Enhancement of oxygen reduction activity by sequential impregnation of Pt and Pd on carbon support

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Abstract—Two Pd-based PtPd bimetallic catalysts (mole ratio of Pt to Pd=1 : 18) were prepared by co-impregnation (Pt-Pt/C) and sequential impregnation of Pt on Pd/C [Pt(Pd/C)] for the application to oxygen reduction reaction (ORR). The prepared bimetallic catalysts had lower ORR activities than Pt/C, while they showed largely enhanced activity compared to Pd/C. In particular, the extent of enhancement was found to be dependent on the surface composition. The observed mass and specific activities of Pt(Pd/C) were more than two times higher than those of Pt-Pd/C. The superior activity of Pt(Pd/C) observed from the performed studies was attributed to its Pt-rich surface.

Key words: Oxygen Reduction Reaction (ORR), Pd Catalyst, Pt Catalyst, Bimetallic Catalyst, Polymer Electrolyte Fuel Cells (PEMFCs)

INTRODUCTION

Polymer electrolyte fuel cells (PEMFCs) have attracted much attention as primary power sources for zero-emission electric vehicles due to their high energy conversion efficiency and environmentally friendly nature. Though there have been many efforts devoted to the technical advancements of PEMFCs on the last decades, several barriers still remain to be overcome for the commercialization of PEMFCs [1-4].

One of them is a sluggish kinetics for oxygen reduction reaction (ORR) at cathode. This induces a large amount of Pt-based metal catalyst utilization, increasing the overall cost of fuel cells. The cost will be effectively reduced either by improving the catalytic activity of Pt catalyst or developing an alternative low-cost catalyst.

Heat-treated metal-porphyrin, in which metal ions such as Co and Fe are bound to nitrogen in carbon structure, has been proposed as an effective alternative cathode catalyst [5-7]. Although the materials may be abundant in nature and consequently can be supplied at lower price, their catalytic activity and stability are currently insufficient for the cathode catalyst utilization.

As a typical method to enhance ORR performance, Pt has been alloyed with transition metals such as Co [8], Ni [3], Fe [9], Ti [10], and Cu [11]. Toda et al. have prepared several Pt alloys with Ni, Co, and Fe using a sputtering method and investigated the several factors which affect the electrocatalytic activity of the catalysts [12]. They reported that Pt-based alloys had 10-15 times higher kinetic current than Pt, depending on the composition of catalysts. The obtained higher kinetic current was attributed to the increased d-electron vacancy of Pt surface layer. Stamenokovic et al. have recently reported an important result on the activity of Pt-based alloy [3]. They demonstrated that the activity of Pt (111) could be enhanced by alloying with Ni, resulting from the modified electronic configuration of surface Pt atom. The interaction between resultant modified Pt surface and oxide species such as hydroxide would be weakened, leaving active site for ORR unpoisoned, which resulted in 90-fold increased activity over a conventional Pt/C. There have been also interesting reports on the catalytic properties of Pt or Pt-M (M= Au, Rh, Ru, etc.) monolayer on Pt (111) [13,14]. The significant enhancement of ORR kinetics is not only due to the geometric effect such as increased surface roughness, but also to a decreased formation of PtOH. This resulted from the modified electronic structure of Pt surface. As can be seen from these examples, it is likely that the deposition of Pt on suitable metal surface such as Pd would be a promising method to increase ORR activity, and therefore to reduce Pt loadings in PEMFCs. In addition, the PtPd binary catalyst would be more economical than Pt monometallic one when considering the cost of metal. Currently, the price of Pd is about a third of that of Pt.

In this work, we prepared carbon-supported PtPd bimetallic catalysts by using a co-impregnation and a sequential impregnation method, respectively. The physico-chemical properties of catalysts were characterized by using XRD, TEM, XPS, and electrochemical methods and were correlated with ORR performances observed in acid solution.

EXPERIMENTAL

1. Materials

Pd and Pt precursors (Na2PdCl4 and H2PtCl6) were purchased from Aldrich and Kojima Chemicals, respectively. NaBH4 (Aldrich) was used for a reducing agent for metal ions and Vulcan XC 72R (Cabot) for a catalyst support. Nafion solution (5 wt%) and isopropyl alcohol (IPA) were obtained from Aldrich and sulfuric acid (H2SO4, 98%) from Showa Chemical. Doubly distilled water was used in this study.

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2. Preparation of Catalysts

Two bimetallic catalysts, Pt-Pd/C and Pt(Pd/C), were prepared using NaBH₄, reducing agent by a co-impregnation and sequential impregnation, respectively. For the preparation of Pt-Pd/C, carbon support (200 mg) was dispersed in a mixed solution of Na₂PdCl₄ (0.34 M, 2.38 ml) and H₂PtCl₆ (0.196 M, 0.23 ml). After making the above solution homogenous through magnetic stirring followed by sonication, an aqueous solution of NaBH₄ (0.048 M, 50 ml) was added slowly to the solution under vigorous stirring. After further stirring for 1 h, a resultant precipitate was washed with copious water followed by drying at 110 °C for 6 h to produce the Pt-Pd/C. For the case of Pt(Pd/C), 30 wt% Pd/C was first prepared by the same method as Pt-Pd/C without the addition of Pt precursor. Prepared Pd/C was then dispersed in an aqueous solution of H₂PtCl₆ (0.196 M, 16 ml), followed by reduction of Pt on Pd/C using NaBH₄. The concentrations of Pt and Pd in two bimetallic catalysts were 3 wt% and 30 wt%, respectively. For the purpose of comparison, 30 wt% Pt/C was prepared by the same method used to prepare the Pd/C catalyst.

3. Characterizations and Measurement of ORR Performance

Crystalline phases of catalysts were identified by XRD (Rigaku D/MAX 2500) measurements using Cu-Kα radiation (λ=1.54056 Å) operated at 40 kV and 30 mA. The particle size and location of Pt on support were confirmed using TEM (JEOL-2010). Surface electronic states of elements in samples were examined with XPS (AXIS-NOVA (Kratos)).

To evaluate electrochemical active surface area and catalytic activity for ORR, electrochemical measurements were conducted with a conventional three-electrode cell in an electrolyte solution. A Pt gauze and a SCE were used as a counter electrode and a reference electrode, respectively. A working electrode was prepared by coating a catalyst ink on a glassy carbon (GC) electrode. For the preparation of catalyst ink, a catalyst (20 mg) was mixed with a few drops of water, IPA (8 ml) and Nafion (75 µl) solution. A repeated stirring followed by sonication to this catalyst slurry was carried out for 1 h to obtain a homogeneous catalyst ink. Cyclic voltammetry was conducted in a N₂ saturated H₂SO₄ (0.5 M) solution. Cyclic voltammograms (CV) of 10 cycles were recorded using CHI700C in the potential range of 0.3-1.1 V.

For the estimation of ORR performance, linear sweep voltammetry (LSV) was carried out with a rotating ring disk electrode (RRDE, NOVA (AFE7R9GCPT)) in oxygen saturated H₂SO₄ (0.5 M) solution.

RESULTS AND DISCUSSION

1. Physical Properties of Catalysts

Table 1. Physical properties of Pd/C, Pt-Pd/C, Pt(Pd/C), and Pt/C.

<table>
<thead>
<tr>
<th></th>
<th>Particle size (nm)</th>
<th>Surface area (m²/g)</th>
<th>Charge (mC/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>5.7</td>
<td>87.7</td>
<td>48.5</td>
</tr>
<tr>
<td>Pt-Pd/C</td>
<td>5.4</td>
<td>86.4</td>
<td>48.1</td>
</tr>
<tr>
<td>Pt(Pd/C)</td>
<td>6.0</td>
<td>77.8</td>
<td>42.6</td>
</tr>
<tr>
<td>Pd/C</td>
<td>4.0</td>
<td>71.4</td>
<td>29.7</td>
</tr>
</tbody>
</table>

\(^{a}\)Computed from XRD analyses

\(^{b}\)Determined from TEM images

\(^{c}\)Charge for the reduction of PdO on Pd/C, Pt-Pd/C, and Pt(Pd/C); Charge for the desorption of hydrogen on Pt/C

angles. It was reported that the diffraction peaks for Pd in Pt/Pd alloys (x=1 and y=1-4) were observed to be shifted to a lower angles resulting from incorporation of Pt into Pd lattice, i.e., lattice expansion of Pd [15]. In this work, however, it is hard to observe the evidence of lattice expansion. Compared to the bimetallic Pt/Pd catalysts in the above reference, our bimetallic catalysts have very low Pt concentration; a mole ratio of Pt to Pd was kept at about 1 : 18. Because both Pt and Pd have an identical crystalline structure as well as a close atomic size to each other, the presence of small amount of Pt seems to have almost no effect on the lattice parameter of Pd in Pt-Pd/C and Pt(Pd/C) catalysts. A similar result to ours was reported in that a bimetallic Pt/Pd/C (x=1 and y=19) compared to Pd/C has no distinct feature in XRD pattern [16].

By applying the Scherrer equation to (220) reflection, the average particle size of metal was calculated as listed in Table 1. The bimetallic catalyst (Pt-Pd/C) had smaller crystallite size than the monometallic catalyst (Pt/C) when both catalysts were prepared by an impregnation method. This is probably because the growth of metal can be suppressed by the presence of different kind of metal ions. On the other hand, the average particle size of Pt(Pd/C) is slightly larger than that of Pd/C, indicating that the reduction of Pt ions was made predominately on the surface of Pd during the impregnation of Pt. In other words, the portion of independent presence of Pt apart from Pd would be very low in the Pt(Pd/C) catalyst. This is very important in designing a bimetallic catalyst because one metal has no influence on the electronic structure of the other metal if they are physically separated from each other. Metal surface area, as listed in Table 1, was calculated by using the following equation: Surface area (m²/g)=6,000/rd, where r stands for the density of metal (Pt:
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21.45 g/cm³ and Pd: 12.02 g/cm³) and d for particle size (nm). Metal surface area was 87.7, 86.4, 77.8, and 71.4 m²/g for Pd/C, Pt-Pd/C, Pt(Pd/C), and Pt/C, respectively.

Fig. 2 shows TEM images of the catalysts. The particle size of the catalysts is similar to those observed from XRD. Average particle size was 5.8, 5.7, 6.4, and 4.1 nm for Pd/C, Pt-Pd/C, Pt(Pd/C), and Pt/C respectively.

To investigate the electronic state and surface concentrations of Pt, XPS analyses were conducted for two bimetallic catalysts and displayed in Fig. 3. The Pt 4f₂ and 4f₅₂ photoelectron lines were fitted into three components that can be assigned to zero-valent Pt, PtO, and PtO₂, respectively [17]. Table 2 summarizes the fitting results including binding energies and relative intensities for Pt species. A common feature of two bimetallic catalysts is that the binding energies for zero-valent Pt are slightly shifted to high binding energy compared to that of pure Pt (70.8 eV). This is usually observed on the supported Pt catalysts and is due to effects of small Pt cluster and Pt-support interaction [18]. Although the relative intensity of zero-valent Pt is fitter to be higher for Pt(Pd/C) than for Pt-Pd/C, its difference between two catalysts is unlikely to be significant because the fitting accuracy for Pt-Pd/C would not be as good as that for Pt(Pd/C) due to the considerable noise in the XP spectra of the former catalyst. It is worth to note that the peak area of Pt 4f₅₂ normalized to that of Pd 3d₅₂ is higher for Pt(Pd/C) than for Pt-Pd/C. This result indicates that the Pt(Pd/C) has higher Pt concentration on its surface than the Pt-Pd/C. It is known that the stand-

Fig. 2. TEM images of Pd/C, Pt-Pd/C, Pt(Pd/C), and Pt/C.

Fig. 3. Pt 4f photoelectron lines for (a) Pt-Pd/C and (b) Pt(Pd/C).
ard potentials for the $[\text{PdCl}_4]^{2-}/\text{Pd}$ and $[\text{PtCl}_4]^{2-}/\text{Pt}$ are 0.623 V and 0.758 V [19], respectively, indicating that the Pt precursor would be more easily reduced than Pd precursor. In other words, Pt precursor tends to be reduced to form a Pt-rich core, followed by the reduction of Pd precursor to form a Pd-rich shell, when the reductions are simultaneously carried out in a mixed solution of two metal precursors. Considering an extremely low concentration of Pt precursor in this work, however, the core of Pt-Pd/C is unlikely to be a Pt-rich phase; on the contrary, it seems that a Pd-rich core is first formed followed by the formation of a Pt-rich phase, this does not indicate that the surface of Pt-Pd/C is mainly composed of Pt; instead, it is reasonable to take the view that most of Pt would be residing in the bulk phase rather than on the surface, as illustrated in Fig. 4.

Fig. 4. Schematics for the description of bimetallic composition; (a) Pt-Pd/C and (b) Pt(Pd/C).

### Table 2. Summary of fitting results for Pt 4f photoelectron lines

<table>
<thead>
<tr>
<th>Species</th>
<th>Binding energy (eV)</th>
<th>Relative intensity (%)</th>
<th>Relative peak area (%)</th>
</tr>
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<tbody>
<tr>
<td>Pt-Pd/C</td>
<td>0</td>
<td>71.2</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;+&lt;/sup&gt;</td>
<td>72.0</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>4&lt;sup&gt;+&lt;/sup&gt;</td>
<td>72.9</td>
<td>15</td>
</tr>
<tr>
<td>Pt(Pd/C)</td>
<td>0</td>
<td>71.4</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>2&lt;sup&gt;+&lt;/sup&gt;</td>
<td>72.3</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>4&lt;sup&gt;+&lt;/sup&gt;</td>
<td>73.2</td>
<td>5</td>
</tr>
</tbody>
</table>

2. Electrochemical Characterization and ORR Performance

Fig. 5 shows the cyclic voltammograms for the catalysts measured at 10<sup>th</sup> cycle in N<sub>2</sub>-purged 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. A common feature of all catalysts in the forward sweep is the evolution of currents for hydrogen desorption and oxide formation, while the current for the reduction of surface oxide and hydrogen adsorption would be observed in the reverse sweep. Based on the charge transferred for hydrogen adsorption or desorption, the electrochemically active surface area (EAS) for Pt/C catalyst was calculated to be 57.4 m<sup>2</sup>/g. As far as Pd-based catalyst is involved, it is known that the hydrogen adsorption is concurrent with hydrogen absorption in the same potential region, which makes it impossible to determine the charge density value for the calculation of EAS [20]. Alternatively, one of the most widely accepted methods for the estimation of EAS of Pd is to use the charge transferred for the reduction of PdO, for which the potential range should be controlled to form the monolayer of PdO [20]. Although the experimental condition in this work might be unsuitable for the calculation of real EAS, it would be possible to use the charge value for the reduction of PdO with the aim of a simple comparison of EAS [21]. As listed in Table 1, the reduction charge of PdO per unit mass is decreased in the following order: Pt-Pd/C>Pd/C>Pt(Pd/C), which is in agreement with the results from XRD and TEM.

To evaluate ORR performances of catalysts, the polarization curves including ring currents were obtained with an RRDE in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, as presented in Fig. 6. The fraction of peroxide, $X_{\text{H}_2\text{O}_2}$, was calculated by using following equation: $X_{\text{H}_2\text{O}_2} = \frac{2I_{\text{O}}(N)}{(2I_{\text{O}}+I_{\text{E}}+I_{\text{L}})/(N)}$, where $I_{\text{O}}$, $I_{\text{E}}$, and $N$ represent ring current, disk current, and collection efficiency (N=0.37), respectively. For all the catalysts, the value of $X_{\text{H}_2\text{O}_2}$ at the kinetically controlled poten-
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The ORR performance in terms of ring current (proportional to the fraction of hydroxide formation) and onset potential is enhanced in the order of Pd/C < Pt-Pd/C < Pt(Pd/C) < Pt/C. In addition, it is worthwhile to compare the mass (the kinetic currents normalized to overall metal loadings) and specific activities (the kinetic currents normalized to the surface area) at fixed potentials (0.8 V and 0.85 V), as shown in Fig. 7. The kinetic current was calculated by using the following equation: \( i_k = i_L / (i_L - i) \), where \( i_k \), \( i_L \), and \( i \) represent the kinetic current, limiting current, and measured current, respectively. The surface area obtained from XRD measurement was used for the evaluation of specific activity. The Pt/C shows the highest activity, while the Pd/C has the lowest. Bimetallic catalysts exhibit lower activities than Pt/C. When considering very low activity of Pd/C, however, an enhancement in activity would be achieved by the addition of small amount of Pt to Pd/C.

CONCLUSIONS

Two Pd-based PtPd bimetallic samples supported on carbon were prepared by a co-impregnation (Pt-Pd/C) and a sequential impregnation [Pt(Pd/C)] method, and applied as an electro-catalyst for ORR. Depending on the catalyst preparation method, a different surface composition was obtained on each bimetallic catalyst. Due to higher standard potential of Pt precursor compared to Pd precursor, most of the Pt in the Pt-Pd/C was believed to be in the bulk phase of Pd, while the surface of Pt(Pd/C) was likely rich in Pt.

Although bimetallic catalysts showed lower activity than Pt/C, the addition of small amount of Pt to Pd/C was effective to obtain a catalyst with an enhanced ORR activity when considering a low activity of Pd/C. Compared to the Pt-Pd/C, the Pt(Pd/C) had higher ORR performance in terms of both mass activity and specific activity. This was believed to result from the Pt-rich surface on Pt(Pd/C).

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