ABSTRACT

In this paper, through-plane liquid water distribution is analyzed for two polymer electrolyte membrane fuel cell (PEMFC) gas diffusion layers (GDLs). The experiments were conducted in an ex situ flow field apparatus with 1 mm square channels at two distinct flow rates to mimic water production rates of 0.2 and 1.5 A/cm² in a PEMFC. Synchrotron radiography, which involves high intensity monochromatic X-ray beams, was used to obtain images with a spatial and temporal resolution of 20-25 μm and 0.9 s, respectively. Freudenberg H2315 I6 exhibited significantly higher amounts of water than Toray TGP-H-090 at the instance of breakthrough, where breakthrough describes the event in which liquid water reaches the flow fields. While Freudenberg H2315 I6 exhibited a significant overall decrease in liquid water content throughout the GDL shortly after breakthrough, Toray TGP-H-090 appeared to retain breakthrough water levels post-breakthrough. It was also observed that the amount of liquid water content in Toray TGP-H-090 (10%.wt PTFE) decreased significantly when the liquid water injection rate increased from 1 μL/min to 8 μL/min.

INTRODUCTION

The porous gas diffusion layer (GDL) plays an important role in liquid water management in the polymer electrolyte membrane fuel cell (PEMFC), by providing pathways for product water to reach the exhaust channels. In addition to facilitating this liquid water transport, the GDL also helps to facilitate the distribution of reactants to the catalyst layer [1]. As well, the GDL provides pathways for electronic transport, and structural support to the membrane electrode assembly (MEA) [1]. Although the GDL is typically treated to be hydrophobic to enhance liquid water wicking, excess liquid water presence, commonly observed in a PEMFC, prevents reactants from reaching the catalyst layer thereby decreasing the performance of the fuel cell.

Numerous numerical models have been developed [2-5] to predict the distribution of liquid water within the PEMFC GDL, and those authors provided valuable insight into the resultant pathways available for reactant transport. However, the availability of experimentally determined liquid water distributions with a microscale resolution in the GDL is still scarce due to the challenges associated with the opacity of fuel cell materials. Imaging techniques such as NMR imaging, neutron imaging, electron microscopy, and X-ray techniques have been investigated for their applicability in visualizing the liquid water transport in a fuel cell [6]. These techniques have been employed to provide new insights into the dynamic behaviour of liquid water transport in the GDL and PEMFC; however, there are often trade-offs between achievable temporal and spatial resolutions [6].

Synchrotron radiography has been recently proposed as a novel technique for imaging the liquid water distribution in the GDL of an operating PEMFC [7-16]. Synchrotron-based imaging is advantageous for providing nearly parallel monochromatic beams with high intensities of $10^{11}$-$10^{15}$ photons/cm² to obtain images with high temporal (0.9 s) and spatial (upto 4 μm) resolutions [12].

Buchi et al. [13] employed synchrotron x-ray microtomography to acquire water saturation profiles of free-floating GDLs at distinct water invasion pressures. Using Toray TGP-H-060 (20% PTFE) GDL, they observed that after purging liquid water was retained in the denser regions of the GDL. Additional work in quantifying the through-plane water present in a GDL of an operating fuel cell was undertaken by Hartnig et al. [14], Lee et al. [15], and Sasabe et al. [16]. Hartnig et al. [14] employed synchrotron radiography and
observed that two liquid agglomerations on the cathodic GDL (Sigracet SGL 10 BB) were acting as diffusion barriers for reactant transport, which resulted in decreased fuel cell performance. Sasabe et al. [16] employed soft x-ray radiography to image a PEMFC with a Sigracet SGL 24 BA GDL. They observed that the majority of the water was found near the catalyst GDL interface or under the rib of the flow field. Lee et al. [15] investigated the temporal through-plane water evolution in a PEMFC using synchrotron radiography and observed that liquid water accumulated in the anodic and cathodic GDLs with similar frequency. Though significant insights into the process of water evolution were obtained from these above mentioned studies, further investigations are necessary to determine the influence of GDL material selection on liquid water transport behaviour.

In this paper, we present our synchrotron radiography visualization of liquid water injection through PEMFC GDLs in an ex situ flow field apparatus. We provide a comparison of the through-plane water thickness profiles of two compressed GDLs at the point of liquid water breakthrough and shortly after breakthrough. Furthermore, we provide insights into the impact of the GDL microstructure on liquid water transport behaviour.

**EXPERIMENTAL APPARATUS AND METHODOLOGY**

In this study, a commercially available paper GDL (Toray TGP-H-090) and felt GDL (Freudenberg H2315 I6) with 10% wt. polytetrafluoroethylene (PTFE) were studied. These GDLs were placed in an ex situ flow field apparatus composed of polycarbonate with 1 mm x 1 mm flow fields, shown in Figure 1. A rubber gasket, the GDL, and a plastic gasket were compressed together using four bolts (20 in-lb/bolt). The rubber gasket was employed to prevent liquid water leakage, while the plastic gasket was used to prevent the GDL from being over-compressed between the compression and the base plates. Liquid water was injected through the base of the apparatus at two flow rates: 1 μL/min and 8 μL/min, which when considering the area of the GDL exposed to the liquid water injection (1 cm²), would represent current densities of 0.2 and 1.5 A/cm² in an operating PEMFC.

All visualizations were performed at the biomedical imaging and therapy beamline (BMIT-BM) at the Canadian Light Source Inc. (Saskatoon, Canada). Labview (National Instruments, Texas, USA) was employed along with a pressure transducer (PX309-005G5V Omega Engineering, Connecticut, USA) and a syringe pump (Harvard 11Plus:70-2212 Harvard Instruments, MA, USA) to remotely control the liquid water injection into the GDL while measuring the liquid water pressure during invasion. The beamline was directed parallel to the in-plane direction of the apparatus, which facilitated the capture of through-plane liquid water distributions (with the orientation shown in Figure 1) with a pixel resolution of 4.2 μm/pixel, a physical spatial resolution of 20-25 μm and a temporal resolution of 0.9 s. Injected volume, liquid water pressure measurements, and visualizations were simultaneously captured throughout invasion, from the initial injection of liquid water into the apparatus until past breakthrough, where breakthrough describes the event in which liquid water reaches the flow fields. Invasion was halted after breakthrough, once the liquid water pressure dropped to 70% of the maximum observed pressure. Given the apparatus design however, a sample once invaded cannot be used again to conduct any more investigations. So the order of parametric investigations (pumping water through a GDL at a flow rate) is not important. For each reported microstructure, a total of two parametric investigations (one at 1 μl/min and another at 8 μl/min) were conducted. The preliminary results presented in this paper were obtained by analyzing a single paper GDL and a single felt GDL for each parametric investigation. In our future work, we plan to increase the number of GDL samples employed per parametric experiment.

**GDL Determination**

The spatial resolution of 20-25 μm is not sufficient to resolve the individual fibres in the GDL. Hence, careful consideration is required when determining the position of the GDL in synchrotron radiographic visualizations. During the invasion of liquid water from the primary reservoir into the GDL, two advancing liquid/gas interfaces were observed. Figure 2(b) illustrates the position of these liquid/gas interfaces beneath the GDL prior to invasion. These liquid/gas interfaces were associated with the existence of a gap between the base plate and the bottom face of the GDL. This gap facilitated liquid water accumulation, forming a secondary reservoir of liquid water in the plane of the rubber gasket (see Figure 1). These round-shaped water droplets expanded in radius, before spreading laterally. The point at which these droplets began to spread laterally was the point at which liquid initially contacted the bottom face of the GDL. We employed the observation of this event to determine the lower boundary of the GDL, which would not otherwise be clear if simply observing a single post-processed image, such as Figure 2(b).
The base of the flow field was assumed to be in contact with the top face of the GDL.

Figure 2: Synchrotron radiographic images illustrating the through-plane distribution of liquid water in the ex situ flow field apparatus with Freudenberg H2315 I6: a) Pre-processed image showing the region of interest and b) post-processed image showing the hemispherical droplets formed inside the gasket-GDL assembly.

**Image Analysis**

Pre-processed (raw) images, such as Figure 2(a), were processed using an open-source software package (Fiji) to calculate the water thickness profile of a GDL along its through-plane direction. All the obtained raw images were first adjusted for the nearly linear decrease in intensity of the synchrotron beam over the course of our investigation. Then images are processed to obtain the water thickness values using the Beer’s law. According to the Beer-Lambert equation, the intensity of the beam after traveling a distance of \( X \) through a material is given by [15]:

\[
I = I_0 e^{-\mu X}
\]  

(1)

where \( I_0 \) is the incident intensity of the beam, and \( \mu \) is the combined attenuation coefficient of the material with respect to the beam energy. According to equation (1), the intensity of the beam upon passing through the dry GDL is given by:

\[
I_{dry} = I_0 e^{-\mu_{nonwater}X_{nonwater}}
\]  

(2)

where \( \mu_{nonwater} \) is the attenuation coefficient of all the other materials combined together except water at 23 keV, and \( X_{nonwater} \) is thickness of all the other materials combined together except water.

Similarly, the captured intensity of the beam that passes through the wet GDL at a given instant, \( j \), after the initialization of invasion is given by:

\[
I_{wet,j} = I_0 e^{-(\mu_{water}X_{water,j} + \mu_{nonwater}X_{nonwater})}
\]  

(3)

Combining (3) and (2), we have the following expression for through-plane water thickness in the GDL:

\[
X_{water,j} = -\frac{\log(I_{wet,j} / I_{dry})}{\mu_{water}}
\]  

(4)

where \( \mu_{water} \) for monochromatic beams with energy of 23 keV is 0.644 cm\(^{-1}\) [17].

Post-processed images are also filtered using a Gaussian filter with a standard deviation of 2.0 to reduce noise. All the other GDL results (two GDLs at two flow rates) were processed similarly to obtain water thickness profiles. Water thickness profiles across the through-plane of the GDL are presented, where the water thickness is the in-plane integration of liquid water detection.

**RESULTS**

Figure 3 illustrates the water thickness profiles as a function of GDL thickness for Toray TGP-H-090 (treated paper) and Freudenberg H2315 I6 (treated felt) at the moment of breakthrough, when liquid water was injected at a flow rate of 1 \( \mu \)L/min. At breakthrough for Toray TGP-H-090, the injected liquid water reached a pressure of 0.98 psi (breakthrough pressure), whereas the breakthrough pressure Freudenberg H2315 I6 reached 0.92 psi. Despite the similarity in breakthrough pressures (Table 1), the water thickness profiles vary significantly, as shown in Figure 3. It is noteworthy that at the liquid water inlet side of the GDL (where GDL through-plane position \( = 0 \)µm) both materials exhibit high water contents, where Freudenberg H2315 I6 exhibits nearly double the water content of Toray TGP-H-090 at the inlet face. Throughout the thickness of the GDL, Freudenberg H2315 I6 also exhibited a higher water content compared to Toray TGP-H-090. We observed that the liquid water front first travelled laterally within the surface pores of the GDL, and then invaded the through-plane pores in the GDL. This is in agreement with the capillary fingering mechanism proposed by Litster et al. [18] and concurred upon by Sinha and Wang [2] and Medici and Allen [19]. This phenomenon was observed to occur in both materials investigated here.

Figure 4 illustrates the water thickness profiles for Freudenberg H2315 I6 at breakthrough and 1.1 min after breakthrough. A significant decrease in the liquid water content of the felt was observed after breakthrough; whereas, Toray TGP-H-090 did not exhibit any significant decrease in the liquid water content after breakthrough. Although the liquid water content in Toray TGP-H-090 did not vary significantly between the moment of breakthrough and 1.1 min after breakthrough, we found that the rate of liquid water injection has a major impact on the liquid water content of the material.
DISCUSSION

The effective porosity can be defined as the percentage of total porosity available for reactant transport in a fuel cell. From the obtained data, though nothing conclusive can be said about the effective porosity distribution of GDLs without considering their compressed porosity distributions; given the water thickness profile data it can be concluded that the effective porosity of treated felt increased after breakthrough. Some of the pores that were occupied by the water before or at breakthrough appear to have been purged. This implies that there could be a substantial interconnectivity between the pores in the felt GDL as compared to those in the paper GDL. It is possible that the binder, polyvinyl alcohol [1], used in the paper making step of the manufacturing process of carbon paper to hold the carbon fibres together, could be blocking the pores from being interconnected. The presence of this binder may lead to fewer interconnections in the paper GDL as compared to those formed in the felt GDL. It should also be noted that a binder is not used to hold together the carbon fibres while manufacturing the felt GDL [20]. The unexpected increase in the water content in the felt GDL towards the outlet face of the GDL (Figure 3) cannot be satisfactorily explained at this point in time and needs further investigation. However, during the course of the invasion, the inlet water pressure might have pushed the GDL material upwards, shifting the pixel data towards the right to give the appearance of a spike in the water thickness values towards the outlet face of the GDL. This decrease in the water content in felt GDL, after breakthrough, also demonstrates the importance of considering the transient effects of water content while modeling liquid water distribution in felt GDLs.

Table 1: Material properties and breakthrough pressures for Freudenberg H2315 I6 and Toray TGP-H-090

<table>
<thead>
<tr>
<th>GDL</th>
<th>Treatment</th>
<th>Measured GDL Thickness (µm)</th>
<th>Breakthrough pressure (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Liquid injection at 1 µL/min</td>
</tr>
<tr>
<td>Freudenberg H2315 I6</td>
<td>10 wt. % PTFE</td>
<td>287</td>
<td>0.92</td>
</tr>
<tr>
<td>(treated felt)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toray TGP-H-090</td>
<td>10 wt. % PTFE</td>
<td>300</td>
<td>0.98</td>
</tr>
</tbody>
</table>

This table provides a summary of the material properties and breakthrough pressures for Freudenberg H2315 I6 and Toray TGP-H-090, including the measured GDL thickness and breakthrough pressures at liquid injection rates of 1 and 8 µL/min. The effective porosity of treated felt increased after breakthrough, as indicated by the higher injection pressures at a constant injection rate. The table highlights the importance of considering the transient effects of water content while modeling liquid water distribution in felt GDLs.

Figure 5 shows the water thickness profiles at breakthrough for the two liquid water injection flow rates (1 and 8 µL/min) for Toray TGP-H-090. In contrast, the liquid water content of Freudenberg H2315 I6 was not sensitive to the liquid water injection rate. We observed that the water content at the inlet face of Toray TGP-H-090 nearly doubled upon decreasing the water injection rate from 8 µL/min to 1 µL/min. Throughout the thickness of the material, there was an overall increase in water content associated with this decrease in injection rate. Uncertainty in the water thickness values can be attributed to the intensity fluctuations over time of the synchrotron beam. The maximum error in the water thickness values is calculated to be 0.0025 cm.
Fishman et al. [20] characterized the porosity distributions of uncompressed GDLs. They reported that the porosity distribution for Freudenberg H2315 (untreated felt) is constant in the core region and that it is sinusoidal in the core region of untreated Toray papers. From the results of subsequent pore network modeling work done by the Hinebaugh et al. [21], we expect the breakthrough water content to correlate directly with the heterogeneous porosity profile i.e. we should see more water in the regions with higher porosity and lesser water in the regions with lower porosity. Since liquid water accumulated in Freudenberg H2315 I6 and Toray TGP-H-090 (Figure 3) in such a way that would have been expected for untreated materials, it would be worthwhile to investigate whether the heterogeneous porosity distributions for these materials differ significantly from their untreated and uncompressed counterparts.

At higher flow rates a trend of lesser water accumulation at the inlet face of the GDL, at breakthrough, has been observed in both paper and felt GDLs. However, in felt the difference is not as pronounced as it is in paper. This could be attributed to the difference in breakthrough pressures of felt and paper at 1 and 8 µL/min. As can be seen from Table 1, the difference in breakthrough pressures at 1 and 8 µL/min, for felt and paper are 0.2 and 0.6 psi, respectively. The greater the breakthrough pressure difference, the lesser the amount of water accumulated at the bottom face. This decrease in the water content at the inlet face with the increase in the flow rate is also in contrast to what has been observed in modelling [22]. Further investigations are required to better explain the increase in liquid water content in Freudenberg H2315 I6 when the liquid water injection rate decreased (Figure 5).

CONCLUSION

In this paper, we determined the liquid water thickness profiles as a function of through-plane position in the GDL. Synchrotron radiography was employed to measure the water content, and we compared the liquid water content at breakthrough and shortly after breakthrough for both Freudenberg H2315 I6 and Toray TGP-H-090. We found that Freudenberg H2315 I6 exhibited significantly higher amounts of water than Toray TGP-H-090 at breakthrough, and particularly so at the inlet face of the GDL. Freudenberg H2315 I6 exhibited a significant overall decrease in liquid water content throughout the GDL shortly after breakthrough; whereas Toray TGP-H-090 appeared to retain breakthrough water-levels post-breakthrough. Finally, while the water content of Freudenberg H2315 I6 did not vary significantly when altering the liquid water injection rates; we observed that the liquid water content of Toray TGP-H-090 decreased when the liquid water injection rate increased from 1 to 8 µL/min. The preliminary results presented in this manuscript were obtained by analyzing a single paper GDL and a single felt GDL for each parametric investigation. For each reported microstructure, a total of two experiments were conducted; one at 1 and another at 8 µL/min. In our future work, we plan to increase the number of GDL samples employed per parametric experiment in our next visit to the synchrotron facility.

However, these results provide valuable insight into material-specific behavior of liquid water in the two commercially available materials, and future work will be extended to investigate the effect of the PTFE content and that of the micro-porous layer (MPL) on the liquid water content.

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