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Effect of PTFE contents in the gas diffusion media on the performance of PEMFC

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Abstract

The behavior of water in the gas diffusion layers of a polymer electrolyte membrane fuel cell (PEMFC) was investigated analytically. To understand the water transportation phenomena systematically, the gas diffusion layers were divided into two parts. One is the gas diffusion medium (GDM) and the other is micro-layer (ML). In this work, the GDM with different PTFE contents was intensively investigated under various single cell operation conditions. I–V performance curves of single cells were compared and analyzed with respect to water transportation in the GDM. The increased PTFE contents disturb the ejection of liquid-phase water from the electrodes to the flow channels via the GDM, especially at higher relative humidity conditions. I–V performance curves in this work can also be interpreted as an evidence that capillary force in the GDM is not the main driving force for the water transportation. Other forces, for example shear force of fluid and water evaporation etc. are more dominant driving forces, at least with in the GDM itself. This is because of the relatively larger pore diameter of the GDM compared to that of electrodes and ML. When a ML was used in the GDM, the I–V performance of fuel cell became more stabilized as well as enhanced. In regard to water management, the ML might have important roles as buffer zone which prevent serious drying and flooding of the electrode. So, when the entire gas diffusion part is designed, the capillary-force-driven water movement and the shear-force- or vaporization-driven water transportation should be considered carefully for both the ML and the GDM structures.

Keywords: PEMFC; Gas diffusion layer; PTFE; Capillary; Flooding

1. Introduction

In the polymer electrolyte membrane fuel cell (PEMFC) system, which uses Nafion® membrane as electrolyte, water plays a critical role in proton conduction. Though more water in the membrane is desirable in the aspect of proton conduction, excess water can be condensed to liquid-phase water in the electrode and in the gas diffusion layer. This liquid water can dramatically decrease the fuel cell performance by hindering gas diffusion as well as by covering the active sites of eletrocatalysts. So, in order to get stable and good fuel cell performance the water contents in the PEMFC system should be precisely controlled.

In the PEMFC system, hydrogen and air are usually supplied in relatively humid conditions to the cells. The humid reactants can supply the desired water and reduce the extreme evaporation of water in the anode and cathode side, respectively. But when considering total system efficiency, it's difficult to supply air in a fully hydrated condition except in some specialized cases. Therefore, the cathode side of an ordinary PEMFC is generally in a relatively dry condition during operation. This means that water-related research should be focused on effective water management under relatively dry cell operating conditions.

Gas diffusion layers should have properties such as good electric conductivity, water and gas transportation, corrosion resistance, etc. Until now, there have been many attempts to increase fuel cell performance by developing, or modifying, the gas diffusion layer (GDL). In this work GDL means gas diffusion medium (GDM) with micro-layer (ML) [1–5]. Carbon paper or carbon cloth have been used most widely as GDM materials [1–7], and sometimes expanded or sintered metals have also been used [8]. Most reports showed enhanced fuel cell performance after a unique treatment process on the GDL. In such cases, it was difficult to distinguish which factors affected the final fuel cell performance most. Actually, most reports concluded that the results came from the improved gas permeability and electrical conductivity. There have also been mathematical or numerical approaches

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on the GDL [9,11,12]. In this work, the driving forces of water and gas transportation in the GDM were treated separately. Among them, capillary force, shear force and evaporation were considered the main driving forces.

On the cathode side of the GDL of a PEMFC, most of the product water moves in the direction of the flow channel by gas-phase diffusion or liquid-phase transport. When humid air is provided to the cathode, the generated water vapor is difficult to diffuse out of the GDL. As a result, partial or complete water condensation occurs. So, the GDL is generally treated with PTFE to render it hydophobic and to reduce water saturation and to help water transport. This means that the management of liquid-phase water is important to get good fuel cell performance.

In this work, to get optimum GDL design parameters, the GDM and ML were investigated separately in order to know which driving forces (capillary, shear or evaporation) are more dominant for controlling water transport in the GDM and ML. With different amounts of PTFE coated on the GDM, the I–V performance of fuel cells was evaluated at various relative humidity conditions. By analyzing the physicochemical characteristics and the patterns of the I–V curve in fuel cell performance, the dominant driving forces of water transportation were suggested for the GDM and the ML, respectively.

2. Experimental

2.1. Preparation of gas diffusion media

TGP-H-060 and TGP-H-090 carbon papers (Torary) which have different thicknesses of 190 and 250 μm, respectively, were used for GDM. As received carbon papers were cut out and washed in acetone to remove dust or undesirable things. Later, the washed papers were dried at 110 °C for 2 h. Sixty weight percent of PTFE emulsion (Du Pont) was diluted to make 5–45 wt.% aqueous solutions. The dried carbon papers were dipped entirely in the different PTFE solutions for 30 s and dried again at room temperature for 5 h. After then, the samples were heat-treated in four temperature steps (80, 110, 290 and 350 °C) in air. The amount of PTFE and the calculated porosity of treated samples are shown in Table 1. In Table 1, the description CP190-0 is for the 0 wt.% PTFE containing-TGP-H-060 carbon paper, and other GDMs are designed in an equivalent fashion.

2.2. Permeability measurement of prepared gas diffusion media

Air permeability of GDM with different amounts of PTFE was measured with Automated Perm Porometer 6.0 (ASTM D 737-75, D737-96, F 316-86, F778 and B.S. 3321, 6410; Porous Materials Instruments). The diameter of samples and the wetting fluid used were 21.5 mm and Prowick 16.0, respectively. With this apparatus air permeability, pore-size distributions as well as mean pore diameter were measured for the GDM samples. The measured mean pore diameters and permeability can be seen in Fig. 1.

Table 1
Porosity of prepared gas diffusion media with various PTFE contents

GDM	PTFE contents (wt.%)	Porosity (%)
CP190-0	0	77.73063141
CP190-5	5.84958217	77.09158907
CP190-15	17.1855542	75.29935718
CP190-25	27.1939328	71.67463804
CP190-35	34.7490347	69.45141562
CP190-45	49.321267	62.85032565
CP250-0	0	72.10033076
CP250-5	4.71785384	71.34075175
CP250-15	14.2367067	69.4320419
CP250-25	27.925341	64.82743197
CP250-35	28.0172414	65.12519958
CP250-45	44.3237371	55.61163074

2.3. Fabrication of membrane electrode assembly

Before fabricating the electrode layer on the electrode, Nafion 112 (Du Pont) membrane was pretreated with H_2O_2 and H_2SO_4 solutions step-by-step to remove the remaining organic and inorganic contaminants [13]. Forty weight percent of Pt/C electrocatalyst (Johnson Matthey) and 5 wt.% Nafion solution (Du Pont) were used to make electrodes for both anode and cathode. The prepared membrane electrode assembly (MEA) had platinum loadings of 0.3 and

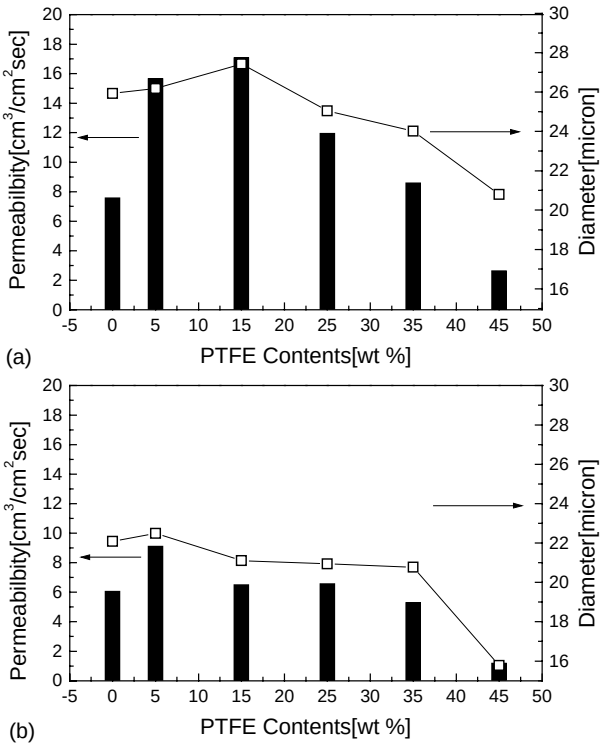

Fig. 1. Effect of PTFE contents on the air permeability and pore diameter of GDM. (a):CP190 GDM, and (b): CP250 GDM.

0.4 mg Pt/cm^2 for anode and cathode, respectively. The active area of MEA was 50 cm^2.

2.4. Evaluation by single cell

Water behavior in the prepared GDMs was analyzed by single cell evaluation of a PEMFC. All kinds of GDMs were tested with the same MEA to minimize the performance differences between MEAs. To gain confidence in the data, the MEA was tested twice with one reference GDL before and after testing the prepared GDMs. The current densities at 0.6 V were 668 and 692 mA/cm^2 for the case of before and after, respectively. The data had good consistency during whole experimental period, showing slightly increased current density of about 3.6%.

GDM which had the same amount of PTFE was applied both to the anode and the cathode at the same time. The assembled single cells were tested at various relative humidity by changing the combinations of temperature between the cell and the humidifiers. The tube temperatures between the humidifier and the cell were controlled to the same temperature during evaluations. The detailed test conditions and relative humidity are shown in Table 2.

Table 2
Operation conditions of single cells with varying relative humidity

Cell temperature (°C)	Air humidifier temperature (°C)	Relative humidity (%)
60	45	48
	55	79
	65	125
	75	193
	85	290
70	55	50
	75	123
	85	185
80	45	20
	65	53
	85	122

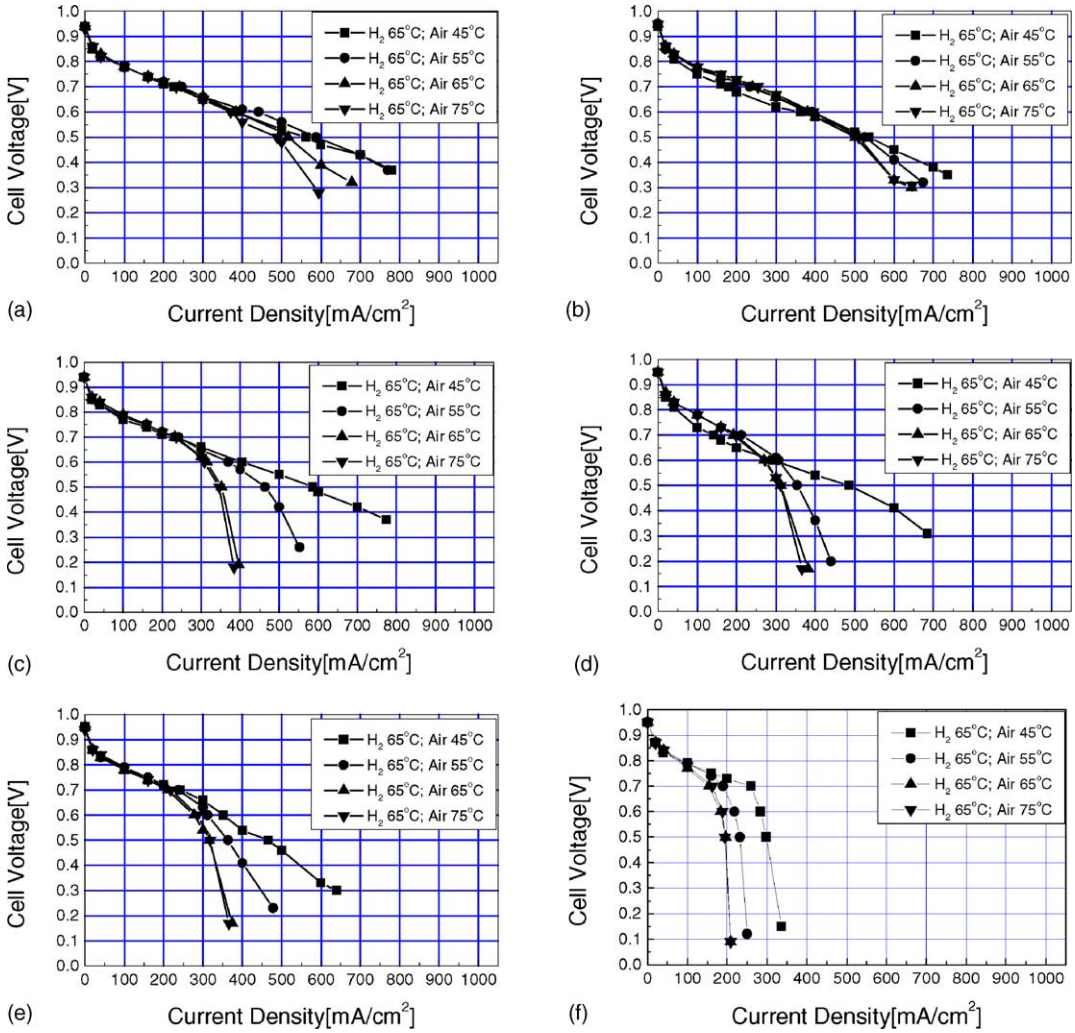

Fig. 2. I–V performance of single cells with PTFE treated CP250 GDMs at various relative humidity conditions of cathode. Cell = 60 °C; anode humidifier = 65 °C (slightly flooding anode condition). (a): CP250-0, (b): CP250-5, (c): CP250-15, (d): CP250-25, (e): CP250-35, and (f): CP250-45. Legend means the temperature of the humidifier.

All tests were conducted at atmospheric pressure and fuel utilization were controlled to 70 and 40% for hydrogen and air, respectively.

3. Results and discussion

The hydrophobicity, mean pore diameter and porosity of the GDM were changed with the contents of PTFE. Table 1 shows the result of PTFE coating for the GDMs which have different thickness. The porosity of CP190 GDM was decreased from 77.7 to 62.8% when nearly 50% PTFE was coated. In Fig. 1, the permeability and the mean pore diameter were compared for the PTFE-coated CP190 and CP250 GDM. Besides untreated GDMs, all samples showed a decrease of permeability and pore diameter with PTFE contents. This is because the coated PTFE filled the pores without increasing GDM thickness. Despite their similar mean pore diameter, CP190-0 and CP250-0 revealed much smaller air permeability as compared with CP190-5 and CP250-5. This result means that even at the low RH condition, the air flux can be hindered remarkably by a hydrophilic surface of the carbon fiber. It can also be expected that a hydrophobic coating on the GDM can facilitate water and air transportation by increasing the apparent contact angle of water from 1 to about 120° [9].

Various I–V performances of fuel cells can be seen in Fig. 2. When the different PTFE-loaded CP250 GDMs were used as diffusion layer, single cells showed much different patterns of performance with prevailing relative humidity conditions. On the whole, as the relative humidity increased the degree of flooding also increased resulting in a decrease of I–V performance, especially in the high current density regime. Deactivation caused by water flooding clearly appeared in the highly PTFE-loaded GDM, CP250-45. In regard to I–V performance and water removal, it looks like PTFE coating had no positive effect. And this result says that the water produced at the electrode can be prone to condense into liquid at the catalyst/GDM interface or in the GDM. Fig. 2 also shows that water condensation may occur more easily and that liquid water is difficult to remove in the higher PTFE-loaded GDM. This can be explained by a capillary condensation phenomenon. Water can be condensed at a lower saturation pressure at the smaller pore diameter than that of larger pore size. And it can be inferred that, at least in this kind of GDM structures, without a ML, the dominant driving force for water removal is not the capillary force but shear or evaporation.

Fig. 3 shows the effect of GDM thickness on water transport and fuel cell performance. The thicker GDMs were less sensitive to the change of relative humidity, but the performance at the high current density was certainly inferior to that of the thinner GDMs. This can be explained because the larger volume of the GDM might help to capture more water, but the exiting water can increase the resistance to air diffusion.

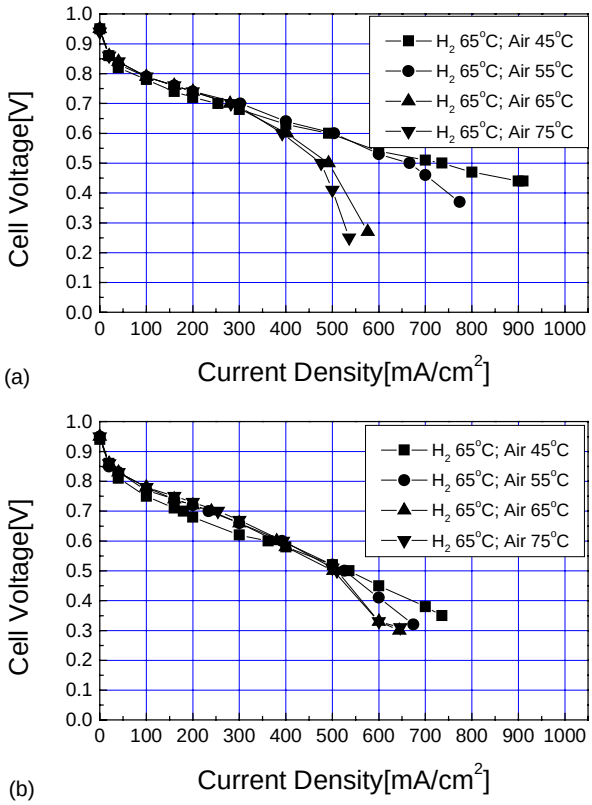

Fig. 3. Effect of GDM thickness on the I–V performance of single Cell = 60 °C; anode humidifier = 65°C (slightly flooding anode condition). (a): CP190-5, and (b): CP250-5. Legend means the temperature of the humidifier.

Water behavior in the GDM can be analyzed more clearly in Fig. 4. For the CP250 GDMs, I–V performances were compared at the more carefully controlled relative humidity conditions. The detailed conditions are in the Table 2. This figure shows that, at the low PTFE-loaded GDMs, the performance curves build up groups for the similar relative humidity. But as the contents of PTFE increased there were no more groups, and better performances could be obtained in relatively dry conditions. This figure also shows that water in high PTFE-coated GDM is more difficult to be removed just by using capillary force. As a result, the water produced became the main cause of performance deactivation by flooding. When all the I–V performances were put together, the best performance could be obtained at about 100% relative humidity conditions.

This phenomenon can be explained by the concept of breakthrough pressure in capillary pores. The breakthrough pressure can be understood to be the minimum pressure to eject water from the pore [10]. As summarized in Table 3, since the pore size or the contact angle decreased it needed more pressure to expel water from the pores. The calculated numbers in Table 3 conduct well with the graphs of Fig. 4.

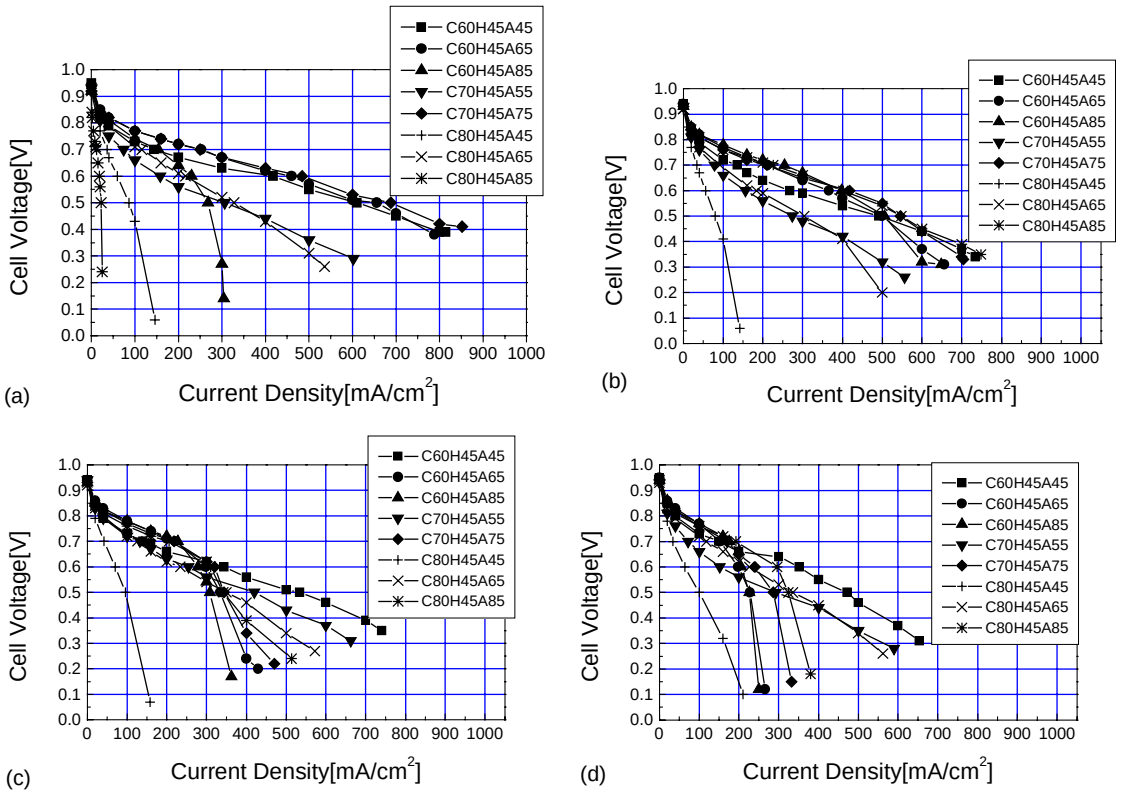

Fig. 4. Effect of relative humidity on the I–V performance of single cells with PTFE treated CP250 GDMs. (a): CP250-0, (b): CP250-5, (c): CP250-35, and (d): CP250-45. Legend C, H, and A is for the temperature of the cell, anode, and cathode, respectively.

In Fig. 5, the roles of ML in the GDL are clearly shown. At the various relative humidity conditions, a single cell, which used the GDL containing a ML, showed a dramatically stable performance as well as an enhanced I–V performance. The performance enhancement may be mainly due to the increased electrical conductivity. When the ML was applied even at a relative humidity of about 190% there was no severe flooding, unlike the GDM-only diffusion layers. It is clear that the ML is an essential factor to get

Table 3
Breakthrough pressure ($4\sigma\cos\theta/d_p$) of prepared gas diffusion media

GDM	Contact angle θ (°)	Pore diameter (μM)	Breakthrough pressure (kPa)
CP190-0	1	25.93325	11.24809139
CP190-5	120	26.17635	5.572663874
CP190-15	120	27.43126667	5.317727459
CP190-25	120	25.0455	5.824279811
CP190-35	120	24.0162	6.073900117
CP190-45	120	20.79376667	7.015179228
CP250-0	1	22.08555	13.20771119
CP250-5	120	22.49166667	6.485602075
CP250-15	120	21.10226667	6.912622341
CP250-25	120	20.94153333	6.965679049
CP250-35	120	20.771	7.022868422
CP250-45	120	15.53603333	9.389269247
GDM (ML)	120	9.1787	15.89244664

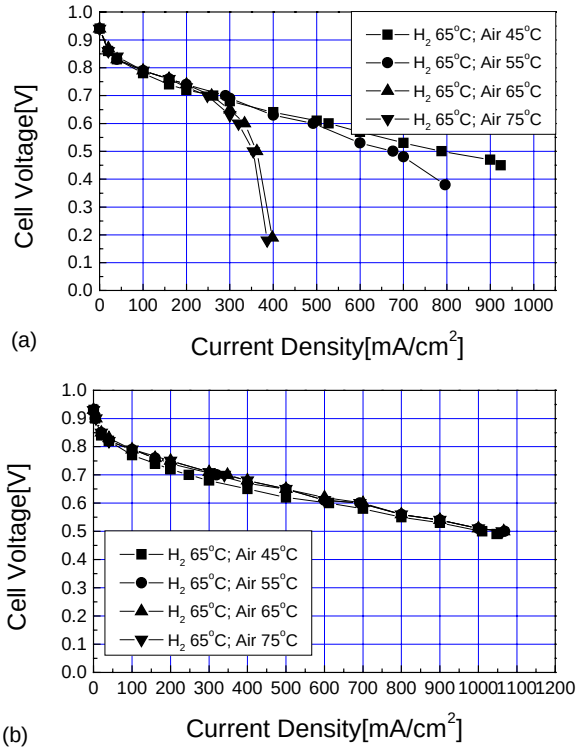

Fig. 5. Effect of ML on the I–V performance of PEMFC. (a): CP190-15, (b): GDM with ML. Legend means the temperature of the humidifier.

stable and good fuel cell performance in regard to water management.

4. Conclusion

The dominant driving forces for water transportation in the gas diffusion layer were elucidated for the GDM and ML by an experimental approach. PTFE-treated GDMs were systematically evaluated by single cell test to get the I–V performance curves in controlled relative humidity conditions. The results showed that the water produced is prone to be easily condensed at the catalyst/GDM interface and in the inner part of the GDM. The condensed water was difficult to remove even in the PTFE-coated GDM. So, it can be deduced that the driving force of water removal from the catalyst to the GDM might be the capillary force, but with in the GDM the driving forces of liquid water ejection might be other forces (shear force or evaporation etc.) rather than capillary force. When fuel cell performances of the CP190-15- and ML-coated GDM were compared, it was clear that the ML plays an important role in water management in regard to stability as well as electrical conductivity. For the GDM design, at least in the range of this work, the thinner thickness and the larger pore diameter is better for water management and fuel cell performance.

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References

[1] J. Soler, E. Hontanon, L. Daza, J. Power Sources 118 (2003) 172.
[2] S. Gamburzev, A.J. Appleby, J. Power Sources 107 (2002) 5.
[3] E. Passalacqua, G. Squadrito, F. Lufrano, A. Patti, L. Giorgi, J. Appl. Electrochem. 31 (2001) 449.
[4] L.R. Jordan, A.K. Shukla, T. Behrsing, N.R. Avery, B.C. Muddle, M. Forsyth, J. Appl. Electrochem. 30 (2000) 646.
[5] D. Bevers, R. Rogers, M. von Bradke, J. Power Sources 63 (1996) 193.
[6] N. Djilali, D. Lu, Int. J. Therm. Sci. 41 (2002) 29.
[7] G.-G. Park, T.-H. Yang, Y.-G. Yoon, W.-Y. Lee, C.-S. Kim, Int. J. Hydrogen Energy 28 (2003) 645.
[8] T. Hottinen, M. Mikkola, T. Mennola, P. Lund, J. Power Sources 118 (2003) 183.
[9] J.H. Nam, M. Kaviany, Int. J. Heat Mass Transfer 46 (2003) 4595.
[10] Y. Gu, C. Yang, J. Petro. Sci. Eng. 40 (2003) 77.
[11] J.S. Yi, T.V. Nguyen, J. Electrochem. Soc. 146 (1999) 38.
[12] D. Natarajan, T.V. Nguyen, J. Electrochem. Soc. 148 (2001) A1324.
[13] Y.-G. Yoon, T.-H. Yang, G.-G. Park, W.-Y. Lee, C.-S. Kim, J. Power Sources 118 (2003) 189.