.1. Preparation of carbon-supported Pt nanoclusters

Carbon-supported Pt nanoclusters were prepared by using a modified polyol synthesis method as reported before [9,10]. Carbon materials (500 mg) were suspended and stirred with ultrasonic treatment for 20 min in ethylene glycol (EG) solution and then 104 mg hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) (Pt: 50 mg, Pt weight percent is 10% against the carbon materials) dissolved EG solution was added dropwise slowly to the above solution and stirred mechanically for 4 h. A 1.0 M NaOH solution was

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added to adjust pH of the solution, and then the solution was heated at 140 °C for 3 h for a complete reduction of Pt. The whole preparation process was conducted under flowing argon gas. The solid of carbon-supported Pt (Pt/C) was filtered and washed with 2 L of deionized water and then dried at 70 °C for 24 h.

## 2.2. Chemical treatments and parameter measurements of carbon blacks

The virgin carbon blacks (VCB) supplied by Korea Carbon Black Co. was used in our experiments. This has an average particle size of 24 nm, DBP adsorption of 153 cm<sup>3</sup>/100 g and specific surface area of 112 m<sup>2</sup> g<sup>-1</sup>. The neutral-treated carbon blacks (NCB), base-treated carbon blacks (BCB), and acid-treated carbon blacks (ACB) were prepared by treating CBs with 0.2N C<sub>6</sub>H<sub>6</sub>, 0.2N KOH, and 0.2N H<sub>3</sub>PO<sub>4</sub>, respectively.

The acid and base values of the surface functional groups of the samples were determined by Boehm's titration method [11]. The specific surface areas ( $S_{\text{BET}}$  [12]) of the samples were determined by gas adsorption. The physical adsorption of gases was used to characterize the CBs support, and adsorbate used was N<sub>2</sub> at 77 K with automated adsorption apparatus (Micromeritics, ASAP 2400). To analyze the functional group of carbon surface, infrared (IR) spectroscopy for the chemical-treated CBs was investigated (FTS-165 spectrometer, Bio-Rad Co.).

## 2.3. Structural measurements of Pt-supported carbon blacks

All of the carbon-supported Pt catalyst (Pt/C) samples were characterized by recording their X-ray diffraction (XRD) patterns on a Rigaku X-ray diffractometer (Model D/Max-III B) using Cu K $\alpha$  radiation with Ni filter. Pt loading level was calculated by considering the atomic ratio of Pt intensity against carbon intensity by using energy dispersive X-ray spectroscopy (EDS) method.

## 3. Results and discussion

Table 1 shows the results of surface and adsorption properties of the carbon blacks before and after chemical treatments. It can be clearly seen that the chemical treatments influences acid–base surface values, and specific surface areas ( $S_{\text{BET}}$ ) of the CBs. As shown in Table 1, the base surface value, and specific surface area of the sample ACB show the prominent changes in compared to VCB. This result indicates that the strong acid–base

Table 1  
Results of surface and adsorption parameters of the carbon blacks

Carbon blacks	Acid value (mequiv. g <sup>-1</sup> )	Base value (mequiv. g <sup>-1</sup> )	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )
VCB	50	70	112
NCB	40	58	114
BCB	70	90	118
ACB	110	13	28

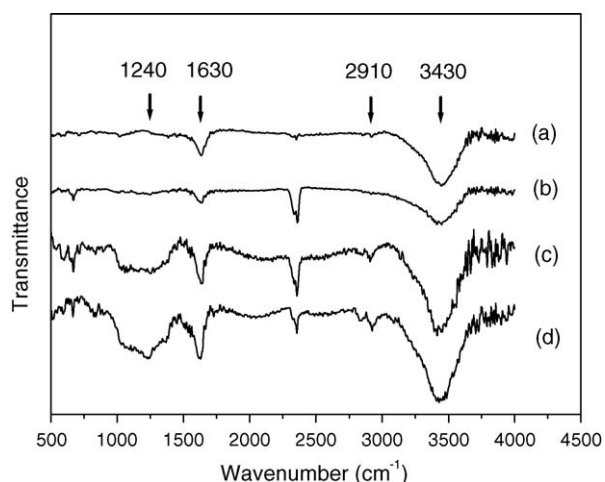


Fig. 1. IR spectra of (a) VCB, (b) NCB, (c) BCB, and (d) ACB.

reaction is happened between the originally rather basic carbon surface and the acidic chemical solution. This can bring the micro-pore degradation or blocking. It is thought that the acidic treatment leads to an increase of aggregation of CBs, resulting in increasing the crystalline size and the concentration of crystalline boundaries as a typical turbostratic structure of CBs. On the other hand, BCB shows an increased base value and a slight enhanced specific surface area.

To analyze the functional groups of carbon surface, IR spectroscopy for the treated CBs was investigated and demonstrated in Fig. 1. The VCB shows the characteristic peaks at 3430, 2910, 1630 and 1240 cm<sup>-1</sup>. These peaks can be assigned to hydroxyl group (O–H), aliphatic (C–H), carboxyl/ester groups (C=O), and ether groups (C–O–C), respectively [13]. ACB shows the enhanced peak intensity at 2910, 1630, and 1240 cm<sup>-1</sup>, because the oxidized groups are developed by an acid treatment with carbon surface. BCB shows that the intensity of peaks is slightly increased due to the oxidized reaction of carbon surface with oxygen in basic solution. In contrast to this, NCB shows a decreased peak intensity of all characteristic peaks. Consequently, the functional groups of carbon surface were changed effectively by acid or base chemical treatments.

Fig. 2 shows the detailed Pt (2 2 0) peaks in the powder XRD patterns of carbon-supported Pt (Pt/C) catalysts. It clearly shows that Pt/VCB, Pt/NCB, Pt/BCB shows a broad peak at 67.6°. However, Pt (2 2 0) peak do not exists in the case of Pt/ACB. It explains that Pt is not effectively deposited onto carbon surface. It is probably thought that Pt reduction reaction is not fully performed due to the high acidic characteristics of CBs surface.

The average size of Pt nanoclusters was calculated by using Scherrer equation [14] and was demonstrated in Table 2:

$$L_c = \frac{K\lambda}{B \cos \theta} \quad (1)$$

where  $L_c$  is the average crystalline size of the Pt particles,  $K$  the Scherrer constant ( $\approx 0.89$ ),  $\lambda = 0.154$  nm,  $B$  the half-height width of the (2 2 0) diffraction line, and  $\theta$  is the Bragg angle in radian unit.

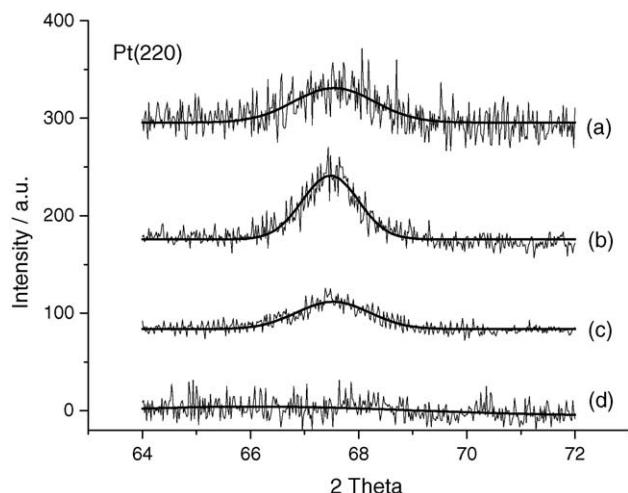


Fig. 2. Pt (2 2 0) peaks of X-ray diffraction patterns for (a) Pt/VCB, (b) Pt/NCB, (c) Pt/BCB, and (d) Pt/ACB.

In the case of Pt/BCB, the broadness of the peak is rather increased, meaning the size decrease of Pt nanoparticles. In the case of Pt/VCB, the average size of Pt is 3.01 nm, which is a typical size of Pt nanoparticles in the range of 3–5 nm [1,2]. In the case of Pt/BCB, the average size decreases to 2.65 nm. It is reported that basic condition is favored in the preparation of Pt nanoclusters-incorporated carbon supports because Pt precursor ( $\text{H}_2\text{PtCl}_6$ ) has to be reduced by a reducing agent [9,10]. On the other hand, ACB shows the smallest surface BET area of all samples due to a high degree of aggregation. In this viewpoint, Pt incorporation of carbon support is not easily available for the decreased specific surface area of ACB.

Platinum loading level can be calculated from the EDS experiments and summarized in Table 2. In the viewpoint of Pt loading level, Pt/BCB shows the highest value of 97% and Pt/ACB shows the lowest value of 65%. It explains that Pt incorporation onto carbon surface is favored in the case of basic chemical-treated CBs.

Fig. 3 shows the electroactivity of Pt catalysts supported on the various carbon supports by linear sweep voltammograms in 0.5 M  $\text{H}_2\text{SO}_4$  + 1.0 M MeOH. Anodic peaks for a methanol oxidation were shown at 640–670 mV for each sample. Pt/BCB and Pt/NCB show an increase in current density of anodic peak such as 0.83 and 0.76 mA, respectively, and more definite peak shape in compared to Pt/VCB. This means that the electrocatalytic activity has been enhanced when the CBs were treated by basic or neutral agents. However, Pt/ACB shows a decrease of cur-

Table 2  
Size and loading levels of platinum nanoclusters of Pt/VCB, Pt/NCB, Pt/BCB, and Pt/ACB

Sample	Average size (nm)	Loading level <sup>a</sup> (%)
Pt/VCB	3.07	91
Pt/NCB	3.74	93
Pt/BCB	2.65	97
Pt/ACB	–	65

<sup>a</sup> EDS measurements.

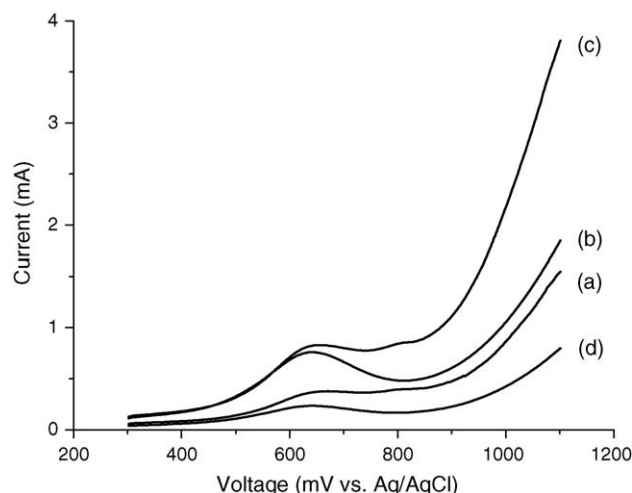


Fig. 3. Linear sweep voltammograms of (a) Pt/VCB, (b) Pt/NCB, (c) Pt/BCB, and (d) Pt/ACB.

rent density meaning that the electrocatalytic activity has been decayed. From this result, it can be concluded that the electrocatalytic activity are the best for the base-treated CBs-supported Pt.

Fig. 4 shows impedance plots of electrocatalysts in above solution. These plots were obtained by measuring ac impedance with changing a frequency from 1 to 100 MHz. The plots show a semi-circle like part at a higher frequency range and a linear part at a lower frequency range. When the imaginary part of impedance value is almost zero, the real part of impedance value indicates the charge-transfer resistance for catalyst electrode. In the case of Pt/NCB, the resistance decreased to  $23 \Omega \text{ cm}^{-1}$  when compared to  $29 \Omega \text{ cm}^{-1}$  for Pt/VCB. In the case of Pt/BCB, the resistance decreased further to  $11 \Omega \text{ cm}^{-1}$ , which shows the

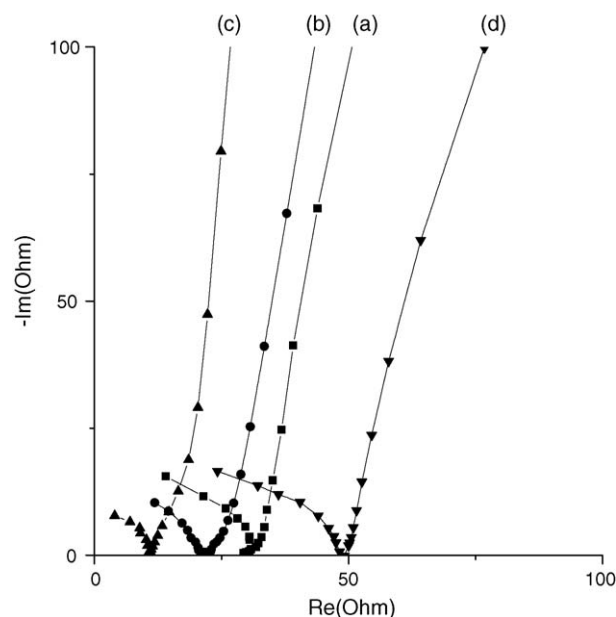


Fig. 4. Impedance plots of (a) Pt/VCB, (b) Pt/NCB, (c) Pt/BCB, and (d) Pt/ACB.

lowest resistance. In contrast with this, in the case of Pt/ACB, the resistance increased to  $49 \Omega \text{ cm}^{-1}$ , which shows the highest resistance. These resistance behaviors as a function of chemical treatments can explain the above electroactivity results. In other words, the resistance decrease can be one of the reasons for the enhancement of the electroactivity of Pt catalysts.

#### 4. Conclusions

The surface characteristics and the degree of aggregation of CBs had been changed by a chemical treatment. After Pt incorporation, base-treated CBs showed the smallest particle size of 2.65 nm and the highest loading level of 97%. In comparison with this, acid-treated CBs showed the lowest loading level. This result could be explained by the fact that probably base-treated carbon surface showed the well-distributed basic functional groups for the effective Pt reduction. A rather low loading level of Pt nanocluster deposited on acid-treated CBs was originated from the decreased specific surface area due to a high degree of aggregation and the strong acidic surface characteristics of CBs. The electroactivity of catalysts had been enhanced when the CBs supports were treated by basic or neutral agents, while the electroactivity had been decayed for the acid-

treated CBs-supported Pt. From the impedance results, Pt/BCB or Pt/NCB showed the reduced charge-transfer resistance, while Pt/ACB showed the increased resistance.

#### References

- [1] A.S. Arico, P. Creti, E. Modica, G. Monforte, V. Baglio, V. Antonucci, *Electrochim. Acta* 45 (2000) 4319.
- [2] T.C. Deivaraj, J.Y. Lee, *J. Power Sources* 142 (2005) 43.
- [3] Z. Liu, J.Y. Lee, W. Chen, M. Han, L.M. Gan, *Langmuir* 20 (2004) 181.
- [4] A. Hamnett, *Catal. Today* 38 (1997) 445.
- [5] H. Bonnemann, R. Brinkmann, W. Brijoux, E. Dinjus, T. Jousen, B. Korall, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1312.
- [6] M. Gotz, H. Wendt, *Electrochim. Acta* 43 (1998) 3637.
- [7] S.J. Park, H.J. Jung, C.W. Nah, *Polymer (Korea)* 27 (2003) 46.
- [8] H. Tang, J.H. Chen, Z.P. Huang, D.Z. Wang, Z.F. Ren, L.H. Nie, Y.F. Kuang, S.Z. Yao, *Carbon* 42 (2004) 191.
- [9] W. Li, C. Liang, J. Qiu, W. Zhou, H. Han, Z. Wei, G. Sun, Q. Xin, *Carbon* 40 (2002) 791.
- [10] W. Li, C. Liang, J. Qiu, W. Zhou, J. Qiu, Z. Zhou, G. Sun, Q. Xin, *J. Phys. Chem. B* 107 (2003) 6292.
- [11] H.P. Boehm, *Adv. Catal.* 16 (1966) 179.
- [12] S. Brunauer, P.H. Emmett, E. Teller, *J. Am. Chem. Soc.* 60 (1938) 309.
- [13] S.J. Park, K.D. Kim, *J. Colloid Interface Sci.* 212 (1999) 186.
- [14] K. Kinoshita, *Carbon: Electrochemical and Physicochemical Properties*, John Wiley, New York, 1988, pp. 31–34.