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Short communication

Influence of plasma treatment of carbon blacks on electrochemical activity of Pt/carbon blacks catalysts for DMFCs

Seok Kim [a], Mi-Hwa Cho [a], Jae-Rock Lee [a], Soo-Jin Park [b,*]

[a] *Advanced Material Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon 305-600, South Korea*
[b] *Department of Chemistry, Inha University, 253, Nam-gu, Incheon 402-751, South Korea*

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Abstract

In this work, in order to improve the dispersion of platinum catalysts deposited on carbon materials, the effects of surface plasma treatment of carbon blacks (CBs) were investigated. The surface characteristics of the CBs were determined by fourier transformed-infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), and Boehm's titration method. The electrochemical properties of the plasma-treated CBs-supported Pt (Pt/CBs) catalysts were analyzed by linear sweep voltammetry (LSV) experiments. From the results of FT-IR and acid–base values, N_2-plasma treatment of the CBs at 300 W intensity led to a formation of a free radical on the CBs. The peak intensity increased with increase of the treatment time, due to the formation of new basic functional groups (such as C–N, C=N, $–NH_3^+$, –NH, and =NH) by the free radical on the CBs. Accordingly, the basic values were enhanced by the basic functional groups. However, after a specific reaction time, N_2-plasma treatment could hardly influence on change of the surface functional groups of CBs, due to the disappearance of free radical. Consequently, it was found that optimal treatment time was 30 s for the best electro activity of Pt/CBs catalysts and the N_2-plasma treated Pt/CBs possessed the better electrochemical properties than the pristine Pt/CBs.
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Keywords: Carbon blacks; Platinum catalyst; Plasma treatment; Electrochemical behaviors

1. Introduction

Direct methanol fuel cells (DMFCs) are one of the promising candidates for a next generation of power sources for portable electronic devices. The ideal support material of electrocatalysts should have the following features: provide a high electrical conductivity, have adequate water-handling capability, and also show good corrosion resistance under oxidizing conditions [1–5].

A widely used supporting materials of catalysts are a carbon materials, on which metallic nanoclusters should be well dispersed to minimize a metal loading. Generally, electrocatalysts with a small particle size and a high dispersion results in high electrocatalytic activities. However, the effects of the preparation method and the structure of various carbon materials as a supporting material have not fully studied to our best knowledge [6–8].

Plasma treatment is one of the most popular treatments of carbon materials. This treatment takes place only on the carbon black surfaces without changing its bulk properties. Besides, it was possible to process under oxidative, reductive, or inactive atmospheres [9].

Therefore, in this work, the effects of the plasma treatment for CBs on the modification of surface functional groups and the deposition of Pt catalyst were investigated.

2. Experimental

Plasma treatment for the carbon blacks was carried out using a radio frequency for N_2 gas (Tegal Plasmod). The radio frequency (13.56 MHz) generated by N_2-plasma was operated at 300 W. The input treatment time for N_2-plasma treatment varied between 0 and 50 s, namely, P0, P10, P20, P30, and P50 under a pressure of about 0.75 Torr and a flow rate of about 100 ml/min.

One hundred and twenty five milligrams of N_2-plasma treated CBs was suspended in 25 ml of ethylene glycol solution and stirred with ultrasonic treatment for 20 min, 4.0 ml of hexachloroplatinic acid ethylene glycol solution (58.3 mg Pt + 4 ml

* Corresponding author. Tel.: +82 42 860 7234; fax: +82 42 860 7234.
E-mail address: sjpark@inha.ac.kr (S.-J. Park).

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ethylene glycol) was added to the solution dropwise also under mechanically stirred conditions for 4 h. NaOH was added to adjust the pH of the solution to above 13. Formaldehyde was added to the solution to reduce Pt at 120 °C for 1.5 h, and a flow of argon was passed through the reaction system to isolate oxygen and to remove organic by-products. The powder of Pt deposited CBs was filtered and washed with de-ionized water and finally dried in vacuum oven for 1 day.

3. Results and discussion

Fig. 1 shows FT-IR spectra of the carbon blacks as a function of N_2-plasma treatment time. As shown in Fig. 1, functional groups of the N_2-plasma treated CBs were observed at peak of 650, 1050, 1490, 1550, 1630, and 3430 cm^{-1}, such as, –NH, C–N, =NH, $–NH_3^+$, C=N, and $–NH_2$. The band intensity at 1050, 1630, and 3430 cm^{-1} of the P0 was rather weak than that of the N_2-plasma treated CBs. In case of the N_2-plasma treated CBs samples, the intensity of 1050, 1630, and 3430 cm^{-1} was increased with N_2-plasma treatment time, due to the changes of functional groups. XPS is used to determine the elemental composition on CBs surfaces. Fig. 2 shows the XPS survey scan spectra of the N_2-plasma treated CBs. The C_{1s} and O_{1s} peaks of N_2-plasma treated CBs are found at the binding energy of about 284.6 and 532.8 eV, respectively [10]. Also, the peak of Pt_{4f} is observed 74 eV. The intensity of Pt_{4f} peak on the N_2-plasma treated CBs is increased. This indicates that the intensity of Pt_{4f} is increased due to the reaction between the radical on N_2-plasma treated CBs and Pt_{4f}. However, after N_2-plasma treatment, the peak of N_{1s} is hardly observed because the content of the nitrogen is very low. Therefore, to estimate the content of nitrogen, elemental analysis (EA) is used.

Table 1 shows the EA results of the N_2-plasma treated CBs surfaces. The content of nitrogen is increased by the N_2-plasma treatment. This is clearly attributed to the increase of nitrogen-containing functional groups on the CBs surfaces. The result can also be explained that the N_2-plasma treatment produces various nitrogen-containing functional groups, i.e., –NH, C–N, =NH, $–NH_3^+$, C=N, and $–NH_2$ groups on the CBs surfaces.

Therefore, it can be seen that the N_2-plasma treatment of CBs surfaces lead to the increase of nitrogen-containing functional groups, resulting in improving the deposited capacity of Pt catalyst.

The powder XRD patterns for N_2-plasma treated Pt/CBs are shown in Fig. 3. Fig. 3 shows that Pt deposited on both P0 and N_2-

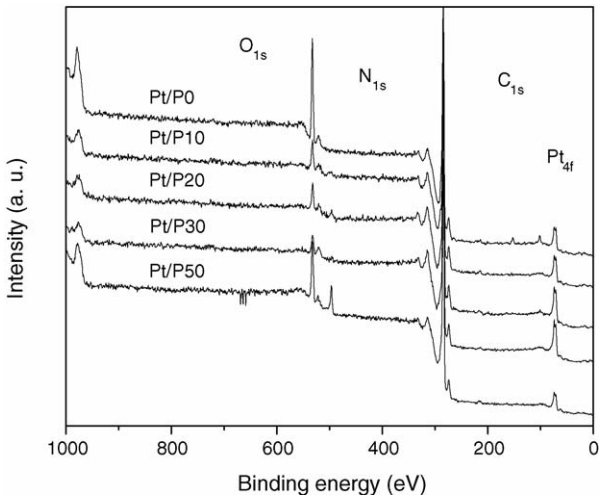

Fig. 2. XPS survey scan spectra of the N_2-plasma treated Pt/carbon blacks catalysts.

Table 1
EA results of N_2-plasma treated carbon blacks

Sample	Elemental analysis	
	C_{1s}	N_{1s}
P0	98.1	1.2
P10	91.8	3.8
P20	83.4	5.3
P30	80.6	10.6
P50	87.8	10.7

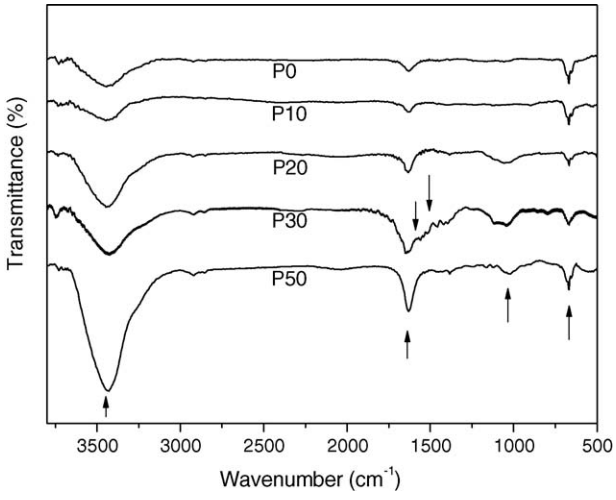

Fig. 1. FT-IR spectra of the N_2-plasma treated carbon blacks as a function of N_2-plasma treatment time.

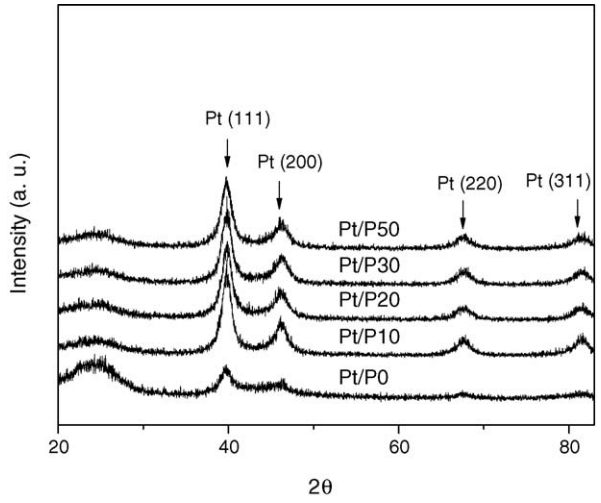

Fig. 3. XRD spectra of the N_2-plasma treated Pt/carbon blacks catalysts.

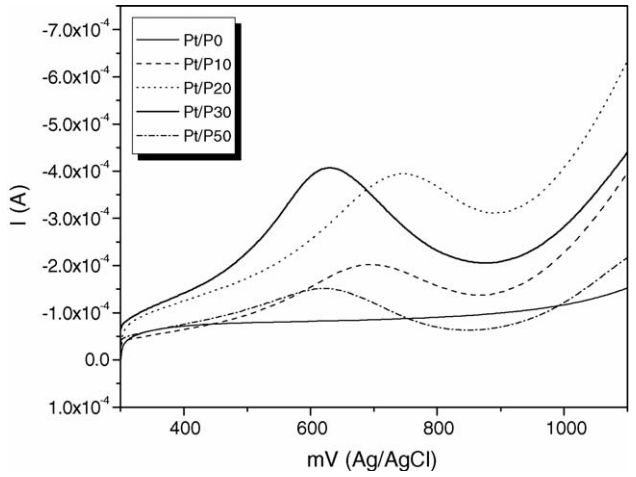

Fig. 4. Cyclic voltammetry of the N_2-plasma treated Pt/carbon blacks catalysts.

plasma treated CBs forms a face centered cubic (fcc) structure and has major peaks at around $2\theta = 39.7^\circ$ (1 1 1), 46.2° (2 0 0), 67.4° (2 2 0), and 81.2° (3 1 1). The broader diffraction peaks for the catalysts also lead to smaller averages alloy particle size as calculated by the Scherrer equation [11]. The calculation results estimated the average size of Pt catalysts.

The sharpening of the XRD peaks indicates an increase of the average crystallite size with increasing the N_2-plasma treatment generated by radio-frequency.

Fig. 4 shows linear sweep voltammograms (LCV) of N_2-plasma treated Pt/CBs catalysts in 0.5 M H_2SO_4 containing 1.0 M CH_3OH. Pt/P30 show the best electroactivity among the samples due to its highest current density of anodic peak. This is evidence that the N_2-plasma Pt/P30 has high activity towards methanol oxidation.

Anodic peaks of methanol oxidation are observed at about 750–850 mV. The current density of anodic peak is greatly enhanced and the peak potential is shifted negatively when the plasma treatment time is 30 s. It means the higher electroactivity and better redox reversibility. However, further treatment has brought the decrease of current density and positive shift of anodic peak potential. This means that the electrocatalytic activity and redox reversibility has been decayed. From this result, it can be concluded that the electrocatalytic activity is the best when the treatment time is 30 s.

4. Conclusions

A characterization of surface functionalities for carbon blacks is important in understanding and controlling the surface properties. Microwave nitrogen plasma treatment can change the surface chemistry of carbon blacks considerably and bring surface nitrogen functionality such as –NH, C–N, =NH, $–NH_3^+$, C=N, and $–NH_2$ groups. It is probably related to the fact that the N_2-plasma treatment of CBs surfaces lead to the increase of nitrogen-containing functional groups, resulting in improving the deposited capacity of Pt catalyst. The electrochemical activity is enhanced by the plasma treatment up to 30 s. Further treatment over 30 s leads to the decrease of the electrochemical activity. It is primarily attributed to the degradable change of functional groups of CBs.

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