Carbon-supported ultra-high loading Pt nanoparticle catalyst by controlled overgrowth of Pt: Improvement of Pt utilization leads to enhanced direct methanol fuel cell performance

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Abstract
Carbon-supported Pt nanoparticle catalysts with ultra-high loading up to 85% are prepared by multi-step reduction (Pt/C-nR), in which additional Pt precursors are reduced upon a preformed Pt/C catalyst (Pt/C-1R). Transmission electron microscopy images show that the Pt/C-nR catalysts are composed of multilayers of Pt nanoparticles. The multiply stacked morphology in the Pt/C-nR catalysts may originate from the local overgrowth of additionally reduced Pt nanoparticles on the pre-existing Pt nanoparticles in the Pt/C-1R catalyst rather than conformal growth. The electrochemical characterizations by cyclic voltammograms in HClO4 solution reveal that Pt/C-2R catalyst exhibits an increased Pt utilization over the Pt/C-1R catalyst of the same Pt loading on the carbon support where a significant portion of catalytically active surfaces are buried within micropores of carbons. Furthermore, a direct methanol fuel cell (DMFC) single cell employing Pt/C-2R catalyst exhibits an enhanced DMFC performance compared to a single cell using the Pt/C-1R catalyst, demonstrating the importance of morphological control of Pt nanoparticles that can improve the catalyst utilization.

1. Introduction
Direct methanol fuel cells (DMFCs) have been recognized as one of the most promising power sources for portable electronic devices because this type of fuel cell can be manufactured into simple and compact structures as well as liquid methanol has high specific energy [1–6]. It is well known that Pt nanoparticles loaded on carbon support (Pt/C) is still the best cathode catalyst for DMFC primarily owing to the better dispersion and larger surface area resulting from the
smaller size of Pt nanoparticles compared to the Pt black catalyst [7].

Although the Pt/C catalyst is the most prevalent electrocatalyst for oxygen reduction reaction (ORR), the use of carbon support gives rise to inherent adverse effects. One such effect is low catalyst utilization in the supported Pt/C catalyst where a significant portion of fine Pt nanoparticles is buried inside the micropores of carbon supports. This embedded structure of Pt nanoparticles consequently results in limited interaction of metal particles with ionomer molecules, which is a critical region for the formation of triple phase boundary [8]. The fraction of buried nanoparticle in Pt/C catalysts can be minimized with the use of a micropore-free, low surface area carbon support, which is, however, unsuitable for attaining high metal dispersion. Therefore, a new structural design of supported catalyst that can improve the utilization of catalytically active surface is in great demand.

For example, Daimon et al. synthesized Pt alloy catalyst of which exposed surface area was maximized using a lower surface area carbon support by addition of phosphorous as a dispersion agent, which led to an improvement in catalyst utilization [8]. Kim et al. adopted a new carbon support with hollow core mesoporous shell (HCMS) to increase the catalyst utilization [9]. They reported an improved fuel cell performance with Pt catalyst supported on HCMS carbon and the improvement was attributed to the decreased fraction of buried Pt nanoparticles. Recently, Unni et al. modified the carbon surface by the polymerization of pyrrole monomer to minimize the micropores of carbon. This process has helped to significantly extend the triple phase boundary as a greater number of Pt particles can contact directly with Nafion, resulting in a substantial enhancement of the overall catalyst utilization [10].

Another disadvantage in using the supported Pt/C catalyst is a high resistance in the electrode caused by the thick catalyst layer in the membrane electrode assembly (MEA). To decrease the thickness of catalyst layer in the MEA, especially for the DMFC, the catalytic metal should be supported on the carbon support with very high loading above 60 wt.%. In this regard, a variety of preparation methods have been developed to achieve a high metal loading on carbon support while maintaining a high dispersion of small particle size and uniform distribution. In particular, the polyol process has been considered as a promising method of choice because of its advantages such as simplicity of preparation and facile control of particle size without using any additional stabilizer [11,12].

The present work was undertaken to resolve the two aforementioned issues by developing a new synthesis strategy to carbon-supported ultra-high Pt loading catalyst that can enhance the catalyst utilization. The Pt/C catalysts with ultra-high Pt loading were prepared by multi-step reduction method and the electrochemical characterization including DMFC single cell operation was conducted.

2. Experimental

2.1. Preparation of Pt/C catalyst

The Pt/C catalysts were prepared by polyol method in a single- or multi-step reduction. The Pt/C catalyst having 67 wt.% Pt in a single reduction step (denoted as Pt(67)/C-1R) was synthesized as follows. 0.146 g of Pt precursor (H2PtCl6·6H2O from Unimicro) was dissolved in 20 g of ethylene glycol (EG), and separately 0.25 g of carbon (Ketjen Black 300J of which surface area is 800 m²/g) was suspended in a mixture of EG (160 g) and deionized water (120 g). The Pt precursor solution and the carbon suspension were mixed, and subsequently the pH of the mixture was adjusted to 11 by using 1 M NaOH solution. The temperature of the mixture was raised to 110 °C over 1 h and kept for 4 h to reduce Pt under refluxing conditions. After filtering and washing with water, Pt/C samples were dried. A higher Pt loading of 76 wt.% Pt/C with a single reduction step (Pt(76)/C-1R) was similarly prepared with the Pt(67)/C-1R catalyst except the amounts of Pt precursor.

The preparation of Pt/C-nR (n ≥ 2) catalysts was carried out by reducing additional Pt precursor onto pre-formed Pt/C catalyst. For instance, Pt(76)/C-2R catalyst with the same Pt loading on the carbon support as Pt(76)/C-1R was synthesized by repeating reduction step with the Pt(67)/C-1R catalyst and the same Pt precursor solution for the first reduction process to produce Pt(67)/C-1R. Pt(85)/C-3R catalyst was similarly prepared by applying reduction step once more to Pt(76)/C-2R.

2.2. Characterization of Pt/C catalyst

X-ray diffraction (XRD) patterns were obtained by Philips X'pert Pro X-ray diffractometer equipped with a Cu-Kα source at 40 kV and 40 mA. The crystalline size of Pt particle from XRD patterns was calculated from the Scherrer’s equation [13]. Transmission electron microscopy (TEM) images were obtained using the G2 FE-TEM Tecnai microscope at an accelerating voltage of 200 kV. The composition of Pt and carbon in the catalyst was determined by ICP-AES (RF source: Jobin Yvon 2301, 40.68 MHz).

Electrochemical characterization was performed by following the thin active layer rotating disk electrode (RDE) method using Nafion as a binder with a three-electrode electrochemical cell [14]. The catalyst layer was obtained in the following way: (i) Catalyst suspension of 2 mg/ml was produced by ultrasonically dispersing the catalyst in water. A 13 μl aliquot of the ultrasonically re-dispersed suspension was pipetted onto the glassy carbon substrate for working electrode, yielding a Pt loading of 60 μg/cm²; (ii) Nafion solution (0.05 wt.% Aldrich) of 13 μl was applied onto top of the dried catalyst and dried in an oven. Pt gauze and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively.

Cyclic voltammogram (CV) for estimating the electrochemical surface area (ECISA) was recorded in the potential range of 0.05–1.2 V versus normal hydrogen electrode (NHE) at a scan rate of 10 mV/s after the cycling for 20 cycles with 50 mV/s in 0.1 M HClO4 solution at room temperature (RT), which was saturated with nitrogen by bubbling pure nitrogen gas for 30 min. Linear scan voltammetry for the ORR was obtained at a scan rate of 5 mV/s at RT. For the ORR, the solution was saturated with oxygen by bubbling pure oxygen gas for 30 min.

2.3. Evaluation of MEA performance

Cathode catalyst ink was prepared by dispersing the catalysts in isopropanol with ionomers. The catalyst ink was sprayed
onto a gas diffusion layer to form a catalyst layer. The anode was prepared similarly except the use of PtRu-black (HiSpec 6000, Johnson Matthey). The catalyst loading was 2 mg/cm² for the cathode and 5 mg/cm² for anode, respectively. Then, an MEA of 10 cm² was assembled by hot pressing at 125 °C for 3 min using Nafion 115 as a membrane. The performance of DMFC was evaluated by using Wonatech fuel cell test station. Polarization curves were obtained with circulating 1 M methanol through the anode at a rate of 0.1 cc/min and feeding air to the cathode at a flow rate of 52.5 cc/min at 50 °C. More details on single cell preparation and evaluation can be found elsewhere [15].

3. Results and discussion

Fig. 1 shows the relationship between the Pt particle sizes of the Pt/C catalysts determined from the XRD patterns (as in the inset) and the loading of Pt nanoparticles on carbon support. As shown in the reference data of Pt/C catalysts from E-Tek [16], the Pt particle size of the Pt/C catalysts rapidly increases as the Pt loading exceeds 60 wt.%. Although such a particle growth would be inevitable with a very high Pt loading, we

![Graph showing the relationship between Pt particle sizes and Pt loading](image)

**Fig. 1** Relationship between the Pt particle sizes determined from XRD and the loading of Pt nanoparticles on Ketjen Black carbon with multiple reduction steps (reference data from [16] and the inset is the XRD patterns of Pt/C catalysts of single step and multi-step reduction).

![TEM images](image)

**Fig. 2** TEM images of (a) Pt(67)/C-1R, (b) Pt(76)/C-1R, (c) Pt(76)/C-2R, and (d) Pt(85)/C-3R (the insets are high magnification images).
were able to keep the Pt particle size less than 4 nm up to as high as 76 wt.% Pt loading in a single step reduction by optimizing the polyol synthesis parameters such as pH value, amounts of deionized water in the total reaction mixture and the concentration ratio of Pt precursor to the total reaction mixture. In particular, the pH of the reaction mixture has been found to be critical for obtaining highly dispersed Pt/C with a small particle size. In the polyol reduction method, metal ions are reduced to form a metal colloid by receiving electrons through the oxidation of EG to glycolic acid, which is present in its deprotonated form as glycolate anions in alkaline solution (high pH value) [17]. The glycolate anions adsorbed on the surface of the metal act as a stabilizer and the glycolate anion concentration increases with increasing pH. Therefore, it is more favorable to perform the polyol process in an alkaline solution in order to decrease the Pt particle size. The role of water in EG solution is believed to retard the growth rate of the nuclei for the Pt particles on the carbon support and to obtain a homogeneous size distribution of Pt particles [18,19]. In our preparation conditions, the optimum water content is 40–60 wt.% in the total reaction mixture.

As shown in Fig. 1, the particle size of Pt/C-1R determined from the XRD was around 3 nm in the investigated Pt content range (67 and 76 wt.%) when the catalysts were prepared in a single reduction step. Pt(76)/C-2R, which was prepared by using Pt(67)/C-1R as a preformed seed and applying an additional Pt precursor solution for a subsequent reduction step, has a larger particle size (3.85 nm) than that (3.17 nm) of Pt(76)/C-1R. The particle size (4.60 nm) of Pt(85)/C-3R is larger than that of Pt(76)/C-2R by a similar margin.

The microstructure of Pt/C catalysts prepared with a single step reduction and multi-step reduction are expected to affect the catalyst utilization and the ORR activity. To investigate the relationship between the microstructure and the Pt utilization, the ECSAs of Pt(76)/C-1R and Pt(76)/C-2R were measured by cyclic voltammetry (CV). The different microstructures of Pt nanoparticles from a single step reduction and multi-step reduction are expected to affect the catalyst utilization and the ORR activity. To investigate the relationship between the microstructure and the Pt utilization, the ECSAs of Pt(76)/C-1R and Pt(76)/C-2R were measured by cyclic voltammetry (CV). The ECSAs of Pt(76)/C-1R and Pt(76)/C-2R were measured under the following conditions: scan rate 50 mV/s, electrolyte 0.1 M HClO₄, and gas phase N₂.

![Fig. 3 – Schematic illustration of a single step and multi-step reduction.](image)

![Fig. 4 – Cyclic voltammograms of Pt(76)/C-1R and Pt(76)/C-2R in N₂-saturated 0.1 M HClO₄ electrolyte with a scan rate of 50 mV/s.](image)
Table 1 – Pt particle size (d) from XRD, geometric surface area (GSA), electrochemical surface area (ECSA), Pt utilization, inter-particle distance (X) and the ratio of inter-particle distance to Pt particle size (X/d) of Pt(76)/C-1R and Pt(76)/C-2R catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt particle size, nm (d)</th>
<th>GSA a, m²/gPt</th>
<th>ECSA b, m²/gPt</th>
<th>Pt utilization c, %</th>
<th>Inter-particle distance d, nm (X)</th>
<th>X/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(76)/C-1R</td>
<td>3.17</td>
<td>88.4</td>
<td>60.2</td>
<td>68</td>
<td>10.20</td>
<td>3.22</td>
</tr>
<tr>
<td>Pt(76)/C-2R</td>
<td>3.85</td>
<td>72.8</td>
<td>65.3</td>
<td>90</td>
<td>13.65</td>
<td>3.55</td>
</tr>
</tbody>
</table>

a $S/m²/gPt = \rho/(\pi d²/4)$ where $\rho$ is the density of platinum metal (21.4 × 10⁶ gm⁻³) and d is the diameter of the particle in nm determined from XRD.

b $S/m²/gPt = Q_{c}/(0.21 \times 10^{-3} \times gPt)$, where $Q_{c}$ is the amount of charge exchanged during the electro-desorption of hydrogen atoms on Pt, $gPt$ is the amount of Pt on the glassy carbon disk in μg determined by CV.

c Pt utilization = (ECSA/GSA) × 100.

d Inter-particle distance $(X) = z√(/π d²S/(100 - y))/(3√y)$ where $\rho$, $d$, $S$, and $y$ is the density of supported catalyst particles (g/nm³), the diameter of the particle in nm determined from XRD (nm), specific surface area of carbon supports (nm²/g) and catalyst loading on carbon black (wt.%).

were calculated based on the CVs from 0.01 V—0.4 V as shown in Fig. 4. It is known that the ECSA of Pt particles is one of the most important parameters to represent the catalytic activity of their surface [21]. The ECSA of Pt in the supported catalyst could be estimated from the integrated charge of the hydrogen desorption region of the CV. The areas in m²/g are calculated from the following formula assuming a correlation value of 0.21 mC/cm and Pt loading [22], that is, ECSA (m²/gPt) = $Q_{c}/(0.21 \times 10^{-3} \times gPt)$, where $Q_{c}$ is the amount of charge exchanged during the electro-desorption of hydrogen atoms on Pt and $gPt$ is the weight of Pt in the electrode. Table 1 summarizes the size of Pt nanoparticle estimated from XRD, geometric surface area (GSA) on the assumption of sphere nanoparticles [23], ECSA calculated from CV, and Pt utilization, defined by a percentage of ratios of ECSA to GSA, of the two catalysts. The GSA of Pt(76)/C-1R catalyst (88.4 m²/gPt) is higher than that of Pt(76)/C-2R catalyst (72.8 m²/gPt) in the same metal loading due to the smaller particle size. Yet, the ECSA of Pt(76)/C-1R (60.2 m²/gPt) is smaller than that of Pt(76)/C-2R catalyst (65.3 m²/gPt), which indicates the stacked morphology of Pt in Pt(76)/C-2R can provide more exposed surface of Pt. Thus, the Pt utilization was increased from 68% for Pt(76)/C-1R to 90% for Pt(76)/C-2R catalyst.

To investigate the relationship between the microstructure and the ORR activity, Fig. 5 displays the linear scan voltammetry of Pt(76)/C-1R and Pt(76)/C-2R in O₂-saturated 0.1 M HClO₄ electrolyte with a scan rate of 5 mV/s at 900 rpm. The mass activity for the ORR of Pt(76)/C-2R is larger than that of Pt(76)/C-1R, which is 1.7 times higher at 0.85 V (see the inset). The higher activity of the Pt(76)/C-2R could be attributed to the morphology of more exposed Pt surface on the carbon support as suggested from the above results.

As an alternative explanation, the ORR characteristics of the catalysts could be explained by inter-particle distance effect suggested by the formula of Watanabe et al. [24], which is particularly useful when the particles are very close together. The ratio of inter-particle distance (X) to particle size (d) can be related to the utilization and the catalytic activity of carbon-supported Pt catalysts. The greater the inter-particle distance and the smaller the particle size is (that is, the greater the X/d ratio is), the higher the specific activity of Pt on carbon support becomes. As shown in Table 1, the catalytic activity of Pt(76)/C-2R catalyst is higher than that of Pt(76)/C-1R, which can be ascribed to the higher X/d ratio of Pt(76)/C-2R.

To further validate the effect of Pt microstructure, the above two catalysts were used in the cathode catalyst layer of MEA for DMFC, and their single cell performances are compared as shown in Fig. 6. The cell performance of Pt(76)/C-2R cathode exceeds that of Pt(76)/C-1R cathode. For example,
the current density at 0.4 V was increased from 63.4 mA/cm² for Pt(76)/C-1R to 79.7 mA/cm² for Pt(76)/C-2R. Accordingly, the maximum power density of two MEAs reached 49.4 and 40.9 mW/cm² for Pt(76)/C-2R and for Pt(76)/C-1R, respectively. These single cell data indicate that an improved Pt utilization in the Pt(76)/C-2R catalyst is realized in the MEA for DMFC in terms of higher operating cell voltages throughout the whole current density range than the Pt(76)/C-1R catalyst.

4. Conclusions

A modified polyyol process was developed for the preparation of ultra-high loading Pt/C catalysts to enhance the utilization of Pt. By using Pt/C-1R as a preformed seed and applying additional Pt precursor solutions for subsequent reduction steps, Pt/C having a loading as high as 85 wt.% was synthesized. Despite of slightly larger Pt particle size in the Pt/C-nR catalysts from multi-step reduction than that of Pt/C with a single reduction step on the same Pt loading basis, the stacked microstructure of Pt nanoparticles in the Pt/C-nR catalysts was found to be more favorable to the improvement of Pt utilization than the Pt/C-1R catalyst. Significantly, the stacked morphology of the Pt/C-2R catalyst further led to the enhancement in the single cell performance in DMFC. Overall, the ultra-high loading Pt/C-nR catalyst prepared by multi-step reduction method is a promising candidate for the future design of high performance MEA for DMFC.

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