Effect of Hydrophobic Polymer Treatments on the Capillary Properties of Gas Diffusion Layers for Polymer Electrolyte Membrane Fuel Cells

Jeff T. Gostick, Marios A. Ioannidis, Michael W. Fowler and Mark D. Pritzker
Dept. of Chemical Engineering, University of Waterloo, Waterloo ON, N2L 5N5

1. Introduction

Increasing the current density of polymer electrolyte membrane fuel cells (PEMFC) leads to reduced stack size and materials cost, both of which are necessary if fuel cells are to become commercialized. Increasing current density, however, also means increased production of water inside the cell. The presence of liquid water in the porous electrode layers, particularly the gas diffusion layer (GDL), dramatically reduces the flux of gaseous reactants to the catalyst sites by blocking pores, thereby imposing mass transfer limitations on the maximum current that can be attained in a cell (1). To mitigate the negative effect of liquid water, a hydrophobic coating is usually applied to the GDL to alter its capillary properties. Although this approach is known to improve cell performance under high current density operation, the actual change in the GDL capillary properties is unclear since reliable experiments have not been available. In this paper, a recently developed method for measuring water-air-GDL capillary pressure curves (2) is applied to GDLs with varying amounts of PTFE coatings to quantitatively determine changes in water behavior. Access to such direct information about the capillary properties of GDLs will allow coating procedures to optimized and tailored to provide the desired water behavior in the cell.

2. Literature Review

Previous attempts to determine the air-water capillary properties of GDLs have not been entirely satisfactory. Although mercury intrusion porosimetry is a well established technique for measuring capillary properties of many porous materials, this method is not useful for GDLs for several reasons. Firstly, mercury is highly non-wetting to both the graphite substrate and the PTFE coating in GDLs, so it is insensitive to changes in the surface heterogeneity, which is precisely the information of interest. Secondly, converting mercury intrusion pressure data to an equivalent air-water pressure requires knowing the contact angle of mercury and water on the GDL surfaces. Even if a single contact angle can be determined for mercury in the GDL, which is not straightforward (3), the water contact angle will vary for the graphite and PTFE surfaces, making this conversion impossible without additional knowledge of the PTFE distribution. Furthermore, this conversion requires the use of the Young-Laplace equation based on a bundle-of-tubes model, which is not necessarily valid for highly porous and fibrous GDLs. Clearly, there is a need for direct measurement of the air-water capillary properties of GDLs.

In an earlier work (3) we reported on the method of standard porosimetry (MSP) for measuring capillary pressure properties with water as the working fluid. This technique was limited, however, since it could only measure along a path of decreasing water saturation and only for $P_C < 0$, where $P_C = P_L – P_G$. These early results suggested that GDLs possessed a network of hydrophilic pores since suction ($P_C < 0$) was required to remove water from the GDL. This finding was in contrast to the results of Benziger *et al*. (4) who found that positive liquid pressure was required for water to penetrate a GDL, even without a PTFE coating. Fairweather *et al*. (5) have recently reported a technique that uses a syringe pump to inject microliter volumes of water into a GDL. This technique, called the microfluidic approach (MFA), can scan along both increasing and decreasing water saturation paths and over a wide range of capillary pressures, $P_{C,MIN} < 0 < P_{C,MAX}$. Their results revealed for the first time a strong hysteresis effect, with water injection occurring at $P_C > 0$, as observed by Benziger *et al*. (4) and water withdrawal occurring at $P_C < 0$, as observed with MSP (3). Despite the insights gained by the MFA approach, this technique is not entirely satisfactory since the controlled parameter is the injected volume. The danger with adding volume in fixed amounts is that the pore space made accessible, V, at any given pressure, P_i, may not be completely filled by the amount of fluid injected, V_i (i.e. $V_i < V(P_i)$). A capillary pressure curve is generally expected to represent the amount of pore volume accessible at a given pressure, making the results of the MFA experiment difficult to interpret.

An alternative approach to measuring the water-air capillary pressure curves for GDLs has been recently reported (2). In this method the capillary pressure is controlled by adjusting the gas pressure above the sample while maintaining the liquid pressure at a constant value. Liquid enters the sample from a water reservoir and liquid saturation is monitored by tracking the changing mass of the reservoir with an analytical balance. Like the method of Fairweather et al. (5), this approach allows scanning along both increasing and decreasing saturation paths, and over a wide range of capillary pressures ($P_{C,MIN} < 0 < P_{C,MAX}$).

3. Experimental

In this work, the effect of PTFE loading on the capillary pressure curve is analyzed for two different substrate materials, Toray090 and SGL10. The specifications of each sample are given in Table 1. The PTFE loading values were specified by the supplier (SGL Carbon for the SGL10 samples and E-Tek for the Toray090 samples). The thickness of each sample was measured with a micrometer and porosity was determined from mercury intrusion porosimetry tests. The present set of experiments uses the setup and procedure detailed previously (2).

Table 1 – Specifications of samples tested

	Toray 090			SGL10		
Sample Name	090A	090C	090D	10AA	10BA	10EA
PTFE Loading [wt%]	0	10	20	0	5	30
Thickness [μm]	290	290	290	380	360	380
Porosity [-/-]	0.78	0.75	0.73	0.90	0.88	0.84

4. Results and Discussion

The results for the Toray 090 samples are given in Figure 1 and for the SGL10 samples in Figure 2. These curves show the results from -15000 to +15000 Pa to highlight the important features, although data were obtained for a range of -25000 to +30000 Pa for all samples. Each sample was tested from an initially dry state beginning at -15000 Pa, and then the capillary pressure was increased stepwise to 30000 Pa. The system was held at each pressure point until the saturation stopped changing. After 30000 Pa was reached the capillary pressure was decreased incrementally to a value of -25000 Pa. This loop from -25000 to 30000 and back to -25000 was repeated again. In general, the water injection followed a different path on the second injection, while the initial and secondary water withdrawal was identical. Further loops all followed the secondary injection path exactly and are not shown for clarity.

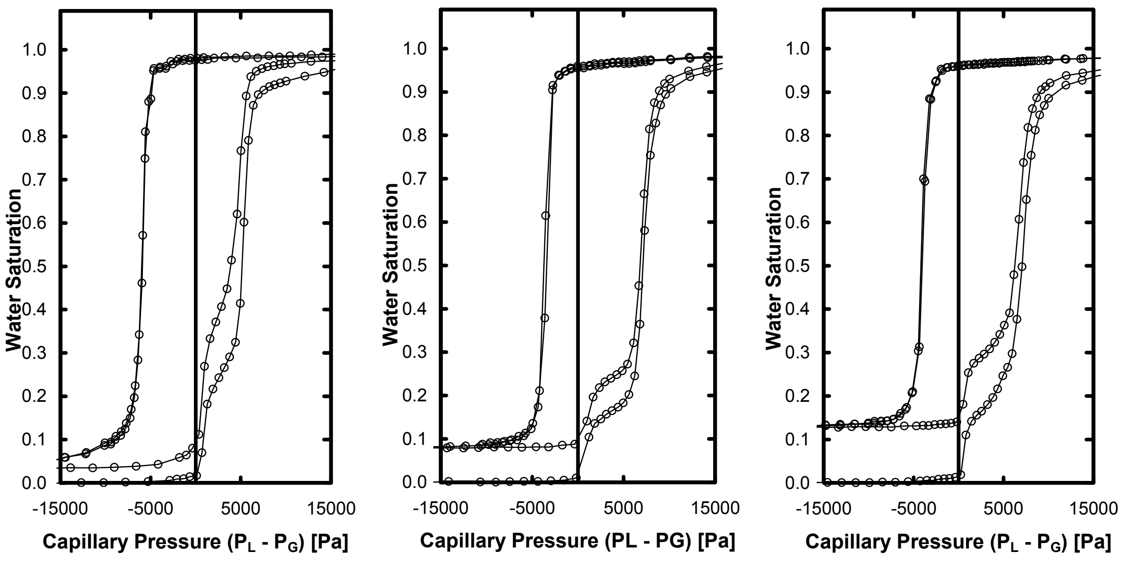

Figure 1 – Water-air capillary pressure curves of Toray 090. Left: 090A (0%PTFE). Middle: 090C (10%PTFE). Right: 090D (20%PTFE).

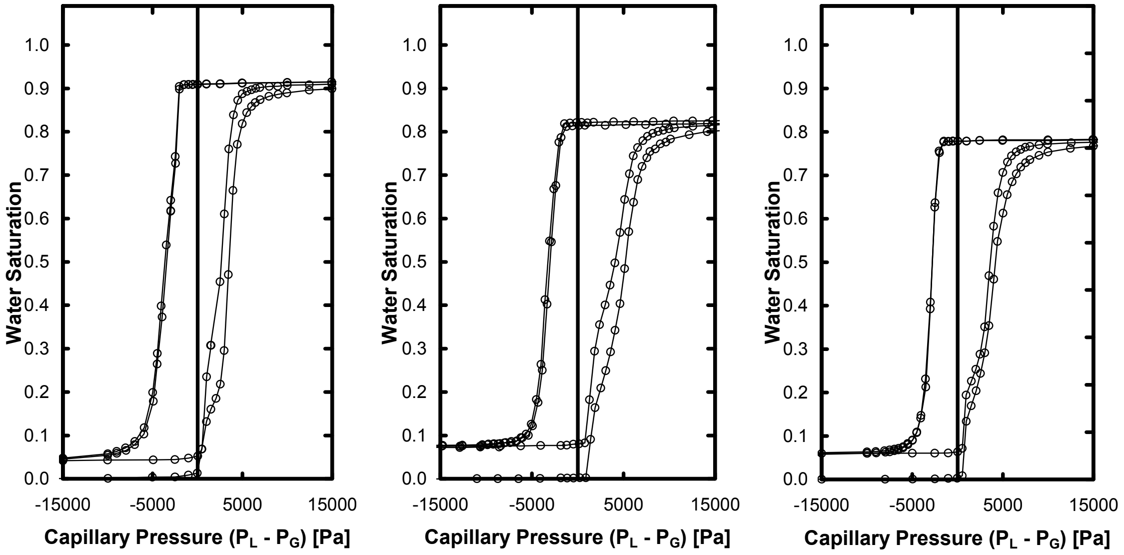

Figure 2 – Water-air capillary pressure curves of SGL10. Left: 10AA (0%PTFE). Middle: 10BA (5%PTFE). Right: 10EA (30%PTFE).

Perhaps the most striking feature of these curves is how little difference there is between different PTFE loadings on a given substrate. Intuitively, one might have expected the addition of PTFE to dramatically alter the shape of these curves. Instead, the differences are more subtle and quantitative. For instance, the water withdrawal for the 090A sample occurs at -4600 Pa while for the 090C and 090D samples it occurs at -2100 Pa. Similarly, water removal begins at -2100 for 10AA and at -1500 for 10BA and 10EA. This suggests that the addition of PTFE does significantly reduce the capillary pressure required to remove water, despite no apparent change in the qualitative features of the capillary pressure curves. Similar evidence can be found by comparing the primary injection legs of Toray 090 samples. The main injection (the sharp rise beginning at about s = 0.3) occurs at 4400 Pa for 090A and 6000 Pa for 090C and 090D. This indicates that the addition of PTFE increases the resistance to water penetration, as expected.

Another interesting feature of these results is that there appears to be little advantage to adding excessive PTFE. There are quantitatively noticeable differences between SGL10AA and SGL10BA or Toray090A and Toray090C, but there is no significant change between SGL10BA and SGL10EA or Toray090C and Toray090D. This is an important finding since it means that PTFE loading can be kept to a minimum, which enhances electrical conductivity of the GDL. This also suggests that higher PTFE contents result in thicker hydrophobic coatings, and not necessarily more hydrophobic surfaces, indicating that PTFE application procedures might be improved by finding ways of promoting more PTFE surface coverage.

5. Conclusions

The water-air capillary pressure properties of two gas diffusion layer materials for polymer electrolyte fuel cells were tested. The two substrate materials (SGL10 and Toray090) were each tested with varying amounts of hydrophobic polymer content. The addition of PTFE did not quantitatively alter the capillary pressure curve when compared to sample with no PTFE added. It was found, however, that significant quantitative differences, consistent with increased hydrophobicity, appeared when PTFE was added. The addition of excess PTFE did not noticeably alter the capillary properties from those of a modest PTFE loading. This indicates that excess PTFE creates thicker hydrophobic layers, but not more hydrophobic surface, and that an improved PTFE application technique could be sought to maximize the coverage of GDL internal surfaces.

6. References

1. Gostick JT, Ioannidis MA, Fowler MW, Pritzker MD 2007 Pore network modeling of fibrous gas diffusion layers for polymer electrolyte membrane fuel cells. J Power Sources 173:277-290

2. Gostick JT, Ioannidis MA, Fowler MW, Pritzker MD 2008 Direct measurement of the capillary pressure characteristics of water-air-gas diffusion layer systems for PEM fuel cells. Electrochem Comm In Press

3. Gostick JT, Fowler MW, Ioannidis MA, Pritzker MD, Volfkovich YM, Sakars A 2006 Capillary pressure and hydrophilic porosity in gas diffusion layers for polymer electrolyte fuel cells. J Power Sources 156:375-387

4. Benziger J, Nehlsen J, Blackwell D, Brennan T, Itescu J 2005 Water flow in the gas diffusion layer of PEM fuel cells. J Membrane Sci 261:98-106

5. Fairweather JD, Cheung P, St Pierre J, Schwartz DT 2007 A microfluidic approach for measuring capillary pressure in PEMFC gas diffusion layers. Electrochem Comm 9:2340-2345