**Effect of the Structure of Microporous Layer on the Performance of High-Temperature Proton Exchange Membrane Fuel Cells**

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**Abstract.** High-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) operate at 120-200°C, avoiding water flooding, tolerating CO, and improving reaction kinetics. The gas diffusion layer (GDL), which consists of the microporous layer (MPL) and carbon paper/cloth, is crucial for mass transport, heat transfer, and electricity conduction. The presence of the MPL can enhance electrochemical surface area (ECSE) and prevent phosphoric acid from leaching toward the channel. Those aspects are essential to improve performance and durability. In this work, the role of MPL in enhancing HT-PEMFC performance, with a focus on MPL structure, is investigated. The MPL with various polytetrafluoroethylene (PTFE) compositions (5, 10, and 20%) and thickness (10 to 50 μm are prepared in-house employing ultrasonic spray technology. The commercial carbon paper (GDS310, CeTech, Taiwan) is sprayed with MPL followed by 1 mg Pt cm -2, while the anode is commercial carbon paper (GDL 340, CeTech, Taiwan) sprayed with 0.5 mg Pt cm -2. HT-PEMFC is operated at 180oC, with stoichiometric ratios of 1.2 and 2 for hydrogen and air, respectively. The results indicate that, for lower binder composition, increasing MPL thickness can enhance HT-PEMFC performance. However, this trend does not hold for higher binder composition. The optimal MPL structure in this study is 50 μm in thickness with 5% PTFE. The cell voltage is 0.6 V at 0.324 A cm -2, while maximum power density peaks at 0.3864 W cm -2. When the MPL thickness is constant, the performance decreases with increasing binder composition: a decrease of 22% at 10% PTFE and 26% at 20% PTFE. The EIS test confirms that the ohmic resistance is 2.7% and 9.7% higher at 5% PTFE compared to 10% and 20% PTFE, respectively, at a thickness of 50 μm. However, further observation is needed for 10% and 20% PTFE cases to obtain comprehensive results.

**Keywords:** High-temperature polymer electrolyte membrane fuel cell, Microporous Layer, Gas Diffusion Layer

1. **Introduction**

High-Temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFCs) operate at elevated temperatures between 120-200°C [5-7], offering significant advantages over their low-temperature counterparts. These advantages include mitigating water flooding, enhancing carbon monoxide (CO) tolerance, and improving electrochemical reaction kinetics [1]. The high operational temperature prevents the condensation of water within the cell, thus eliminating the issue of water flooding, which can impede gas transport and reduce performance [1-2]. Furthermore, higher temperatures reduce CO poisoning of the platinum catalyst, a common issue in hydrogen fuel produced from reforming processes, by enhancing CO desorption [1-3]. These improvements contribute to the overall efficiency and reliability of HT-PEMFCs.

A critical component in HT-PEMFCs is the gas diffusion layer (GDL), which consists of a microporous layer (MPL) and a carbon paper or cloth substrate [3-4]. The GDL is vital in facilitating mass transport, heat transfer, and electrical conduction within the cell [5]. The MPL, in particular, is essential for enhancing the electrochemical surface area (ECSA) and preventing phosphoric acid from leaching into the flow channels [5-6]. By optimizing the structure and composition of the MPL, the performance and durability of HT-PEMFCs can be significantly enhanced [5-6]. The interaction between the MPL and the catalyst layer directly impacts the efficiency of reactant gas distribution and water management, which are crucial for maintaining high performance [7].

This study investigates the role of the MPL in improving HT-PEMFC performance, mainly through variations in MPL structure. Using ultrasonic spray technology, MPLs with different polytetrafluoroethylene (PTFE) compositions (5%, 10%, and 20%) and thicknesses (10 to 50 μm) were prepared and applied to commercial carbon paper substrates.

1. **Experimental**
	1. **Preparation of gas diffusion electrode**

MPL inks were prepared by dispersing carbon black (Vulcan XC-72), PTFE (60%, Aldrich, USA) in deionized (DI) water and Isopropyl Alcohol (IPA) using an ultrasonic bath and planetary mixer. The details of these cases are shown in Table 1. Catalyst inks in this study consist of commercial catalyst (46.7% Pt/C), Polyvinylidene Fluoride (PVDF) binder, and DMAc as solvent. All contents were mixed using an ultrasonic bath and planetary mixer to ensure that the particle size of the mixture was sufficiently small. All of the Gas Diffusion Electrodes (GDEs) employed in this investigation had platinum loading of 0.5 mg cm-2 and 1 mg cm-2 for the anode and cathode side, respectively.

* 1. **Preparation of MEA and Fuel Cell Test**

Membrane Electrode Assembly (MEAs) were constructed in a single stack fuel cell by sandwiching the Phosphoric Acid (PA)-doped Polybenzimidazole (PBI) membrane between two Gas Diffusion Electrodes (GDEs) with an active area of 5x5 cm2. The endplate, current collector, gasket, bipolar plate, GDLs, and membrane comprise a single cell. In the galvanostatic mode, polarization curves were measured while an external load applied the necessary current. The single cell was operated for 24 hours at 180 C with a constant voltage of 0.6 before I-V measurements. Tests were conducted on Hephas Energy’s HS-150 fuel cell test station.

**Table 1.** The specification of the GDL in this study

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| **5%PTFE** | **10% PTFE** | **20% PTFE** |
| 10 µm | 50 µm  | 50 µm |
| 30 µm |
| 40 µm |
| 50 µm |

1. **Results and Discussion**
	1. **The Effect of Various MPL Thickness**

Figure 1a illustrates the performance of cells with varying microporous layer (MPL) thicknesses, precisely ten μm, 30 μm, 40 μm, and 50 μm. The current densities are 0.292 A cm -2, 0.324 A cm -2, 0.336 A cm -2, and 0.348 A cm -2 for the respective MPL thicknesses at 0.6 voltage. Notably, the 50 μm MPL exhibits the highest current density of 0.348 A cm -2, coupled with a maximum power density of 0.5 W cm -2. This superior performance can be primarily attributed to the lowest activation loss area observed for the 50 μm MPL. This reduction in activation losses indicates more efficient catalytic activity and improved reaction kinetics, enhancing the cell's overall performance.

The results above correlate with the SEM test results in Figure 2. The even coverage of the carbon paper likely increases the ECSA by maximizing the utilization of the available surface area for electrochemical reactions. This, in turn, improves the cell's overall performance by increasing the number of active sites, enhancing catalyst utilization, improving reaction kinetics, and ensuring better mass transport and reduced local resistance. These factors collectively contribute to the higher current density and power density observed in the cell.

Figure 1b presents the Nyquist plots derived from Electrochemical Impedance Spectroscopy (EIS) measurements, providing insights into the cells' ohmic and charge transfer resistances. The ohmic resistances are 0.10202 Ω.cm², 0.095 Ω.cm², 0.0901 Ω.cm², and 0.0846 Ω.cm² for the MPL thicknesses of 10 μm, 30 μm, 40 μm, and 50 μm, respectively. Similarly, the charge transfer resistances are 0.538 Ω.cm², 0.440 ohm.cm², 0.506 Ω.cm², and 0.515 Ω.cm² for the respective MPL thicknesses. While the 50 μm MPL demonstrates the lowest ohmic resistance, signifying minimal losses due to ionic transport, it exhibits a relatively high charge transfer resistance. This paradox may be due to a complex interplay between the thickness of the MPL and the resultant porosity and catalyst utilization. While a thicker MPL reduces ohmic losses by enhancing ionic conductivity, it may also lead to a suboptimal pore structure that impedes efficient charge transfer, thereby increasing the charge transfer resistance.

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| (a) | (b) |

**Fig. 1.** (a) Performance curve and (b) Nyquist plots of 5%PTFE under various microporous layer thickness



**Fig. 2.** SEM images of microporous layer surface of (a) 10 µm, (b) 20 µm, (c) 40 µm, and 50 µm

* 1. **The Effect of Various PTFE Binder Percentages**

Figure 3a presents the performance curves of cells under various percentages of PTFE binder in the microporous layer (MPL), all at a constant thickness of 50 μm. The current densities at 0.6 V are 0.348 A cm -2, 0.292 A cm -2, and 0.272 A cm -2 for MPLs with 5%, 10%, and 20% PTFE, respectively. Among these, the 5% PTFE case exhibits the highest performance, achieving a current density of 0.348 A cm -2 and a maximum power density of 0.5 W cm -2. The superior performance of the 5% PTFE MPL can be attributed to its lowest activation loss area. Activation loss, associated with the energy required to initiate electrochemical reactions, is minimized in the 5% PTFE MPL, indicating more efficient catalytic activity and better kinetics of the electrochemical processes. This reduction in activation loss significantly contributes to the overall enhanced performance of the cell.

Figure 3b shows the Nyquist plots from the Electrochemical Impedance Spectroscopy (EIS) tests, providing insights into the cells' ohmic and charge transfer resistances. The ohmic resistances are 0.0846 Ω.cm², 0.0925 Ω.cm², and 0.0988 Ω.cm² for the 5%, 10%, and 20% PTFE MPLs, respectively. Similarly, the charge transfer resistances are 0.515 Ω.cm², 0.526 Ω.cm², and 0.563 Ω.cm² for the exact PTFE percentages. The 5% PTFE MPL demonstrates the lowest ohmic and charge transfer resistance values. The lower resistance in the 5% PTFE MPL can be attributed to an optimal balance between electronic conductivity and structural integrity. A lower

PTFE content ensures sufficient porosity for effective ion transport and minimizes the insulation effect that higher PTFE content can cause. This balance facilitates efficient charge transfer and reduces overall resistive losses, enhancing cell performance.

The percentage of PTFE binder in the MPL significantly impacts the cell's performance, even when the MPL thickness is constant. The results indicate that increasing the PTFE binder percentage from 5% to 20% leads to decreased performance, as evidenced by reduced current and power density. Increases in both ohmic and charge transfer resistances accompany this decline in performance. Higher PTFE content increases the insulation within the MPL, which hampers ionic conductivity and obstructs effective charge transfer at the electrode-electrolyte interface. Consequently, higher PTFE percentages result in more significant resistive losses, thereby diminishing the overall efficiency and performance of the cell.

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| (a) | (b) |

**Fig. 3.** (a) Performance curve and (b) Nyquist plots of 5%PTFE under various binder percentage

1. **Conclusions**

The best performance for 5% PTFE is achieved with a 50 µm MPL thickness, showing a current density of 0.348 A cm -2 and a maximum power density of 0.5 W cm -2. Despite having a relatively high charge transfer resistance, it has the lowest ohmic resistance among the tested samples, with values of 0.0846 Ω·cm² for ohmic resistance and 0.515 Ω·cm² for charge transfer resistance. When the MPL thickness is constant, performance decreases with increasing binder composition: a decrease of 19.8% at 10% PTFE and 27% at 20% PTFE. The EIS test confirms that at a thickness of 50 μm, the ohmic resistance is 9.3% and 16.7% higher at 5% PTFE compared to 10% and 20% PTFE, respectively. The charge transfer resistance is also 2.1% and 9.2% higher at 5% PTFE compared to 10% and 20% PTFE, respectively.

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