

Investigation of oxygen gain in polymer electrolyte membrane fuel cells

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Abstract

The polymer electrolyte membrane fuel cell (PEMFC) faces an efficiency loss, so called “oxygen gain”, when the cathode gas is changed from oxygen to air due to the reduced oxygen partial pressure. To reduce the oxygen gain of a PEMFC, performance and oxygen gain of the single cells were evaluated as a function of carbon support, Pt content in the catalyst, membrane electrode assembly (MEA) fabrication process and the cathode humidification temperature. Among the tested carbon supports, Black Pearl 2000 and an undisclosed carbon produced the best performance and the lowest oxygen gain with their high surface area and high pore volume. As the Pt content in the catalyst increased from 10 to 60 wt.%, Pt surface area and the electrode thickness decreased leading to decreases in active catalyst surface area, and an ohmic and mass transfer resistance of the electrode. Due to trade-off effects, 20 wt.% Pt exhibited the highest performance. Compared to the conventional MEA, the MEA prepared using catalyst-coated membrane (CCM) method showed better performance with reduced catalyst loss into the gas diffusion media (GDM). As the cathode humidification temperature increased from 55 to 85 °C, the amount of water supplied to the cathode increased, leading to an increase in ionic conductivity of the membrane and another probability of water flooding. Thus, in the low current density region, performance of the single cell was improved with cathode humidification temperature, while in the high current density region, the single cell showed the highest performance at the cathode humidification temperature of 65 °C with water flooding at 75 and 85 °C.

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1. 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 advantages to reduce the oxygen gain.

According to previous studies [1–19], 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 [5–19]. The oxygen partial pressure could be increased by using a compressor or by enrichment, which has resulted in a decrease in oxygen gain [1–4]. However, the compressed reactants reduced lifetime of the PEMFC and

the oxygen enrichment lowered the whole system efficiency due to a high energy consumption of the enrichment process with current technologies. 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 into 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 [7]. Wang et al. [6] 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 obtain 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

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the modification of catalytic layer structure to improve cell performance [9–17].

As described above, oxygen gain is affected by operating conditions and the electrode characteristics, which, in turn, are influenced by the catalyst, carbon support and MEA fabrication process. To improve performance of the PEMFC operating on air, Prasanna et al. investigated oxygen gain as a function of MEA fabrication and operating conditions [18]. In the first part of the study [18], they measured oxygen gain with changing thickness and hydrophobicity of gas diffusion media (GDM), and reported that 20% PTFE-coated carbon paper with thickness of 175 μm produced the best cell performance among the tested gas diffusion media. In this study, as the second part, oxygen gain was investigated by measuring the cell performance as a function of oxygen concentration in the cathode gas, carbon support, Pt content in the catalyst, membrane electrode assembly fabrication process and cathode humidification temperature.

2. Experimental

2.1. Preparation of membrane electrode assemblies

Catalyst ink was prepared by mixing catalyst powder with isopropyl alcohol and then, the mixture was ultrasonicated for 1 h. 5 wt.% Nafion[®] solution (Du Pont, Inc.) was added to the catalyst ink, which was sonicated again for 1 h. 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 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 cm^2 with platinum loading of 0.3 and 0.4 mg/cm^2 for anode and cathode, respectively, and the hot pressing was conducted at 140 $^\circ\text{C}$ and 200 kg/cm^2 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. As the cathode gas, air and gas mixtures of oxygen and nitrogen were used. Oxygen concentration in the gas mixture was changed from 40 to 100%. Operating temperature and pressure were 80 $^\circ\text{C}$ and 1 atm, respectively. Cathode humidification temperature was changed from 55 to 85 $^\circ\text{C}$ with a constant anode humidification of 80 $^\circ\text{C}$. If otherwise unspecified, the cathode humidification was 65 $^\circ\text{C}$.

Performance of the single cell was evaluated by measuring the I - V characteristics using an electronic loader (Daegil Electronics, EL 500P). Polarization resistance of the single cells was investigated by measuring AC impedance of the single cells with the oxygen electrode as the working electrode and the hydrogen electrode as the reference and counter electrode. IM6 (ZAHNER) was used for the impedance measurement and the applied frequency was varied from 10 mHz to 10 kHz with an excitation voltage of 5 mV (peak-to-peak). The electrochemical active surface area was estimated from cyclic voltammograms measured at a scan rate of 50 mV/s and at a cell temperature of 80 $^\circ\text{C}$. During the measurement of cyclic voltammograms, humidified nitrogen was fed to the working electrode and humidified hydrogen to the counter electrode. For the measurements of AC impedance and cyclic voltammograms, the counter electrode also served as a reference electrode since the overpotential at the counter electrode for the hydrogen oxidation or evolution reaction is negligible [19].

3. Results and discussion

3.1. Oxygen gain

Before examining effects of MEA fabrication condition and cathode humidification temperature on oxygen gain, oxygen gain was examined by measuring the performance of the single cell with feeding air or gas mixture of oxygen and nitrogen to the cathode, as presented in Fig. 1. The MEA was prepared using 20 wt.% Pt/Vulcan XC 72 and by the CCM method. The operating temperature of the cell was 80 $^\circ\text{C}$ with humidifying the anode and cathode gas at 80 and 65 $^\circ\text{C}$, respectively. The cathode gases were physically mixed using mass flow controllers with oxygen concentration from 40 to 100%. With decreasing oxygen concentration from 100 to 21% (air), the cell voltage was lowered in the whole current density region, which could be attributed to the decrease in oxygen partial pressure and the blanketing effect of nitrogen. On the performance curve obtained with air, cell voltage dropped sharply at the high current region probably due to mass transport limitation.

To investigate effects of oxygen concentration on the ohmic and charge transfer resistance of the single cell, the impedance of the single cell was measured at a cell voltage of 0.85 V. Fig. 2 presents Nyquist plots for the single cell obtained with air and the gas mixtures. The Nyquist plots are semi-circular; the left point of intersection with the

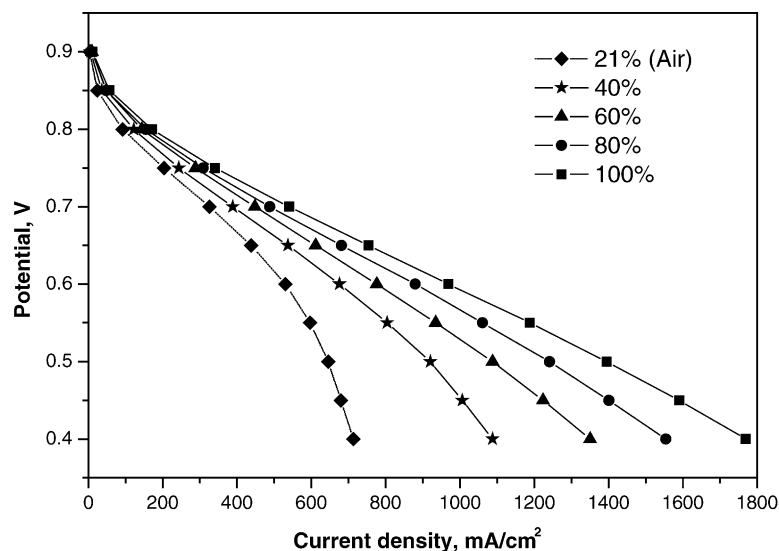


Fig. 1. Effects of oxygen concentration in the cathode gas on the cell performance measured at a cell temperature of 80 °C.

x -axis corresponds to the ohmic resistance and the diameter of the semi-circle to the charge transfer resistance [20]. In the AC impedance measurement, the oxygen electrode served as the working electrode and hydrogen electrode as the counter electrode. The counter electrode also served as the reference with its negligible overpotential for the hydrogen oxidation or evolution reaction [19]. Thus, the charge transfer resistance obtained through the AC impedance study primarily could be attributed to the oxygen reduction reaction. Ohmic resistance of the single cell was almost constant to be $0.125 \Omega \text{ cm}^2$, independent of oxygen concentration in the cathode gas. On the other hand, with decreasing oxygen concentration from 100 to 21%, the charge

transfer resistance of the cell increased significantly from 0.73 to $1.72 \Omega \text{ cm}^2$ due to low oxygen concentration in the catalytic layer even though at the cell potential of 0.85 V , consumption of oxygen was relatively low. Figs. 1 and 2 reflect that oxygen gain could originate from the increase in charge transfer resistance caused by dilution of oxygen in the catalytic layer and also from the mass transport resistance particularly observed with air performance at high current densities.

3.2. Effects of MEA fabrication conditions on the oxygen gain

The electrode structure of the PEMFC strongly depends upon the MEA fabrication conditions, such as carbon support, Pt content and MEA fabrication process. Carbon supports of the catalyst are used to provide high dispersion for 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 [21]. Thus, the 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 the Pt catalyst supported on the different carbons, nitrogen adsorption and BET analysis were carried out, and the results are summarized in Table 1. 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, the BET surface area of the catalysts were considerably different; BET surface areas of Pt/Shawinigan acetylene black, Pt/Vulcan XC72, Pt/C-UD and Pt/Black Pearl 2000 were 58 , 127 , 382 and $776 \text{ m}^2/\text{g}$, respectively. Volume of micro-

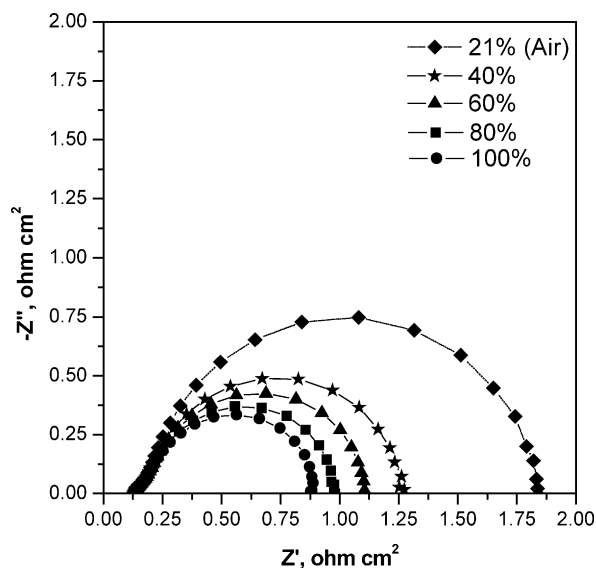


Fig. 2. Effects of oxygen concentration in the cathode gas on Nyquist plots for the single cell at a cell temperature of 80 °C.

Table 1

Physical properties of the 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

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

^a Undisclosed.

^b From the manufacturer.

(diameter $<0.002 \mu\text{m}$), meso- (0.002 \sim 0.05 μm) and macro- ($>0.05 \mu\text{m}$) pores also increased in the same order. These 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. 3 shows performance and oxygen gain of the single cells employing the catalysts. In the whole current range,

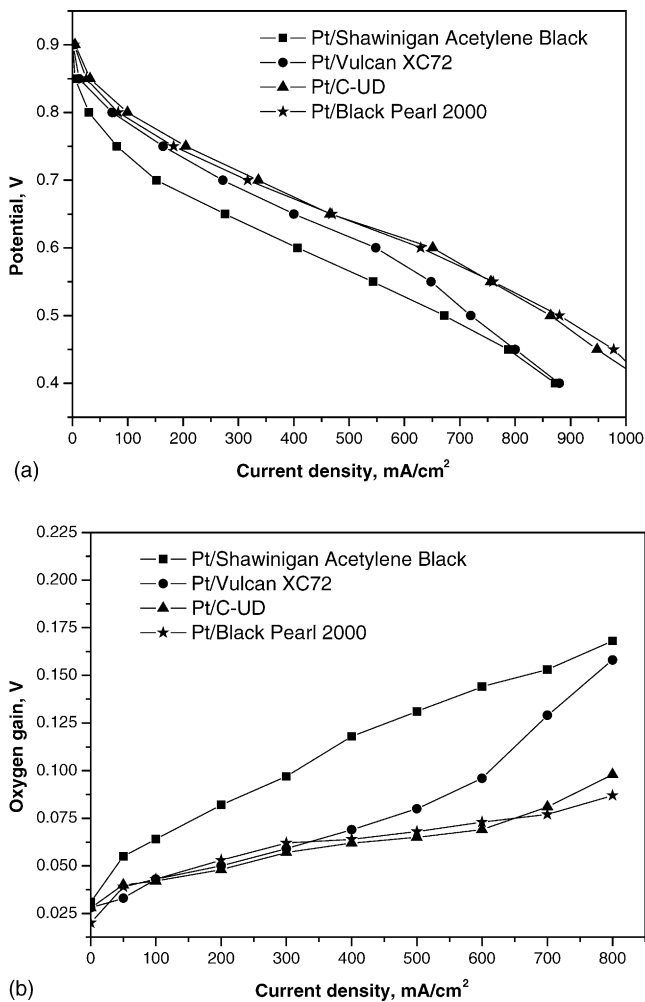


Fig. 3. Effect of carbon support on (a) the cell performance and (b) oxygen gain measured at a cell temperature of 80 °C.

Pt/C-UD and Pt/Black Pearl 2000 produced almost the same and the best performance, and the lowest oxygen gain, followed by Pt/Vulcan XC 72 and Pt/SAB. These 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 the roughness factor (electrochemical surface area/apparent electrode area) calculated from the charge of hydrogen oxidation peak observed on cyclic voltammograms. Fig. 4 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], the roughness factors of the Pt/SAB, Pt/Vulcan XC 72, Pt/C-UD and Pt/Black Pearl 2000 were calculated to be 45.3, 109.8, 260.5 and 263.1 cm^2/cm^2 . In accordance with the cell performance shown in Fig. 3, Pt/C-UD and Pt/Black Pearl 2000 exhibited the highest roughness factors, 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 were almost same. According to a previous study [22], above a critical porosity limit, catalyst utilization can be reduced since the catalyst particles are embedded in the micropores, not in contact with the electrolyte, and thus cannot participate in the electrochemical reaction.

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. The thickness of the catalytic layer was measured from cross-sectional scanning electron microscopy (SEM) images for the MEAs with same Pt loading of 0.4 mg/cm^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

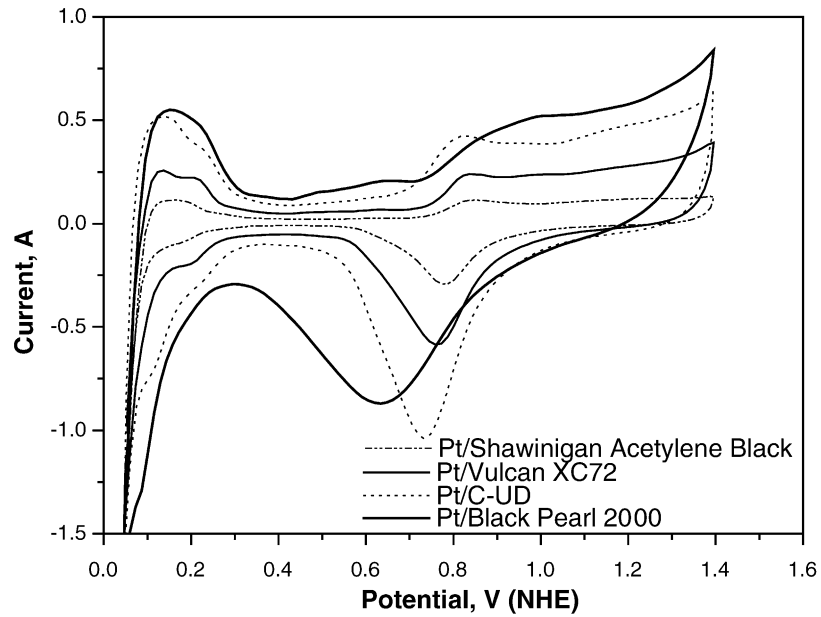


Fig. 4. Effects of carbon support on cyclic voltammograms obtained at 80 °C. Scan rate was 50 mV/s.

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.

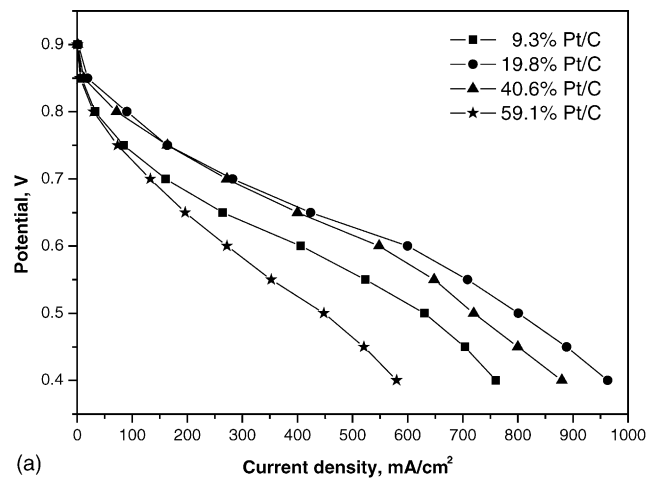
Fig. 5 demonstrates performance and oxygen gain of the single cells employing 10, 20, 40 and 60 wt.% Pt/C with constant Pt loading of 0.3 and 0.4 mg/cm² for anode and cathode, respectively. In the whole current density region, 20 wt.% Pt/C produced the highest performance and the lowest oxygen gain followed 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 contents 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. These results

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

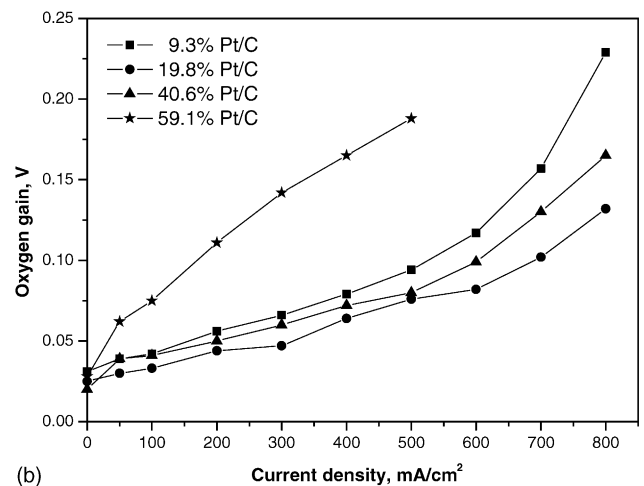
Pt/Vulcan XC72 ^a (%)	Average Pt particle size ^a (Å)	Pt surface area ^a (m ² /g)	Thickness of catalyst layer ^b (μm)
9.3	20	140	34.0
19.8	25	112	23.0
40.6	39	72	11.7
59.1	88	32	3.5

^a From manufacturer.

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



(a)



(b)

Fig. 5. 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.

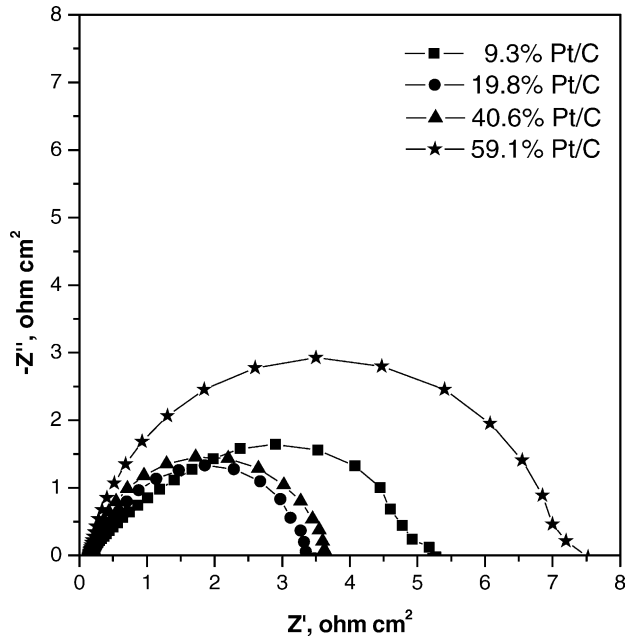


Fig. 6. Effects of Pt content in Pt/Vulcan XC 72 catalyst on Nyquist plots for the single cell at a cell temperature of 80°C; H₂/Air.

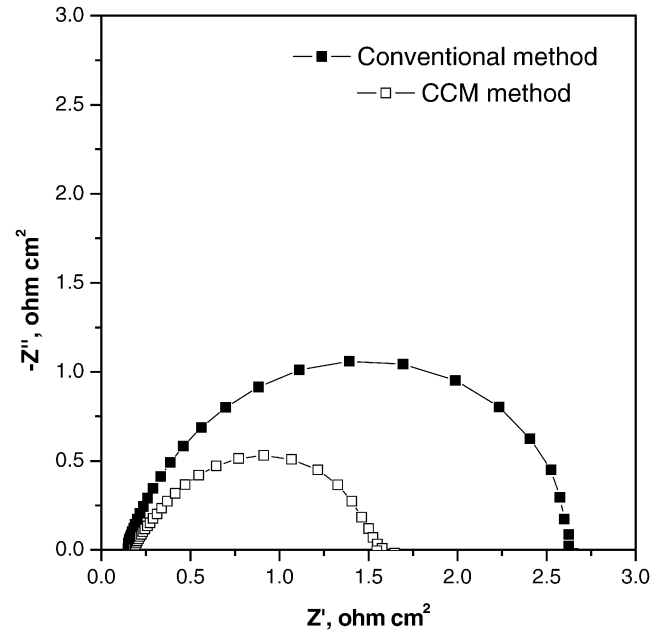
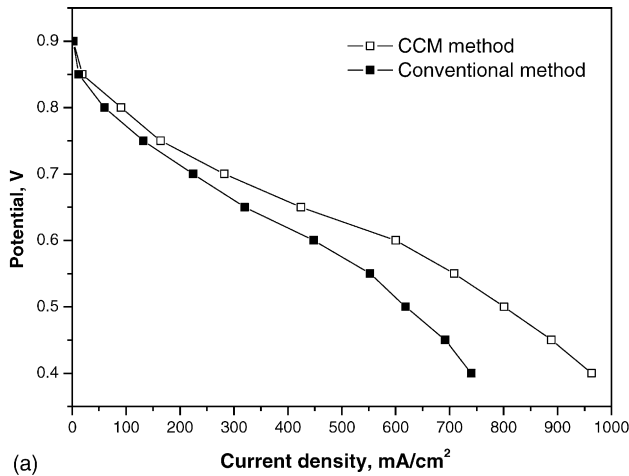
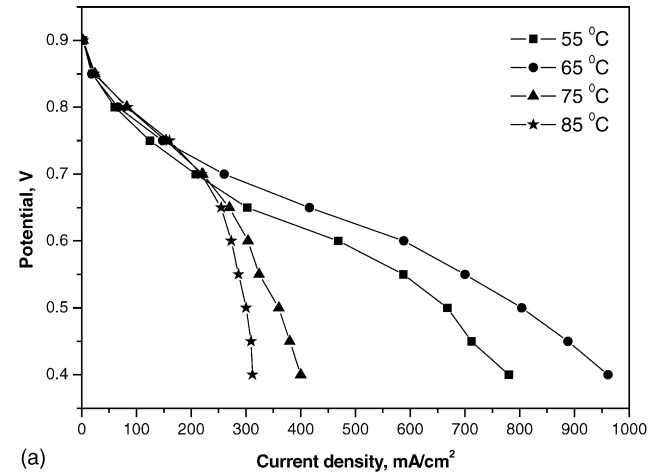


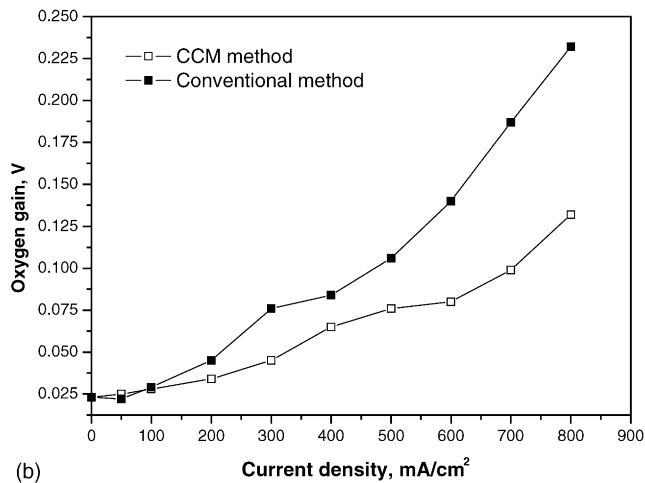
Fig. 8. Effects of MEA fabrication process on Nyquist plots for the single cell at a cell temperature of 80°C.



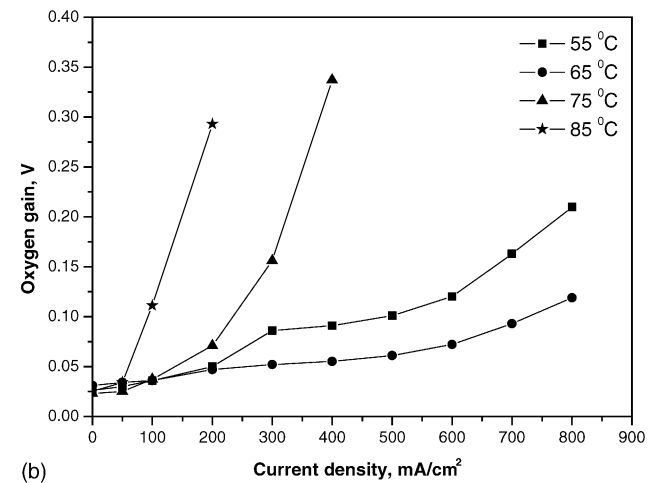
(a)



(a)



(b)



(b)

Fig. 7. Effects of MEA fabrication process on (a) the cell performance and (b) oxygen gain measured at a cell temperature of 80°C.

Fig. 9. Effects of cathode humidification temperature on (a) the cell performance and (b) oxygen gain measured at a cell temperature of 80°C.

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. 6 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. 5. The ohmic resistance of the single cell was about $0.18 \Omega \text{ cm}^2$, independent of Pt content in the catalyst powder. On the other hand, with increasing Pt content from 10 to 60%, the charge transfer resistance of the cell changed significantly from 3.16 to $7.05 \Omega \text{ cm}^2$ also due to the trade-off between platinum surface area and mass transfer resistance.

In addition to catalyst support and Pt content, the MEA fabrication process would have significant effects on the electrode structure. To study the effects of the MEA fab-

rication process on the cell performance, MEAs were prepared by two methods: the conventional method and the CCM method as described in the experimental section. Catalyst loading in the active layer was same for both methods. Fig. 7 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 [16]. Nyquist plots presented in Fig. 8 confirm the lower charge transfer resistance of the MEA prepared by the CCM method than the conventional MEA method.

3.3. Effects of operating conditions on the oxygen gain

The effects of cathode humidification on the cell performance were studied at a cell temperature of 80°C . Fig. 9

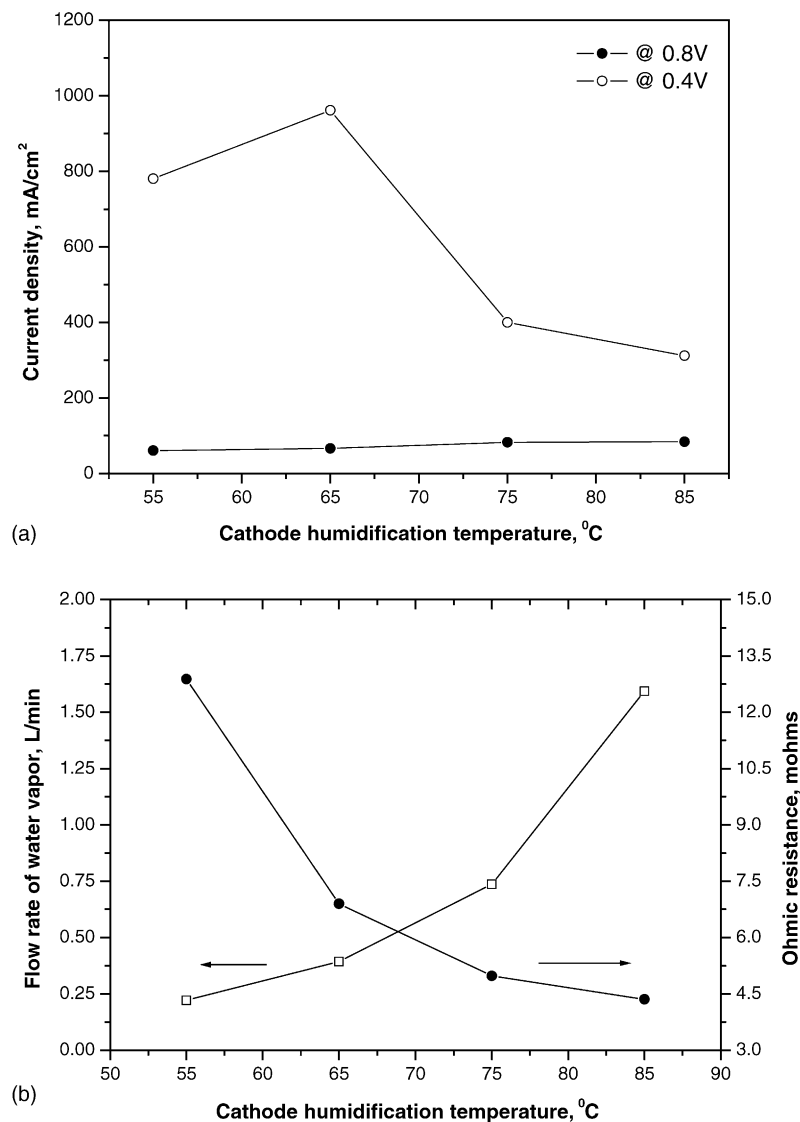


Fig. 10. Dependence of current density (a), ohmic resistance and saturated water vapor (b) as a function of cathode humidification temperatures; air flow rate = 1.2 L/min .

shows the performance and the oxygen gain of the single cell with changing the cathode humidification temperature from 55 to 85 °C, exhibiting the maximum performance and the lowest oxygen gain at 65 °C. The anode humidification temperature was 80 °C. In detail, cathode humidification had different effects on the cell performance according to the current density and hence the amount of product water. Fig. 10(a) shows current density as a function of the cathode humidification temperature, at cell voltages of 0.8 and 0.4 V, which corresponded to low and high current density regions, respectively. In the low current density region (below about 180 mA/cm²), as the cathode humidification temperature increases, the cell performance was improved due to enhanced hydration and ionic conductivity of the membrane, as shown in Fig. 10(b). On the other hand, in the high current density region (above about 180 mA/cm²), at cathode humidification temperatures of 75 and 85 °C, the cell performance was reduced due to water flooding, which was reflected in the sharp voltage decrease in the high current region in Fig. 9(a). As shown in Fig. 10(b), the amount of water supplied to the cathode significantly increases with the cathode humidification temperature, resulting in a more probable occurrence of water flooding. Thus, with the trade-off of ion conductivity and water flooding, the cell performance exhibited maximum performance at an intermediate cathode humidification temperature, i.e. 65 °C in this study.

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, the 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 carbons, 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. In the cathode humidification temperature range from 55 to 85 °C, higher cathode humidification was favored in the activation (low current density) region due to enhanced hydration and ionic conductivity of the membrane. On the other hand, in the mass transport (high current density) region, cathode humidification at 65 °C provided the best performance, and the performance was substantially lowered at the cathode humidification temperatures above 75 °C due to water flooding.

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