Supporting PtRu catalysts on various types of carbon nanomaterials for fuel cell applications

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Abstract: PtRu catalysts were supported on five types of carbon nanomaterials of various shapes, sizes, and graphitic properties and the catalyst supports evaluated. The carbon nanomaterial used included three types of nanoparticles: Arc Black (AcB), Vulcan XC-72 (Vulcan) and graphene oxide (GO), and two types of nanofibers: carbon nanocoil (CNC) and carbon nanotube (CNT). Pt and Ru were supported by the reduction method using sodium borohydride. The metal catalyst loading was confirmed by thermo-gravimetric analysis (TGA), electron microscopy, and X-ray diffraction (XRD). Transmission electron microscopy (TEM) and XRD revealed that the diameter of PtRu catalyst nanoparticles loaded on reduced GO (rGO) and AcB were ~2 nm and was the smallest among all the samples. Shifts in Pt (111) XRD peaks of CNC and CNT were larger than those of AcB, Vulcan, and rGO. These results suggest that the diameters of catalyst nanoparticles became smaller by loading on the carbon nanoparticles with a large surface area including rGO, AcB, and Vulcan. Loading onto the carbon nanofibers enhanced the degree of PtRu alloying.

1. Introduction

Direct methanol fuel cells (DMFC) are applicable to portable electric power supply because the liquid fuel has a high energy density and DMFC is operated in a low temperature range (room temperature–100°C) [1]. In order to apply DMFCs to commercial electronic devices, low cost, miniaturization, and high efficiency issues needs to be solved [2-7]. As fuel cells employ precious metals including platinum (Pt) and ruthenium (Ru) for the oxidation of fuel and reduction of oxygen, these catalyst metals are required to be used effectively. This can be achieved by using their nanoparticulate form. Carbon nanomaterial is efficient for supporting nanometer-sized metal catalysts and has been used as a catalyst support in energy
devices. There are various types of carbon nanomaterials including carbon nano-onions, carbon nanocapsules, carbon nanohorns, and carbon nanotubes [8-10]. Recently, fibrous carbon nanomaterials including carbon nanofibers (CNFs) [11, 12] and CNTs [13, 14] have been studied for applications as catalyst supports in fuel cells. These fibrous carbon nanomaterials are capable of having minute structures as well as high electric conductivity in the fuel cell electrode. In contrast, other type fibrous CNFs have a helical shape. These are called carbon nanocoils (CNCs) [15-18]. It was shown that CNCs could also be used as a catalyst support for fuel cells [19-21].

The properties of carbon nanomaterials as a catalyst support have been studied for the following parameters: (1) electric conductivity and graphitic property of carbon nanomaterials, (2) dispersion of the catalyst nanoparticles on carbon nanomaterials with the aim of having a narrow size distribution [22, 23], (3) catalytic activity by electrochemical characterization, and (4) fuel cell performance of the anode/cathode electrode of the catalyst-supported carbon nanomaterials [24]. In this study, we supported PtRu catalysts on five types of carbon nanomaterials with different shapes, sizes, and graphitic properties and evaluated the state of the catalyst loading. The carbon nanomaterials used included the following nanoparticles: Arc Black (AcB), Vulcan XC-72 (Vulcan) and graphene oxide (GO), and two types of nanofibers: carbon nanocoil (CNC) and carbon nanotube (CNT). A quantity synthesis apparatus of AcB [23, 24] and CNC was developed [15]. The properties of Vulcan, CNT, and GO were compared with those of AcB and CNC.

2. Experimental
2-1. Preparation of carbon nanomaterials
2-1-1. Carbon nanocoil (CNC)

Carbon nanofiber with a helical shape is called helical carbon nanofiber (HCNF). HCNFs are classified into four types: angular-type CNC and carbon nanotwist (CNTw), and round-type CNC and CNTw by their coil diameter and surface morphology of the fiber. These classifications are determined by their coil diameter and by the surface morphology of the fiber [15]. Angular-type CNC with fiber diameters of 120–400 nm and coil diameters of 400–1000 nm were used in this study. This angular-type CNC is composed of two, or more, thin helical carbon nanofibers with an edged surface [15]. CNC was synthesized on a Fe/Sn catalyst which was deposited on a graphite substrate using an automatic chemical vapor deposition (CVD) system with consecutive substrate transfer mechanism [15] that was developed in our laboratory. Conventional CVD apparatus requires cooling down after synthesis in every operation, resulting in a longer process time. This apparatus employs two gate valves to separate the load lock, synthesis, and cooling chambers. The sample synthesized can be replaced by a new catalyst while keeping the synthesis chamber heated. By using this apparatus, CNC was obtained at a production rate of 2 g/h. The CVD conditions to produce CNC are listed in Table 1.
2-1-2. Graphene oxide (GO)

Graphene oxide (GO) is a sheet-like graphite and is obtained by treating with strong oxidizers. GO was synthesized from graphite powder (JEOF carbon SNO-3) by a modification of the Hummers method. 2.5 g of potassium peroxodisulfate (K$_2$S$_2$O$_8$) and 2.5 g of phosphorus pentoxide (P$_2$O$_5$) were added to 12 mL of sulfuric acid (H$_2$SO$_4$) aqueous solution, which was heated at 90°C. This mixture was then cooled to 80°C. Then 3 g of graphite powder was added to the mixture and stirred at 80°C for 4.5 h. After cooling to room temperature, 500 mL of ultrapure water was added for dilution. The solution was filtered and dried in clock glass overnight. 15 g of potassium permanganate (KMnO$_4$) was slowly added while stirring. The rate of addition was carefully controlled to avoid sudden increases in temperature. The mixture was then maintained at 35°C for 2 hours. 250 mL of deionized water was gradually added; causing an increase in temperature that was kept below 50°C. After 2 hours, the mixture was further treated with 700 mL of deionized water and 20 mL of 30% hydrogen peroxide (H$_2$O$_2$) solution. The mixture was washed with a 1:10 hydrochloric (HCl) and water solution by repeated centrifugation. The solution was filtered and further washed with deionized water.

2-1-3. Arc-black

Arc-black (AcB) is a spherical particulate of carbon nanomaterial with an amorphous structure. AcB was synthesized by the twin-torch arc discharge apparatus developed in our laboratory [23, 24]. In the discharge chamber, two graphite rod electrodes are mounted at sharp angles, and an arc discharge with a AC current of 200 A occurred between the electrodes in an 80-kPa N$_2$ gas environment. During the discharge, the anode electrode was vaporized and the generated carbon particles of atoms, molecules, and clusters were cooled down by inelastic collisions with ambient N$_2$ gas molecules, forming AcB.

2-1-4. Other Materials

Commercial Vulcan XC-72R (Cabot Corp) and vapor grown carbon fiber (VGCF; SHOWA DENKO K.K.) were used as a Vulcan and carbon nanotubes (CNTs), respectively.
2-2. Catalyst preparation

PtRu catalysts were loaded by the reduction method using sodium boron hydrate (NaBH₄). Hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆•6H₂O) and Ruthenium trichloride (RuCl₃) were respectively used as precursors of Pt and Ru. The molar ratio of Pt and Ru was set at 1:1 and the precursors were balanced between 20wt.% and 30wt.% with respect to the weight of the carbon nanomaterials. The carbon nanomaterial was dispersed in 500 mL of deionized water by sonication for 20 min. H₂PtCl₆•6H₂O and RuCl₃ were stirred in 50 mL of deionized water at 60 rpm for 10 min. This metal precursor solution was added to the carbon nanomaterial solution and the mixture stirred at 600 rpm for 10 min. NaBH₄, with 30-fold mole of the metal precursors, was added to 400 mL deionized water. This NaBH₄ solution was added to the metal precursor solution and stirred at 600 rpm for 2 hours. The solution was filtered by a membrane and washed repeatedly with deionized water, and the catalyst was obtained after drying.

It is reported that GO was reduced during the catalyst preparation [25, 26]. The reduced GO shall be referred to as rGO.

2-3. Characterization

The carbon nanomaterials were characterized using a scanning electron microscope (SEM; Hitachi, S-4500II), a compressive resistivity meter, and a laser Raman spectroscope (JASCO NRS-1000, excitation wavelength = 532 nm). The crystalline structure of the carbon nanomaterials was analyzed by a Raman spectrometer and the intensity ratio of the G-peak (1581 cm⁻¹) to the D-peak (1360 cm⁻¹) (I_G/I_D) in the Raman spectra was noted. The morphological characteristics of the prepared catalysts were analyzed using a transmission electron microscope (TEM; JEOL, JEM-2100F). Before and after catalyst loading, the carbon nanomaterials were analyzed by a thermo-gravimetric analyzer (TGA; Shimadzu, DTG-60) in a temperature range of 100–1000°C. The rate of temperature increase was 10°C/min under a flow rate of 50 ml/min of ambient air. By determining the residual weight after heating, the catalyst load was measured. The catalytic activities of the catalysts loaded on carbon nanomaterials were measured by a three-electrode cell with an electrolyte of 0.5 M H₂SO₄ and a voltage scan rate of 50 mV/s.

3. Results and discussion

3-1. Configuration and graphitic structure of carbon nanomaterials

Scanning electron microscopy (SEM) micrographs of the carbon nanomaterials are shown in Fig. 1. Aerogel (Aer) and Vulcan are spherical particles with diameters of 50 nm and 30 nm, respectively. CNC and CNT are confirmed to be of a fibrous configuration. The fiber diameters of CNC and CNT are similar at 150 nm, and the coil diameter of CNC ranges between 400 and 1000 nm. GO is applied in the form of thin sheets with a thickness of 3 µm.
Fig. 1. SEM micrographs of carbon nanomaterials: (a) AcB, (b) Vulcan, (c) CNC, (d) CNT (VGCF), and (e) GO.

Fig. 2. Raman spectra of (a) AcB, (b) Vulcan, (c) CNC, (d) CNT, and (e) GO.

Table 2 $I_G/I_D$ ratios in the Raman spectra of the carbon nanomaterials

|       | AcB | Vulcan | CNC | CNT | GO |
|-------|-----|--------|-----|-----|----|
| $I_G/I_D$ | 0.86 | 0.90   | 0.90| 2.61| 0.91|

Raman spectra of the carbon nanomaterials are shown in Fig. 2. The G-peak (1581 cm$^{-1}$), which represents the graphite crystalline structure, and the D-peak (1360 cm$^{-1}$), which indicates the defect in crystalline graphite, can be seen in all the spectra. G’-peak (2700 cm$^{-1}$) which appears in crystalline graphite is also seen in the spectra of AcB, CNC, and CNT. The intensity ratios of the G-peak to the D-peak ($I_G/I_D$) in the Raman spectra was evaluated and shown in Table 2. CNT has the highest $I_G/I_D$ ratio among the carbon nanomaterials, while those of the other four are more similar.
3-2. TEM observation of catalyst loaded on carbon nanomaterials

Fig. 3 shows the TEM micrographs of catalyst nanoparticles loaded on the carbon nanomaterials. Nanometer scale particles are well dispersed on all the carbon nanomaterials. Energy-dispersive X-ray analyzer equipped with TEM revealed that the nanoparticles loaded are of Pt and Ru.

![TEM micrographs of catalyst nanoparticles loaded on carbon nanomaterials](image)

Fig. 3. TEM micrographs of catalyst nanoparticles loaded on carbon nanomaterials: (a) AcB, (b) Vulcan, (c) CNC, (d) CNT, and (e) rGO. The weight ratio of Pt and Ru to carbon nanomaterial was 30wt.%. Scale bar = 20 nm.

For each sample, 70 nanoparticles in the TEM micrographs were counted and their size distributions shown in Fig. 4. The catalyst nanoparticles loaded were in the range of 1 and 6 nm. The average diameters of catalyst nanoparticles loaded on rGO and AcB were ~2 nm and were the smallest among those on all
the carbon nanomaterials. These results show that the form of nanofibers including CNC and CNT tended
to load larger catalyst nanoparticles than the form of particulates including AcB, Vulcan, and rGO. The
surface areas of the carbon nanomaterials without catalysts are listed in Table 3.

3-3. Thermo-gravimetric analysis (TGA)

Fig. 5 shows the TGA results of the carbon nanomaterials without PtRu catalysts. CNT has the highest
combustion temperature among all the carbon nanomaterials because of the highest crystalline order of
graphite. However, the combustion temperature of CNC was very low. The combustion temperature of
GO was the lowest and this is probably because of the high surface area.

The TGA results of the PtRu-catalyst-loaded carbon nanomaterials with two different catalyst weight
ratios are shown in Fig. 6. After heating these catalyst-loaded carbon nanomaterials to 1000°C, the error
of the residue weights were within 5% with respect to the weight ratio of the PtRu precursor to carbon
nanomaterial. When PtRu catalysts were supported, the combustion temperatures of AcB and Vulcan were
lower than those of CNT and CNC.

![Graphs showing TGA results for different carbon nanomaterials.](image)

Fig. 4. Size distributions of PtRu catalyst nanoparticles observed in Fig. 3. Carbon nanomaterial and the
average diameter are as follows: (a) PtRu/AcB (2.16 nm), (b) PtRu/Vulcan (2.82 nm), (c) PtRu/CNC (3.67
nm), (d) PtRu/CNT (3.86 nm), (e) PtRu/rGO (2.25 nm).

| Table 3 Surface area of carbon nanomaterials measured by Brunauer, Emmett and Teller (BET) method |
|-----------------------------------------------|----------------|----------------|----------------|----------------|----------------|
| Surface area (m² / g) | AcB | Vulcan | CNC | CNT | GO |
|------------------------|-----|--------|-----|-----|-----|
| 153 | 237 | 115 | 13 | 347 |


Fig. 5. TGA results of carbon nanomaterials. (black) AcB, (red) Vulcan, (green), CNC, (blue) CNT, and (purple) GO. Temperature range: 100–1000°C; rate of temperature increase: 10°C/min.

Fig. 6. TGA results of PtRu-loaded carbon nanomaterials (solid line, 30wt.%; dashed line, 20wt.%). (black) AcB, (red) Vulcan, (green) CNC, (blue) CNT, and (purple) GO.

3-4. X-ray diffraction (XRD)

XRD patterns of PtRu-catalyst-loaded carbon nanomaterials are shown in Fig. 7. All the catalysts show typical diffraction peaks of Pt (111), Pt (200), Pt (220), and Pt (311). C (200) peak is also seen in the carbon nanomaterials of AcB, CNC and CNT, which have a high G’ intensity in the Raman spectra. The average diameter, lattice constant, and surface area of the Pt nanoparticles are evaluated by the following formula [27, 28]:

\[
d = \frac{0.9 \lambda_{\text{beam}}}{\beta \cos \theta_{\text{max}}} \\
(1)
\]

\[
\sigma_{\text{ave}} = \frac{\sqrt{2} \lambda_{\text{beam}}}{3 \sin \theta_{\text{max}}} \\
(2)
\]
\[ s = \frac{\lambda_{\text{Kr1}}}{d} \]  

(3)

Where \( d \) is the average diameter (nm), \( \lambda_{\text{Kr1}} \) is the wavelength of the X-ray (0.154 nm), \( \beta \) is the full width of the diffraction peak at half maximum (rad), \( \theta_{\text{max}} \) is the angle at the position of the peak maximum (deg), \( a_{\text{fCc}} \) is the lattice constant (nm), \( S \) is the metal surface area (m\(^2\)/g), and \( \rho \) is the density of Pt (21.4 g/cm\(^3\)). The calculated values are presented in Table 4. The average diameter of catalyst nanoparticles was in the order of: rGO, Vulcan, AcB, CNC, and CNT. This tendency corresponds to the results from TEM observation. The 2\( \theta \) value of Pt (111) in single crystalline Pt is 39.8° [27]. Shifts in the Pt (111) peak in XRD patterns, which indicate the alloying of Pt with Ru, were seen in all the samples. The shifts in the samples of CNC and CNT were larger than those of AcB, Vulcan, and rGO.

From the analysis above, it suggests that the diameter of catalyst nanoparticles became smaller by loading on the carbon nanoparticles with a large surface area including rGO, AcB, and Vulcan, and that the degree of PtRu alloying was enhanced by loading on the carbon nanofibers including CNC and CNT.

![XRD patterns](image)

Fig. 7. XRD patterns of (a) 20wt.% PtRu- and (b) 30wt.% PtRu-loaded carbon nanomaterials. (1) AcB, (2) Vulcan, (3) CNC, (4) CNT, and (5) GO.

| Catalyst     | Peak of Pt (111) (degree) | Lattice constant (Å) | Particle size (nm) | Pt surface area (m\(^2\)/g) |
|--------------|---------------------------|----------------------|--------------------|----------------------------|
| PtRu/AcB     | 40.1, 40.1                | 3.90, 3.90           | 2.98, 3.34         | 94.2, 84.0                 |
| PtRu/Vulcan  | 40.1, 40.2                | 3.89, 3.89           | 3.07, 3.09         | 91.2, 90.6                 |
| PtRu/CNC     | 40.2, 40.3                | 3.89, 3.88           | 3.20, 3.69         | 87.7, 75.9                 |
| PtRu/CNT     | 40.2, 40.3                | 3.89, 3.89           | 3.69, 3.84         | 76.0, 73.0                 |
| PtRu/GO      | 40.1, 40.1                | 3.90, 3.89           | 2.59, 2.90         | 108.2, 96.4                |
Fig. 8. CV curves of (a) PtRu/AcB, (b) PtRu/Vulcan, (c) PtRu/CNC, (d) PtRu/CNT, and (e) PtRu/rGO electrodes in Ar saturated 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution at a potential scan rate of 50 mV s\(^{-1}\).

Table 5 Electrochemically active surface areas of PtRu-loaded carbon nanomaterials.

|                  | PtRu/AcB | PtRu/Vulcan | PtRu/CNC | PtRu/CNT | PtRu/rGO |
|------------------|----------|-------------|----------|----------|----------|
| Electrochemically active Surface area (m\(^2\) g\(^{-1}\)) | 8.14     | 6.46        | 16.45    | 9.20     | 3.52     |

3.5. Electrochemical measurement

The cyclic voltammograms (CVs) of PtRu-loaded carbon nanomaterials (PtRu/C) were obtained in Ar-purged 0.5M H\(_2\)SO\(_4\) solution (Fig. 8). The electrochemically active surface area of PtRu/C was obtained by integrating the total charge corresponding to the desorption peak of hydrogen, and normalizing with scan rate, Pt loading, and the charge value of 210 \(\mu\)C cm\(^{-2}\) for Pt surface [28,29]. Thus, the obtained active surface areas of PtRu/C catalysts were 8.14 m\(^2\) g\(^{-1}\) for PtRu/AcB, 6.46 m\(^2\) g\(^{-1}\) for PtRu/Vulcan, 16.45 m\(^2\) g\(^{-1}\) for PtRu/CNC, 9.20 m\(^2\) g\(^{-1}\) for PtRu/CNT, and 3.52 m\(^2\) g\(^{-1}\) for PtRu/rGO, as listed in Table 5.

4. Conclusion

Various carbon nanomaterials with different configurations and degree of crystalline graphite were used for PtRu catalyst nanoparticle support, which can be applied in fuel cells. When the weight ratio of the catalyst precursor to carbon nanomaterial is constant, the carbon nanomaterials with higher surface area can be loaded to form smaller catalyst nanoparticles. The degree of alloying of Pt with Ru was evaluated by X-ray diffraction pattern, and the form of nanofibers influenced a higher degree of alloying. We initially evaluated the catalytic activity of these catalysts by using a three-electrode cell. The direct methanol fuel cell performance of the anode and cathode electrodes using these catalysts will be presented in future work.
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