

Pd-based PdPt(19:1)/C electrocatalyst as an electrode in PEM fuel cell

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Abstract

A carbon supported Pd-based PdPt catalyst with a Pd:Pt atomic ratio of 19:1 was synthesized and applied to a polymer electrolyte membrane fuel cell (PEMFC). Three different types of single cells with the electrodes containing (PdPt/C:Pt/C), (Pt/C:PdPt/C) and (PdPt/C:Pt/C) as their anode and cathode electrocatalysts were fabricated and the performance of them was compared. The single cell using PdPt/C as the anode electrocatalyst showed a high performance comparable to the cell with a commercial Pt/C electrocatalyst. This indicates that Pd-based electrocatalysts can be used as an anode electrocatalyst in PEMFC with very small amount of Pt (just about 5 at.%).

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1. Introduction

The expense of rare metals such as platinum in a polymer electrolyte membrane fuel cell (PEMFC) is one of the most important barriers to the commercialization of fuel cells. The state-of-art PEMFC uses an expensive carbon supported platinum catalyst. Several methods have been used in an attempt to reduce the amount of platinum used in fuel cells. These include inventing a new MEA fabrication method [1–3], introducing a new supporting material to produce the maximum platinum activity [4–7], discovering a new electrocatalyst [8–11], etc. In addition, there is active research into the development of an alloyed electrocatalyst based on platinum [12–14].

In this study, a carbon supported Pd-based PdPt electrocatalyst with an atomic ratio of 19:1 (Pd:Pt) was applied to a PEMFC. The electrocatalyst used in this paper, contained only 5 at.% platinum. The results suggest that this electrocatalyst can be used in a PEMFC, and will result

in a dramatic reduction in the amount of Pt used and the price of PEMFC electrocatalysts.

This study fabricated three different types of single cells with electrodes containing (PdPt/C:Pt/C), (Pt/C:PdPt/C) and (PdPt/C:Pt/C) as their anode and cathode electrocatalysts compared their performance with that of Pt/C. In addition, the performance of PdPt/C and Pd/C as the anode catalyst and Pt/C as the cathode catalyst were compared.

2. Experimental

The carbon (Vulcan XC-72RTM, Cabot Co.) supported Pd and PdPt electrocatalysts were synthesized by the conventional sodium borohydride reduction method combined with freeze-drying [15,16]. PdCl₂ (Aldrich Co.) and H₂PtCl₆ · xH₂O (Aldrich Co.) were used as metal salts for PdPt/C and Pd/C nanoparticles. For dissolution of PdCl₂, hydrochloric acid (HCl, Aldrich Co.) was used with 5 times equivalence of Pd⁺² [17]. X-ray diffraction (XRD) patterns were taken by Powder X-ray diffractometer (Bruker Co.) using Cu K α source at a room temperature. High resolution-transmission electron spectroscopy (HR-TEM)

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analysis performed with working at 200 kV accelerating potential with a JEOL EM-2000 EXII microscope.

The electrocatalysts used were Pt/C (60 wt%, Johnson Matthey), PdPt/C (60 wt%, synthesized), Pd/C (60 wt%, synthesized). The catalyst ink was produced by mixing the catalysts ultrasonically in isopropyl alcohol (IPA) and a 5 wt% Nafion solution (Dupont). The catalyst-coated membrane (CCM) was fabricated by spraying the catalyst ink directly onto the polymer electrolyte membrane. Nafion 112 was used as the membrane, and the catalyst loading was 0.2 mg/cm² for both sides of Nafion 112. Anode and cathode gas diffusion layers were then placed on both sides of the CCM. The graphite plates with a serpentine channel were used for the single cell test, and the 1.5/2.0 stoichiometric hydrogen/oxygen gases were fed into the fuel cell. The temperature of the anode, cathode and single cell was kept at 70 °C, 75 °C and 70 °C, respectively, and the supplied gases were fully humidified at that temperature. The test was carried out at atmospheric pressure [18–20].

3. Results and discussion

The bulk atomic compositions of electrocatalysts were investigated using energy dispersive X-ray spectroscopy

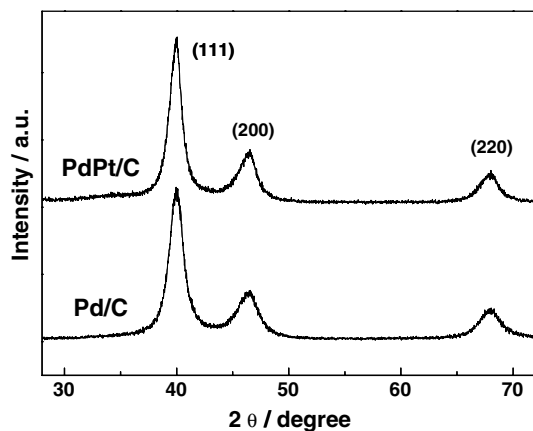


Fig. 1. X-ray diffraction (XRD) patterns of PdPt/C and Pd/C electrocatalysts.

(EDX) (not shown here). EDX results are in good agreement with nominal atomic ratio. Fig. 1 shows face centered cubic (FCC) structure of both PdPt(19:1) and Pd electrocatalyst nanoparticles. The average particle size of PdPt and Pd using Debye–Scherrer equation from the (220) peak broadness was 5.9 nm and 4.2 nm, respectively. In Fig. 2, well-dispersed PdPt and Pd nanoparticles are shown in HR-TEM images on the carbon substrate. However, distinctive feature was not detected by XRD and HR-TEM due to the similar atom size and identical crystal structure of both Pd and Pt [21].

Fig. 3 gives a summary of the single cell test results. The maximum power density using the PdPt/C electrocatalyst for both electrodes was 0.44 W/cm² and the current density was 250 mA/cm² at a cell voltage of 0.6 V. The cell with the Pt/C anode and PdPt/C cathode showed a maximum power density of 0.42 W/cm² and a current density of 150 mA/cm² at a fuel cell voltage of 0.6 V. However, the cell with the PdPt/C anode and Pt/C cathode showed a maximum power density of 0.75 W/cm², which is 170% higher than the other cells, and showed an approximately 340–550% higher performance at a voltage 0.6 V with a current density of 850 mA/cm². When PdPt/C was applied to both the anode and the cathode, the maximum power density was similar to the cell with the Pt/C anode and the PdPt cathode electrocatalysts. These data indicate the suitability of PdPt/C as an anode electrocatalyst in PEMFC.

Fig. 4 shows the single cell performance of the three different anodes with the PtPd/C, Pd/C and Pt/C electrocatalysts using same Pt/C cathode. The single cell with the Pt/C anode electrocatalyst shows a maximum power density of 0.80 W/cm², and a current density of 900 mA/cm² at a cell voltage of 0.6 V. The cell with the PdPt/C anode catalyst showed a power density of 0.75 W/cm². To confirm that PdPt/C has a catalytic activity on hydrogen oxidation as the Pt/C has, we measured the anode polarization curve with the same single cells and the curve. The anode polarization curve was measured in the current density range from 0 to 1 A/cm² at 70 °C of cell temperature while the humidified hydrogen gas was fed into the fuel cell anode and cathode part. In other words, the cathode part was

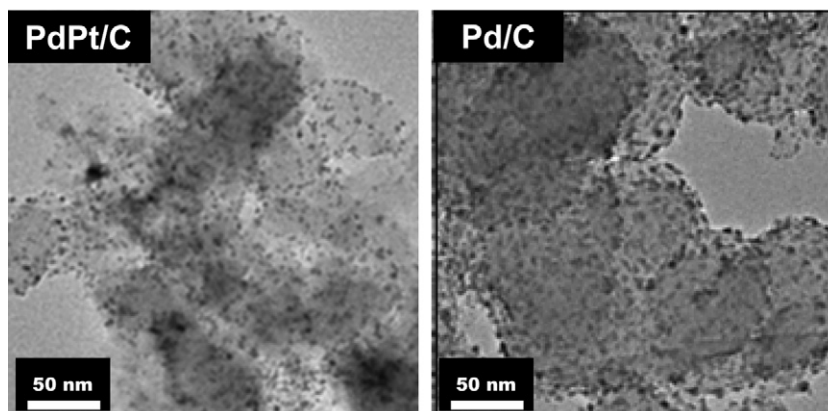


Fig. 2. High resolution-transmission electron spectroscopy (HR-TEM) images of PdPt/C and Pd/C electrocatalysts.

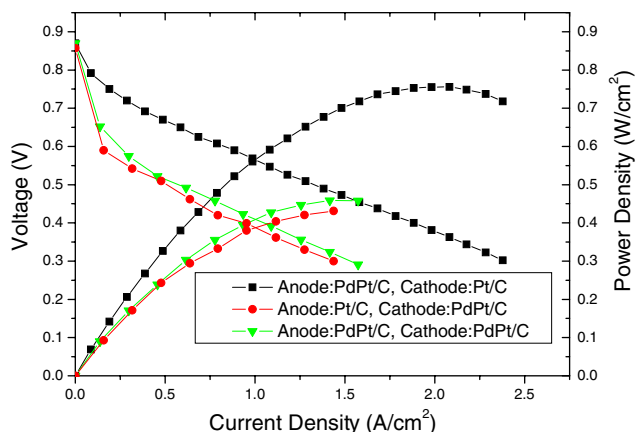


Fig. 3. Comparison of single cell performance fabricated with electrodes of (PdPt/C:Pt/C), (Pt/C:Pt/C) and (PdPt/C:Pt/C) as their anode and cathode electrocatalysts.

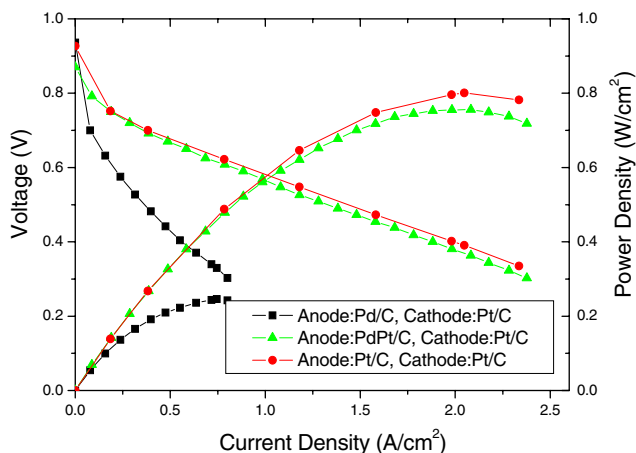


Fig. 4. Comparison of single cell performance fabricated with electrodes of (Pt/C:Pt/C), (Pd/C:Pt/C) and (PdPt/C:Pt/C) as their anode and cathode electrocatalysts.

used as the dynamic hydrogen electrode. PdPt/C catalyst shows a similar polarization curve with the Pt/C catalyst (not shown here). However, the single cell with the Pd/C anode catalyst showed a very low power density of 0.22 W/cm^2 , and a current density of approximately 190 mA/cm^2 at a cell voltage of 0.6 V . This is a very poor performance compared with the others, and suggests that Pd/C is not suitable as an anode electrocatalyst. In contrast, interestingly, the single cell using Pd + 5 at.% Pt as the anode electrocatalyst showed a high performance comparable to the cell with a commercial Pt/C electrocatalyst. These results suggest that Pd-based electrocatalysts with very small amount of Pt can be a good electrocatalyst material for the anode in PEMFC. Detailed studies of the catalyst analysis and origin of the performance enhancement of PtPd(19:1) will be reported in the future.

4. Conclusion

The performance of three different types of single cells fabricated with electrodes containing (PdPt/C:Pt/C), (Pt/

C:Pt/C) and (PdPt/C:Pt/C) as their anode and cathode electrocatalysts. The cell containing the PdPt/C anode electrocatalyst and Pt/C cathode electrocatalyst shows a maximum power density of 0.75 W/cm^2 , which was 170% higher than the other electrocatalysts. This indicates that PdPt/C (Pd : Pt atomic ratio of 19:1) with only 5 at.% Pt is suitable for use as an anode electrocatalyst. In addition, the single cell performance of the three different cells containing the PdPt/C, Pd/C and Pt/C anode electrocatalysts with same Pt/C cathode electrocatalyst were compared. The single cell containing the Pd/C anode catalyst showed a very low power density compared with the other cells. When PdPt/C was used as the anode electrocatalyst, the maximum power density was similar to the cell containing the Pt/C anode electrocatalyst. Based upon these results, it is believed that very small amount of Pt ($\sim 5 \text{ at.}\%$) applied to Pd maximize the hydrogen oxidation reaction. Experiments are underway in an attempt to understand the mechanism.

Acknowledgments

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