Performance of membrane electrode assemblies using PdPt alloy as anode catalysts in polymer electrolyte membrane fuel cell

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Abstract

Pd-based nanoparticles, such as 40 wt.% carbon-supported Pd50Pt50, Pd75Pt25, Pd90Pt10 and Pd95Pt5, for anode electrocatalyst on polymer electrolyte membrane fuel cells (PEMFCs) were synthesized by the borohydride reduction method. PdPt metal particles with a narrow size distribution were dispersed uniformly on a carbon support. The membrane electrode assembly (MEA) with Pd95Pt5/C as the anode catalyst exhibited comparable single-cell performance to that of commercial Pt/C at 0.7 V. Although the Pt loading of the anode with Pd95Pt5/C was as low as 0.02 mg cm⁻², the specific power (power to mass of Pt in the MEA) of Pd95Pt5/C was higher than that of Pt/C at 0.7 V. Furthermore, the single-cell performance with Pd95Pt5/C and Pd90Pt10/C as the anode catalyst at 0.4 V was approximately 95% that of the MEA with the Pt/C catalyst. This indicated that a Pd-based catalyst that has an extremely small amount of Pt (only 5 or 50 at.%) can be replaced as an anode electrocatalyst in PEMFC.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are attractive power generators for vehicles, electronic devices, and stationary generators on account of their low operating temperature and high efficiency of energy conversion [1–4]. On the other hand, the commercialization of PEMFCs will require an increase in the lifespan of the membrane electrode assembly (MEA) on the PEMFC as well as a decrease in manufacturing cost [5–8]. The synthesis of Pt alloy catalysts, development of non Pt catalysts, and the reduced use of Pt catalysts through optimization of the catalyst layer structure to a three-phase boundary are effective ways of reducing the MEA cost [9–12] because electrocatalysts, such as carbon-supported Pt (Pt/C), demand a large fraction of material costs. The use of cathode catalysts for the oxygen reduction reaction (ORR) has been studied extensively to minimize the use of Pt in the MEA because the ORR is considered the kinetic limit for PEMFCs. For instance, Pt based metal alloy catalysts with transition metals such as PtCo/C, PtNi/C, PtCr/C, and PtFe/C were employed to improve the ORR activity [13–15]. In addition, Pd-based metal alloy catalysts such as PdPt/C, PdCo/C,
carbon-supported 60 wt.% Pd95Pt5 electrocatalyst as an anode deionized (D.I.) water, and Pt salt (H2PtCl6) were dispersed in carbon materials (Vulcan XC-72R, Carbot) were dispersed in deionized (D.I.) water, and Pt salt (H2PtCl6, Aldrich Chem. Co.) and Pd salt (Pd(NO3)2, Aldrich Chem. Co.) were added to the solution. After mixing the solutions, the metal salts were reduced by NaBH4. The resulting materials were rinsed with distilled water and dried at 70 °C.

The synthesized PdPt/C catalysts were characterized by X-ray diffraction (XRD, Rigaku D/MAX 2500) using a CuKα source at 40 kV and 100 mA. The prepared PdPt/C catalysts were scanned from 20 to 80° with a 2° min⁻¹. The particle size and dispersion of the synthesized catalysts were observed by high resolution transmission electron microscopy (HR-TEM, JEOL 2010). The differences in chemical composition among the synthesized PdPt/C catalysts were evaluated using energy dispersive X-ray (EDX; 7421, OXFORD).

For electrochemical characterization of the synthesized PdPt catalyst powder, cyclic voltammetry for the half-cell test was performed in a three-electrode electrochemical cell that consisted of a glass carbon electrode coated with a catalyst ink, saturated calomel electrode (SCE), and Pt wire as the working, reference, and counter electrodes, respectively. All potentials are quoted with respect to a reversible hydrogen electrode (RHE). The catalyst ink for the half-cell test was prepared using 0.1 g of catalyst. Cyclic voltammetry was conducted in a 0.5 M H2SO4 solution using a rotating disc electrode (RDE) at 25 °C. Linear sweep voltammetry was conducted from 0 to 0.3 V vs. RHE at 1 mV s⁻¹.

The MEAs were fabricated to test the single-cell performance of the prepared catalysts. The catalyst inks for the anode electrode were fabricated ultrasonically using the synthesized PdPt/C catalyst powders and a 5 wt.% Nafion solution (Aldrich Chem. Co) with D.I. water and isopropyl alcohol (IPA, Aldrich Chem. Co) as the solvent. The carbon-supported Pt catalyst powder (40 wt.% Pt/C, Johnson Matthey) was used as the cathode catalysts. Cathode catalyst inks also were prepared by the above method. For the preparation of MEA, the catalyst inks were sprayed directly onto both sides of the pretreated Nafion 212 membrane fixed to a frame to form the catalyst-coated membrane (CCM). The metal catalyst was loaded with 0.2 mg cm⁻² on all electrodes, and the active surface area on the MEA was 5 cm². The single-cell for the MEA performance test was assembled using a unit cell containing a pair of graphite plates engraved for a flow field with a physically placing gas diffusion layer (GDL, E-TEK). The single-cell was connected to a fuel cell test station to rigorously assess the MEA performance. Then, fully humidified H2 and air were fed to the anode and cathode with a 150 and 800 sccm, respectively. The cell temperature was set at 70 °C and backpressure on the single-cell was at ambient conditions.

### Results and discussion

Fig. 1 shows the XRD patterns of the synthesized Pd-based catalysts. It is well known that Pt and Pd have typical face-centered cubic (FCC) lattice structures, which have intrinsic peaks for (111), (200), and (220) planes, and they have a similar atom size and crystal structure. In all cases, the XRD patterns of Pd50Pt50/C, Pd75Pt25/C, Pd90Pt10/C, and Pd95Pt5/C exhibited similar peak positions, indicating that the PdPt catalysts have a single-phase structure. The XRD patterns of the synthesized Pd50Pt50/C, Pd75Pt25/C, Pd90Pt10/C, and Pd95Pt5/C catalysts are shown in Fig. 1. The diffraction peaks for (111), (200), and (220) planes are labeled in the figure. The XRD patterns confirm that the synthesized PdPt/C catalysts have a single-phase structure, which is important for their electrocatalytic activity.
profiles of the PdPt/C synthesized with various Pd contents showed the main peaks of the FCC structure. The (220) peak was used to calculate the average particle size of catalysts with the Scherrer equation \( L = \frac{0.9l}{B \cos \theta} \), where \( L \) is the average crystallite size, \( l \) is the X-ray wavelength (1.54056 Å) of the CuK\( \alpha \), \( B \) is the Full Width at Half Maximum (FWHM), and \( \theta \) is the Bragg angle because the (111) and (200) peaks with broad C peaks overlap each other [31]. The (220) peak positions were shifted in the negative direction when the Pd ratio was increased to 25% in the PdPt nanoparticles. However, the (220) peak position of Pd50Pt50/C was slightly shifted to the high theta position. Despite the presence of one exceptional sample (Pd50Pt50/C), it can be concluded that PdPt/C catalysts containing various ratios of Pd and Pt were well alloyed, because the feature peaks of all synthesized catalysts were located at intermediate positions between those of Pd and Pt. The average particle sizes of Pd50Pt50, Pd75Pt25, Pd90Pt10, and Pd95Pt5 obtained from XRD are approximately 3.4, 2.5, 2.7, and 2.8 nm, respectively.

Fig. 2 shows the HR-TEM images of prepared (a) Pd50Pt50/C, (b) Pd75Pt25/C, (c) Pd90Pt10/C, and (d) Pd95Pt5/C. PdPt metal particles in all prepared samples are uniformly dispersed on the carbon support without any major agglomeration. Based on measured mean particle size from randomly chosen particles in HR-TEM images, the particle sizes of Pd50Pt50, Pd75Pt25, Pd90Pt10, and Pd95Pt5 are approximately 3.2, 2.6, 2.8, and 2.9 nm, respectively, which are in good agreement with the XRD results. In addition, the (220) peak positions were shifted in the negative direction when the Pd ratio was increased to 25% in the PdPt nanoparticles. However, the (220) peak position of Pd50Pt50/C was slightly shifted to the high theta position. Despite the presence of one exceptional sample (Pd50Pt50/C), it can be concluded that PdPt/C catalysts containing various ratios of Pd and Pt were well alloyed, because the feature peaks of all synthesized catalysts were located at intermediate positions between those of Pd and Pt. The average particle sizes of Pd50Pt50, Pd75Pt25, Pd90Pt10, and Pd95Pt5 obtained from XRD are approximately 3.4, 2.5, 2.7, and 2.8 nm, respectively.

Fig. 2 shows the HR-TEM images of synthesized (a) Pd50Pt50/C, (b) Pd75Pt25/C, (c) Pd90Pt10/C, and (d) Pd95Pt5/C. PdPt metal particles in all prepared samples are uniformly dispersed on the carbon support without any major agglomeration. Based on measured mean particle size from randomly chosen particles in HR-TEM images, the particle sizes of Pd50Pt50, Pd75Pt25, Pd90Pt10, and Pd95Pt5 are approximately 3.2, 2.6, 2.8, and 2.9 nm, respectively, which are in good agreement with the XRD results. In addition, insets of Fig. 2(a)–(d) display that all catalysts have a narrow size distribution in metal particles. Fig. 3 shows histograms in particle size distributions of (a) Pd50Pt50/C, (b) Pd75Pt25/C, (c) Pd90Pt10/C, and (d) Pd95Pt5/C, which also are found to be well dispersed on the carbon with a narrow particle size distribution.

Fig. 4 shows the cyclic voltammograms of carbon-supported Pd50Pt50, Pd75Pt25, Pd90Pt10, and Pd95Pt5. The curve shapes in the cyclic voltammograms of the carbon-supported Pd50Pt50 and Pd95Pt5 representing the Pd-rich catalysts were similar to that of the typical Pd/C; whereas the curve shapes of carbon-supported Pd90Pt10 and Pd75Pt25 were similar to that of PdPt alloy nanoparticles in literature [23, 32]. When a positive scan was conducted, the curves of Pd50Pt50/C and Pd95Pt5/C showed two peaks that were similar to that of a typical Pd catalyst in the hydrogen adsorption/desorption region (around 0.1–0.2 V vs. RHE), but only one broad peak for the curves of Pd50Pt50/C and Pd95Pt5/C was observed in the hydrogen desorption region. In addition, the peak position of oxide reduction shifted to a positive potential with increasing Pt content in the PdPt/C nanoparticles.

Fig. 5 demonstrates the CO-stripping voltammograms of the commercial Pt/C, prepared Pd/C, and PdPt/C catalysts. The
main peaks of CO oxidation on the prepared PdPt/C were located at the intermediate position between that of CO oxidation on the Pt/C and Pd/C catalysts. The main peaks of CO oxidation on the Pd90Pt10/C and Pd95Pt5/C catalysts were closer to that on the Pd/C. The curve shapes of CV and the position of main peaks of CO oxidation on the prepared PdPt/C indicate that the surface enrichment of Pd in the Pd90Pt10/C and Pd95Pt5/C catalysts [24,33]. In addition, the onset potentials and main peaks of CO oxidation moved to more positive values with the Pd content in the PdPt/C catalysts. The electronic modification leads to change the position of CO oxidation peak. The shifts in the CO oxidation peaks suggest that the prepared PdPt/C catalysts were well alloyed [25,34]. The expected Pd and Pt atomic ratio in the synthesized PdPt/C catalysts was confirmed by EDX. As shown in Table 1, the Pd and Pt atomic ratios of the specimens showed a difference of approximately 2% from those of target materials but were close to the expected nominal value. This also suggests that the prepared PdPt/C catalysts were well alloyed.

Fig. 3 – Particle size histograms of (a) Pd50Pt50/C, (b) Pd75Pt25/C, (c) Pd90Pt10/C and (d) Pd95Pt5/C catalysts measured from the TEM images in the insets in Fig. 2.

Fig. 4 – Cyclic voltammograms of synthesized Pd50Pt50/C, Pd75Pt25/C, Pd90Pt10/C and Pd95Pt5/C catalyst powder.

Fig. 5 – CO-stripping voltammograms of the commercial Pt/C, synthesized Pd/C, Pd50Pt50/C, Pd75Pt25/C, Pd90Pt10/C and Pd95Pt5/C catalyst powder.
Fig. 6 shows the polarization curves for the HOR of the Pd95Pt5/C and commercial Pt/C at various rotating speeds. In all cases, the limiting current reaches at approximately 70 mV and the polarization curves of Pd95Pt5/C were similar to that of commercial Pt/C. The current density for the Pd95Pt5/C was slightly lower than that for commercial Pt/C. To determine the number of electrons involved in HOR, Koutecky–Levich plots of Pd 95Pt5/C and commercial Pt/C were obtained at 0.2 V. The measured total current density in RDE was composed of the kinetic current density \(j_k\) and diffusion limited current density \(j_d\) since the film resistance of Nafion is sufficiently small. Therefore, Koutecky–Levich equation is following as:

\[
\frac{1}{j} = \frac{1}{j_d} + \frac{1}{j_k} = \frac{1}{B \omega^{1/2}} + \frac{1}{j_k}
\]

where \(B\) is the Levich constant and \(\omega\) is the electrode rotation rate. The Levich constant defined as:

\[
B = 0.62nFD^{2/3}v^{-1/6}C_0
\]

where \(n\) is the number of electrons, \(F\) is the Faraday constant, \(D\) is the diffusion coefficient for hydrogen, \(v\) is the kinematic viscosity of electrolyte, and \(C_0\) is the concentration of hydrogen. Using this equation, number of electrons was calculated from the slope of Koutecky–Levich plots shown in Fig. 7. In both cases, approximately 2 electrons were involved in HOR.

Fig. 8 shows the single-cell performance of the MEA with Pd50Pt50/C, Pd75Pt25/C, Pd90Pt10/C, and Pd95Pt5/C for comparison with that of the MEA containing commercial Pt/C. As expected, the MEA with Pt/C as the anode catalyst showed the highest current density of the fabricated MEAs through the entire cell voltage region, which is in good accord with the half-cell test using RDE. On the other hand, as shown in the inset of Fig. 8, the current density of the MEA with the Pd95Pt5/C electrocatalyst at 0.7 V was sufficient to replace the MEA used in Pt/C, which is as much as 350 mA cm\(^2\). However, performance of the MEA with Pd95Pt5/C decreased gradually from below 0.65 V compared to that of the MEA containing commercial Pt/C and after all, dropped the lowest value at 0.4 V among prepared MEAs, which was 1210 mA cm\(^2\) and was approximately 22% lower than the MEA with Pt/C (1550 mA cm\(^2\)). For the MEAs used in Pd50Pt50/C and Pd75Pt25/C, the curvature of the polarization curve is similar (through the entire cell voltage region) to that of the MEA containing Pt/C, and the performance at 0.4 V, which is 1500 mA cm\(^2\), showed only a 5% difference from that of the MEA with Pt/C. Furthermore, the Pt loading on the anode with Pt/C, Pd50Pt50/C, Pd75Pt25/C, Pd90Pt10/C, and Pd95Pt5/C were 0.2, 0.13, 0.09, 0.03, and 0.02 mgPt cm\(^2\), respectively. The specific power (power to mass of Pt in the MEA) of Pd95Pt5/C (0.96 W mg\(^{-1}\)) at 0.7 V was higher than that of commercial Pt/C (0.74 W mg\(^{-1}\)). Yoo et al. reported that Pd in PtPd alloy modifies the electronic structure of Pt, which affects to improve the HOR activity [26].

<p>| Table 1 – The Pd/Pt atomic ratios from EDX analysis. |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd(<em>{50})Pt(</em>{50})</th>
<th>Pd(<em>{75})Pt(</em>{25})</th>
<th>Pd(<em>{90})Pt(</em>{10})</th>
<th>Pd(<em>{95})Pt(</em>{5})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/at.%</td>
<td>52.75</td>
<td>78.02</td>
<td>92.07</td>
<td>93.97</td>
</tr>
<tr>
<td>Pt/at.%</td>
<td>47.25</td>
<td>21.98</td>
<td>7.93</td>
<td>6.03</td>
</tr>
</tbody>
</table>

Fig. 6 – Polarization curves for HOR of (a) Pd\(_{50}\)Pt\(_{50}\)/C and (b) Pt/C catalyst powder at various rotation speeds.

Fig. 7 – Koutecky–Levich plots for HOR of Pd\(_{55}\)Pt\(_{5}\)/C and Pt/C catalyst powder.

Yoo et al. reported that Pd in PtPd alloy modifies the electronic structure of Pt, which affects to improve the HOR activity [26].
result, the Pd-based PdPt catalysts can be good candidates for replacing Pt as an anode electrocatalyst. It is well known that the synthesis method has a strong influence on the composition, dispersion, morphology, and performance of catalysts. The synthesized Pd-based catalysts in this study might not be well optimized for the HOR. Pd-based catalysts containing extremely small amounts of Pt are expected to replace the commercial Pt/C catalyst as the anode catalyst once adequate HOR activity can be achieved. Detailed studies of electrocatalytic activity with Pd:Pt compositions will be reported in at further study.

4. Conclusions

PdPt nanoparticles on carbon supports were synthesized with atomic ratios of Pd:Pt = 50:50, 75:25, 90:10, and 95:5. The prepared PdPt nanoparticles had unique electrochemical and structural characteristics associated with the Pd content. The mean particle size of prepared nanoparticles was 2–3 nm and showed a narrow size distribution and good dispersion on the carbon supports. Although the Pt loadings of Pd50Pt50/C and Pd75Pt25/C were as low as 0.13 and 0.09 mg cm$^{-2}$, respectively.

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