



Microporous layer coated gas diffusion layers for enhanced performance of polymer electrolyte fuel cells

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ABSTRACT

The influence of microporous layer (MPL) design parameters for gas diffusion layers (GDLs) on the performance of polymer electrolyte fuel cells (PEFCs) was clarified. Appropriate MPL design parameters vary depending on the humidification of the supplied gas. Under low humidification, decreasing both the MPL pore diameter and the content of polytetrafluoroethylene (PTFE) in the MPL is effective to prevent drying-up of the membrane electrode assembly (MEA) and enhance PEFC performance. Increasing the MPL thickness is also effective for maintaining the humidity of the MEA. However, when the MPL thickness becomes too large, oxygen transport to the electrode through the MPL is reduced, which lowers PEFC performance. Under high humidification, decreasing the MPL mean flow pore diameter to 3 μm is effective for the prevention of flooding and enhancement of PEFC performance. However, when the pore diameter becomes too small, the PEFC performance tends to decrease. Both reduction of the MPL thickness penetrated into the substrate and increase in the PTFE content to 20 mass% enhance the ability of the MPL to prevent flooding.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) with high efficiency and low environmental impact have been developed in recent years. However, further improvement in performance and reliability is required to ensure that PEFCs constitute a large proportion of future power generation devices. In order to enhance PEFC performance, an appropriate water balance between the conservation of membrane humidity and the discharge of water produced in the cell is essential. Loss of water content in the membrane decreases ionic conductivity, thereby increasing the internal resistance of the cell. The basic configuration of a PEFC includes a membrane electrode assembly (MEA), a gas diffusion layer (GDL) and a separator. The design parameters for the GDL, such as thickness, pore size distribution, electrical resistivity, gas permeability and hydrophobicity, play an important role in determining the characteristics of electron transport, gas diffusion and water management during PEFC operation.

Several investigations have demonstrated that a hydrophobic microporous layer (MPL) coated on the GDL substrate is effective for improvement of the water management characteristics, which thereby enhances PEFC performance [1–4]. The authors have

also reported that a MPL coated GDL significantly reduces flooding on the electrode, and enhances PEFC performance under high humidity conditions. The MPL is also effective to prevent drying-out of the MEA under low humidity conditions [5–7]. The pore size, porosity, thickness and hydrophobicity of the MPL have a significant influence on the gas diffusion and water management characteristics of the GDL. Therefore, it is important to clarify appropriate design parameters for the MPL to enhance PEFC performance.

The present study was carried out to determine appropriate design parameters for MPL coated GDLs. The in-plane and through-plane air permeabilities of the GDL were measured under compression conditions typical of PEFCs under operation. The maximum pore and mean flow pore diameters were measured using an air permeability test apparatus, in which a low-surface-tension wetting liquid filled the pores of the GDL. The MPL thickness considering the penetration into the substrate was estimated by comparison of the in-plane permeability obtained using GDLs with and without the MPL. A water permeability test was also carried out using the same apparatus. When the maximum pore diameter measured using the water permeability test was assumed to be the same as that measured using the air permeability test, the contact angle inside the GDL pores could be accurately estimated. The influences of the MPL design parameters on the PEFC performance were clarified under high and low humidity conditions.

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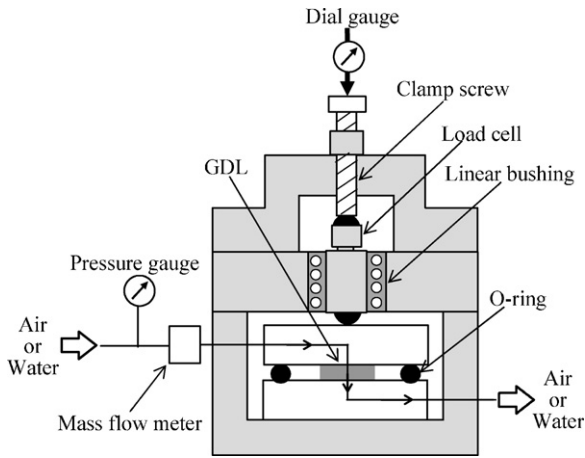


Fig. 1. Schematic diagram of air and water permeability tests apparatus.

2. Experimental

2.1. Air permeability test

Fig. 1 shows a schematic diagram of the GDL permeability test apparatus [8]. The GDL to be tested was placed between two cylindrical plates. A soft O-ring was used for gas sealing between the plates. The force required to deform the O-ring was negligible compared with the compression force acting on the GDL. The compression force was controlled using a clamp screw and was measured with a load cell. For air permeability tests, the compression pressure was set at 1 MPa, as measured in a typical PEFC [9]. Fig. 2 shows the major dimensions of the GDL used for the through-plane and in-plane permeability tests. The supplied air pressure P was set at 1.23 kPa. The air flow rate Q was measured using a mass flow meter. The permeance q was defined as the flow rate divided by the supplied air pressure and permeable cross-sectional area.

Maximum pore and mean flow pore diameters of MPL coated GDLs were measured from through-plane permeability tests according to the ASTM standard test method for pore size characteristics [10] as shown in Fig. 3. The dry flow curve represents the relationship between the flow rate and the supplied air pressure obtained with a completely dry GDL and the wet flow curve represents that obtained with a wetted GDL, in which a low-surface-tension ($=0.0157 \text{ N m}^{-1}$) wetting liquid (Galwick [11]) fills the pores of the GDL. The half-dry flow curve corresponds to one half the measured dry flow curve at a given air pressure.

By applying an air pressure across the wetted GDL, the liquid is displaced from the pores. The equilibrium relationship between the surface tension of the liquid and the air pressure, as shown in Fig. 4, was used to calculate the pore diameter:

$$d = \frac{4\gamma \cos \theta}{P} \quad (1)$$

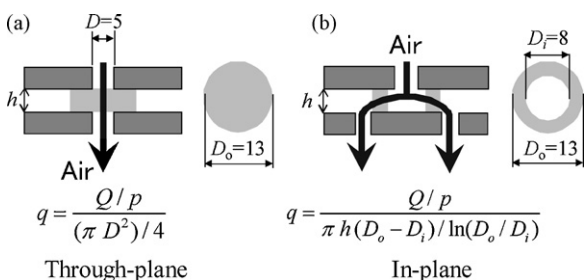


Fig. 2. Major dimensions of GDL used for through-plane and in-plane permeability tests.

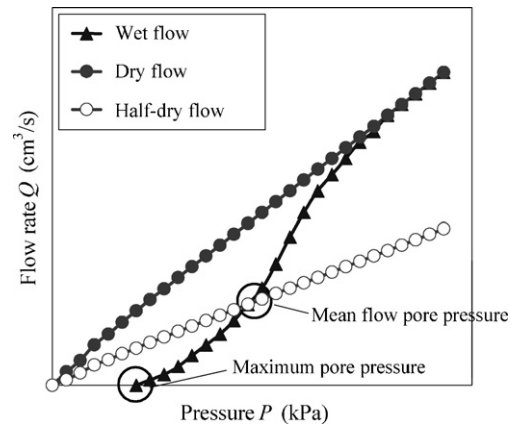


Fig. 3. Typical changes in flow rate with the supplied air pressure obtained using dry and wetted GDLs.

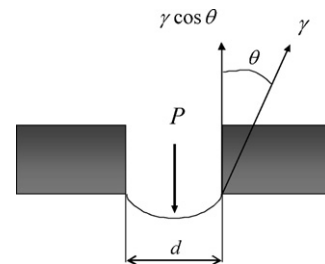


Fig. 4. Equilibrium relationship between the surface tension of the liquid and the air pressure.

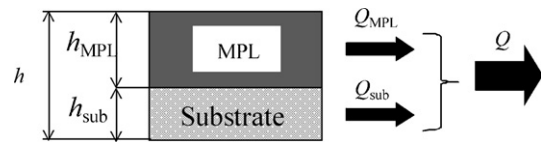


Fig. 5. MPL thickness considering the penetration into the GDL substrate calculated from in-plane permeability.

where d is pore diameter, γ and θ are the surface tension and contact angle of the wetting liquid, respectively, and P is the air pressure acting on the liquid in the pore. The contact angle of the wetting liquid is close to 0° [11]. The minimum pressure at which air begins to flow by clearing of the first pore is the maximum pore (bubble point) pressure, which is used to calculate the maximum pore diameter d_{max} . The pressure is further increased and progressively smaller pores are cleared until the GDL is fully dried. The mean flow pore diameter d_m is calculated using the mean flow pressure that corresponds to the intersection of the wet flow and half-dry flow curves.

The cross-sectional view of the MPL coated GDLs demonstrates that the MPL is not simply coated on the substrate surface, but penetrates deeply into the porous substrate. Because the boundary between the MPL and the substrate observed from the micrograph is neither clear nor uniform, it is difficult to measure the MPL thickness considering the penetration into the substrate. Therefore, the average thickness of the MPL h_{MPL} considering the penetration into the substrate was evaluated by a comparison of the measured in-plane permeance using GDLs with and without MPLs, as shown in Fig. 5 [8].

The in-plane permeance q of the MPL coated GDL is given as follows:

$$q = \frac{q_{\text{MPL}} h_{\text{MPL}} + q_{\text{sub}} h_{\text{sub}}}{h} \quad (2)$$

where h is the total thickness of the GDL, q_{sub} and q_{MPL} are the permeance of the substrate and the MPL, respectively, and h_{sub} and h_{MPL} are the thickness of the substrate and the MPL, respectively. From Eq. (2), the MPL thickness can be obtained as follows:

$$h_{\text{MPL}} = \frac{h}{1-k} \left(1 - \frac{q}{q_{\text{sub}}} \right) \quad (3)$$

where $k (=q_{\text{MPL}}/q_{\text{sub}})$ is the in-plane permeance ratio of the MPL to the substrate. The in-plane permeance ratio could not be obtained directly. In the present study, the values of k were set at either 1/80 for a mean flow pore diameter of 3 μm or 1/150 for a mean flow pore diameter of 1 μm , assuming that the in-plane permeance ratio was equal to the through-plane permeance ratio, which was measured using the substrate and the MPL coated GDL with a MPL thickness of 110 μm and a PTFE content of 20 mass%. Evidence for the through-plane permeance is presented later in the paper (see Fig. 8).

2.2. Contact angle measurement

The hydrophobic properties of the GDL are generally evaluated using the contact angle, which is commonly measured by the sessile drop method [12]. In this method, a droplet of water is placed on the GDL surface and the contact angle is measured by fitting a tangent to the three-phase point where the liquid surface touches the solid surface. However, because the contact angle measured using this method is significantly dependent on the surface roughness of the GDL and the weight of the water droplet, it is difficult to evaluate an accurate contact angle. Therefore, a new technique was developed to measure the contact angle inside the GDL pore. The water permeability test in the through-plane direction of the GDL was carried out using the same apparatus as shown in Fig. 1. The water flow rate increases with the increase in the water supply pressure. The minimum pressure at which water begins to flow through the largest pore of the GDL is the maximum pore pressure. The maximum pore diameter is calculated using Eq. (1). The surface tension of water at 25 °C was set at 0.0720 N m⁻¹ [13]. When the maximum pore diameter measured using the water permeability test was assumed to be the same as that measured using the air permeability test, the contact angle inside the GDL pore could be accurately estimated.

2.3. PEFC performance test

The PEFC performance tests were carried out under conditions of high and low humidity of the supplied gas. The cell temperature was set to 75 °C. The utilization of hydrogen at the anode was set at 70% and the utilization of air at the cathode was set at 60%. The relative humidity of the gas supplied at the cathode was set at either 100% or 0%, while maintaining a relative humidity of 100% at the anode. The back pressure of the supplied gases was set at zero. The active area of the MEA (PRIMEA® 5580) was 4.2 cm².

The IR (ohmic loss), activation and concentration overpotentials were measured separately as follows [14]:

- Anode overpotential (η_A) was obtained as the difference between the anode cell voltage and the reference hydrogen electrode.
- Open circuit voltage (OCV) overpotential (η_{OCV}) was measured as the potential drop between the Nernst potential (E_0) and OCV.
- IR overpotential (η_{IR}), or ohmic loss, was measured using the current-interruption method.
- Cathode concentration overpotential (η_{CC}) was determined by separating the voltage given by Tafel's equation from the cathode overpotential.

- Cathode activation overpotential (η_{CA}) was calculated by subtracting the above overpotentials and the output voltage (V_{eff}) from E_0 as follows:

$$\eta_{\text{CA}} = E_0 - \eta_A - \eta_{\text{eff}} - \eta_{\text{CC}} - \eta_{\text{OCV}} - \eta_{\text{IR}} \quad (4)$$

The differences in the activation overpotentials obtained for all GDLs were not significant. Therefore, the influences of the MPL design parameters on the IR and concentration overpotentials could be discussed with the following test results.

2.4. MPL coating on the substrate

The GDL substrate used was a commercial carbon paper (SGL SIGRACET® 24BA) that was treated with 5% PTFE (polytetrafluoroethylene) loading to impart hydrophobicity. The substrate had a thickness of 190 μm , an areal weight of 54 g m⁻², a porosity of 84% and a mean flow pore diameter of 42 μm . The MPL, which consists of PTFE and carbon black, was coated on the substrate as follows. A slurry containing PTFE, carbon black, distilled water and a surface-active agent was mixed using an impeller blade-type mixer, and then spread on the substrate using a bar coating machine. The MPL was dried in an oven and then finally heated at 350 °C to remove any remaining solvent and to sinter the PTFE and carbon black on the substrate. The PTFE content in the MPL was varied between 5 and 40 mass%.

Figs. 6 and 7 show SEM micrographs of the surface and cross-section of GDLs with and without MPLs, respectively. The mean flow pore diameter of the MPL d_m decreased from 10 to 1 μm when the water concentration in the slurry was reduced from 89% to 76%. The MPL thickness h_{MPL} , considering the penetration in the substrate, was controlled to between 90 and 240 μm by the clearance and pressure of the doctor blade in the coating machine. The total thickness h of all MPL coated GDLs was set at 250 μm .

3. Results and discussion

3.1. Influence of the MPL on air permeability

Fig. 8 shows the influence of the MPL mean flow pore diameter d_m on the through-plane and in-plane air permeance. The MPL thickness h_{MPL} was set at 110 μm and the PTFE content in the MPL was also set at 20 mass% for all GDLs. Decrease in the MPL pore diameter significantly reduces through-plane permeability, but reduces in-plane permeability only slightly. Fig. 9 shows the influence of the MPL thickness h_{MPL} on the through-plane and in-plane air permeance. The mean flow pore diameter of the MPL d_m was set at 3 μm and the PTFE content in the MPL was also set at 20 mass% for all GDLs. The in-plane permeance is enhanced when the MPL thickness decreases; however, enhancement of the through-plane permeance is not significant.

For the through-plane permeability tests, all of the supplied air flows out through the dense MPL, so that any decrease in the MPL pore diameter significantly reduces the through-plane permeability. The influence of the substrate porosity and pore diameter for the MPL coated GDLs on the through-plane permeance is not significant [8]. The relationship between the through-plane permeability and the MPL pore diameter will be discussed later. For the in-plane permeability tests, the permeance of the MPL coated GDL could be described by Eq. (2). Although the MPL penetrates into the substrate, most of the supplied air flows out through the porous GDL substrate. Therefore, the influence of the MPL pore diameter on in-plane permeability is not significant. A decrease in the MPL thickness penetrated into the substrate increases the porous substrate cross-sectional area, which significantly enhances the in-plane permeability.

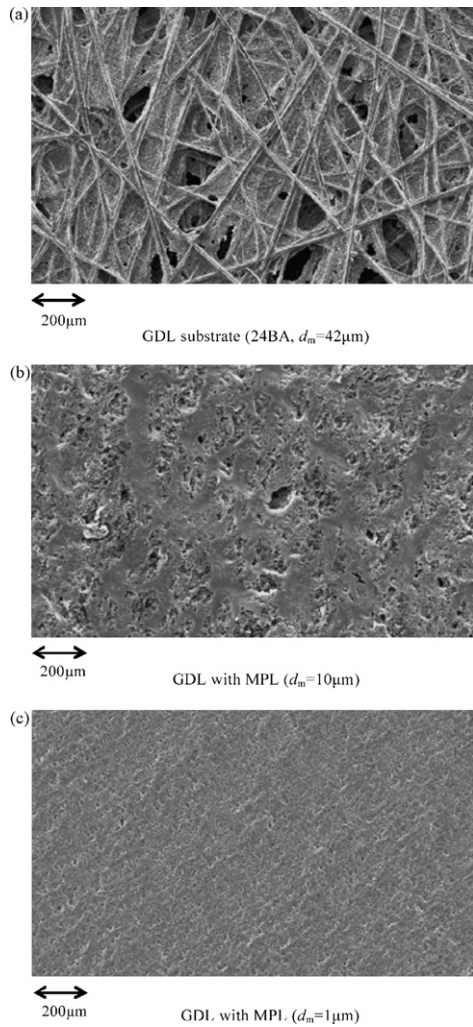


Fig. 6. SEM micrographs of GDL surface with and without MPLs (PTFE 20%, $h_{MPL} = 110 \mu\text{m}$).

Fig. 10 shows the relationship between the through-plane permeance q , porosity ε and mean flow pore diameter d_m obtained using GDLs with and without MPLs. For the tested GDLs without the MPL, the porosity was varied between 83 and 91% and the thickness was varied between 190 and 300 μm [8]. For the tested GDLs with the MPL, the MPL mean flow pore diameter was varied between 1 and 10 μm , the MPL thickness was varied between 90 and 180 μm , and the PTFE content in the MPL was varied between 5 and 40 mass%. Permeance increases in proportion to the porosity multiplied by the squared mean flow pore diameter (εd_m^2) obtained for GDLs without the MPL (white circles) [8]. Although the GDL has a very complex porous structure, a familiar relationship for a porous material consisting of straight capillary tubes with a porosity of ε and a diameter of d_m [15] can be obtained. On the other hand, for the MPL coated GDLs, there is no appropriate method to evaluate the porosity of the MPL. However, if the same relationship between permeance and εd_m^2 is assumed, then the porosity of the MPL can be evaluated using the measured permeance and mean flow pore diameter [8]. The relationship for the MPL coated GDLs (black circles) shown in Fig. 10 was obtained according to the previously described procedure. Fig. 11 demonstrates that the porosity of the MPL decreases from 50% to 35% when the MPL mean flow pore diameter is reduced from 10 to 1 μm .

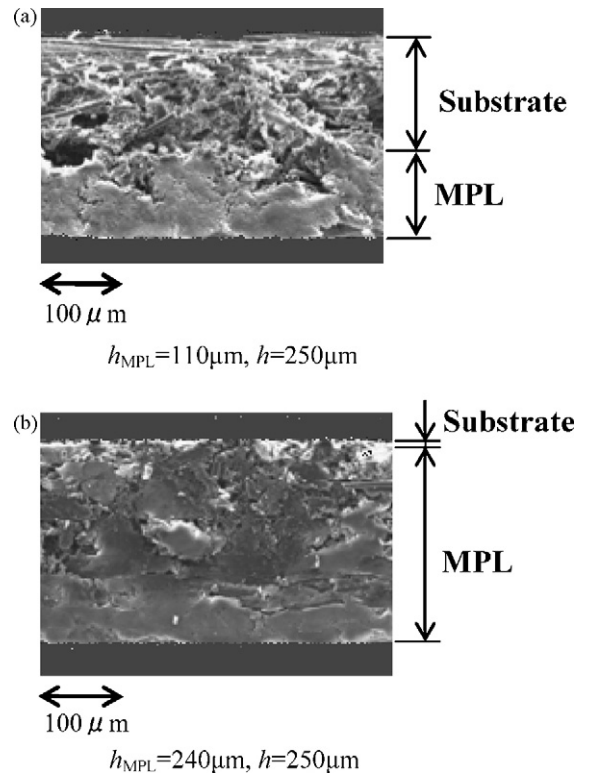


Fig. 7. Cross-sectional SEM micrographs of MPL coated GDLs (PTFE 20%, $d_m = 1 \mu\text{m}$).

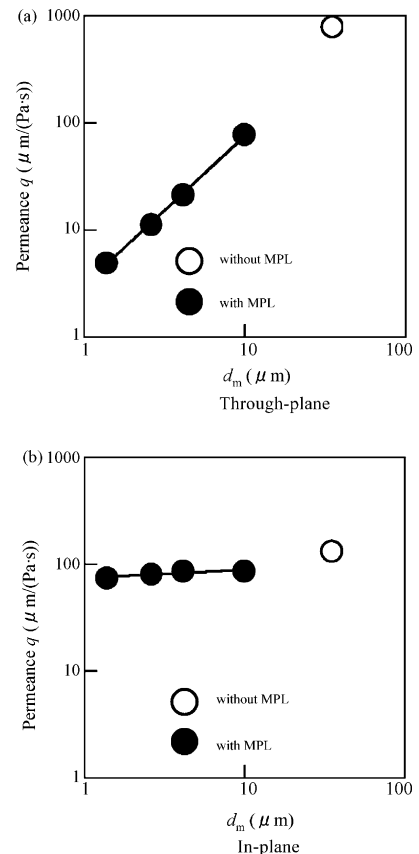


Fig. 8. Influence of MPL mean flow pore diameter on GDL permeability (PTFE 20%, $h_{MPL} = 110 \mu\text{m}$).

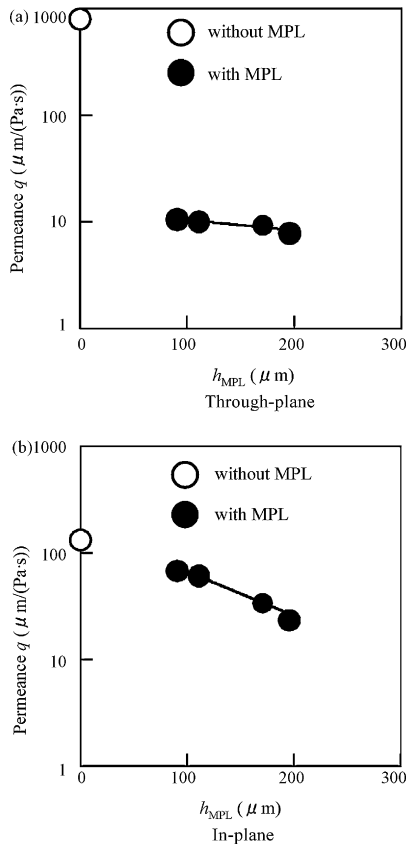


Fig. 9. Influence of MPL thickness on GDL permeability (PTFE 20%, $d_m = 3 \mu\text{m}$).

3.2. Influence of the PTFE content in the MPL on hydrophobicity

Fig. 12 shows the contact angles measured using the conventional sessile drop method at 25 °C. The mass of the water droplet placed on the GDL surface was set at 0.04 g. The PTFE content in the MPL was varied between 5 and 40 mass%. The mean flow pore diameter d_m was set at 3 μm and the MPL thickness h_{MPL} was set at 90 μm for all GDLs. The contact angle is almost the same value of 126°, even when the PTFE content in the MPL is increased from 5 to 40 mass%. This is because the contact angle could not be accurately measured due to the influence of the surface roughness of the GDL and the weight of the water droplet.

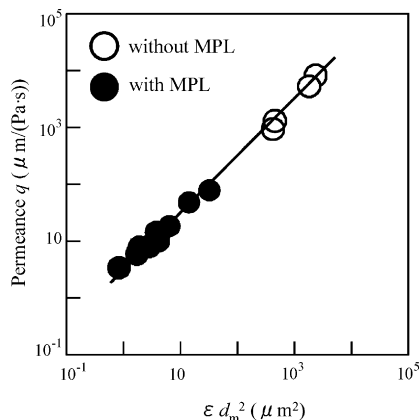


Fig. 10. Relationship between through-plane permeance and ϵd_m^2 obtained using GDLs with and without MPLs.

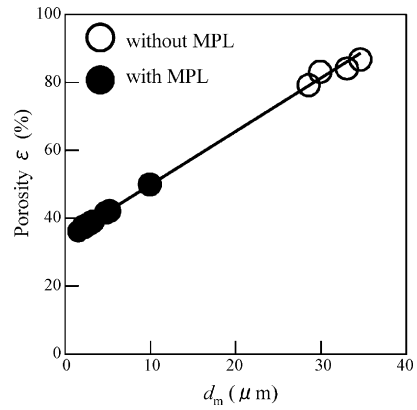


Fig. 11. Relationship between porosity and mean flow pore diameter obtained using GDLs with and without MPLs.

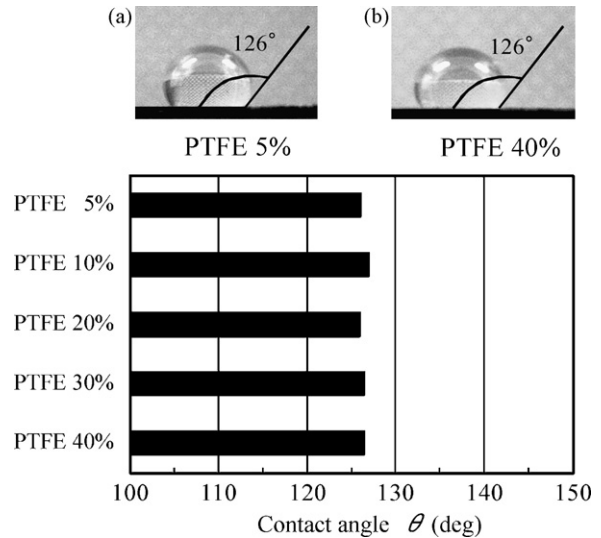


Fig. 12. Influence of PTFE content in MPL on contact angle measured using the sessile drop method ($d_m = 3 \mu\text{m}$, $h_{\text{MPL}} = 90 \mu\text{m}$).

Therefore, a new technique was developed to measure the contact angle inside the GDL pore, assuming that the maximum pore diameters obtained from both air and water permeability tests were the same values. Fig. 13 shows the influence of the PTFE content in the MPL on the contact angle. When the PTFE content increases from 5 to 40 mass%, the contact angle is extended from 119° to 142°, which enhances the hydrophobic properties of the GDL.

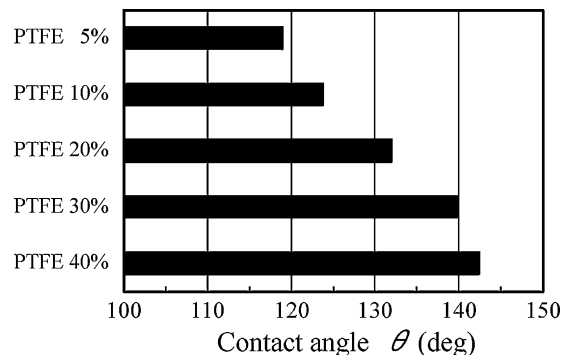


Fig. 13. Influence of PTFE content in MPL on contact angle measured using air and water permeability tests ($d_m = 3 \mu\text{m}$, $h_{\text{MPL}} = 90 \mu\text{m}$).

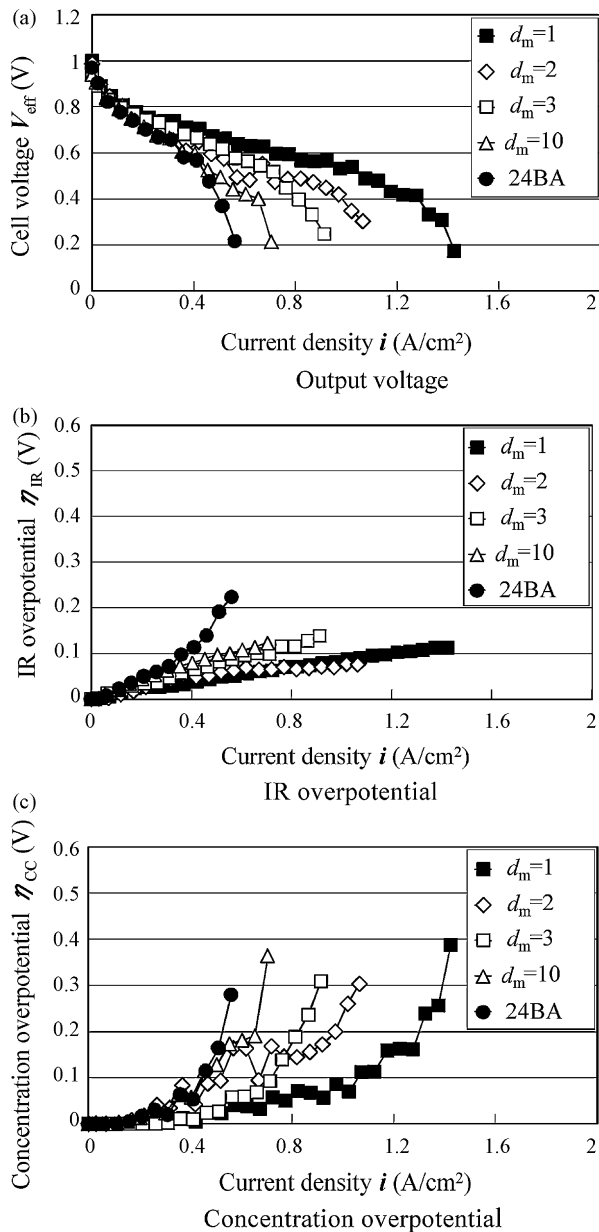


Fig. 14. Influence of mean flow pore diameter of cathode GDL on PEFC performance under no-humidity condition at cathode (PTFE 20%, $h_{MPL} = 110 \mu\text{m}$).

3.3. Influence of the MPL on PEFC performance under low humidity

Fig. 14 shows the influence of the MPL on the PEFC performance under low humidity when the MPL mean flow pore diameter d_m of the cathode GDL is varied between 1 and 10 μm . The MPL thickness h_{MPL} of 110 μm and the PTFE content of 20 mass% were applied to all MPLs. The relative humidity of the gas supplied at the cathode was set to 0%, while maintaining a relative humidity of 100% at the anode. A 24BA GDL without MPL was used at the anode [7]. The IR and concentration overpotentials obtained using the MPL coated GDLs were lower than that of the 24BA GDL without MPL, which indicates that the MPL is effective for enhancement of the PEFC performance under low humidity. Even when the relative humidity of the air supplied to the cathode is zero, water is transported into the MEA from the humidified hydrogen gas by electro-osmotic drag, and is also produced by electrochem-

ical reaction at the cathode. The wetness of the MEA is affected by the water balance between the conservation of membrane humidity and the discharge of water at the cathode. In the case of the cathode GDL without MPL, dehydration of the MEA caused by dry air at the cathode cannot be avoided. When the water content in the MEA becomes low, the ionic conductivity is reduced, which results in an increased IR overpotential. Moreover, when the wetness at the cathode catalyst layer is lowered, the effective reaction area at the triple-phase boundaries, that is, the intersection of the ion-conductive electrolyte, the electrically conductive electrode and the gas-phase pores, is reduced. As a result, it is considered that oxygen transport to the active reaction sites becomes insufficient to keep required electrochemical reaction, thereby increasing the concentration overpotential [7]. Further study is required to determine the detailed mechanism for the increased concentration overpotential due to the reduced wetness at the cathode catalyst layer.

The ability of the MPL to prevent dehydration of the MEA varies significantly, according to the MPL pore diameter. Decreasing the MPL pore diameter reduces through-plane permeability, so that it is difficult for the MEA water to be expelled to the GDL substrate where it can be removed via dry air in the separator gas channel. This enhances the ability of the MPL to prevent dehydration of the MEA.

Fig. 15 shows the influence of the MPL on the PEFC performance under low humidity when the MPL thickness h_{MPL} of the cathode GDL is varied between 110 and 240 μm . The mean flow pore diameter of 1 μm and the PTFE content of 20 mass% were applied to all MPLs. Increasing the MPL thickness reduces both the through-plane and in-plane permeability of the GDL, which is effective for maintaining the humidity of the MEA. However, when the MPL thickness becomes too large, oxygen transport to the electrode through the MPL is decreased, which increases the concentration overpotential, thereby lowering PEFC performance.

Fig. 16 shows the influence of the MPL on the PEFC performance under low humidity when the PTFE content in the MPL is varied between 5 and 40 mass%. A mean flow pore diameter of 1 μm and MPL thickness of 180 μm , for which excellent performance was demonstrated (Figs. 14 and 15), were applied to all MPLs. The electrical resistivity deteriorates with increasing PTFE content in the MPL. However, the difference in IR overpotential obtained for all MPL coated GDLs was not significant. This indicates that the influence of the GDL electrical resistivity on the PEFC performance is negligible for the PTFE content in the MPL in the range between 5 and 40 mass%.

When the PTFE content is lowered from 40 to 5 mass%, the concentration overpotential is reduced, which enhances the PEFC performance. Because the pore diameter and the thickness of the tested GDLs were set at the same values, the differences in the in-plane and through-plane permeability were negligible. When the PTFE content is lowered from 40 to 5 mass%, the hydrophobicity of the MPL is reduced, thereby enhancing the ability of the MPL to conserve membrane humidity. This is probably effective to prevent dehydration at the triple-phase boundaries in the cathode catalyst layer, thereby reducing the concentration overpotential.

The present study was carried out to evaluate appropriate MPL coated GDLs under a relative humidity of 0% at the cathode, while maintaining a relative humidity of 100% at the anode. If a PEFC could be operated under very low humidity at the anode, external humidification may be removed, resulting in a very simplified overall PEFC system with increased total efficiency and reduced cost. As a next step, the authors will evaluate appropriate design parameters of GDLs without humidification at both the anode and cathode.

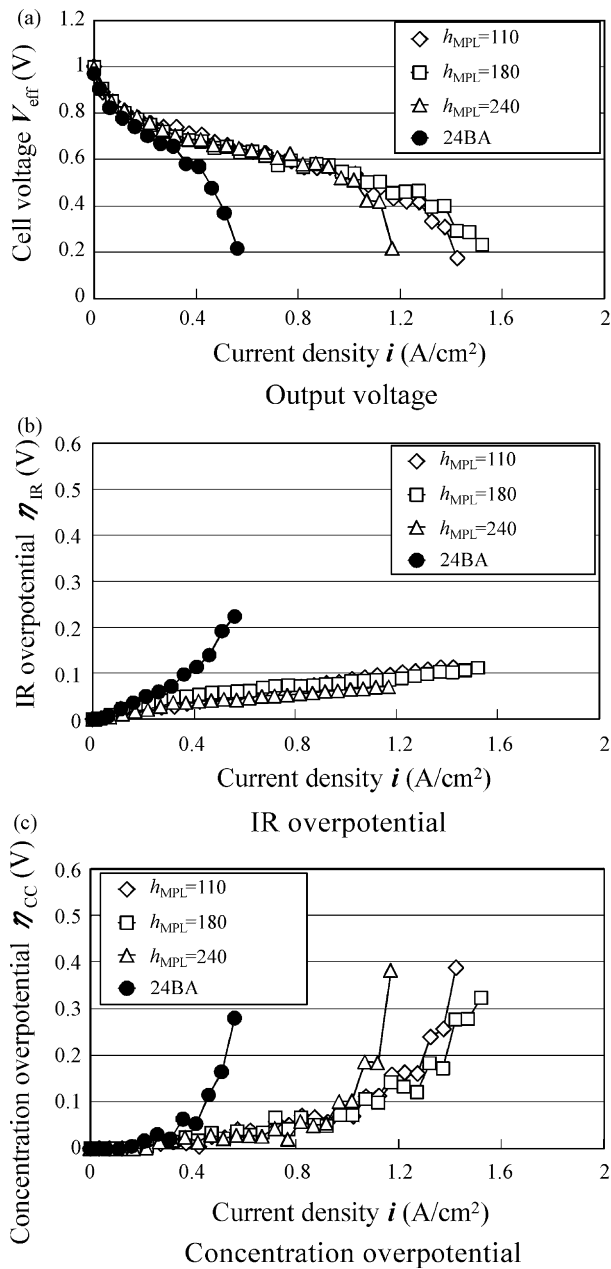


Fig. 15. Influence of MPL thickness of cathode GDL on PEFC performance under no-humidity condition at cathode (PTFE 20%, $d_m = 1 \mu\text{m}$).

3.4. Influence of the MPL on PEFC performance under high humidity

Fig. 17 shows the influence of the MPL on the PEFC performance under high humidity when the MPL mean flow pore diameter d_m of the cathode GDL is varied between 1 and 10 μm . A MPL thickness of 110 μm and PTFE content of 20 mass% were applied to all MPLs. The relative humidity of the gases supplied to both the anode and cathode was set to 100%. A 24BA GDL without MPL was used at the anode. The performance obtained using the 24BA GDL without MPL at the cathode was low, due to flooding caused by the product water, which inhibits the transport of oxygen to the electrode and increases the concentration overpotential at high current densities. The performance obtained using the MPL coated GDLs was superior to the 24BA GDL without the MPL, due to a lower concentration overpotential, although the IR overpotential was relatively uniform for all GDLs. MPL coating is effective for enhancement of the PEFC

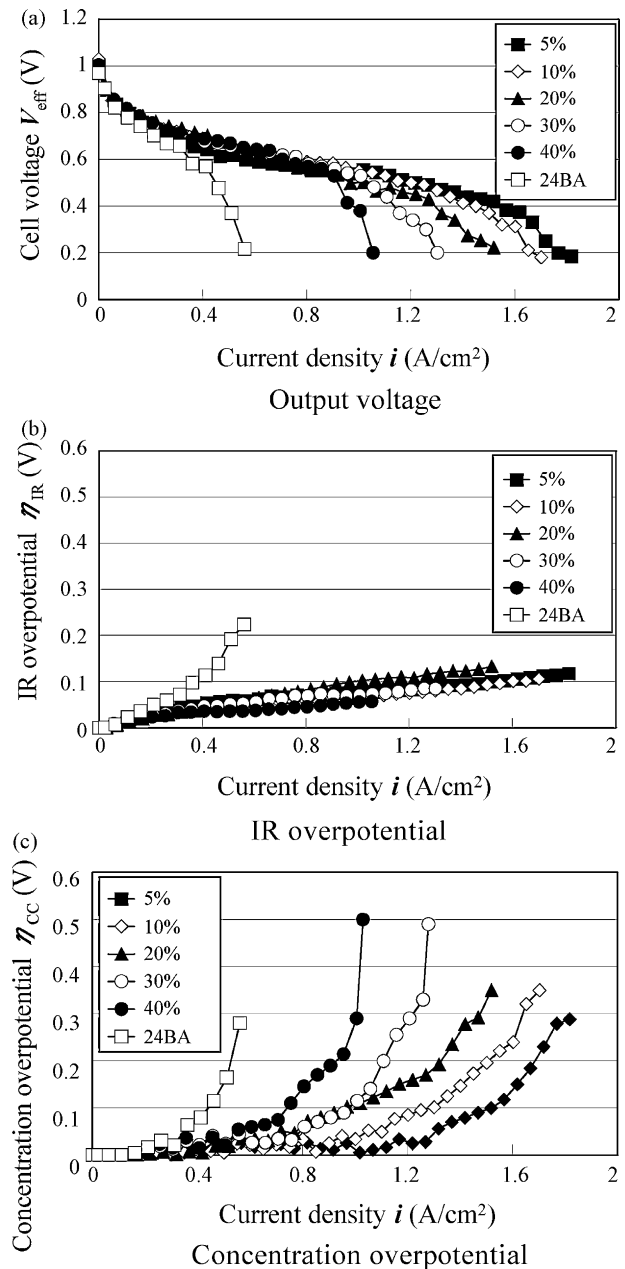


Fig. 16. Influence of PTFE content in MPL on PEFC performance under no-humidity condition at cathode ($d_m = 1 \mu\text{m}$, $h_{MPL} = 180 \mu\text{m}$).

performance, which varies significantly depending on the MPL pore diameter. Decreasing the MPL pore diameter to 3 μm is effective to reduce flooding and enhance PEFC performance. However, when the pore diameter becomes too small, the PEFC performance tends to decrease.

The best performance was obtained for the MPL mean flow pore diameter of 3 μm . It is considered that an appropriate MPL coating between the electrode and the substrate reduces flooding on the cathode electrode, as shown in Fig. 18. The water vapor produced from the electrochemical reaction at the cathode electrode is expelled through the MPL to the GDL substrate. When water vapor is condensed in the substrate, the water droplets accumulate in a large portion of the pores. For the MPL diameter of 3 μm , most of the liquid water is expelled to the gas channel in the separator, because the MPL is effective to prevent the back transport of liquid water from the substrate to the electrode, which leads to reduced flooding at the cathode electrode [16]. However, when

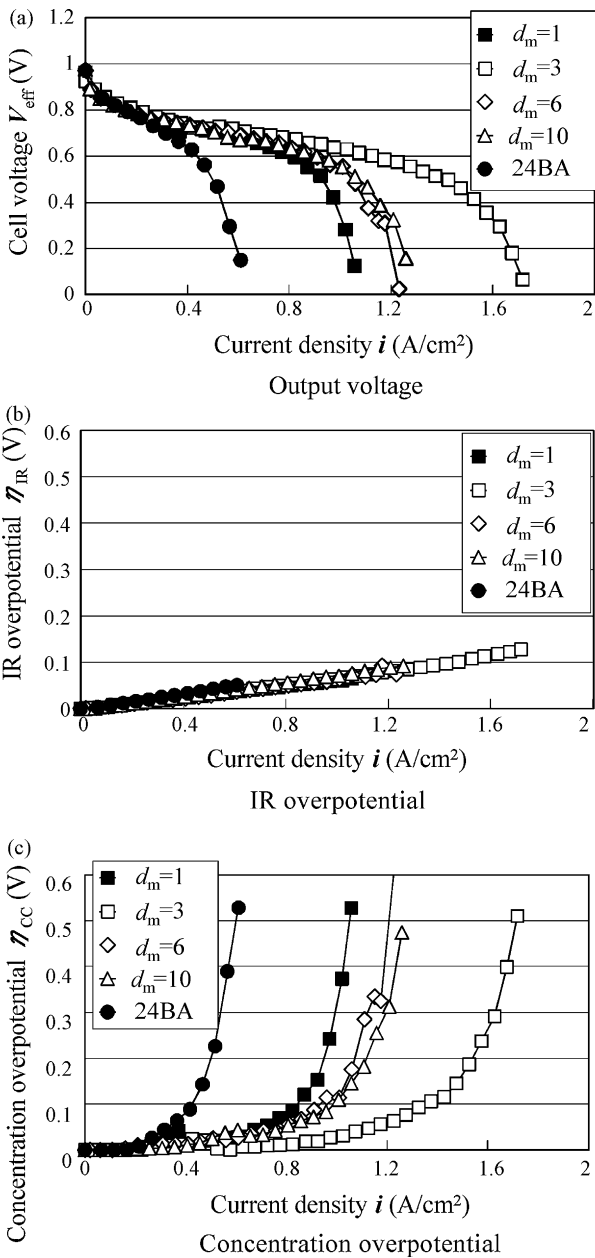


Fig. 17. Influence of mean flow pore diameter of cathode GDL on PEFC performance under high humidity condition (PTFE 20%, $h_{MPL} = 110 \mu\text{m}$).

the MPL pore diameter is too large, the water droplets in the substrate are transported readily from the substrate to the electrode, resulting in an increase in accumulated liquid water at the cathode electrode. This promotes flooding at the cathode electrode, thereby lowering the PEFC performance, as shown in Fig. 17. When the MPL pore diameter is too small, the gas permeability is significantly decreased, the transport of generated water vapor from the electrode to the substrate is inhibited, and the diffusion of oxygen gas to the electrode is also reduced. This increases the concentration overpotential, thereby lowering the PEFC performance.

Fig. 19 shows the influence of the MPL on the PEFC performance under high humidity when the MPL thickness of the cathode GDL is varied between 90 and 190 μm . A mean flow pore diameter of 3 μm and PTFE content of 20 mass% were applied to all MPLs. Reducing the MPL thickness increases the porous GDL substrate cross-sectional area, thereby improving in-plane permeability. This is effective to promote the discharge of water droplets accumu-

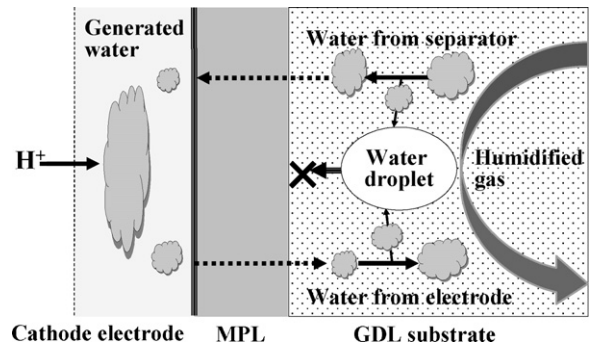


Fig. 18. Appropriate MPL to prevent flooding at cathode electrode.

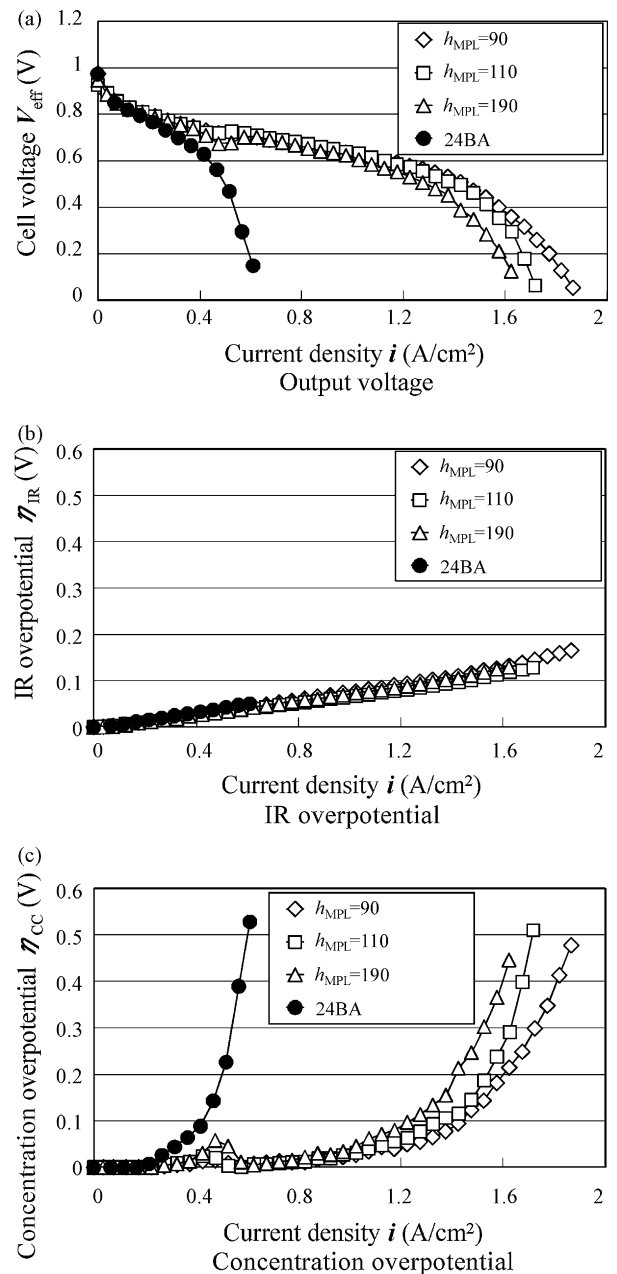


Fig. 19. Influence of MPL thickness of cathode GDL on PEFC performance under high humidity condition (PTFE 20%, $d_m = 3 \mu\text{m}$).

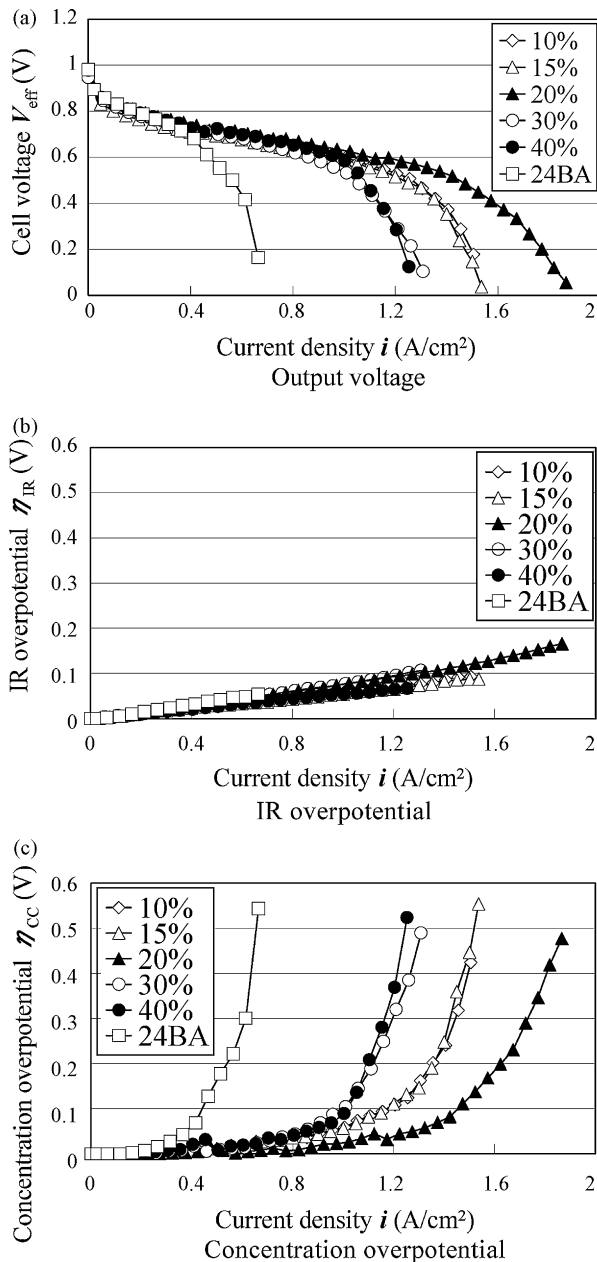


Fig. 20. Influence of PTFE content in MPL on PEFC performance under high humidity condition ($d_m = 3 \mu\text{m}$, $h_{\text{MPL}} = 90 \mu\text{m}$).

lated in the GDL substrate, which enhances the ability of the MPL to prevent flooding. The ability of the MPL coated GDL to reduce flooding has been discussed using only the measured permeability of the GDL. However, the capillary pressure gradient along the GDL through-plane direction also influences liquid water transport. Therefore, further study is required to evaluate the appropriate MPL coated GDL with respect to the capillary pressure gradient inside the GDL.

Fig. 20 shows the influence of the MPL on the PEFC performance under high humidity when the PTFE content in the MPL is varied between 10 and 40 mass%. A mean flow pore diameter of $3 \mu\text{m}$ and MPL thickness of $90 \mu\text{m}$, which demonstrated excellent performance (Figs. 17 and 19), were applied to all MPLs. For low PTFE content in the MPL, the hydrophobicity of the MPL was insufficient to prevent electrode flooding, so that significant enhancement in the PEFC performance could not be expected. Increasing the PTFE content to 20 mass% enhances the hydrophobicity of the MPL,

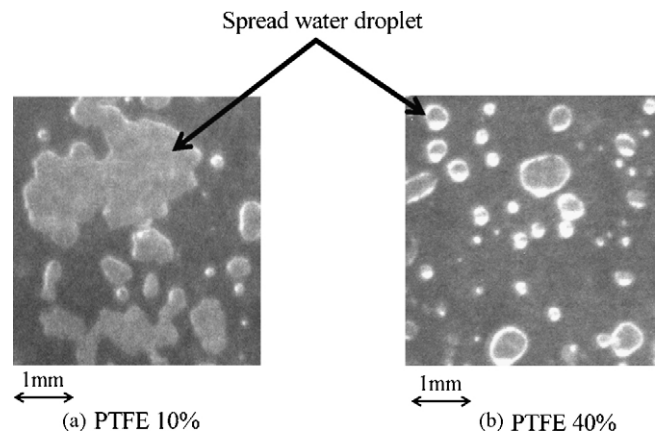


Fig. 21. Liquid water droplets spread between MPL and glass plate.

which promotes the discharge of the water through the MPL to the GDL substrate and effectively enhances the ability of the MPL to prevent flooding under high humidity.

However, when the PTFE content becomes too high, the PEFC performance tends to decrease. This is probably because significantly enhanced MPL hydrophobicity inhibits the spread of water droplets between the electrode and the MPL. In order to evaluate the water droplet spread on the MPL surface, small water droplets (0.0006 g cm^{-2}) were sprayed on the MPL and then pressed with a glass plate. Fig. 21 shows the liquid water droplet spread between the MPL and the glass plate. When the PTFE content in the MPL is increased to 40 mass%, the significantly enhanced hydrophobicity inhibits water droplet spreading. Therefore, the wetness at the interface between the electrode and the high PTFE content MPL is not sufficient during PEFC operation, and the effective reaction area at triple-phase boundaries is reduced. This probably increases the concentration overpotential, which lowers the PEFC performance, as shown in Fig. 20. However, further investigations are needed to clarify the exact mechanism for enhanced performance obtained with the appropriate hydrophobicity of the MPL.

4. Conclusions

The influence of MPL design parameters for the GDL on the PEFC performance under high and low humidity was investigated and the following conclusions were obtained:

- (1) Decreasing the MPL pore diameter significantly reduces through-plane permeability, but reduces in-plane permeability only slightly. The in-plane permeability of the MPL coated GDL is significantly enhanced by reducing the MPL thickness penetrated into the substrate. The permeance increases in proportion to the porosity multiplied by the squared mean flow pore diameter obtained using all GDLs with and without MPLs.
- (2) When the maximum pore diameter measured using the water permeability test was assumed to be the same as that measured for the air permeability test, the contact angle inside the GDL pore could be accurately estimated. Increasing the PTFE content in the MPL extends the contact angle, which enhances the hydrophobic properties of the GDL.
- (3) Under low humidity, decreasing both the MPL pore diameter and the PTFE content in the MPL is effective to prevent dehydration of the MEA. Increasing the MPL thickness is also effective to maintain the humidity of the MEA. However, when the MPL

thickness becomes too large, the oxygen transport to the electrode through the GDL is decreased, which lowers the PEFC performance.

- (4) Under high humidity, decreasing the MPL mean flow pore diameter to 3 μm is effective for the prevention of flooding and the enhancement of PEFC performance. However, when the pore diameter becomes too small, the PEFC performance tends to decrease. Reducing the MPL thickness improves in-plane permeability, and enhances the ability of the MPL to avoid flooding. Appropriate enhancement of the hydrophobicity by increasing the PTFE content in the MPL to 20 mass% is effective for the prevention of flooding and the enhancement of PEFC performance.

References

- [1] Z. Qi, A. Kaufman, *Journal of Power Sources* 109 (2002) 38–46.
- [2] P.M. Wilde, M. Mändle, M. Murata, N. Berg, *Fuel Cells* 4–3 (2004) 180–184.
- [3] J. Chen, T. Matsuura, M. Hori, *Journal of Power Sources* 131 (2004) 155–161.
- [4] G.G. Park, Y.J. Sohn, T.H. Yang, Y.G. Yoon, W.Y. Lee, C.S. Kim, *Journal of Power Sources* 131 (2004) 182–187.
- [5] T. Kitahara, T. Konomi, M. Murata, N. Berg, P.M. Wilde, *ECS Transactions* 5–1 (2007) 27–36.
- [6] M. Murata, T. Kitahara, T. Konomi, H. Nakajima, *Transactions of the Japan Society of Mechanical Engineers Series B* 74–737 (2008) 183–189.
- [7] T. Kitahara, T. Konomi, H. Nakajima, Y. Tateishi, M. Murata, N. Haak, P.M. Wilde, *ECS Transactions* 16–2 (2008) 1603–1613.
- [8] T. Kitahara, T. Konomi, H. Nakajima, Y. Tateishi, *Transactions of the Japan Society of Mechanical Engineers Series B* 74–746 (2008) 2221–2228.
- [9] T. Kitahara, T. Konomi, *Transactions of the Japan Society of Mechanical Engineers Series B* 72–716 (2006) 1007–1012.
- [10] American Society for Testing, Materials Committee, *Standard Test Methods for Pore Size Characteristics of Membrane Filters by Bubble Point and Mean Flow Pore Test*, ASTM, F316–86, 1970, pp. 722–727.
- [11] A. Jena, K. Gupta, *Journal of Power Sources* 96 (2001) 214–219.
- [12] M. Mathias, J. Roth, J. Fleming, W. Lehnert, in: W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), *Handbook of Fuel Cells—Fundamentals Technology and Applications*, vol. 3, John Wiley & Sons Ltd., England, 2003, pp. 517–537.
- [13] The Society of Chemical Engineers, Japan, *Chemical Engineering Handbook*, Maruzen, Japan, 2004, p. 96.
- [14] T. Konomi, Y. Sasaki, *Transactions of the Japan Society of Mechanical Engineers Series B* 71–705 (2005) 1428–1435.
- [15] The Society of Chemical Engineers, Japan, *Chemical Engineering Handbook*, Maruzen, Japan, 2004, p. 147.
- [16] T. Konomi, T. Kitahara, Y. Iwata, *Transactions of the Japan Society of Mechanical Engineers Series B* 72–715 (2006) 764–770.