Effect of Properties of Hydrophilic Microporous Layer (MPL) on PEFC Performance

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For better water management in polymer electrolyte fuel cells (PEFCs), microporous layers (MPLs) are generally used. In this paper, hydrophilic MPLs having various pore volumes and diameters were prepared using a range of carbon materials, and the effect of the MPL on the membrane electrode assembly (MEA) performance was investigated under dry and wet conditions. Under the dry condition (80 °C, 30%RH), the MEA employing an MPL with a larger median pore diameter showed higher cell voltage, suggesting that the MPL with a larger pore diameter has better gas diffusivity, leading to better MEA performance. Under the wet condition (80 °C, 100%RH), it was confirmed that pore volume of the MPL has a significant impact on the MEA performance and that the hydrophilic MPL with a large pore volume was effective in reducing water flooding in the cathode catalyst layer. When used in an MPL, VGCF-H (carbon fiber with a fiber diameter of 150 nm) gives the largest pore diameter and pore volume. This MEA with a hydrophilic MPL (made of VGCF-H and ionomer) showed the best MEA performance under both dry and wet operating conditions.

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CX320, hydrophobically treated GDL with an MPL, Freudenberg-NOK) was used.

**Pore size distribution.**—The pore size distribution of the MPL-coated GDLs was measured using mercury intrusion porosimetry (Auto Pore IV 9500, Shimadzu Co.).

**MEA performance testing.**—The single cell fixture was composed of an MEA and a pair of graphite plates with a single serpentine flow channel of 0.8 mm width and 0.7 mm depth for the anode, and a single serpentine flow channel of 1.0 mm width and 1.0 mm depth for the cathode. Hydrogen and air/oxygen were supplied in a counter-flow configuration. The polarization curves were recorded under two different operating conditions, 30%RH (ambient pressure) and 100%RH (50 kPa, gauge pressure). For the dry condition, the cell temperature was kept at 80°C, whereas the inlet anode and cathode humidity was maintained at 30%RH. For the wet condition, the cell temperature was kept at 80°C, while the inlet anode and cathode humidity was maintained at 100% RH. For both conditions, the stoichiometric ratios of hydrogen and air were 1.4 and 2.0, respectively.

**Estimation of mass transfer loss.**—Cell voltages and voltage losses in a typical PEFC are shown in Fig. 1. The actual cell voltage is much lower than the theoretical one, which is mainly due to activation loss, ohmic loss, and mass transfer loss. Activation loss can be calculated by extrapolating the $iR$-free cell voltage at a very low measured current density over the entire current density range using a Tafel slope, which was obtained based on the actual cell voltage range of 0.01–0.1 A/cm$^2$. There are some techniques to measure mass transport loss; in this paper, the mass transfer loss ($\eta_{mt}$) is estimated to be the difference between the corrected cell voltage $E_{cor}$ (theoretical cell voltage) and the $iR$-free cell voltage ($E_{cell} + iR$), where $E_{cor}$ is estimated to be the difference between the corrected cell voltage $E_{cor}$ (theoretical cell voltage) and the $iR$-free cell voltage ($E_{cell} + iR$), where $E_{cor}$ is.

- For the dry condition, the cell temperature was kept at 80°C, whereas the inlet anode and cathode humidity was maintained at 30%RH. For the wet condition, the cell temperature was kept at 80°C, while the inlet anode and cathode humidity was maintained at 100% RH. For both conditions, the stoichiometric ratios of hydrogen and air were 1.4 and 2.0, respectively.

### Table I. Comparison of Carbon Materials and MPL Properties.

| Carbon Material | Vulcan-XC-72R | MDCNF | 24PS | VGCF-H | CF-X |
|-----------------|--------------|-------|------|--------|------|
| Note            | Carbon black | multi-walled CNT | cup-stacked CNT | vapor grown CF | CF by melt spinning |
| Carbon Properties |              |       |      |        |      |
| Fiber Diameter (nm) | particle     | 10–20 | 70–80 | 150    | 250  |
| Fiber Length (μm) | 30 nm        | 0.1–10 | 5    | 10–20  | >30  |
| Properties of MPLsa |              |       |      |        |      |
| Pore Volume (mL/g-MPL) | 0.84         | 0.67  | 1.22 | 1.33   | 0.68 |
| Median Pore Diameter (μm) | 0.068       | 0.052 | 0.25 | 0.77   | 0.49 |

*Mercury intrusion porosimetry.

CNT: Carbon Nanotube, CF: Carbon Fiber, cf. Catalyst Layer (median pore diameter): 0.051 μm.

![Figure 1](image1.png)

**Figure 1.** Cell voltages and voltage losses in a typical PEFC.

![Figure 2](image2.png)

**Figure 2.** (a–c). Surface SEM images of MPLs made of various carbon materials.
obtained by using the empirical Tafel equation ($E_{\text{cor}} = a + b \log i$):

$$\eta_{\text{mt}} = E_{\text{cor}} - (E_{\text{cell}} + iR) \ [1]$$

In this equation, $\eta_{\text{mt}}$ represents the estimated mass transfer loss, $a$ is constant, $b$ is the Tafel slope, $i$ is the current density, $E_{\text{cell}}$ is the actual cell voltage, and $R$ is the cell resistance.

Results and Discussion

Properties of the MPLs.—In order to clarify the effect of hydrophilic MPL properties, we collected various carbon materials shown on Table I, which compares the properties of the carbon material and those of MPLs formed on the GDL substrate. The properties of MPLs coated on the GDL substrate, such as median pore diameter and pore volume, shown on this table, are based on measurements using mercury intrusion porosimetry. The MPLs made of very thin carbon fiber (MDCNF) and carbon black (Vulcan XC-72R) have the smallest median pore diameters, 0.052 and 0.068 μm, respectively, and that made of carbon fiber (VGCF-H) has the largest pore diameter (0.77 μm). Although carbon fiber CF-X has the largest fiber diameter of 250 nm, the MPL made of CF-X is not as porous as that made of 24PS or VGCF-H. This is probably because carbon fibers of CF-X are thick and straight, tending to align in the MPL, which is confirmed by the surface and cross-section SEM images of the MPL (Fig. 2e and Fig. 3e).

Figures 2a and 2b show that there is no visible pores in MPLs made of carbon black Vulcan with a particle size of 30 nm or carbon nanotube MDCNF with a fiber diameter of around 10 nm. When comparing the SEM images of MPLs in Figures 2 and 3, the MPLs made of carbon fiber 24PS and VGCF-H have obviously larger pores than the other MPLs.

Figure 4, obtained using the mercury intrusion porosimeter, shows the pore size distribution of the various MPLs coated on the hydrophobically treated GDL substrate. The GDL substrate has pores of around 20 μm, and the pores in the range of 0.01 to 2 μm are from the pores in the MPLs.

Effect of pore properties of the MPL on MEA performance under a dry condition.—The MEAs were evaluated at 80°C under a dry condition. The comparison of IR free cell voltage at 1 A/cm² for the MEAs each using a different MPL and the one with no MPL (80°C, 30%RH, Stoic: $H_2$/Air = 1.4/2.0).
Figure 6. (a). Relationship between IR free cell voltage (@0.1 A/cm², 80°C, 30%RH, Stoic: H₂/Air(O₂) = 1.4/2.0) and the median pore diameter of MPL.
(b). Relationship between IR free cell voltage (@1.0 A/cm², 80°C, 30%RH, Stoic: H₂/Air(O₂) = 1.4/2.0) and the median pore diameter of MPL.

Figure 7. Pore diameter and gas diffusivity in the MEA.

Effect of pore properties of the MPL on MEA performance under a wet condition.—The polarization curves were measured under the condition of 80°C, 100%RH, 50 kPa. In order to evaluate flooding levels, the mass transfer loss (ηₘₜ) at a high current density (2.0 A/cm²) was estimated. Figure 8 shows the estimated mass transfer loss at 2.0 A/cm² for the MEAs each using different MPLs made of five different carbon materials and one with no MPL, demonstrating that MPLs are contributing to the reduction of mass transfer loss.

First, we plotted fiber diameter or median pore diameter against mass transfer loss. However, no distinct relationship was found in either case. Next, the estimated mass transfer loss based on the polarization curves for the five MEAs are plotted against the pore volume of MPLs in Fig. 9. In this figure, in addition to the five MPLs with a coating of 2 mg/cm², a data point for comparison using VGCF-H with a higher coating of 3 mg/cm² was plotted. It is apparent that the larger the pore volume of MPL, the smaller the mass transfer loss, indicating that the MPL with a large pore volume is effective in reducing mass transfer loss. However, no distinct relationship was found in either case.

Whereas in the case of the MPL with a large pore diameter, oxygen diffuses to the region under the lands of a separator, resulting in higher catalyst utilization and higher performance of the MEA. Under dry conditions, the difference in MEA performance is mostly attributed to pore diameter (gas diffusivity) in the MPL rather than water distribution in the rib and channel regions. There were very few apparent cracks in the MPLs used in this work, but it is significant to note that cracks in the MPL generally enhances facilitation of liquid water transportation to the GDL as reported in some papers.21,22
Conclusions

In order to clarify the effect of MPL properties on MEA performance, MEAs using a range of hydrophilic MPLs were prepared and evaluated under dry and wet conditions. Under the dry condition (80 °C, 30%RH), the major contributing MPL property was median pore diameter. The MPL with a larger pore diameter has better gas diffusivity, leading to better MEA performance. Under the wet condition (80 °C, 100%RH), the larger median pore diameter was not sufficient. In addition to better gas diffusivity, larger pore volume is necessary to reduce flooding at the cathode. When used in an MPL, carbon fiber, VGCF-H, gives the largest pore diameter and pore volume. The MEA with a hydrophilic MPL (made of VGCF-H and ionomer) showed the highest cell voltage under both dry and wet operating conditions.

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