

Investigation of Mass transport in Polymer Electrolyte Membrane Fuel Cells

M. Prasanna, H.Y. Ha, E.A. Cho, S.-A. Hong and I.-H. Oh*

Fuel cell Research Center, Korea Institute of Science and Technology,
39-1 Hawolgok-dong, Sungbuk-gu, Seoul 136-791, South Korea

Introduction

Performance of the proton exchange membrane fuel cell (PEMFC) is lowered when the cathode gas is changed from oxygen to air, due to the reduced oxygen partial pressure and the blanketing effect of nitrogen. The difference in the cell potential obtained using pure oxygen and air at a given current density is called as oxygen gain. Since air would be used as the cathode gas in most applications, it is strongly required to reduce the oxygen gain.

According to previous studies [1-17], oxygen gain could be reduced by increasing oxygen partial pressure in the cathode gas [1-4] or by modifying the structure of cathode catalytic layer [5-17]. The oxygen partial pressure could be increased by using a compressor or by enrichment, which resulted in a decrease in oxygen gain [1-4]. Modification of the structure of cathode catalytic layer was also effective in reducing oxygen gain [5-17]. Yoon *et al.* [5] reported that addition of pore forming agents to the catalytic layer reduced oxygen gain by facilitating the oxygen transport in the catalytic layers even though accompanied by an increase in ohmic resistance. Oxygen transport in the catalytic layer could also be facilitated by self-organizing the nanostructure of the electrode [6]. Xin Wang *et al.* [7] employed binary mixtures of carbon support (Vulcan XC72 and Black Pearl 2000) having different surface area to provide the electrode with good electrical conductivity and obtained an improved cell performance. Cell performance was also improved either by increasing Pt surface area or by using higher Pt content of the catalyst [8]. On the other hand, various membrane-electrode assembly (MEA) fabrication methods such as spraying, powder deposition, spreading, decal/direct coating on membrane and sputter deposition of catalyst were applied to the modification of catalytic layer structure to improve cell performance [9-17].

In this study, oxygen gain which is an index of mass transfer resistance was investigated by measuring the cell performance as a function of carbon support, Pt content in the catalyst and membrane electrode assembly (MEA) fabrication process.

2. Experimental

2.1. Preparation of Membrane electrode assemblies (MEAs)

Catalyst ink was prepared by mixing catalyst powder with isopropyl alcohol and then, the mixture was ultrasonicated for 1 hr. 5 wt% Nafion[®] solution (Du Pont, Inc) was added to the catalyst ink, which was sonicated again for 1 hr. To examine effects of carbon support and Pt content on oxygen gain, two sets of catalyst powder were used; 40 wt% Pt supported on Shawinigan acetylene black (SAB), Vulcan XC 72, an undisclosed carbon (C-UD) and Black Pearl 2000; 10, 20, 40 and 60 wt% Pt on Vulcan XC 72.

Membrane electrode assemblies (MEAs) were fabricated by the conventional and the catalyst coated membrane (CCM) methods. For a conventional MEA, the prepared catalyst ink was sprayed on the wet-proofed carbon paper. Then, the electrodes were placed at both sides of a pre-treated Nafion 115 membrane and hot pressed. On the other hand, a CCM was fabricated by spray-coating the prepared ink on a pre-treated Nafion 115 membrane. Then, the prepared CCM was kept inside a polythene cover and dried at room temperature to avoid the formation of cracks prior to hot pressing with gas diffusion media at the same condition to form a MEA. In both methods, the active electrode area was 25 cm² with platinum loading of 0.3 and 0.4 mg/cm² for anode and cathode, respectively, and the hot pressing was conducted at 140 °C and 200 kg/cm² for 90 s. Without specific notification, the MEA was fabricated using 20 wt% Pt/Vulcan XC 72 by the CCM method as a standard condition.

2.2. Single Cell Tests

Single cells were assembled with the prepared MEAs, Teflon gaskets and graphite blocks. Hydrogen and a cathode gas were fed to the anode and cathode, respectively, after passing through a bubble humidifier. Operating temperature and pressure were 80 °C and 1 atm, respectively. Cathode and anode humidification temperatures are 65 and 80 °C. Performance of the single cell was evaluated by measuring the *I-V* characteristics using an electronic loader (Daegil Electronics, EL 500P).

3. Results and Discussion

3.1. Effects of carbon support of the catalyst on the oxygen gain

Carbon supports of the catalyst are used to provide high dispersion to platinum particles and good electronic conductivity to the electrode. Additionally, the high porosity of the carbon support contributes to improvement of mass transport at high current densities [18]. Thus, carbon support would affect the electrode structure, gas transport and hence the oxygen gain. In this study, Pt supported on Shawinigan acetylene black (SAB), Vulcan XC 72, an undisclosed carbon (C-UD) and Black Pearl 2000 were applied to the MEA fabrication. To examine porosity of Pt catalyst supported on the different carbon, nitrogen adsorption and BET analysis was carried out and the results are summarized in Table 1.

Table 1. Physical properties of Pt catalyst supported on Shawinigan Acetylene Black (SAB), Vulcan XC 72, an undisclosed carbon (C-UD) and Black Pearl 2000 obtained from BET surface analysis.

	Pt/SAB	Pt/Vulcan XC 72	Pt/C-UD	Pt/Black Pearl 2000
Catalyst Purchased	E-Tek	E-Tek	UD ^{a)}	E-Tek
Pt ^{b)} (%)	39.7	40.6	46.5	38.6
BET surface area (m ² /g)	58	127	382	776
Microporous volume (cm ³ /g)	0.0097	0.0321	0.0884	0.2164
Mesoporous volume (cm ³ /g)	0.0789	0.1505	0.3351	0.8531
Macroporous volume (cm ³ /g)	0.0472	0.1554	0.2423	0.4561
Average pore diameter (nm)	6.1	5.7	4.3	5.3

^{a)} Undisclosed.

^{b)} From the manufacturer

Micro-, meso-, and macro-pores were defined to be pores whose diameter was below 0.002 μm, from 0.002 to 0.05 μm and above 0.05 μm,

BET surface area and pore volumes were calculated based on the total weight of Pt catalyst and the carbon support. Even though all the catalysts contained similar wt% Pt, BET surface area of the catalysts were considerably different; BET surface area of Pt/Shawinigan acetylene black (SAB), Pt/Vulcan XC72, Pt/C-UD and Pt/Black Pearl 2000 was 58, 127, 382 and 776 m²/g, respectively. Volume of micro- (diameter < 0.002 μm), meso- (0.002 ~ 0.05 μm) and macro- (>0.05 μm) pores also increased in the same order. Those results imply that Pt/Black Pearl 2000 has the smallest particle size and the highest porosity among the studied catalysts, followed by Pt/C-UD, Pt/Vulcan XC 72 and Pt/SAB.

Fig. 1 shows performance and oxygen gain of the single cells employing the catalysts. In the whole current range, Pt/C-UD and Pt/Black Pearl 2000 produced almost same and the best performance and the lowest oxygen gain, followed by Pt/Vulcan XC 72 and Pt/SAB. Those results reveal that the catalyst with high BET surface area could improve the cell performance probably due to high electrochemical active surface area, which can be estimated in terms of roughness factor (electrochemical surface area/apparent electrode area) calculated from the charge of hydrogen oxidation peak observed on cyclic voltammograms.

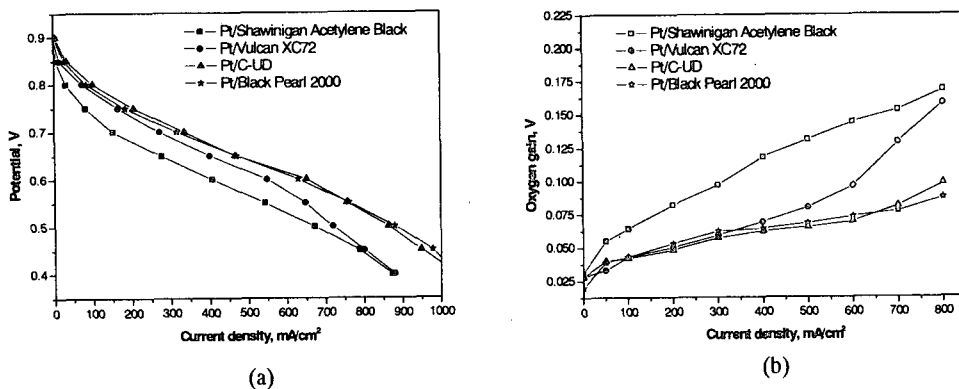


Fig. 1 Effects of carbon support on (a) the cell performance and (b) oxygen gain measured at a cell temperature of 80 °C.

Fig. 2 demonstrates cyclic voltammograms for the single cells, exhibiting the current density of the hydrogen oxidation peak observed at about 100 mV. During the measurement of cyclic voltammograms, humidified nitrogen was fed to the working electrode (cathode) and humidified hydrogen to the counter and reference electrode (anode). Thus, the roughness factor estimated from cyclic voltammograms could be associated with the cathode catalytic layer. Under the assumption that the adsorption/desorption charge for the hydrogen monolayer on platinum is $210 \mu\text{C}/\text{cm}^2$ [8], roughness factor of the Pt/SAB, Pt/Vulcan XC 72, Pt/C-UD and Pt/Black Pearl 2000 was calculated to be 45.3, 109.8, 260.5 and $263.1 \text{ cm}^2/\text{cm}^2$. In accordance with the cell performance shown in Fig. 1, Pt/C-UD and Pt/Black Pearl 2000 exhibited the highest roughness factor, followed by Pt/Vulcan XC 72 and Pt/SAB. It should be noted that even though Pt/Black Pearl 2000 has the higher BET surface area and the higher porosity than Pt/C-UD, performance and roughness factor of the cells using Pt/Black Pearl 2000 and Pt/C-UD was almost same. According to a previous study on the electrode structure [19], above a critical porosity limit, catalyst utilization can be reduced since the catalyst particles are embedded in the micro-pores, not in contact with the electrolyte, and thus cannot participate in the electrochemical reaction.

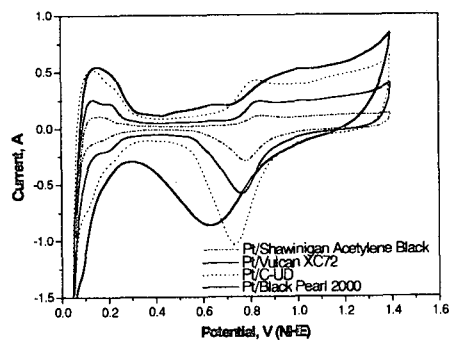


Fig. 2 Effects of carbon support on cyclic voltammograms obtained at 80 °C. Scan rate was 50 mV/s.

3.2. Effects of Pt content of the catalyst on the oxygen gain

To examine effects of Pt content of the catalyst on the cell performance, single cells were fabricated using 10, 20, 40 and 60 wt% Pt on Vulcan XC 72, whose properties were summarized in Table 2.

Generally, Pt content of the carbon-supported catalyst affects the cell performance mainly in two ways. As shown in Table 2, platinum particle size increases with increasing the Pt content due to agglomeration, resulting in a lowered Pt surface area at a given loading. On the other hand, as the Pt content increases, thickness of the catalytic layer decreased leading to a decrease in ohmic and mass transfer resistance since smaller amount of carbon was included in the catalytic layer at a given Pt loading. Thus, there would be an optimal Pt content.

Table 2. Physical properties of Pt/Vulcan XC72 containing 10, 20, 40, and 60 wt% Pt.

Pt/Vulcan XC72 ^{a)} (%)	Average Pt Particle size ^{b)} (Å)	Pt surface area ^{c)} (m ² /g)	Thickness of catalyst layer ^{d)} (µm)
9.3	20	140	34.0
19.8	25	112	23.0
40.6	39	72	11.7
59.1	88	32	3.5

^{a)-c)} From manufacturer

^{d)} Measured from cross-sectional SEM images for the cathode with a platinum loading of 0.4 mg/cm².

Fig. 3 demonstrates performance and oxygen gain of the single cells employing 10, 20, 40 and 60 wt% Pt/C with constant Pt loading of 0.3 and 0.4 mg/cm² for anode and cathode, respectively. In the whole current density region, 20 wt% Pt/C produced the highest performance and lowest oxygen gain followed by 40, 10, and 60 wt% Pt. Therefore, in this case, 20 wt% is the optimal Pt content of the catalyst due to the trade-off between platinum surface area and thickness of the catalytic layer. The oxygen gains at 500 mA/cm² were around 70~80 mV for Pt content below 40 wt% and about 180 mV for 60 wt% Pt/C, much higher than the others. Thickness of the catalytic layer and Pt surface area of 60 wt% Pt/C were 1/7 and 1/4, respectively, of those of 20 wt% Pt/C, as shown in Table 2.

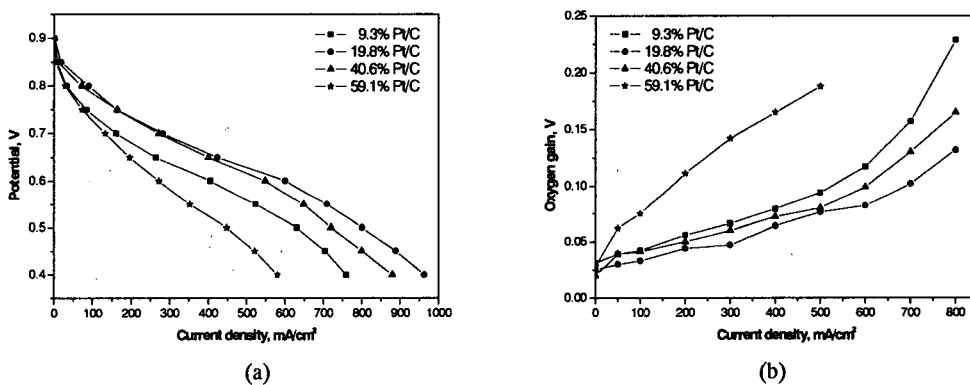


Fig. 3 Effects of Pt content in Pt/Vulcan XC 72 catalyst on (a) the cell performance and (b) oxygen gain measured at a cell temperature of 80 °C.

Those results imply that the decrease in mass transport rate could not compensate for the decrease in Pt surface area for the 60 wt% Pt/C catalyst layer and that Pt surface area could be more important than mass transport resistance in the catalyst layer when air is used.

Fig. 4 exhibits Nyquist plots for the single cells, revealing that the single cell using 20 wt% Pt/C had the lowest charge transfer resistance in accordance with the cell performance shown in Fig. 3. Ohmic resistance of the single cell was almost constant to be 0.125 Ωcm², independent of Pt content in the catalyst powder. On the other hand, with increasing Pt content from 10 to 60 %, charge transfer resistance of the cell changed significantly from 0.73 to 1.72 ohm cm² also due to the trade-off between platinum surface area and mass transfer resistance.

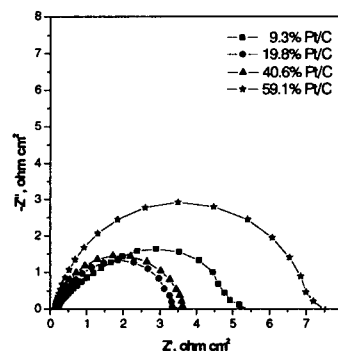


Fig. 4 Effects of Pt content in Pt/Vulcan XC 72 catalyst on Nyquist plots for the single cell at a cell temperature of 80 °C.

3.3. Effects of MEA fabrication condition on the oxygen gain

In addition to catalyst support and Pt content, MEA fabrication process would have significant effects on the electrode structure. To study the effects of MEA fabrication process on the cell performance, MEAs were prepared by two methods; the conventional method and the CCM (catalyst coated membrane) method as described in the experimental section.

Catalyst loading in the active layer was same for both methods. Fig. 5 (a&b) demonstrates performance and oxygen gain of the single cells. The MEA made by the CCM method exhibited the better performance and the lower oxygen gain than the conventional MEA, probably due to the reduced catalyst loss to the gas diffusion media (GDM) [16]. Nyquist plots presented in Fig. 5(c) confirms that the lower charge transfer resistance of the MEA prepared by CCM method than the conventional MEA.

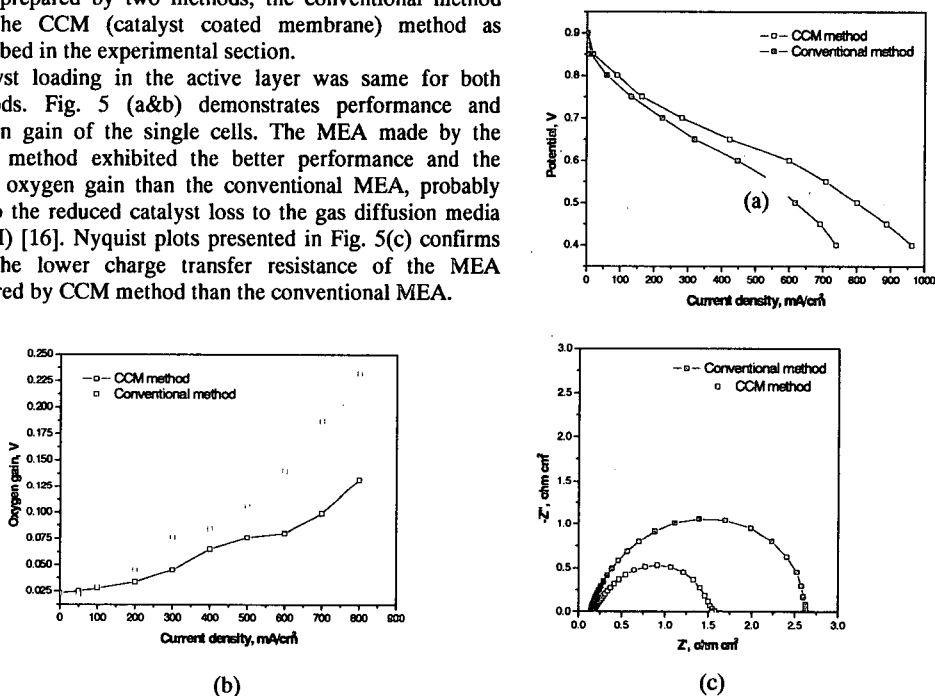


Fig. 5 Effects of MEA fabrication process on (a) the cell performance (b) oxygen gain measured and on (C) Nyquist plots for the single cell at a cell temperature of 80 °C..

4. Conclusions

Oxygen gain of the PEMFC was investigated as a function of oxygen concentration, catalyst, MEA fabrication process and cathode humidification. With decreasing oxygen concentration in the cathode gas, performance of the cell was lowered due to the decrease in oxygen partial pressure and blanketing effect of nitrogen. For the Pt catalysts supported on various carbon, the cell performance was improved as surface area and porosity of the catalyst increased to a certain level, above which a large portion of catalyst particles were embedded in the micropores of the carbon support and could not participate in the electrochemical reaction. Among 10, 20, 40 and 60 wt% Pt supported on Vulcan XC72, 20 wt% Pt/C exhibited the best performance due to the trade-off between platinum surface area and thickness of the catalytic layer. The MEA fabricated by the CCM method showed higher performance than the conventional MEA probably due to the reduced catalyst loss into the GDM.

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