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APPLICATION OF A MICROPOROUS LAYER WITH PLANAR WETTABILITY TO IMPROVE THE COLD-STARTING PERFORMANCE OF A POLYMER ELECTROLYTE FUEL CELL

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ABSTRACT

To improve the cold-starting performance of a polymer electrolyte fuel cell (PEFC), we devised a microporous layer (MPL) with a planar wettability distribution. Hydrophilic and hydrophobic strips in the MPL were arrayed in alternating rows in the in-plane direction. Due to the exclusion of liquid water from the hydrophobic regions, the water moved towards the hydrophilic areas and was absorbed. Since frozen water near the interface between the MPL and catalyst layer (CL) was thought to inhibit the continuation of power generation, minimizing the amount of water on the CL was important. We extended the continuous operating temperature range to encompass lower temperatures and improved the operating time of the PEFC at sub-freezing temperatures.

Keywords: fuel cell, cold start, microporous layer, wettability distribution

NOMENCLATURE

Abbreviations	
PEFC	Polymer electrolyte fuel cell
MPL	Microporous layer
CL	Catalyst layer
GDL	Gas diffusion layer
PTFE	Polytetrafluoroethylene

1. INTRODUCTION

During operation of a polymer electrolyte fuel cell (PEFC), hydrogen and oxygen move into the catalyst layer (CL), where water is generated via electrochemical reactions. The generated water passes through the microporous layer (MPL) and the gas diffusion layer (GDL) in the opposite direction of oxygen diffusion and flows from the cell through the gas channel. However, when PEFC operation is initiated at sub-freezing temperatures, the water is in a super-cooled state and may freeze inside the fuel cell. The MPL and GDL are porous materials and provide channels for gas diffusion and the movement of water in the PEFC under normal operating conditions [1]. However, when water freezes in the channels, volume expansion due to ice formation can damage the internal structures of the GDL and MPL. The ice blocks internal pores, preventing hydrogen and oxygen from reaching the CL. In addition, the PEFC will stop working if the CL surface is covered with ice [2]. To enable a PEFC to start successfully at sub-freezing temperature, water within the MPL and GDL must be managed effectively.

During operation of a PEFC, water generated through electrochemical reactions is generally distributed randomly in the planar direction [3]. The MPL and GDL are usually subjected to hydrophobic treatment to facilitate the rapid draining of water [1]. Researchers have designed various MPL and GDL structures to improve water management. Hirakata et al. [4] showed that a hydrophilic MPL could increase the water storage capacity and improve the cold-starting performance of a PEFC. However, a hydrophilic MPL makes water accumulation within the PEFC more likely if it is run below the normal operating temperature of 60–80 °C [5]. Utaka et al. [6–8] designed a wettability distributed GDL capable of planar water distribution, which facilitated the movement of liquid water within it from hydrophobic to hydrophilic regions. The GDL continued to allow gas diffusion as the liquid water drained, so hydrogen and oxygen could still reach the CL by passing through the GDL. However, the GDL reported by Utaka et al. was only tested with a MPL of uniform wettability.

The objective of this study was to improve PEFC performance at sub-freezing temperatures. To improve cold starting, we fabricated a hybrid MPL to control the distribution of water in the microporous layer. The wettability of the hybrid MPL had a planar distribution. The performance of a PEFC using the hybrid MPL was analyzed and compared to that of a PEFC built with a MPL of conventional, uniform wettability.

2. HYBRID MPL AND EXPERIMENTAL SYSTEM

2.1 Structure and function of the hybrid MPL

The structure and function of the hybrid MPL designed in this study is shown schematically in Fig. 1. The hybrid MPL was composed of two types of nanoporous media with different wettabilities, one hydrophobic and the other hydrophilic. Alternating strips of the hydrophobic and hydrophilic media were placed parallel to one another in the in-plane direction. After startup of the PEFC, water was generated in the CL. Since the water between CL and hydrophobic MPL moved to hydrophilic MPL region due to nature of repelling water on the hydrophobic surface and capillary pressure difference between both regions, most of generated liquid water collected to the hydrophilic area and was absorbed inside the hydrophilic MPL. Furthermore, the difference in capillary pressure enabled water that had entered the hydrophobic regions of the MPL to move into the hydrophilic regions. Thus, gas diffusion paths in the hydrophobic regions were maintained, and the PEFC was expected to operate continuously even at sub-freezing temperatures.

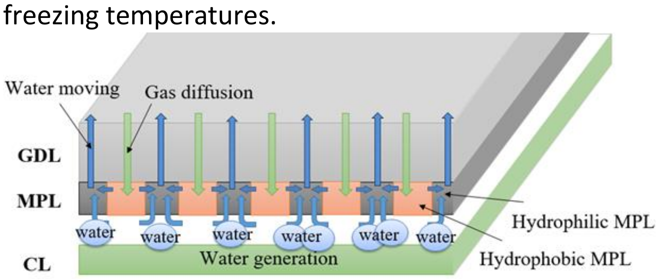

Fig. 1. Structure and function of the MPL exhibiting planar wettability.

2.2 Experimental system for measuring fuel cell performance

The structural and operational parameters of the PEFC used in this study are shown in Table 1. Carbon bipolar plates were used, and a parallel gas flow channel was adopted. The PEFC assembly screw torque was set at 1 N·m, which made it possible to fix the assembly pressure in the active area at ~0.5 MPa. SGL 29BC (including MPL) and Toray 060 were used as the anode and cathode GDLs, respectively. The cathode MPL was either the hybrid MPL or a conventional MPL. The conventional MPL and the hydrophobic components in the hybrid MPL were primarily composed of carbon black and polytetrafluoroethylene (PTFE). The hydrophilic portions of the hybrid MPL were comprised of carbon black and polyamide resin. Each hydrophilic and hydrophobic MPL strip was 1.0 mm wide, twice the width of the gas channels (0.5 mm) and ribs (0.5 mm). When the PEFC was assembled, it can be controlled that each hydrophilic or hydrophobic region of hybrid MPL was in parallel to channel and rib.

Table 1 Parameters of the PEFC cold-start experiment.

PEFC parameter	Value
Active area (cm^2)	5.0 × 5.0
MPL area (cm^2)	5.0 × 5.0
Gas channel width (mm)	0.5
Rib width (mm)	0.5
Gas channel depth (mm)	0.3
Proton exchange membrane	Nafion 212
Pt load in cathode CL (mg/cm^2)	0.6
Pt load in anode CL (mg/cm^2)	0.4
Bipolar plate thickness (mm)	10.0
GDL thickness (μm)	140
MPL thickness (μm)	35 ± 5
Air flux (sccm)	95
H_2 flux (sccm)	226
Current density (A/cm^2)	0.04

The PEFC was placed in a constant-temperature chamber for the cold-start experiment. The temperatures of the PEFC and reaction gas were controlled by adjusting the air temperature in the chamber. The reaction gas of cathode was a mixture of N_2 and O_2, hereafter referred to as air. The reaction gas was first cooled in the cooling coil until its temperature equaled that of the constant-temperature chamber, at which point it entered the PEFC. To prevent water vapor from freezing in the reaction gas, the H_2 and air were not humidified. The ohmic resistance of the PEFC was measured during the experiments with an electrochemical workstation.

3. RESULTS AND DISCUSSION

3.1 PEFC cold-start performance with the hybrid MPL

Changes in PEFC voltage over time with the conventional and hybrid MPLs at various sub-freezing temperatures are shown in Fig. 2. The PEFC using the conventional MPL could operate for over 30 min at -4.2 °C, and its operational time decreased when the cold-start temperature was reduced. Since the conventional MPL exhibited uniform hydrophobicity, water was randomly distributed at the interface between the MPL and CL. The reaction was inhibited by ice that had solidified on the CL, which covered the entire CL surface. The lower the temperature, the greater the probability of freezing. Thus, sub-freezing temperatures reduced the operating time of the PEFC. In contrast, the PEFC with the hybrid MPL worked for over 30 min at -4.2 °C and -5.5 °C and possibly would have operated continuously at these temperatures. The operating time of this PEFC was significantly longer than that of the PEFC with a conventional MPL from -6.5 °C to -10.0 °C. This was due to the presence of alternating hydrophilic and hydrophobic regions in the hybrid MPL. Water at the MPL/CL interface of the hybrid MPL was repelled by the hydrophobic MPL and driven into the hydrophilic regions by the difference in capillary pressure. The water was then absorbed into the hydrophilic MPL. Furthermore, super-cooled water in the hydrophobic regions of the MPL moved to the hydrophilic regions. The concentration of water in the hydrophobic regions of the hybrid MPL would be thus lower than that it would be in a conventional MPL under the same conditions. Even if the supercooled water froze, the hydrophobic MPL could still maintain channels for the diffusion of air. Air continued to reach the cathode CL, and the PEFC could work continuously.

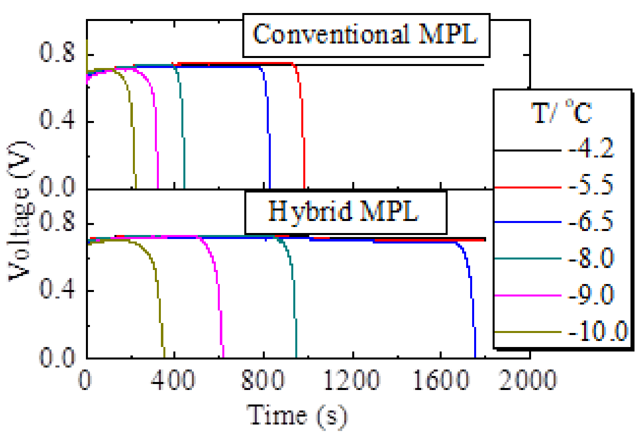

Fig. 2. Voltage changes of PEFCs using conventional and hybrid MPLs when cold starting.

At -5.5 °C, the operating time of the PEFC using hybrid MPL was significantly longer than that of the PEFC with a conventional MPL (Fig. 2). The operating times of the PEFC using the hybrid MPL at -6.5 °C ~ -10.0 °C were 2.11, 2.14, 1.90 and 1.59 times longer, respectively, than those of the PEFC using a conventional MPL. Therefore, use of the hybrid MPL significantly improved the cold-starting performance of the PEFC.

3.2 Ohmic resistance

During a PEFC cold-starting with either a conventional or hybrid MPL, the ohmic resistance gradually decreases and then stabilizes. When freezing conditions in the PEFC cause cold-start failure, the ohmic resistance will increase. Figure 3 shows changes in the ohmic resistance of both PEFCs over time during operation at several sub-freezing temperatures. During operation of the PEFC using a conventional MPL at -4.2 °C, the ohmic resistance decreased and became generally stable. At temperatures from -5.5 °C to -10.0 °C, shutdown caused by freezing increased the ohmic resistance arose. When shutdown occurred at -5.5 °C or -6.5 °C, ohmic resistance increased suddenly. Ohmic resistance increased more slowly when shutdown occurred at either -9.0 °C or -10.0 °C. It was possible that a larger volume of water accumulated in the PEFC prior to shutdown at -5.5 °C and -6.5 °C, because the water remained in a super-cooled state for a longer period of time. After a period of continuous contact, the super-cooled water suddenly froze, and the ohmic resistance rose rapidly. With the PEFC using the hybrid MPL, ohmic resistance initially decreased and stabilized during operation at -4.2 and -5.5 °C, and no voltage increase was observed. Although the steep increases in ohmic resistance commenced at different times, the qualitative trends observed with the conventional and hybrid MPLs were similar at temperatures of -6.5 °C and lower.

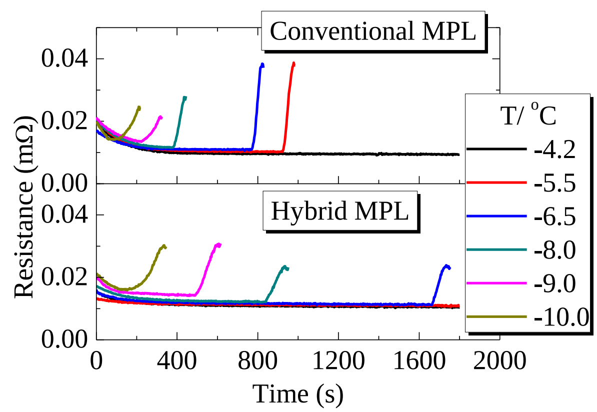

Fig. 3. Ohmic resistance changes of PEFCs using conventional and hybrid MPLs when cold starting

3.3 Analysis of freezing behavior

When H_2 and air travel through a gas flow channel, the pressure drops between the inlet and outlet of the flow channel. When water generated in the CL enters the gas flow channel and accumulates or freezes within it, the pressure drop would gradually increases due to constriction of the channel. The influence of the MPL on the pressure drop between the inlet and outlet of the cathode gas flow channel at several super-cooled temperatures is shown in Fig. 4. In the PEFC using a conventional MPL, there was no significant change in the pressure drop in the cathode flow channel during the first 800 s at -4.2 °C. The pressure drop gradually grew larger after 800 s. This was because water accumulated in the MPL and GDL and eventually reached the cathode flow channel. Variations in the loss of pressure up to the time of shutdown were nearly the same at -5.5 and -6.5 °C as they were at -4.2 °C, and the pressure drop remained nearly unchanged. In these cases, shutdown due to freezing occurred before liquid water reached the gas channels.

In the PEFC using the hybrid MPL, the pressure drop remained stable until 1200 s, which was longer than that of the PEFC using a conventional MPL. This indicated that water in the PEFC using a conventional MPL reached the gas channels more quickly. Water generated in the PEFC using the hybrid MPL accumulated in the hydrophilic regions of the MPL and/or GDL, which was in accordance with the results discussed in section 3.1. The pressure loss at -5.5 °C was similar to that observed at -4.2 °C; but after 1400 s at -6.5 °C, the magnitude of the pressure loss was smaller. A smaller volume of water reached the gas channels at -6.5 °C, indicating that icing occurred more quickly at the lower temperature. In addition, the larger water storage capacity of the hybrid MPL enabled the PEFC to operate longer at sub-freezing temperatures. This also contributed to the better cold-starting performance of the PEFC using the hybrid MPL. When the PEFC was operated at temperatures below -5.5 °C, the generated water and ice accumulated primarily in the MPL and GDL. The lower the super-cooled temperature became, the higher the probability of freezing. Therefore, the liquid water generated in this PEFC remained in a supercooled state for a shorter time, which reduced the distance over which the liquid water moved. At this time, the ability of the MPL to manage water was crucial to the cold-starting performance of the PEFC.

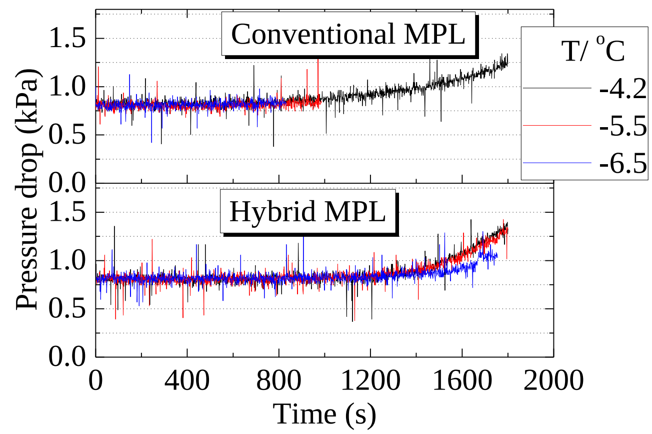

Fig. 4. Influence of the MPL on pressure drop in the cathode gas channel at different super-cooling temperatures.

4. CONCLUSION

A novel MPL with a planar wettability distribution was constructed with an alternating arrangement of hydrophilic and hydrophobic regions to improve the cold-starting performance of a PEFC. The hydrophilic regions in the MPL could store water generated by the PEFC, and the reactant gas pathways were maintained in the hydrophobic regions due to the movement of liquid from the hydrophobic to the hydrophilic regions. Two types of PEFCs, one using the hybrid MPL and the other using a conventional MPL, were tested at sub-freezing temperatures. The range of continuous operating temperatures was extended at the lower-temperature end, and the duration of PEFC operation until shutdown at sub-freezing temperatures was significantly increased.

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