Effects of Structure and Hydrophobic Treatment on Water Transport Behaviour in PEM Fuel Cell Gas Diffusion Layers

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Abstract. This paper examines the effects of structure and wettability on water transport behaviour in PEM fuel cell gas diffusion layers (GDLs). Different GDL materials, including carbon cloth and carbon paper with and without PTFE and MPL coatings, were used in this study. The breakthrough pressure of liquid water, water flow rate and water retention in the GDL were measured. For the GDL with and without MPL, the results indicate that the paper GDLs require higher breakthrough pressure than the cloth ones. Compared to the untreated GDL, applying PTFE on the GDL increases breakthrough pressure up to 1.5 times while it decreases water flow rate and water retention up to about 3.8 and 0.5 times respectively, over the tested conditions. The results also show that applying MPL on the GDL surface has greater impact on breakthrough pressure than applying PTFE. Liquid water requires up to about 4 times greater pressure to break through the other side of the GDL with the MPL. By applying MPL, the amount of water retention and flow through the GDL also reduced greatly, to almost zero. In addition, the results suggest that the GDLs are degraded after being exposed to water, which causes a significant decrease in breakthrough pressure and an increase in water retention.

1. Introduction

A gas diffusion layer (GDL) plays a crucial role in the overall performance of a proton exchange membrane (PEM) fuel cell by providing pathways for gaseous reactant transport from a supply channel to a catalyst layer, and product water removal from the catalyst layer to the gas channel. Excessive amounts of liquid water in the GDL hinder the reactant gases from accessing the active sites of the catalyst layer leading to decreased performance of the PEM fuel cell. Therefore, GDLs are commonly treated with a hydrophobic substance to render their fibres more hydrophobic and, thus, facilitate gas transport and water removal. Bevers et al. [1] studied the effect of PTFE (polytetrafluoroethylene) contents on water saturation in carbon paper GDL, and the results indicate a decrease in water saturation levels with an increase in PTFE content. Several works [2–6] have demonstrated numerically the phenomenon of saturation reduction with increasing hydrophobicity. Benziger et al. [7, 8] provided insight into water permeation properties under the effect of GDL wettability. They concluded that PTFE treatment of the GDL reduces the amount of water that can be trapped in the GDL and, thus, facilitates good gas transport through the GDL. In addition, a fine microporous layer (MPL) is usually applied on one side of the GDL to improve cell performance and
fuel cell water management. This is an additional layer between the GDL and catalyst layer, typically consisting of carbon powder and PTFE particles. Lu et al. [9] reported that water saturation in the GDL sample with MPL is significantly lower than that of GDL without MPL. They found that MPL also restricts the number of locations where water can enter the GDL allowing a greater number of pathways for gas transport. Likewise, Gostick et al. [10] illustrated that water saturation in the GDL was considerably decreased when MPL was introduced.

Since the application of PTFE and MPL has shown great promise for water and gas transport in the GDL, the present study aims to investigate the effects of these treatments on liquid water transport, including breakthrough behaviour, water flow rate and water retention in the GDL. Accordingly, different GDL structures, including paper and cloth GDL with and without MPL, were used in this study. Wettability of the GDL was also altered so that the effect on water transport could be examined. By varying GDL structure and PTFE loading, their effects on liquid water behaviour in the GDL can be compared. This could improve the understanding of water transport behaviour in the GDLs, which is essential for the development of effective PEM fuel cell water management and the design of future GDL materials.

2. Experimental

2.1. Materials
The GDL samples used in this study were: a carbon paper, a carbon paper with MPL, a carbon cloth and a carbon cloth with MPL. They are commercially available and have similar thickness of about 350 μm. Carbon paper consists of several layers of carbon fibres, whilst carbon cloth is composed of woven bundles of carbon fibres. The individual carbon fibres are about 7-10 μm in diameter and the bundles are in the region of around 350-450 μm. The micrographs of the GDL samples are shown in figure 1. Paper without MPL was also examined under different PTFE loadings, from 0 wt.% to 30 wt.%, in order to evaluate its effect on water behaviour in the GDL.

![Figure 1. Micrographs of (a) carbon paper (b) carbon paper with MPL (MPL side) (c) carbon cloth (d) carbon cloth with MPL (MPL side).](image)

2.2. Experiments
This work sets out to examine breakthrough pressure, water flow rate and water retention in the GDL. A circular GDL sample of 12 mm in diameter was mounted between two acrylic plates in the test apparatus. The apparatus, as illustrated in figure 2, consists of a 2 m high acrylic tube of 10 mm in diameter standing on top of the two acrylic plates where the tested sample is placed. The acrylic tube allows a water column to build up creating hydrostatic pressure for the experiments. A peristaltic pump is used to add water into the acrylic tube. Each tested sample is weighed both before and after the experiment to measure the amount of water trapped in the GDL.

For the breakthrough experiment, water was slowly added to the acrylic tube on top of the tested GDL sample. As water commenced to flow through the GDL, the height of the water column corresponding to hydrostatic pressure was recorded. The influence of wettability on breakthrough pressure was examined by altering the PTFE loadings on the GDL surface from 0 wt.% to 30 wt.%. The required minimum pressures to break through the GDLs were then compared. Each GDL sample was weighed after the first set of samples, i.e. virgin GDLs, was tested to measure the amount of water trapped in the GDL.
retained in it. The samples were then dried at 70°C in a hot-air oven for 3 hours and the tests were repeated with the dried samples.

For the flow experiment, the outlet of the GDL sample was initially blocked to allow for higher hydrostatic pressure, and the peristaltic pump was used to maintain the water level during the experiment. As the GDL outlet was unblocked, water could pass through the GDL. The amount of water drainage was then measured with time.

![Figure 2. Schematic of the apparatus.](image)

3. Results and discussion

3.1. Effects of PTFE on breakthrough pressure

The plain paper and paper with PTFE loadings of 10 wt.%, 20 wt.% and 30 wt.% were used in this study to investigate the effects on breakthrough behaviour. Figure 3 shows breakthrough pressure at varying PTFE loadings for virgin GDL, represented by a solid line, and dried GDL, represented by a dashed line. The figure indicates that PTFE loading has a significant effect on the minimum pressure required to push liquid water through the GDL samples. By applying PTFE, the required pressure has increased by about 0.5 and 1.5 times for the virgin and dried GDLs respectively. Since the wettability of the GDL was altered towards becoming more hydrophobic by applying PTFE, capillary resistance also increased according to the Young-Laplace equation. As a result, larger pressure needed to be applied in order to overcome the increased resistance.

![Figure 3. Effect of PTFE loading on the breakthrough pressure.](image)

The results also show that the dried GDL, i.e. previously used GDL, requires significantly lower breakthrough pressure than that required by the virgin GDL. The reduction in breakthrough pressure
observed in the dried GDL agrees with the results reported by Benziger et al. [7]. The possible reason for this is the loss of hydrophobicity of the GDL as it is exposed to water, found in the work of Ha et al. [11], which demonstrated a continuous decrease of hydrophobicity over time.

3.2. Effects of PTFE on water flow rate
In order to investigate the effect of PTFE loading on the flow of water through the GDL, the amount of water drainage was measured as a function of time. The outlet of the GDL sample was initially blocked to allow for higher hydrostatic pressure. Water was then freely drained through the sample by gravity and the amount of drained water was recorded. At the same time, the pressure head was maintained by adding water into the acrylic tube using the peristaltic pump. In this experiment, the GDL samples were tested over the applied hydrostatic pressures of 7.4 kPa, 9.8 kPa and 12.3 kPa.

Figure 4 shows the water flow rate according to the amount of PTFE. The dotted, dashed and solid lines represent the flow rate of drained water out of the GDL sample with varying PTFE loadings at a hydrostatic pressure of 7.4 kPa, 9.8 kPa and 12.3 kPa respectively. As expected, the largest hydrostatic pressure gives the highest flow rate, while the smallest hydrostatic pressure gives the lowest flow rate, suggesting that liquid water permeation depends on the applied hydrostatic pressure. It was observed that all hydrostatic pressures show similar trends, where the flow rate significantly decreases as the amount of PTFE increases. At the hydrostatic pressure of 12.3 kPa, the flow rate of water decreased to about a third, from 3,390 mg s\(^{-1}\) to 1,040 mg s\(^{-1}\) over the range of tested PTFE loadings, while the flow rate decreased to about a fifth, from 1,760 mg s\(^{-1}\) to 370 mg s\(^{-1}\), and to about a quarter from 740 mg s\(^{-1}\) to 190 mg s\(^{-1}\) over the same range of PTFE loadings for the 9.8 kPa and 7.4 kPa cases respectively.

Interestingly, for the case of 12.3 kPa, applying 10 wt.% PTFE on the GDL had only a minor effect on the rate of water flowing through the GDL compared to the plain GDL. This suggests that at a large hydrostatic pressure, a small amount of PTFE might not be able to reduce the amount of water travelling through the GDL, since the applied pressure is great enough to overcome the large capillary resistance created by small pores and is, thus, able to push liquid water through the GDL.

3.3. Effects of PTFE on water retention
In order to investigate the effect of PTFE loadings on water retention in the GDL, the plain paper and paper coated with 10 wt.%., 20 wt.% and 30 wt.% PTFE were used. After the virgin GDL samples were tested, all samples were dried at 70°C in a hot-air oven for 3 hours and were repeatedly tested at the same condition.
Figure 5 shows the amount of water retention in the paper GDL under different PTFE loadings. It can be observed that applying PTFE considerably reduces the amount of water retention in the GDL, which amounts to over 50% reduction in water retention compared to the untreated GDL.

This study also compares the water retention capability of the virgin GDL, represented by the solid line, with the dried GDL, represented by the dashed line. The result shows that a larger amount of water is trapped in the dried GDL than in the virgin. For example, the dried GDL with 30 wt.% PTFE could retain 60.3 g m\(^{-2}\) of water, while the virgin GDL retained 22.5% less at 46.7 g m\(^{-2}\), indicating that the GDL tends to hold more water over time. This is again due to the loss of hydrophobicity of the dried GDL, as mentioned in [11], which allows more water to be retained in it.

![Figure 5. Effect of PTFE loading on water retention in the GDL.](image)

3.4. Effects of GDL structure on breakthrough pressure

Figure 6 compares the minimum pressure required to force water through different GDL structures, including paper GDL and cloth GDL with and without MPL. The solid bar represents virgin GDL, whilst the striped bar represents dried GDL. For both GDLs with and without MPL, it is seen that paper GDL requires larger breakthrough pressure than the cloth GDL. For example, the virgin paper GDL requires 4 times larger pressure than the virgin cloth GDL. The reason is that the paper GDL has a smaller average pore size than the cloth GDL, which creates large capillary resistance, thus leading to larger pressure being required to push water through the pores of the paper GDL. This corresponds to the results in [7], which reported a significant reduction in the required breakthrough pressure for the cloth GDL. For the paper and cloth GDLs with MPL, the diminutive pore size of the MPL, as shown in figure 1 (b) and (d), creates even more resistance to water flow. As a result, considerably larger pressure is required to force water to break through the GDL with MPL, which is almost 2 and 4 times higher for the paper and cloth GDLs respectively.
As observed, the required hydrostatic pressure for the dried GDL is less than that of the virgin GDL. This implies that the required pressure would change over time, possibly due to GDL degradation. A similar phenomenon is reported by Tamayol and Bahrami [12], who observed a significant reduction in the required breakthrough pressure for the dried GDL.

3.5. Effects of GDL structure on water retention

The paper and cloth GDLs with and without MPL were used to examine the effect of structure on water retention. As seen in figure 7, both plain paper and cloth show a similar ability to keep liquid water within their structure. In contrast, the paper and cloth with MPL exhibit a different trend where almost no water is kept within their structure. The reason is that the MPL has very small pore sizes creating large capillary resistance, which might limit the amount of water entering the sample, thus causing very little water being retained in it. Conversely, the GDL without MPL has relatively large pore sizes creating smaller capillary resistance, which allows more water to flow through its structure, possibly increasing water retention.
Considering the paper and cloth without MPL, it is seen that the cloth GDL can retain more water than the paper GDL, which is about 1 time and 0.25 times for the virgin and dried GDLs respectively. The possible reason is that the woven structure of the cloth GDL allows water accumulation within its bundle of carbon fibres, while the randomly dispersed carbon fibres of the paper GDL can retain significantly less water. For the paper and cloth GDLs with and without MPL, the dried GDL can retain a larger amount of water than the virgin GDL of the same structure, suggesting that there is a structural or surface wettability change after drying the GDL, which causes a change in the water retention properties of the GDL. This, again, corresponds to the observations by Ha et al. [11], who illustrated the loss of hydrophobicity of the GDL over the duration of the test.

4. Conclusion
In this work, the effects of GDL structure and PTFE treatment on breakthrough pressure, rate of flow and water retention were examined. The conclusions that can be drawn from the results are as follows.

- Applying PTFE on the GDL surface increases the minimum pressure required to break through the GDL. This suggests that altering GDL surface wettability to more hydrophobic creates greater capillary resistance for liquid water to pass through the pores of the GDL. As a result, the rate of water draining out of the GDL and the amount of water trapped in the GDL also decreases significantly compared to the untreated GDL.

- Applying MPL on the GDL has greater impact on breakthrough pressure than applying PTFE. Liquid water requires considerably higher pressure to travel through the GDL with the MPL due to the diminutive size of MPL pores creating greater capillary resistance, which implies that water can only travel in vapour form through the GDL with applied MPL in PEM fuel cell working conditions. In applying the MPL, the amount of water retention and flow through the GDL also reduce greatly to almost zero.

- The degradation of the GDL due to the loss of hydrophobicity can cause a significant decrease in breakthrough pressure, while at the same time cause an increase in water retention over time.

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