

Effect of O₂ Plasma Treatments of Carbon Supports on Pt-Ru Electrocatalysts

Soo-Jin Park,* Jeong-Min Park, and Min-Kang Seo

Department of Chemistry, Inha University, Incheon 402-751, Korea. *E-mail: sjpark@inha.ac.kr

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In the present study, carbon supports mixed with purified multi-walled carbon nanotubes (MWNTs) and carbon blacks (CBs) were used to improve the cell performance of direct methanol fuel cells (DMFCs). Additionally, the effect of O₂ plasma treatment on CBs/MWNTs supports was investigated for different plasma RF powers of 100, 200, and 300 W. The surface and structural properties of the CBs/MWNTs supports were characterized by FT-IR, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and inductive coupled plasma-mass spectrometer (ICP-MS). The electrocatalytic activity of PtRu/CBs/MWNTs catalysts was investigated by cyclic voltammetry measurement. In the experimental results, the oxygen functional groups of the supports were increased with increasing plasma RF power, while the average Pt particle size was decreased owing to the improvement of dispersibility of the catalysts. The electrochemical activity of the catalysts for methanol oxidation was gradually improved by the larger available active surface area, itself due to the introduction of oxygen functional groups. Consequently, it was found that O₂ plasma treatments could influence the surface properties of the carbon supports, resulting in enhanced electrocatalytic activity of the catalysts for DMFCs.

Key Words: Carbon supports, DMFCs, O₂ Plasma, Pt/Ru catalysts, Electrocatalytic activity

Introduction

Direct methanol fuel cells (DMFCs) produce electrical energy by means of the direct conversion of methanol fuel. DMFCs offer various attractions such as their high efficiency, portability, and negligible pollutant emission.¹⁻⁴ Not surprisingly then, DMFCs have been spotlighted as the ideal fuel cell system. However, commercialization of DMFCs has been difficult to realize, owing to the high over potentials resulting from the slow kinetics of the methanol oxidation reaction at the anode as well as the methanol 'crossover' from the anode to the cathode through the membrane.⁵⁻⁷ For these reasons, Pt has been used over several decades in anode electrocatalysts as catalyst materials for commercial products.^{8,9}

A common problem is that Pt catalysts are poisoned by side-product of methanol oxidation, such as carbon monoxide. To improve the performance of Pt electrocatalysts, the Pt has been modified by the addition of a second metal (*eg.* Ru, Ni, Sn, Mo, or Pd). Ru is considered to be the most appropriate of these metals, due to the utility it provides in removing CO from Pt atoms. Pt-Ru bimetallic catalysts thus have been regarded as the best materials for methanol electrode-oxidation, and correspondingly have seen widespread use.¹⁰⁻¹³ Nonetheless, it remains fundamentally important to improve the properties of Pt impregnated support materials.

The ideal support materials should have suitable characteristics, such as high electrical conductivity, a large active surface area, and low resistance.¹⁴ Generally, carbon supports have been utilized as a template for Pt-Ru alloy catalysts.¹⁵ Among carbon materials, carbon blacks (CBs), owing to their good electronic conductivity, high surface area, and low cost, -have been most commonly used as a support for electrocatalysts in DMFCs. Recently, carbon nanotubes (CNTs) have become a subject of interest, due to their unique structure and excellent conductivity and accordingly have been introduced as a support

material where the dispersion of Pt catalysts.¹⁶ However, raw carbon materials have a tendency to aggregate together spontaneously on account of their very fine structure and high surface energy. Thus, surface treatment is an indispensable process for carbon materials.¹⁷

Surface modification is accomplished through different types of treatment, such as liquid or gas oxidation, chemical, electrochemical, or plasma treatment.¹⁸ Notably, plasma treatment of carbon materials is probably the most versatile surface treatment technique to alter the physicochemical properties of carbon surfaces without significantly changing the bulk characteristics.^{19,20} The interactions of plasma treated carbon surfaces have an effect on highly active species, such as free radicals, ions, and meta-stable species, according to the nature of the gases used in the plasma zone.²¹⁻²³

In the present study, we investigated the effects of O₂ plasma treatment, at various RF plasma powers, on the surface properties of CBs/MWNTs supports. To optimize the electrocatalytic activity, Pt-Ru catalysts were impregnated into CBs/MWNTs supports by the chemical reduction method. The electrochemical characteristics of the PtRu/CBs/MWNTs catalysts were examined for methanol oxidation.

Experimental

Carbon blacks (CBs, Hi Black 420B, Korea Carbon Corporation) mixed with multi-walled carbon nanotubes (MWNTs, Nano Solution Company) were used as support materials for metal catalysts. The weight content of MWNTs to CBs was maintained at 30 wt %. Prior to the preparation of Pt-Ru catalysts, the residual chemicals of the carbon materials used were removed by nitric acid for 3 h. Two types of carbon materials were washed several times with distilled water and dried in a vacuum oven at 110 °C. And the CBs/MWNT supports were treated by O₂ plasma in order to modify their carbon surfaces.

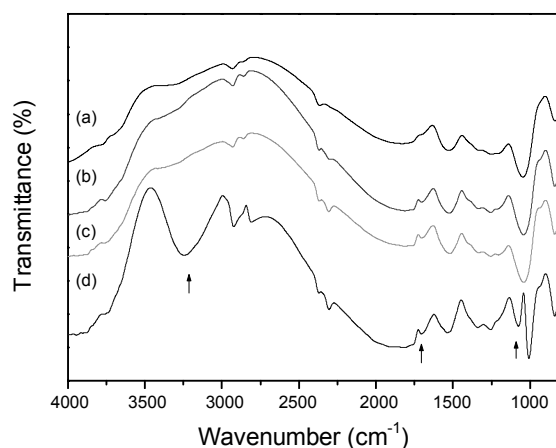
Table 1. O₂ Plasma treatment conditions

Conditions	
Height between electrode and sample plate	40 mm
Length of a sample	5 × 5 cm ²
Process frequency	45 time (s)
Process speed	5 mm/s
Helium gas	5 L/sec
Oxygen gas	5 mL/sec

The plasma treatment for 1 g of CBs/MWNT supports was performed in a sample plate using radio frequency plasma treatment equipment (Tegal Plasmod[®]). This treatment was carried out at several different RF powers, 100, 200, and 300 W. Subsequently, the Pt-Ru catalysts were loaded onto the CBs/MWNT supports by the chemical reduction method. It is widely known that the plasma treatment decays significantly with time. To avoid this ageing phenomenon, catalysts were prepared directly. First, the O₂ plasma treated CBs/MWNTs were dispersed and stirred in distilled water by ultrasonic treatment. Then, H₂PtCl₆ and RuCl₃ from metal precursors (Aldrich Co.) were added to the above suspension under mechanical stirred conditions. The Pt-Ru had a molar ratio of 1:1, and the total loading of the Pt-Ru in the PtRu/CBs/MWNTs was 25 wt %. Next, the reducing agents HCHO and NaOH were both added dropwise to the Pt-Ru slurry and stirring for 5 h at 80 °C.²⁴ Ar gas was passed all process to remove organic by product. The catalysts were then dried in a vacuum oven at 70 °C for 12 h. These prepared samples, according to the different plasma RF powers used in their fabrication, were named P-100, P-200, and P-300. And untreated carbon supports were named as P-0. Table 1 lists the O₂ plasma treatment conditions.

The surface properties of the O₂ plasma treated CBs/MWNTs supports were investigated using Jasco 4000 series FT-IR spectrometer, by which means the enhanced functional groups of the supports, also, were determined. The oxygen groups introduced onto the surface were analyzed by X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB MKII spectrometer equipped with a MgK α X-ray source. The base pressure in the sample chamber was maintained within in the range of 10⁻⁸ to 10⁻⁹ Torr. PtRu loading level was calculated by using an ELAN 6100 inductive coupled plasma-mass spectrometer (ICP-MS). The structural properties of the PtRu/CBs/MWNTs were characterized *via* X-ray diffraction (XRD) performed on Rigaku D/MAX 2200V/PC X-ray diffractometer using a CuK α radiation. The 2 θ angular regions between 20° and 85° were investigated at a scan rate of 5° min⁻¹.

The cyclic voltammetry measurements of the PtRu/CBs/MWNTs catalysts were examined by Autolab equipment with PGSTAT 30 (Eco Chemie, Netherlands) in three-electrode cell system was performed. A three electrode cell, consisting of an Ag/AgCl reference electrode, a Pt wire as a counter electrode, and catalyst sample mixed with Nafion[®] polymer onto a glassy carbon electrode as a working electrode. 1 M CH₃OH in a 0.5 M H₂SO₄ was used as electrolytes. The potential was changed linearly from -200 to 600 mV vs. Ag/AgCl. Cyclic voltammograms were recorded at a scan rate of 20 mV/s.

**Figure 1.** FT-IR spectrum of O₂ plasma treated CBs/MWNTs supports: (a) P-0; (b) P-100; (c) P-200; and (d) P-300.

Results and Discussion

Fig. 1 shows the FT-IR spectrum of the O₂ plasma treated CBs/MWNTs supported Pt-Ru catalysts as a function of plasma treatment power. The peak at 1100 - 1150 cm⁻¹ was attributed to the C-O bond stretching vibration, the broad peak at 3200 - 3500 cm⁻¹ originated from the stretching vibration of the hydroxyl stretching mode of adsorbed H₂O groups, and another peak detected, at about 1700 cm⁻¹ was correlated with C=O stretching in the carboxylic acid groups, which increased in number with RF plasma power, compared with the P-0 sample. In brief, the oxygen functional groups of the supports are more presented with increasing RF power, reaching the maximum at an RF power of 300 W.

Fig. 2 shows the XPS survey scan spectra of the O₂ plasma treated CBs/MWNTs supports. The Fig. 2(a) show carbon and oxygen peaks at binding energies of 283.5 and 530.2 eV, respectively. The oxygen group at 530.2 eV binding energy was observed for the CBs/MWNTs oxygenated by plasma treatment, and introduction of the oxygen functional groups was confirmed, in accordance with the FT-IR results. For the sake of a better understanding of the surface chemistry change, an XPS peak fitting technique was employed to deconvolution of the C_{1s} in Fig. 2(b). The deconvolution of the C_{1s} spectra yielded four peaks is made up of four components, the binding energy of C-C and C-H were normally assigned at 284.6 eV. Chemical shift of +1.5, +2.5, and +4.0 eV are usually used for each functional group, such as C-O, C=O, and COOH.²⁵ Thus, the plasma treatment makes the support surface rich in oxygen functional groups.

It has been reported that plasma treatment changes surface characteristics, such as, layer interaction and light scattering properties, but does not destroy material structures.¹⁹ In that reason, the O₂ plasma treatment leads that active species and free radicals are created on the carbon support during the plasma treatment. Weak or unstable boundary layers on the surfaces of carbon supports are removed by O₂ plasma treatment. So, such changes are easy to introduce the oxygen functional groups on surface of carbon supports.

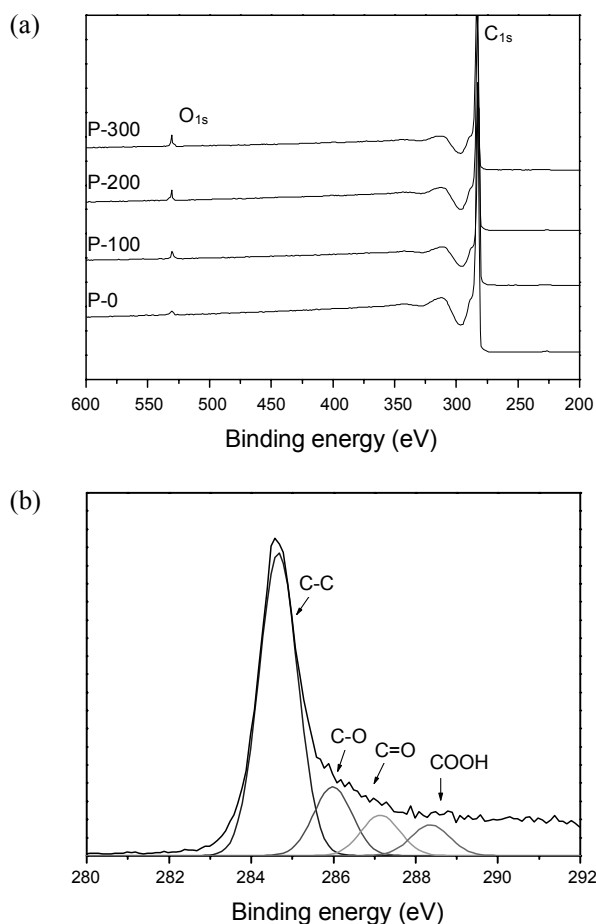


Figure 2. XPS survey spectra of plasma treated CBs/MWNTs (a) and C_{1s} of deconvolution analyses of P-300 (b).

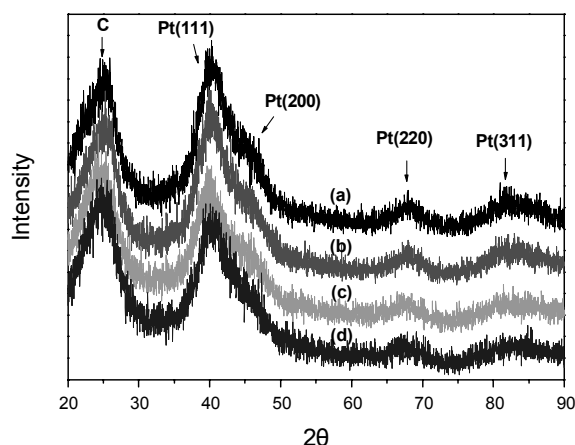


Figure 3. XRD patterns of PtRu/CBs/MWNTs catalysts : (a) P-0; (b) P-100; (c) P-200; and (d) P-300.

Fig. 3 shows the XRD patterns of the PtRu/CBs/MWNTs catalysts. All of them present the main characteristic patterns of Pt face-centered cubic (fcc) crystalline structures at 2θ , that is, of Pt (111) at 40° , Pt (200) at 47° , Pt (220) at 67° , and Pt (311) at 80° . The XRD patterns are verified that the Pt particles were impregnated into the CBs/MWNTs. The characteristic peaks for Ru, however, are not clearly shown in the XRD patterns.

Table 2. Pt particle size and loading contents of PtRu/CBs/MWNTs catalysts

Specimens	2θ (deg) ^a	Particle Size (nm) ^a	Pt (wt %) ^b	Ru (wt %) ^b	Metal Loading (%) ^b
P-0	67.96	4.4076	10.2	6.4	17.6
P-100	67.78	4.3680	11.0	7.6	18.6
P-200	67.46	4.0492	11.6	8.5	20.1
P-300	67.40	3.8672	12.1	8.8	20.9

^aMeasured from XRD results. ^bMeasured from ICP-MS results.

From the XRD results, the Pt particle size (L_c , along the c axis) was calculated using the Scherrer equation.²⁶

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

where K is a constant of Scherrer (0.89), λ is the wavelength of the X radiation (0.154 for CuK α), β is the half-height width of the (220), and θ is the angle, in radian unit, at the peak maximum positioning.

The Pt particle sizes obtained from the fcc peak (220) is listed in Table 2. The Pt particle size gradually decreased from 4.41 to 3.81 nm by increasing the plasma RF power from 0 to 300 W, which is related to affected surface by O₂ plasma treatment. It can be considered that O₂ plasma treated CBs/MWNTs have a secured deposition area for Pt particles, due to the removal of weak or unstable boundary layers on the surfaces of carbon supports. Therefore, deposited Pt particles are more dispersed and become smaller. And consequently, Pt particles size is associated with the modified and oxidized surface characteristics of O₂ plasma treated carbon supports. Also, contents of PtRu in PtRu/CBs/MWNTs are presented in Table 2. The loading contents of Pt are upgraded from 10.2% to 12.1%, and that of Ru is changed from 6.4% to 8.8%. The metal loading has been increased proportionally as a function of plasma power owing to increasing oxygen functional groups. It is probably related to the fact that the O₂ plasma treatments lead to the increase of oxygen-containing functional groups, resulting in improving the deposited capacity of Pt-Ru catalysts.

Fig. 4 shows the CVs of the prepared catalysts in 1.0 M sulphuric acid solution. It was found that the electrocatalytic activities of the samples were enhanced with increasing in the plasma RF power. This is evidence that the O₂ plasma treated supports has higher activity than the pristine support. P-300 show the best electroactivity among the samples due to its largest peak. This was probably related with the small particle size and high loading contents.

Fig. 5 illustrates the electrocatalytic activity of the PtRu/CBs/MWNTs catalysts. The catalysts deposited on O₂ plasma treated CBs/MWNTs show, for the forward scan, a rather definite oxidation peak at about 510 mV vs. Ag/AgCl. The electrocatalytic activity increased with increasing RF power, reaching the maximum at 300 W, owing to the smaller particle size having lead to an improvement in the particle dispersibility. Indeed, the catalysts at 300 W showed a particle size of 3.81 nm. It is thought that smaller particles and high loading contents lead

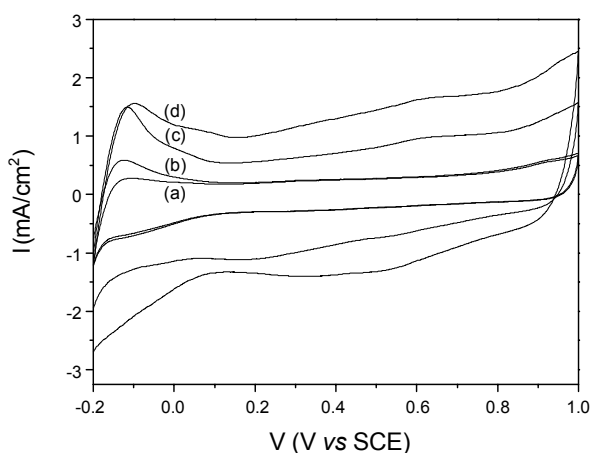


Figure 4. Cyclic voltammograms of PtRu/CBs/MWNTs catalysts : (a) P-0; (b) P-100; (c) P-200; and (d) P-300 (in 0.5 M H₂SO₄ solution, scan rate: 20 mV/s).

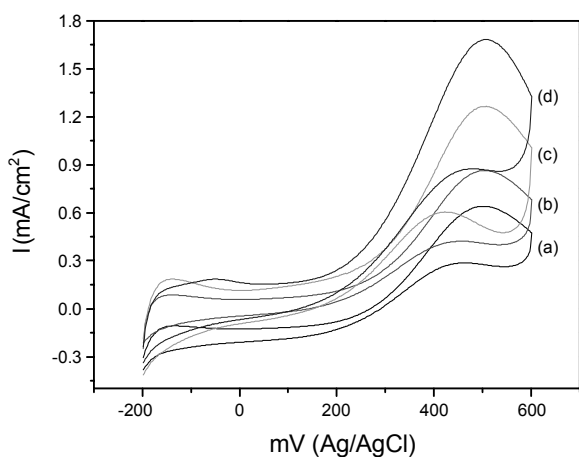


Figure 5. Cyclic voltammograms of PtRu/CBs/MWNTs catalysts : (a) P-0; (b) P-100; (c) P-200; and (d) P-300 (in 1.0 M MeOH + 0.5 M H₂SO₄ solution, scan rate: 20 mV/s).

to larger available active surface of the catalysts, resulting in better electrocatalytic properties for methanol oxidation. Consequently, it can be concluded that the electrocatalytic performance of catalysts can significantly improve with plasma RF power, which decrease Pt particle size of the catalysts.

Conclusions

In the present study, the effect of O₂ plasma treatment of

CBs/MWNTs supports on the electrochemical behaviors of PtRu/CBs/MWNTs catalysts is investigated. The experimental results show that O₂ plasma treatment, with increases (from 0 to 300 W) in plasma RF power, modifies CBs/MWNTs surfaces by increasing oxygen functional groups on them, which led to the optimal conditions of PtRu reduction reaction. And PtRu nanoparticles were deposited on the CBs/MWNTs with good formation with 3.81 - 4.41 nm. In fact, the highest electroactivity for methanol oxidation was obtained with 300 W of plasma RF power. Thus, it could be concluded that plasma treatment of carbon supports leads to enhanced electrocatalytic activity.

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