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Effect of Hydrophilic Treatment of Microporous Layer on Fuel Cell Performance

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The gas diffusion layer in a polymer electrolyte fuel cell is the component primarily responsible for effective water management under a wide variety of conditions. The incorporation of hydrophilic aluminosilicate fibers in the microporous layer leads to an improvement in the fuel cell performance associated with a decrease in the mass transport resistance especially under high RH operation. This improvement in performance is obtained without sacrificing performance under low RH conditions. The aluminosilicate fibers create domains that wick liquid water away from the catalyst layer. The improved mass transport performance is corroborated by AC impedance and neutron radiography analysis and is consistent with an increase in the average pore diameter inside the microporous layer.

Introduction

Water management in polymer electrolyte membrane fuel cells (PEMFCs) is critical to optimizing performance under a variety of conditions. The components that manage the water in a fuel cell need to keep the membrane wet at dry operating conditions and the catalyst layer dry under wet operating conditions. The gas diffusion layer (GDL) plays an important role in the transport of water away from the cathode catalyst layer into the flow channels (1). Most state of the art GDLs consist of a porous substrate and a microporous layer (MPL) facing the cathode catalyst layer. The MPL is primarily composed of heat-treated carbon black and Teflon, and plays a crucial role in providing open gas pathways at high current densities. Optimal GDL performance is obtained when the MPL has enough hydrophobic pores for gas access and enough hydrophilic pores for water wicking (2). In this paper we report on the performance of a new GDL material prepared by SGL Technologies that incorporates hydrophilic pathways in the MPL to facilitate liquid water removal from the cathode catalyst layer (3).

Experimental

Fuel Cell Materials and Characterization

The GDL materials were prepared by SGL Technologies GmbH by treating Sigracet® GDLs (24AA and 25AA) with 5% PTFE using a dip-coating process. A MPL was added to the treated substrates by coating an aqueous paste of PTFE and carbon black (24BC and 25BC). The engineered GDLs (25 BL) were prepared by mixing 10% by weight aluminosilicate fibers into the carbon black PTFE paste (3). The GDLs were then treated at 350 °C before characterization and use. Through plane permeability measurements with air and Galwick™ as the fluid, and mercury and water porosimetry measurements were performed at Porous Materials, Inc (PMI).

Fuel cells were built using the 24BC GDL on the anode and 24BC, 25BC and 25BL on the cathode. Gore Primea® MEAs (A510.2/M710.18/C510.4) were used in a 50 cm² Fuel Cell Technologies (FCT) quad-serpentine cell. The fuel cell characterization (VIRs and AC impedance) was performed in a co-flow configuration with a FCT test station.

Neutron Radiography

Neutron imaging was performed at the NIST Center for Neutron Research (NCNR) on thermal beam tube 2. The measurements were performed using beam #1 and aperture #2 with a fluence rate of 1.9×10^6 neutrons cm⁻² sec⁻¹. The imaging was performed using the newly installed 13 μm resolution detector. The MEAs/GDLs were tested in a specially designed hardware with an active area of 2.5 cm² to optimize the neutron imaging resolution (4). AC impedance measurements were performed *in situ* at NIST using a PARSTAT 2273 potentiostat/galvanostat.

Results and Discussion

The performance of fuel cells using the GDL with the hydrophilic fibers in the MPL (25BL) was significantly better than the baseline hydrophobic GDL (25BC), especially at high current densities. This is illustrated in Fig. 1 that shows the performance of these 2

Figure 1. Polarization curves at 80°C and 100% inlet RH with anode stoich. 1.2 and cathode stoich. 2.0 and 40 psia outlet pressure.

cells operated at 80°C and 100% inlet RHs in both air and HelOx mixture (21%O₂, 79% He). For example, the cell with the 25BL GDL showed a 150mV improvement in the voltage at a current density of 2Acm⁻² when compared to the 25BC cell leading to a 30% improvement in the output power of the cell. However when the cathode gas was changed to HelOx, the performance of the 2 cells were almost identical indicating that the improvement in the performance was primarily due to better mass transport characteristics of the 25BL GDL with the hydrophilic fibers in the MPL. The polarization curves were obtained with a 30 sec wait time at each point and show hysteresis with slightly better performance during the return portion of the curve. This hysteresis can be lowered with longer wait times but was not deemed essential for this study.

The AC impedance spectra of the two cells at 1.4 Acm⁻², 100% inlet RH, 80°C and 40 psia outlet pressure is illustrated in Fig. 2. Although the high frequency resistance (HFR)

Figure 2. AC Impedance spectra (0.1Hz to 1kHz) obtained at 80°C, 1.4Acm⁻², 100% inlet RH with anode stoich. 1.2 and cathode stoich. 2.0 and 40 psia outlet pressure.

of both these cells is the same ($\approx 0.04 \Omega\text{cm}^2$), the low frequency (0.1 Hz) resistance of the cell with the 25BL GDL is $\approx 40\%$ lower. Moreover, the impedance spectra in HelOx of these 2 cells is identical, indicating that the improved performance of the 25BL GDL is due to better water removal resulting in improved oxygen diffusion kinetics. The impedance data obtained in HelOx shows two semicircles with the high frequency one corresponding to charge transfer kinetics at the electrode and the low frequency one corresponding to mass transport. The decreased mass transport resistance in HelOx when compared to air is directly attributed to the 3.7 times better diffusion of O₂ in He vs N₂ (5). These results indicate that the presence of hydrophilic fibers in the MPL leads to significant improvements in O₂ diffusion kinetics under saturated conditions although further improvement in performance are still possible as indicated by the lower mass transport resistance in HelOx.

The impedance spectra of the 2 cells operated at 1.4 Acm⁻², 50% inlet RH, 80°C and 40 psia outlet pressure is illustrated in Fig. 3. The lower RH operation is seen to alleviate the mass transport issues of the cell with the 25BC GDL while the 25BL GDL retains its performance under the drier operating condition. For example, when the inlet RH is

lowered from 100% to 50%, the resistance of the 25BC cell is lowered from $0.67 \Omega\text{cm}^2$ to $0.34 \Omega\text{cm}^2$ while that of the 25BL cell remains at $\approx 0.34 \Omega\text{cm}^2$. The impedance in

Figure 3. AC Impedance spectra (0.1Hz to 1kHz) obtained at 80°C , 1.4Acm^{-2} , 50% inlet RH with anode stoich. 1.2 and cathode stoich. 2.0 and 40 psia back pressure.

HelOx of the 2 cells shows a slight improvement in performance of the 25BC cell when compared to the 25BL cell. This improvement can be attributed to the 3.3 times better H_2O diffusion in He when compared to N_2 (6). This improved water diffusion appears detrimental to the cell under these drier conditions resulting in an increase in the proton transport resistance of the cathode catalyst layer.

Mercury (Hg) and water (H_2O) porosimetry results from these GDLs exhibit a bimodal distribution in pore size with one set of pores around $0.1 \mu\text{m}$ diameter and another around

Figure 4. Mercury and water porosimetry of the 24BC, 25BC and 25BL GDLs. Only the region of the porosimetry corresponding to the MPL pores is represented

10-100 μm in diameter. Porosimetry performed on GDL substrates without and MPL revealed that the smaller pore sizes are associated with the MPL, while the larger pore sizes are associated with the substrate. A comparison of the smaller pores in the various GDLs under both Hg and H_2O porosimetry is shown in Fig. 4. Analysis of the mercury porosimetry reveals that the 25BL GDL has a slightly larger average pore diameter based on volumes (0.1 μm compared to 0.09 μm), and a significantly larger average pore diameter (4V/S) of 0.042 μm when compared to the 25BC (0.024 μm) and 24BC (0.022 μm) GDLs. This increased diameter of the pores in the MPL is probably due to the presence of the aluminosilicate fibers and is responsible for the better water transport properties exhibited by this GDL. Finally, through plane gas and liquid permeability of these GDL materials were controlled by the substrate porosity/treatment and were independent of the MPL used. This is consistent with previous reports in the literature of these materials (3).

In order to investigate the origin of the mass transport improvement, the water profiles of two cells with the 24BC and 25BL GDLs were obtained via neutron radiography with the newly installed 13 μm resolution detector at NIST. The 25BC cell is expected to behave similar to the 24BC one (based on the performance data) and will be imaged. Figure 5

Figure 5. Water profiles in 2.5 cm^2 fuel cells operated at 80°C (100% inlet RH) using the 2 GDLs. 25BL (hydrophilic fibers in MPL) and 25BC (hydrophobic MPL)

shows the water profiles obtained in the cross-section view of these cells. The baseline GDL (24BC) shows a typical profile (4) where a peak in water content is seen close to the location of the cathode catalyst layer. Moreover the MPL ($\approx 50 \mu\text{m}$ thick) exhibits low liquid water content as illustrated by the steep drop in water content as one moves away from the MEA. In contrast, the cell with the 25BL GDL shows significant liquid water in the MPL region as evidenced by the steady water content profile as one moves across the MPL. This higher water content is probably due to hydrophilic regimes formed by the fibers in the MPL. The water content does not peak at the cathode catalyst layer in this GDL and is lower than the comparable baseline GDL. This indicates that the liquid

water saturation in the cathode catalyst layer is lower when using the 25BL GDL. Finally both the GDLs show significant water accumulation in the substrate with the 25BL GDL having greater water saturation. The absolute values of the water contents, expressed in mm of water in a 12 mm active length of the cell indicate a maximum saturation of only 15% in the GDL substrate for the 25BL GDL. Although the absolute water content in the thin catalyst layers and membranes is difficult to obtain due to the smearing of the water content based on the 13 mm detector resolution, these results indicate that the mass transport losses are predominantly due to liquid water in the catalyst layer pores. For example the 25BL GDL has higher liquid water saturation in both the substrate and MPL but exhibits lower water content in the cathode catalyst layer.

Conclusions

The incorporation of hydrophilic aluminosilicate fibers in the MPL of a GDL material leads to improvement in high current density fuel cell performance. This improvement in performance is attributed to a decrease in the mass transport resistance associated with better O₂ diffusion kinetics. The origin of the improved performance can be ascribed to the hydrophilic pathways in the MPL wicking the liquid water away from the cathode catalyst layer.

Acknowledgments

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