



Facilitating mass transport in gas diffusion layer of PEMFC by fabricating micro-porous layer with dry layer preparation

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ABSTRACT

For a proton exchange membrane fuel cell (PEMFC), dry layer preparation was optimized and applied to fabricate a micro-porous layer (MPL) for a gas diffusion layer (GDL). The MPLs fabricated by dry layer preparation and the conventional wet layer preparation were compared by physical and electrochemical methods. The PEMFC using dry layer MPLs showed better performance than that using wet layer MPLs, especially when the cells were operated under conditions of high oxygen utilization rate and high humidification temperature of air. The mass transport properties of the GDLs with the dry layer MPLs were also better than with the wet layer MPLs, and were found to be related to the pore size distribution in GDLs. The differences in surface morphology and pore size distribution for the GDLs with the dry layer and wet layer MPLs were investigated and analyzed. The dry layer preparation for MPLs was found to be more beneficial for forming meso-pores (pore size in the range of 0.5–15 μm), which are important and advantageous for facilitating gas transport in the GDLs. Moreover, the GDLs with the dry layer MPLs exhibited better electronic conductivity and more stable hydrophobicity than those with the wet layer MPLs. The reproducibility of the dry layer preparation for MPLs was also satisfying.

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1. Introduction

To increase the specific power density of proton exchange membrane fuel cells (PEMFCs) is the key objective for PEMFC R&D. In order to meet this goal, improvement of the performance of PEMFCs at high current densities is one of the key issues. However, gas transport in the electrode is always hindered by the large amount of liquid water produced at high current densities.

The gas diffusion layer (GDL) is an essential component in a PEMFC and is placed between the catalyst layer and flow field. The most important function of the GDL is to distribute the reactant gas over the catalyst layer and to remove the generated product (liquid water) out of the cell. Thus, the mass transport in a GDL is the two-phase flow of gas and liquid water. The effective diffusion coefficient of the reactant gas in a porous GDL decreases exponentially with the increase of the degree of water saturation [1]. Therefore, the transport of liquid water is crucial for the transport of the reactant gas. The pores in the GDL will be filled with the liquid water, if the water cannot be removed effectively. The result is high diffusion resistance of gas transport and flooding in the GDL. Furthermore, flooding in the catalyst layer inhibits the transport of reactant gas

to the reaction sites and blocks part of the active reaction surface. The cases mentioned above are the main obstacles for achieving high performance of PEMFCs. Due to the production of water and the electro-osmotic drag of water across the membrane, flooding is more likely to occur in the cathode. The ideal GDL should be effective for transporting the reactant gas and removing the liquid water simultaneously.

A GDL normally comprises two layers. The waterproofed carbon paper or carbon cloth is usually employed as the backing layer in a GDL. Carbon paper and carbon cloth are porous materials, having porosity greater than 70%. More than 90% of the pores in the carbon paper and the carbon cloth are larger than 20 μm . In order to improve water transport in a GDL, an additional layer called MPL (micro-porous layer), prepared with a mixture of carbon powder and PTFE, is coated at the surface of backing layer and sandwiched between the backing layer and the catalyst layer [2,3]. There are abundant micro-pores in the range of tens of nanometers to hundred nanometers in MPLs. The most important role of the MPLs is “water management”, which has been analyzed by modeling and simulation [1,4–8].

The effects of carbon powder [9–14], fabrication process [15], PTFE content [2,16–19], and carbon loading [9,10,20] of MPLs on the performance of PEMFC single cells have been investigated by several groups. By now, MPLs are mainly prepared with the conventional wet layer method, in which a large amount of organic solvents should be applied to prepare the carbon–PTFE paste. Recently, a

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novel process of dry layer preparation for MPLs has been reported by Yu et al. [15]. In that method, carbon powder was directly mixed with PTFE powder by a knife mill. Then the mixture was directly deposited onto the surface of waterproofed carbon paper. In that paper, the surface morphology of the dry layer MPLs fabricated with different kinds of carbon powder and the corresponding performances of PEMFC single cells were investigated. The authors indicated that due to the simpler preparation process, the dry layer preparation is very suitable for industrial MPL fabrication [15]. However, comparison between the wet layer and the dry layer preparations has not been conducted. Especially, the differences in the pore size distribution and the mass transport property of GDLs caused by the MPLs are not clear.

In this paper, the dry layer preparation was optimized and applied to fabricate MPLs. The comparison between the GDLs with dry layer and wet layer MPLs was investigated by the measurement of cell performance, surface morphology, pore size distribution, and wettability of the GDLs. The reasons for facilitating the mass transport in GDLs by the dry layer MPLs are elucidated.

2. Experimental

2.1. GDL sample preparation

GDLs were fabricated with PTFE-treated carbon paper (TGP060, Toray) as a backing layer. The PTFE content in the waterproofed carbon paper was about 10 wt.%.

The process of the dry layer preparation for the MPLs was as follows: Cabot Vulcan XC-72 and PTFE powder (3F Co., Shanghai, China) were mixed thoroughly by a knife mill. Then the mixture was deposited directly onto the waterproofed carbon paper, and spread uniformly using a blade. The carbon paper coated with the mixture of carbon powder and PTFE was baked at 240 °C for 30 min, and finally sintered at 340 °C for 30 min. The PTFE content in the dry layer MPLs was 30 wt.% unless specified otherwise.

For comparison, the conventional wet layer preparation for MPLs was also applied. The process of wet layer preparation for MPLs has been described in details [21,22]. The carbon-PTFE paste was prepared by stirring an alcohol suspension of Cabot Vulcan XC-72 and 10 wt.% PTFE emulsion thoroughly by an ultrasonic machine. Then the paste was spread onto the waterproofed carbon paper with a blade. The carbon paper coated with the paste was baked at 240 °C for 30 min, and finally sintered at 350 °C for 30 min. The PTFE content in the wet layer MPLs was 30 wt.%.

2.2. Membrane electrode assembly preparation and single cell test

The GDL samples were compared at the cathode side, using the same materials for all the other components for membrane electrode assemblies (MEAs). The MEAs were prepared by a hot pressing process. The cathode catalyst layer was prepared by spraying the catalyst ink (46 wt.% Pt/C from Tanaka and 5 wt.% Nafion® solution) onto one side of a Nafion® 212 membrane (DuPont). The Pt loading in the cathode was 0.4 mg cm⁻². A self-prepared gas diffusion electrode with Pt loading of 0.3 mg cm⁻² was used as the anode. The cathode GDL, the Nafion® 212 membrane and the combined cathode catalyst layer, and the anode were hot-pressed together to prepare the MEA. The effective area of the electrode was 5 cm². The MEA was mounted in a single cell with stainless steel end plates and stainless steel mesh flow fields as the current collectors.

The performance of the cell was evaluated at a cell temperature of 80 °C. Hydrogen and air were humidified before entering the cell, and were employed as the fuel and the oxidant, respectively. Unless

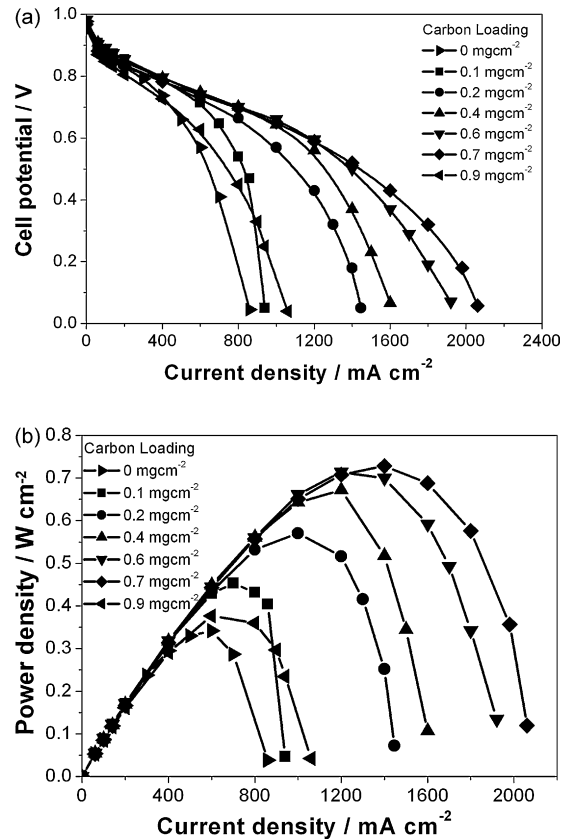


Fig. 1. Performances of PEMFC single cells based on the GDLs with dry layer MPLs. $P_{H_2} = P_{air} = 0.2$ MPa, $T_{a, humi} = 90$ °C, $T_{cell} = 80$ °C, $T_{c, humi} = 85$ °C. The carbon loading in MPL is presented in the figure. The PTFE content in MPL was 30 wt.%. (a) I - V curve, (b) I - P curve.

specified otherwise, the humidification temperature for hydrogen and air were 90 °C and 85 °C, respectively. The flow rates of inlet gases were controlled to maintain constant utilization of hydrogen at 80% and oxygen at 40% for various current densities. In the experiments on the influence of oxygen utilization rate, the different oxygen utilization rates were maintained by regulating the flow rate of air.

2.3. Characterization of GDL samples

A scanning electron microscope (SEM) (JEOL JSM-6360LV) was used to observe the surface and structure morphology of GDL samples.

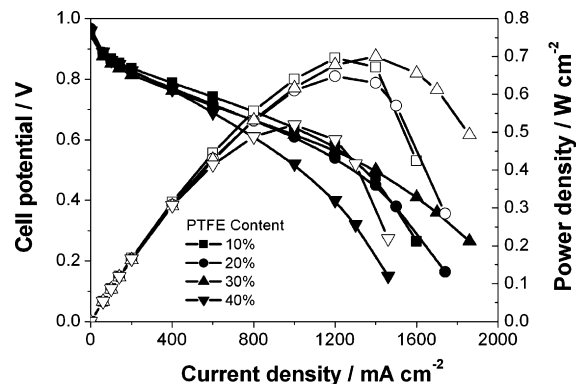


Fig. 2. Performances of PEMFC single cells based on the GDLs with dry layer MPLs containing different contents of PTFE. The carbon loading in MPLs: 0.7 mg cm⁻². $T_{a, humi} = 90$ °C, $T_{cell} = 80$ °C, $T_{c, humi} = 85$ °C, $P_{H_2} = P_{air} = 0.2$ MPa.

The pore size distribution in the GDLs was measured by MIP (mercury intrusion porosimetry) by using a Quantachrome Pore-MasterGT 60.

Due to the low surface energy of decane, both hydrophobic and hydrophilic pores in GDLs can be filled with it. Thus the total porosity of the GDLs was obtained by weighting the increment of decane when the sample was immersed in it. During the measurement, the GDL sample was immersed completely and suspended in decane.

The gas permeability of the GDLs was measured by flowing nitrogen through a GDL sample. The permeability coefficient of the GDLs was calculated by measuring the flow rate of nitrogen through the sample at different pressure drops across it [23–26]. The flow rate of nitrogen was measured using a flow meter, and the pressure difference across the sample was measured using a Dwyer 2000 differential pressure gauge at a range of 0–60 Pa. With the measured data, the permeability coefficient (k) was calculated according to

Darcy's law: $k = v\mu (\Delta X/\Delta P)$, in which v is the velocity, μ is the fluid viscosity, ΔX is the thickness of the GDL, and ΔP is the pressure drop across the GDL sample. The carbon loading in both the dry layer and wet layer MPLs was 0.7 mg cm^{-2} . The size of each sample was $5.0 \text{ cm} \times 5.0 \text{ cm}$.

3. Results and discussion

3.1. PEMFC single cell performance

3.1.1. Influence of carbon loading and PTFE content in dry layer MPLs on the performance of PEMFC single cells

I - V curves of the PEMFC single cells using the dry layer MPLs with different carbon loadings are shown in Fig. 1. For comparison, the polarization curve of single cells based on the GDLs without MPLs is also shown in the figure.

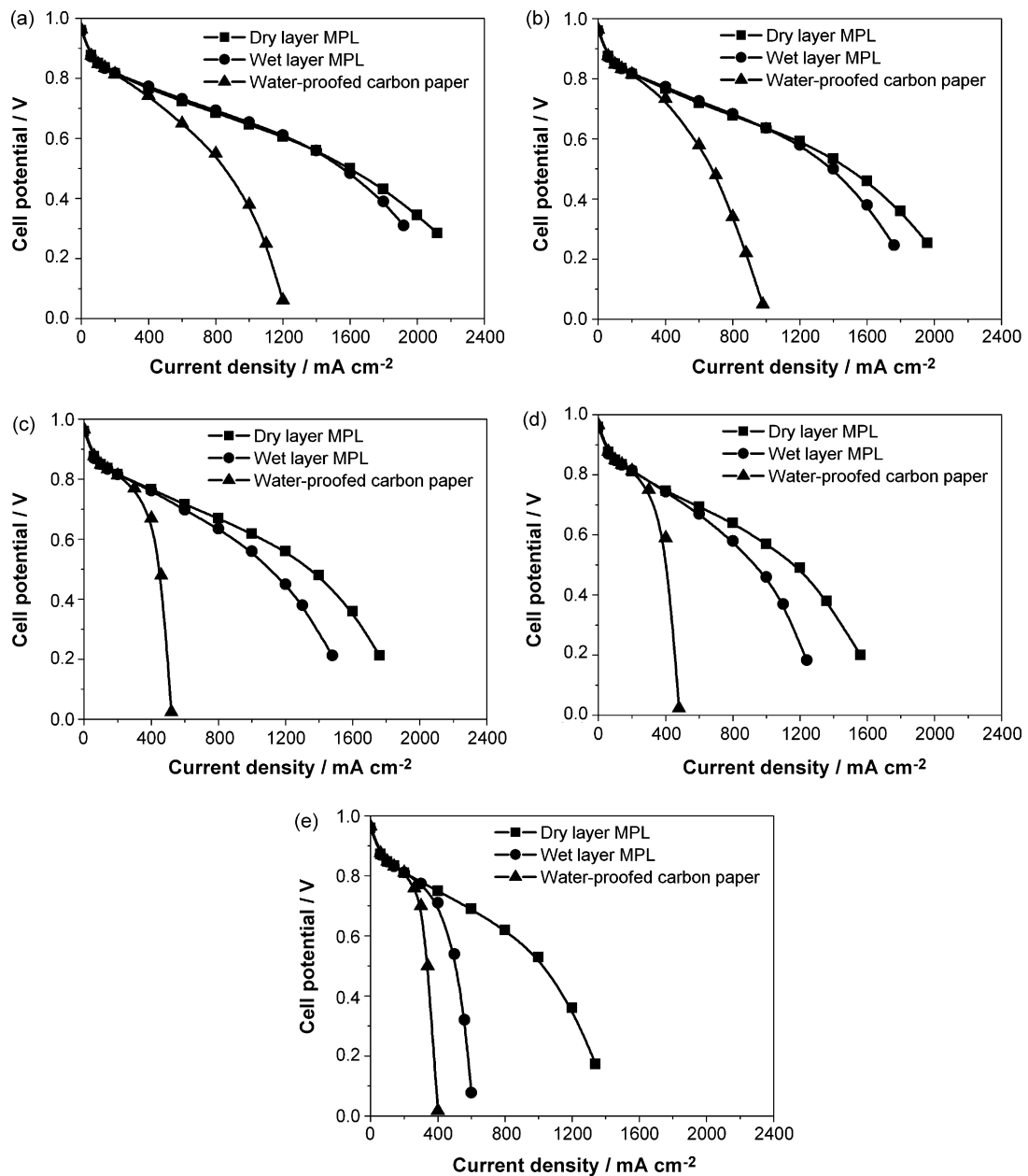


Fig. 3. Influence of oxygen utilization rate for air on the performance of PEMFC single cells. $P_{\text{H}_2} = P_{\text{air}} = 0.2 \text{ MPa}$, $T_{\text{a,humi}} = 90^\circ \text{C}$, $T_{\text{cell}} = 80^\circ \text{C}$, $T_{\text{c,humi}} = 85^\circ \text{C}$. The carbon loading in MPLs was 0.7 mg cm^{-2} . The PTFE content in MPLs was 30 wt.%. The oxygen utilization rate for air: (a) 30%; (b) 40%; (c) 50%; (d) 60%; and (e) 70%.

As can be seen from Fig. 1, the performance of the cells was improved with the increase of the carbon loading in the range of 0–0.7 mg cm⁻². If the carbon loading was larger than 0.7 mg cm⁻², the performance of the cells was decreased. Thus the optimal value of carbon loading in dry layer MPLs was 0.7 mg cm⁻².

It also can be seen from Fig. 1 that the performance of the cells was improved significantly by introducing the dry layer MPLs. For example, for a cell based on a GDL without a MPL, the current density at 0.1 V was about 0.84 A cm⁻². This value for a cell using a dry layer MPL was significantly increased to 2.05 A cm⁻² when the carbon loading was 0.7 mg cm⁻².

The influence of PTFE content in the dry layer MPLs on the performance of PEMFC single cells is shown in Fig. 2. As can be seen, the best performance of the cells was obtained when the PTFE content was 30 wt.%.

3.1.2. Influence of oxygen utilization rate for air on the performance of PEMFC single cells

The performances of the cells based on different GDLs were evaluated at different oxygen utilization rates for air. The results are shown in Fig. 3. In the experiments, the air pressure was 0.2 MPa.

If the air pressure is constant, the oxygen utilization rate for air is in inverse proportion to the air flow rate. The higher the oxygen utilization rate is, the lower the air flow rate. As can be seen from Fig. 3, the performance of the cells at high current densities was significantly affected by the oxygen utilization rate for air. The limiting current densities increased with the decrease of oxygen utilization rate due to the effective removal of the liquid water by the larger air flow rate.

Comparing *I*-*V* curves measured at the same oxygen utilization rate, we see that the performance of the cells using the dry layer MPLs was always the best one. Besides, the advantage of the dry layer MPLs was much more obvious when the cells were operated at high oxygen utilization rates. For example, when the oxygen utilization rate was 70% (as shown in Fig. 3e), the current density at 0.1 V for the cells using the dry layer MPLs was about 2.3 times as large as that for the cells using the wet layer MPLs, and was about 3.5 times as large as that for cells based on GDLs without a MPL. This characteristic is very advantageous for a PEMFC system that contains an air compressor powered by the fuel cell itself. In such a system, the higher the oxygen utilization rate for air, the larger net output power of the system will be obtained.

The experiment on the influence of oxygen utilization rate was also conducted at an air pressure of 0.02 MPa (not shown in this paper). The performance of the cells using dry layer MPLs was also obviously better than that of the cells using wet layer MPLs, especially when the cells were operated at high oxygen utilization rate.

The repeated experiments were done by operating PEMFC single cells at an oxygen utilization rate of 40%. The experimental results indicated that the reproducibility of both the dry layer and wet layer preparations was satisfied. And the cells using the dry layer MPLs exhibited better performance than the cells using the wet layer MPLs.

3.1.3. Influence of humidification temperature of air on the performance of PEMFC single cells

The performances of the PEMFC single cells were evaluated at different humidification temperature of air. The limiting current densities appearing in *I*-*V* curves are shown in Fig. 4. The cell temperature and the humidification temperature of hydrogen were constant in the experiments.

It can be seen from Fig. 4a that the limiting current densities appearing in the *I*-*V* curves obtained with cells using the dry layer MPLs remained close to 2.1 A cm⁻² when the humidification tem-

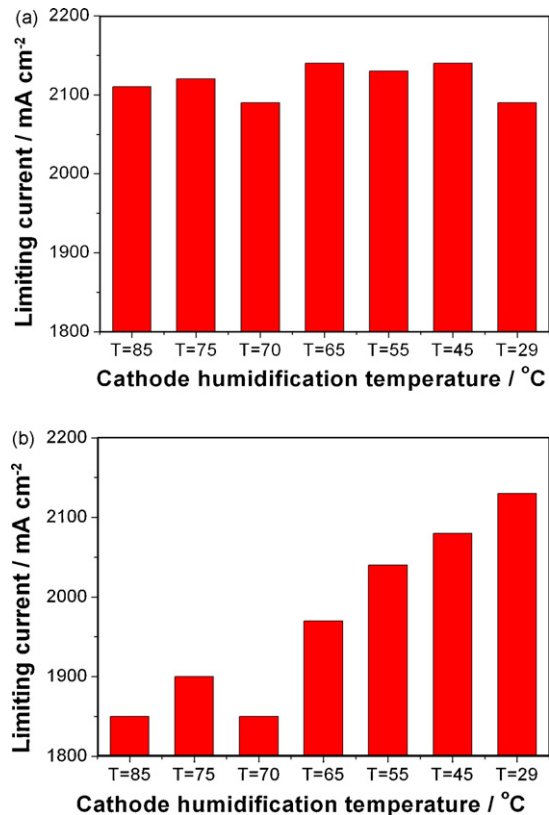


Fig. 4. Influence of the cathode humidification temperature on the limiting current densities. $P_{\text{H}_2} = P_{\text{air}} = 0.2$ MPa, $T_{\text{a,humi}} = 90^\circ\text{C}$, $T_{\text{cell}} = 80^\circ\text{C}$. The carbon loading in MPLs was 0.7 mg cm⁻². The PTFE content in MPLs was 30%. (a) Dry layer MPLs; (b) wet layer MPLs.

perature of the air increased from 29 to 85 °C. On the contrary, as shown in Fig. 4b, the limiting current densities for the cells using the wet layer MPLs evidently increased from 1.82 to 2.13 A cm⁻² with decrease of air humidification temperature from 85 to 29 °C.

If the experimental conditions of gas pressure, cell temperature, and operation current density are constant, the amount of liquid water generated inside a cell is approximately governed by the humidification temperature of the reactant gas. In such a case, the higher the humidification temperature of the air, the larger amount of liquid water will be produced. The results as mentioned above indicate that the gas transport in the cells using the dry layer MPLs was not obviously affected by the relative humidity, which is strongly related to the humidification temperature of the air. But the large resistance of oxygen diffusion in the GDL caused by the liquid water was observed in cells using the wet layer MPLs. It indicates that the gas transport in GDLs with dry layer MPLs is obviously better than that in GDLs with wet layer MPLs.

The reason for the improvement of mass transport in the GDLs employing dry layer MPLs will be discussed with respect to pore size distribution in Section 3.3.

3.2. Characterization of GDLs with dry layer and wet layer MPLs

3.2.1. SEM images

In this work, both dry layer and wet layer MPLs were fabricated on the surface of waterproofed carbon paper. Thus, the structure and pore size distribution in the GDLs (having a two-layer structure of a backing layer and a MPL) were consequently modified by the MPLs. In order to investigate the formation of the MPLs and the consequent change of GDL structure, MPLs with carbon loadings

of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 mg cm^{-2} were fabricated with both the dry layer and wet layer techniques. Meanwhile, the surface morphology of the MPLs and the structure of the GDLs were observed and recorded using a SEM. The SEM images are shown in Figs. 5 and 6.

As can be observed from Figs. 5a and 6a, in the case of wet layer preparation for the MPLs, due to the large density of the carbon-PTFE paste, the latter penetrated into the inner part of the carbon paper. Some pastes adhered to the carbon fibers, and others

were finally held by the texture of the carbon fibers. After sintering treatment, massive and compact carbon conglomerations were formed. The modification of the pore structure and size in the GDLs by wet layer MPLs was achieved mainly by the formation of carbon conglomerations around the original pores in the carbon paper.

As shown in Figs. 5b and 6b, the formation of dry layer MPLs was quite different from that of wet layer MPLs. When applying the dry layer preparation, the carbon-PTFE powder formed ball-shaped carbon clusters after the sintering treatment. The clus-

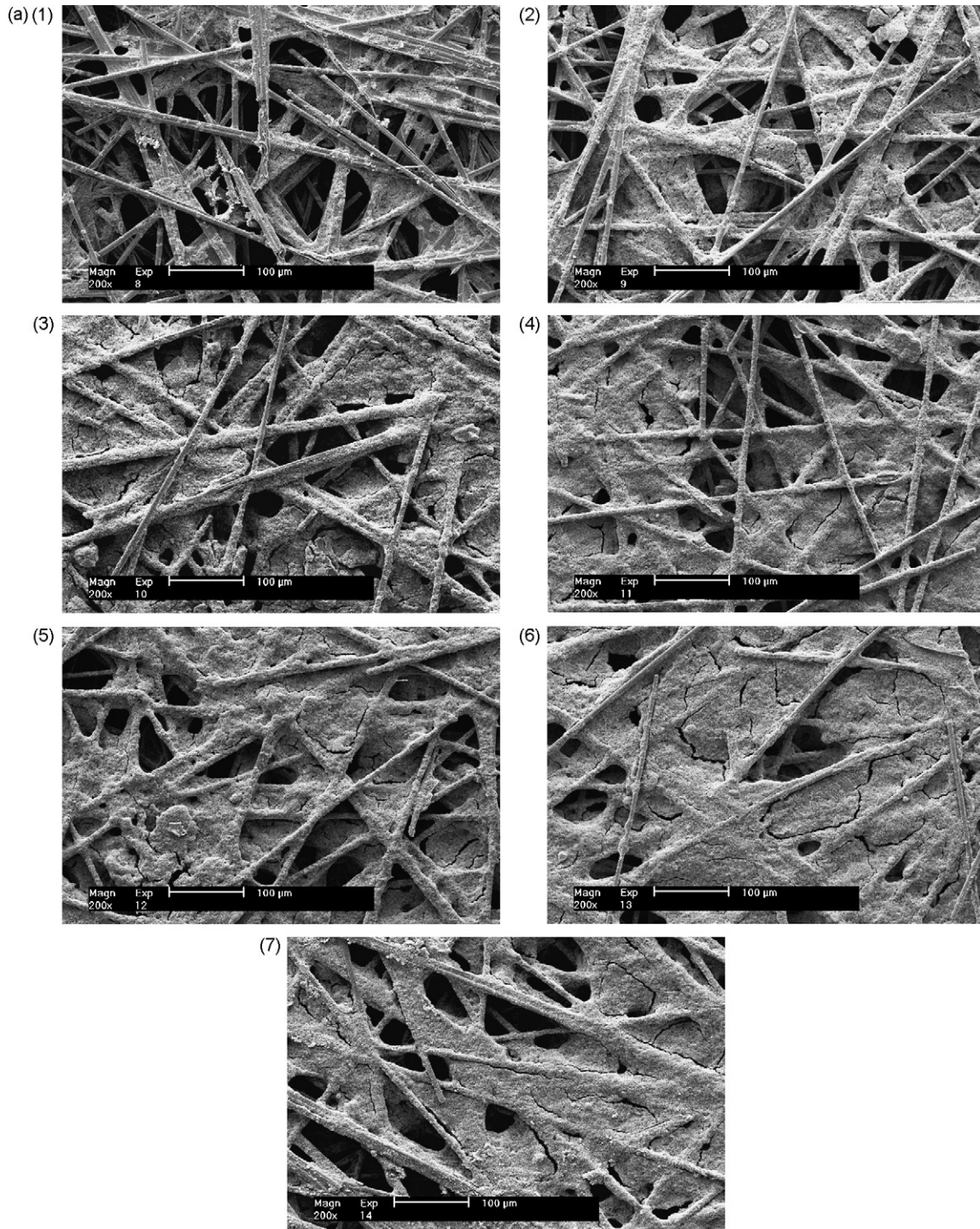


Fig. 5. SEM images of MPLs in GDLs (magnification $200\times$). Carbon loading in MPLs: (1) 0.1; (2) 0.2; (3) 0.3; (4) 0.4; (5) 0.5; (6) 0.6; and (7) 0.7 mg cm^{-2} . The PTFE content in MPLs was 30 wt.%. (a) Wet layer MPLs; (b) dry layer MPLs; (c) waterproofed carbon paper.

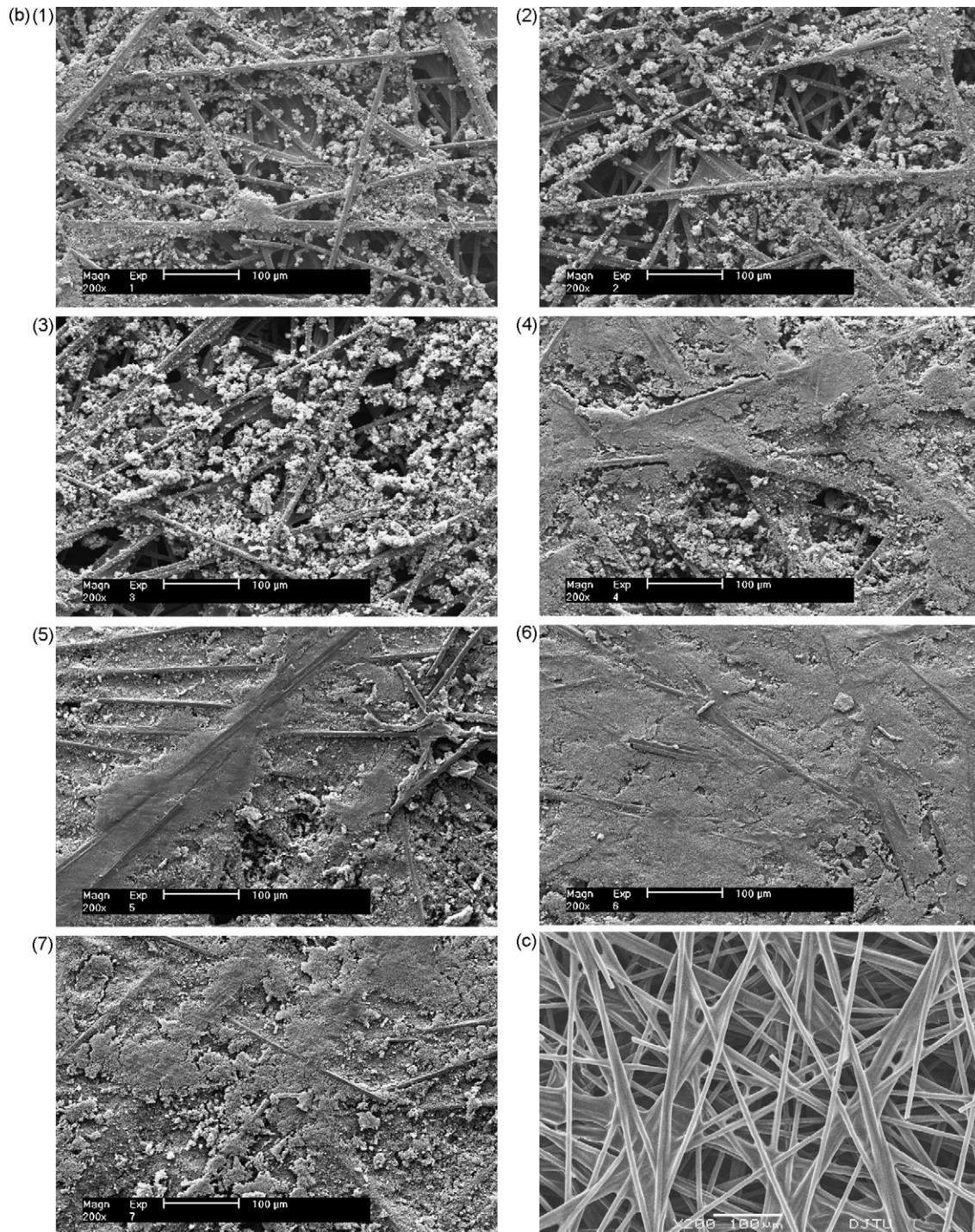


Fig. 5. (Continued).

ters were loose and light, and could not easily penetrate into the inner part of the carbon paper. When more carbon-PTFE powder was added, the clusters filled the vacancies or pressed the former ones to the inner part of the carbon paper. Thus, the large pores in carbon paper were divided into small pores by the clusters.

3.2.2. Porosity of GDLs

The porosity of the GDLs was measured as described in Section 2. The experimental data are listed in Table 1.

Compared with the waterproofed carbon paper (the GDLs without MPLs), the porosity of the GDLs with either dry layer or wet layer MPLs was reduced about 1–2%. Besides, the hot-press treatment caused only a slight decrease of porosity. The difference in the porosities for the GDLs with the dry layer and wet layer MPLs was slight. This is because in this work the MPLs took up only a small part of the total volume of the GDLs. It is apparent that the difference in the performances obtained with the cells using the dry layer and wet layer MPLs was not related to the total porosity of the GDLs.

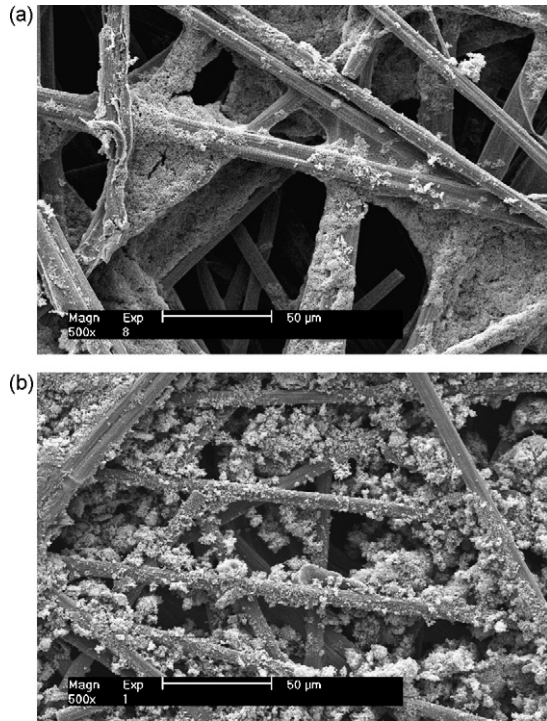


Fig. 6. SEM images of MPLs in GDLs (magnification 500×). The carbon loading in MPLs was 0.1 mg cm⁻². The PTFE content in MPLs was 30 wt.%. (a) Wet layer MPL; (b) dry layer MPL.

Table 1
Porosities of GDLs

Porosity	Before hot-press (%)	After hot-press (%)
Carbon paper	78.0	77.0
Waterproofed carbon paper	76.3	74.8
GDL with dry layer MPL	74.4	73.8
GDL with wet layer MPL	75.0	73.6

The carbon loading in MPL was 0.7 mg cm⁻². The PTFE content in MPL was 30 wt.%. The hot-press treatment was performed at 160 °C, 1 MPa for 1 min.

3.2.3. Pore size distribution in the GDLs

The pore size distribution in the GDLs was measured using mercury intrusion porosimetry. The specific pore volume for the GDLs is shown in Fig. 7. The carbon loading in both the dry layer and wet layer MPLs was 0.7 mg cm⁻². In this paper, the pores in the ranges

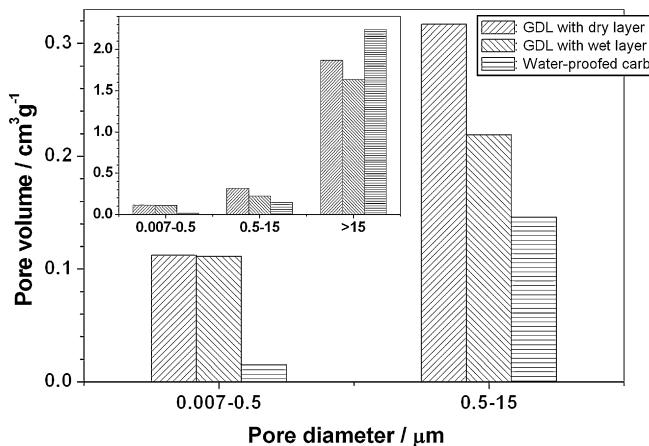


Fig. 7. Pore size distribution of GDLs. The carbon loading in MPLs was 0.7 mg cm⁻². The PTFE content in MPLs was 30 wt.%. The hot-press treatment was performed at 160 °C, 1 MPa for 1 min.

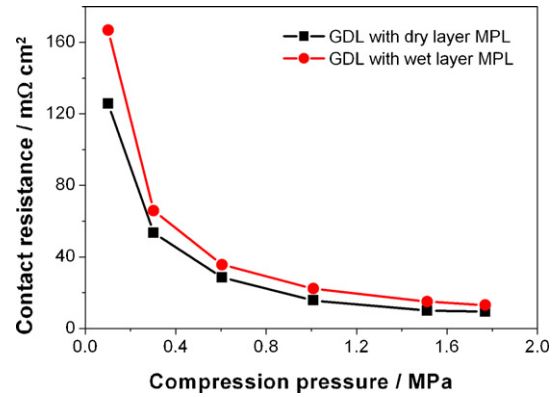


Fig. 8. Through-plane resistance of GDLs. The carbon loading in MPLs was 0.7 mg cm⁻². The PTFE content in MPLs was 30 wt.%. The hot-press treatment was performed at 160 °C, 1 MPa for 1 min.

7 nm–0.5 μm, 0.5–15 μm, and >15 μm are termed as micro-pores, meso-pores, and macro-pores, respectively.

As shown in Fig. 7, the volume of micro-pores in the GDLs with either the dry layer or wet layer MPLs was about 0.110 cm³ g⁻¹, which was about 8 times as large as that in the GDLs without the MPLs (waterproofed carbon paper). The results indicated that the micro-pore volume was increased significantly by addition of the MPLs.

Besides, the volume of meso-pores in the GDLs was quite different. The meso-pore volume for the GDLs with the dry layer MPLs was measured to be 0.317 cm³ g⁻¹, which was obviously larger than that for the GDLs with the wet layer MPLs (0.219 cm³ g⁻¹) and the GDLs without MPLs (0.146 cm³ g⁻¹). Thus, the volume of meso-pores in the GDLs with the dry layer MPLs was the largest.

3.2.4. Gas permeability of the GDLs

First, the GDL samples were treated with 80 °C water for 20 h. Then the permeability of nitrogen through the GDLs was measured as described in Section 2. In order to prevent the removal of the absorbed water from the GDLs, the pressure difference across the sample was controlled to be constant within 10 Pa by regulating the gas flow rate. The gas permeability coefficient for the GDLs with the dry layer MPLs was measured to be 0.38 × 10⁻¹² m², which was obviously larger than the value for the GDLs with the wet layer MPLs (0.17 × 10⁻¹² m²). It indicated that even with the absorbed water, the GDLs with the dry layer MPLs was more effective for gas transport than the GDLs with the wet layer MPLs. The reason will be discussed in Section 3.3.

3.2.5. Electrical conductivity of the GDLs

The through-plane resistance of the GDLs was measured at different compression pressures. The results are shown in Fig. 8. The resistance of the GDLs with the dry layer MPLs was slightly less than that of the GDLs with the wet layer MPLs.

3.2.6. Hydrophobic property of MPL surfaces

The gas transport in a GDL is also influenced by the surface hydrophobicity of the MPLs [6]. The hydrophobicities of the dry layer and wet layer MPLs were compared by treating the GDL samples in 80 °C water for 20 h. Then, the samples were taken out of the water. The images of the MPL surfaces were recorded and shown in Fig. 9.

As can be seen, almost the whole surface area of the wet layer MPLs was wet. But more than 80% of the surface area of the dry layer MPLs remained dry. It indicated that the hydrophobic property of the dry layer MPLs was more stable than that of the wet layer MPLs.

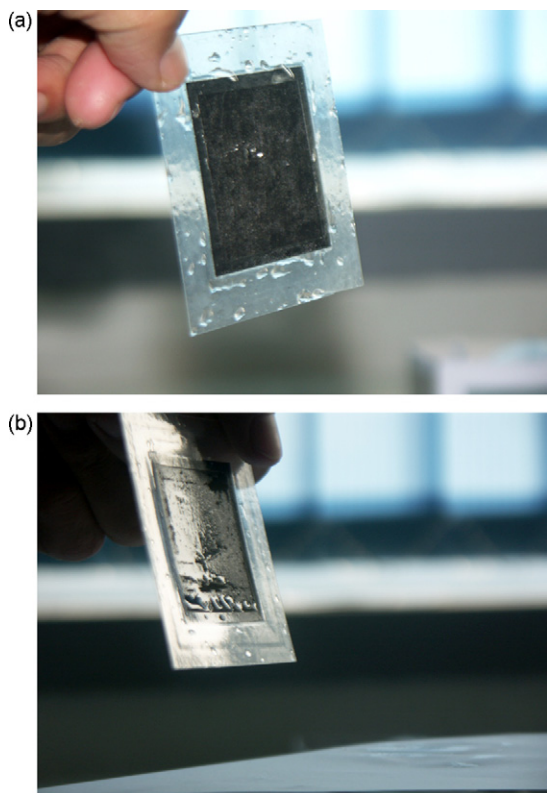


Fig. 9. Images of MPL surface after treating with 80 °C water for 20 h. The carbon loading in MPLs was 0.7 mg cm⁻². The PTFE content in MPLs was 30 wt.%. (a) Dry layer MPLs; (b) wet layer MPLs.

3.3. Relationship between pore size distribution and mass transport in GDLs

As well known, the GDLs have a composite structure, which is made up of Teflon and carbon. Hence, the contact angle within the GDLs can be either hydrophilic or hydrophobic. The critical radius (r_c) of the pore in a GDL that can be filled with liquid water is related to the capillary pressure and the wettability of the pore: $r_c = (2\sigma \cos\theta/P_c)$, in which P_c is the capillary pressure ($P_c = P_l - P_g$), the pressure difference between the liquid phase and the gas phase, σ is the surface tension of water, and θ is the composite contact angle between water in air and carbon.

For the hydrophilic pore, the contact angle is $0^\circ \leq \theta < 90^\circ$. At the condition $P_c < 0$, due to the smaller capillary force needed, the liquid water preferentially penetrates into the smaller hydrophilic pores. Thus the hydrophilic micro-pores are advantageous for the transport of liquid water.

For the hydrophobic pore, the contact angle is $90^\circ < \theta \leq 180^\circ$. At the condition $P_c > 0$, water preferentially penetrates into the larger hydrophobic pores, because the critical P_c for entering a larger pore is lower than that for entering a smaller one. When the fuel cell is operated at high current densities, or at high relative humidity, the pressure of the liquid phase is often larger than that of the gas phase ($P_c > 0$). In such cases, although the hydrophobic macro-pores are beneficial to the gas transport, they are also easily filled with liquid water. However, because the capillary pressure for liquid water penetrating into a smaller hydrophobic pore is much higher, the hydrophobic meso-pores can consequently remain free for gas transport. Therefore, the hydrophobic meso-pores are important and advantageous for gas transport in GDLs. The value of r_c is the smallest water-filled pore radius for a hydrophobic pore [4]. The similar argument on the condensation and transport of liquid water

in hydrophobic pores with different size in a catalyst layer of PEMFC has been reported by Zhang et al. [27].

The above-mentioned analysis is also verified and supported by the experimental results as shown in Figs. 3, 4 and 7. As shown in Figs. 3 and 7, compared with the performance of the cell based on the GDLs without the MPLs, the performances of the cells were all evidently improved by both the dry layer and wet layer MPLs due to the abundant micro-pores in MPLs. This is also consistent with the results reported in the literature [9–20].

As shown in Figs. 3 and 4, PEMFC single cells using the dry layer MPLs always exhibited the best performance, especially at high oxygen utilization rate and high humidification temperature of air. The most important character of the pore size distribution in the GDLs with the dry layer MPLs is that it contains the most abundant meso-pores, which are about 1.5 times as large as that in the GDLs with the wet layer MPLs, and more than 2 times as large as that in the waterproofed carbon paper (as shown in Fig. 7). Thus, the large amount of hydrophobic meso-pores introduced by the dry layer MPLs was the main reason for the improvement of the cell performance.

In the experiments on the influence of the humidification temperature of air, the cells using the dry layer MPLs showed better performance at high current densities than that using the wet layer MPLs, especially at high humidification temperature of air. This is considered to be related to the larger number of meso-pores in the GDLs with the dry layer MPLs. At high humidification temperature (high relative humidity), the hydrophobic macro-pores in the GDLs were easily filled with liquid water, resulting in high resistance for oxygen diffusion in GDLs. However, because the capillary pressure for liquid water entering a hydrophobic meso-pore is much higher, the meso-pores can remain free for gas transport. Thus, it is easily understood that at high relative humidity, the gas transport in the GDLs with the dry layer MPLs that contained the larger number of meso-pores was better than that in the GDLs with the wet layer MPLs. In the case that the experiments were conducted at low humidification temperature of air, due to the low relative humidity, the hydrophobic macro-pores in the GDLs with the wet layer MPLs possibly remained open. Thus, the gas transport in the cell using the wet layer MPLs could be improved at low relative humidity.

The experimental results on the gas permeability of the GDLs as described in Section 3.2.4 also supported the evidence obtained outside the fuel cells for the improvement of gas transport by using the dry layer MPLs. This is considered to be also related to the larger number of meso-pores in the GDLs with the dry layer MPLs. Even if absorbing liquid water, the GDLs with the dry layer MPLs exhibited an obvious advantage for facilitating gas transport.

However, it is necessary to point out that the quantitative researches about the role of meso-pores on the mass transport in GDLs are very important and should be studied further.

The pores larger than 15 μm (the macro-pores) mainly remained from the original ones in the waterproofed carbon paper. The micro-pores were mainly introduced by the MPLs. Concerning the meso-pores, they were mainly formed by the modification of the macro-pores in the carbon paper by the MPLs. It can be concluded that the dry layer preparation for MPLs is more beneficial to forming the meso-pores in GDLs.

4. Conclusions

PEMFC single cells using dry layer MPLs showed better performance than those using the wet layer MPLs, especially when the cells were operated at high oxygen utilization rate and high humidification temperature of air. The mass transport property of the GDLs with the dry layer MPLs was also better than that of the GDLs with the wet layer MPLs. This effect was found to be related

to the pore size distribution in the GDLs. The formation processes of the dry layer MPLs and wet layer MPLs are different. The structure of the carbon paper was modified in different ways depending on the preparation process of the MPLs. The analysis of the pore size distribution and mass transport property of the GDLs indicated that the hydrophilic micro-pores and the hydrophobic macro-pores were advantageous for water transport. Because the capillary pressure for liquid water penetrating into a hydrophobic meso-pore is very high, the hydrophobic meso-pores can remain free for the gas transport. The dry layer preparation for the MPLs was found to be more beneficial to forming the meso-pores, which are important and advantageous for facilitating the gas transport in GDLs. Moreover, the GDLs with the dry layer MPLs exhibited better electronic conductivity and more stable hydrophobicity than those with the wet layer MPLs. The reproducibility of the dry layer preparation for MPLs was also satisfactory.

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References

- [1] J.H. Nam, M. Kaviany, *International Journal of Heat and Mass Transfer* 46 (2003) 4595–4611.
- [2] Z.G. Qi, A. Kaufman, *Journal of Power Sources* 109 (2002) 38–46.
- [3] M. Han, S.H. Chan, S.P. Jiang, *Journal of Power Sources* 159 (2) (2006) 1005–1014.
- [4] A.Z. Weber, R.M. Darling, J. Newman, *Journal of the Electrochemical Society* 151 (10) (2004) A1715–A1727.
- [5] U. Pasaogullari, C.Y. Wang, *Journal of the Electrochemical Society* 151 (3) (2004) A399–A406.
- [6] U. Pasaogullari, C.Y. Wang, *Electrochimica Acta* 49 (2004) 4359–4369.
- [7] D. Natarajan, T.V. Nguyen, *Journal of the Electrochemical Society* 148 (12) (2001) A1324–A1335.
- [8] G. Lin, T.V. Nguyen, *Journal of the Electrochemical Society* 153 (2) (2006) A372–A382.
- [9] L.R. Jordan, A.K. Shukla, T. Behrsing, et al., *Journal of Power Sources* 86 (2000) 250–254.
- [10] L.R. Jordan, A.K. Shukla, T. Behrsing, et al., *Journal of Applied Electrochemistry* 30 (2000) 641–646.
- [11] E. Passalacqua, G. Squadrito, F. Lufrano, et al., *Journal of Applied Electrochemistry* 31 (2001) 449–454.
- [12] E. Antolini, R.R. Passos, E.A. Ticianelli, *Journal of Power Sources* 109 (2002) 477–482.
- [13] A.M. Kannan, A. Menghal, I.V. Barsukov, *Electrochemistry Communications* 8 (2006) 887–891.
- [14] G.G. Park, Y.J. Sohn, S.D. Yim, et al., *Journal of Power Sources* 163 (1) (2006) 113–118.
- [15] J.R. Yu, Y. Yoshikawa, T. Matsuura, et al., *Electrochemical and Solid-State Letters* 8 (3) (2005) A152–A155.
- [16] V.A. Paganin, E.A. Ticianelli, E.R. Gonzalez, *Journal of Applied Electrochemistry* 26 (1996) 297–304.
- [17] E. Antolini, R.R. Passos, E.A. Ticianelli, *Journal of Applied Electrochemistry* 32 (2002) 383–388.
- [18] L. Giorgi, E. Antolini, A. Pozio, et al., *Electrochimica Acta* 43 (24) (1998) 3675–3680.
- [19] J. Moreira, A.L. Ocampo, P.J. Sebastian, et al., *International Journal of Hydrogen Energy* 28 (2003) 625–627.
- [20] J.M. Song, S.Y. Cha, W.M. Lee, *Journal of Power Sources* 94 (2001) 78–84.
- [21] X.L. Wang, H.M. Zhang, J.L. Zhang, et al., *Journal of Power Sources* 162 (2006) 474–479.
- [22] G.G. Park, Y.J. Sohn, T.H. Yang, et al., *Journal of Power Sources* 131 (2004) 182–187.
- [23] M.V. Williams, E. Begg, L.J. Bonville, et al., *Journal of the Electrochemical Society* 151 (8) (2004) A1173–A1180.
- [24] M. Mathias, J. Roth, J. Fleming, et al., *Diffusion media materials and characterization, Handbook of Fuel Cells—Fundamentals, Technology and Applications*, vol. 3 (Chapter 46), 2003.
- [25] M. Prasanna, H.Y. Ha, E.A. Cho, et al., *Journal of Power Sources* 131 (2004) 147–154.
- [26] J.G. Pharoah, *Journal of Power Sources* 144 (2005) 77–82.
- [27] F.Y. Zhang, D. Spornjak, A.K. Prasad, et al., *Journal of the Electrochemical Society* 154 (11) (2007) B1152–B1157.