PEM fuel cell gas diffusion layer modelling of pore structure and predicted liquid water saturation

J. Hinebaugh and A. Bazylak
Microscale Energy Systems Transport Phenomena Laboratory
Department of Mechanical and Industrial Engineering, University of Toronto
Toronto, Ontario, Canada

ABSTRACT
An unstructured, three-dimensional pore network model is employed to describe the effect of through-plane porosity profiles on liquid water saturation within the gas diffusion layer (GDL) of the polymer electrolyte membrane fuel cell. Random fibre placements are based on the porosity profiles of six commercially available GDL materials recently obtained through x-ray computed tomography experiments. The pore space is characterized with a maximal ball algorithm, and invasion percolation-based simulations are performed. It is shown that water tends to accumulate in regions of relatively high porosity due to the lower associated capillary pressures. It is predicted that GDLs tailored to have smooth porosity profiles will have fewer pockets of high saturation levels within the bulk of the material. The results provide a more detailed picture of the possible water distributions in GDLs during operation.

INTRODUCTION
In order to run polymer electrolyte membrane fuel cells (PEMFCs) over a wide range of operating conditions, liquid water within the fuel cell must be actively or passively managed, maximizing reactant diffusion pathways and preventing premature mass transport limitations [1]. Water is introduced into the cathode of the PEMFC at the catalyst layer (CL) as both a product of the electrochemical reaction and through electroosmosis across the polymer electrolyte membrane. Water is also introduced at the flow field (FF) inlet from humidified oxidant streams. At some operating conditions, saturated relative humidity levels have been predicted at the gas diffusion layer (GDL) | CL boundary [2, 3], implying that some liquid water streams within the cathode originate near the GDL|CL boundary.

Pore network models have been employed to simulate liquid water invasion of hydrophobic, porous materials [4-15], where heterogeneity is often provided by randomizing pore and throat radii. These models typically assume capillary forces dominate the transport processes, simplifying the simulations to geometrical searching algorithms [4-6, 9, 11, 12, 15]. Only recently has data been generated that characterizes the through-plane dependence of porosity for various commercial GDL materials [16]. Using micro-computed tomography, Fishman et al. [16] found characteristic through-plane porosity profiles for six commercially available GDL materials, similar to the porosity profile published by Büchi et al. [17].

Stochastically generated fibrous geometries have been generated in [18] to model transport GDL-like structures, providing insight into the tortuosity of the GDL. In this work, similar fibrous geometries are generated, but based on observed, through-plane porosity profiles. Then, a percolation process is simulated to characterize liquid water after invasion in six of the GDL materials investigated in [16]. A comparison between porosity profiles and breakthrough saturation profiles will provide insight into the passive water management qualities of several GDL morphologies.

STOCHASTIC MODEL OF GDL
Unstructured three-dimensional pore spaces are generated with dimensions $l \times l \times l$ by iteratively drawing cylindrical ‘fibres’ into a voxelized domain until a desired porosity is achieved, where porosity is defined as the ratio of non-fibre volume to total volume. All fibres are parallel to the inlet and outlet planes of the domain and have diameter, $d$. To place the fibres according to a specific distribution, each voxel of the network domain is given a probability of being randomly selected as containing a fibre centre, then a random angle, $\theta$, between 0 and $\pi$ is given to the fibre. Voxels are then labelled as material, if their centres are within $d/2$ of an
imaginary line travelling through the center of the originally selected voxel at an angle of θ. Fibre overlap is permitted.

To provide periodic sidewall boundaries, while reducing the effects of fibre ends, four equally sized fibrous domains were generated with dimensions $\mathcal{L} \times h$ as is illustrated in Fig 1(a), where $h$ is the thickness of the fibrous domain extending out of the page. Each domain is generated to have a total porosity value $\frac{1}{3}$ of that of the prescribed material porosity determined from [16]. These four domains were placed such that they would overlap (Fig 1(b)) by a distance of $\alpha$ (overlap parameter), creating a new domain with a length and width of $2\beta + \alpha$, where,

$$\beta = l - \alpha.$$ 

Then, all opposite sections of the domain are added to each other. Following Fig 1 as an example, this results in the four corner sections of the domain equalling the sum of all original corners ($w' = w + x + y + z$ etc.) and each edge section equaling the sum of each pair of edge sections ($A' = A + D$ etc.). Finally, any $\mathcal{L} \times h$ region of the total domain can be taken as a repeating element (Fig 1(d)).

Similar to the work of Luo et al. [6], pore space is described with a maximal ball algorithm. A maximal ball algorithm first assigns a value to each voxel of a pore space. This value represents the distance between that voxel and the nearest material voxel. Then, by applying a set of rules for each voxel, the pore space is reduced to a skeleton, and voxels within the pore space are grouped into clusters, forming pores connected by throat voxels. The steps outlined in [19] are followed with the modification that the maximal ball search algorithm also follows periodic boundary conditions. An example of maximal ball derived pore locations within a fibrous volume is shown in Fig 2.

As is described in Fishman et al. [16], three dimensional x-ray tomography derived data (Table 1) is used to characterize the porosity profiles of various commercially available GDL materials. A porosity profile is defined as the porosity of each thin, in-plane slice of the material with respect to its through-plane position. In [16], each slice represents roughly a 7000 μm by 2500 μm by 6 μm sheet of the material oriented parallel to the plane of the material. It is important to note that the porosities of various materials are found to be strong functions of through-plane position.

To match the approximate diameter of the carbon fibres in typical GDLs [20], fibre diameters of $d = 7$ μm are employed in this study. An overlap parameter of $\alpha = 2l/3$ is applied when creating stochastic pore spaces. A total of 70 random networks are generated for each studied material, with dimensions $l = 100$ μm, and with $h$ equal to the thicknesses reported in Table 1. Pore spaces are created with resolutions of 2.36 μm/voxel.

**INVASION SIMULATIONS**

To simulate the evolution of liquid water clusters within the PEFMC GDL, an invasion percolation algorithm is employed. Invasion percolation, as described by Wilkinson and Willemsen [21], assumes that an advancing fluid interface follows the path of least resistance determined by local capillary pressures, such that the invading phase maintains the lowest possible pressure at each simulation step. When the invading phase is non-wetting, such as water in a hydrophobically treated GDL, the path of least resistance during invasion is determined by throat size [21]. Water is then assumed to invade the largest available throat at each simulation step, and no pressure equations are required.

The quasi-static invasion process simulated employs an invasion percolation algorithm with the following assumptions.

1. The system is isothermal.
2. The gas phase cannot become completely trapped by the liquid and solid phases.
3. Viscous forces within the liquid water clusters at the GDL|CL interface and within the GDL are negligible.
4. The GDL is uniformly hydrophobic; therefore, the capillary pressures associated with pore entry are only inversely proportional to the throat width.
5. A steady-state condition is reached once the cluster invades a pore centered at the GDL|FF interface, an event labelled as breakthrough. At breakthrough, the water cluster ceases to grow within the GDL due to the low capillary pressures associated with a water droplet either in the channel or in contact with a relatively hydrophilic rib.
6. The GDL is initially dry. Liquid water at the gas channel is not considered.

The simulation is initialized by labelling all pores centered at the GDL|CL interface as inlet pores. All inlet pores are labelled as fully saturated with liquid water, and all throats connecting inlet pores to other pores are labelled as interfacial throats. Then the interface advances through the largest interfacial throat, fully saturating the adjacent pore and labelling all of that pore’s throats as interfaces. This process repeats until breakthrough.

**RESULTS & DISCUSSION**

**GDL Characterization**

To apply the experimentally determined porosity profiles [16] to the random fibre distributions of three dimensional pore spaces, porosity levels are linearly interpolated between data points, such that each plane of voxels in the domain has an associated porosity. The weighting of the probability distribution governing fibre placement is then based on these interpolated porosity profiles, following the method described in [15]. Invasion percolation simulations are run until breakthrough in the 70 random networks for each material studied.

After the sequence of pore invasion leading to breakthrough is determined, all voxels belonging to the invaded pores are labelled as fully saturated with liquid water.
Then, calculations of liquid water across the domain are performed using two related methods. In the first, water thicknesses are calculated by determining the total number of voxels in a region of interest that are saturated. The purpose of these results is to display data as it would be seen from image subtraction methods applied to experimentally determined images, such as those used in [22] or [23]. In the second method, saturation levels are calculated by dividing the water thickness levels by the original thickness of pore voxels in that same domain. This provides information not only on the water content in a particular region, but also residual air content, because the saturation of one phase in a two phase system is equal to 1 minus the saturation of the second phase.

A single simulation result is shown in Fig 3, where both saturation and water thickness levels are displayed for each column of voxels perpendicular to the $xz$ plane. Fig 3 shows results from a trial where the experimentally determined [16] porosity profile of Toray TGP-H-060 was used as the input for fibre placement. Both the water thickness and saturation patterns in Fig 3 display fronts of liquid water that resulted from the invasion process at $z$ values near 50 μm and 150 μm. As was predicted by a similar two dimensional model [15], these fronts roughly align with the two local minimums of porosity present in the Toray TGP-H 060 data which can be seen in Fig 4(b).

This example also highlights a noticeable difference between the two methods of displaying the water data. What appear to be air pockets near the inlet region of the water thickness pattern nearly disappear in the saturation pattern, turning out to be pockets of low porosity. Similarly, lateral striations of water thickness near $z$ values of 140 μm also disappear in the saturation pattern. These differences emerge because water thickness values incorporate data from only one of the three possible phases: water, air, and solid. This
emphasizes the importance of incorporating known porosity data into measured water levels.

For each material studied, average saturation profiles, normalized water thickness profiles, and average porosity profiles are generated and provided in Fig 4. An average profile is not the averages of individual profiles, but a profile generated from the combined data of the 70 network definitions and calculated breakthrough saturation distributions generated from a certain porosity input.

Because the GDL samples were uncompressed when the x-ray tomography data were attained, the local porosity values and pore and throat sizes of the resultant pore networks near the GDL/CL and GDL/FF interfaces are expected to be larger than would otherwise be expected in the compressed environment of a PEMFC. Due to the increased throat sizes at the GDL/CL interface, these throats are nearly always invaded by the end of the simulation. As can be seen from Fig. 5, this leads to a prediction of fully saturated conditions at the GDL/CL interface.

To account for the lack of symmetry of porosity profiles, a second set of simulations was performed for each profile, initializing the invasion from the opposite face. As seen in Table 1, the average saturation levels of a specific material vary by as much as 0.11, depending on the orientation of the GDL. Saturation profiles presented in Fig 4 are the results of orientations with the lowest corresponding saturation level.

The saturation profiles displayed in Fig 4 are highly correlated with the applied porosity profiles. This is most apparent with the simulation results of Toray TGP-H materials 060, 090, and 120, where the porosity profiles contain multiple local minimums. The local porosity profile minimums correlate well with the local saturation profile minimums. Similarly, it can be seen in Fig 4 that regions between local porosity minima can create “water traps” causing spikes in the saturation profile.

Toray TGP-H GDL materials are classified as “papers”. Varying thicknesses of Toray TGP-H papers are generated by bonding thin layers together [20]. The results displayed in Figs. 3 and 4 show that this manufacturing process has a large impact on the saturation profiles, as the layering process used to create the thicker Toray papers appears to have resulted in peaks and valleys in the porosity profile [16]. SGL Sigracet 10AA and Freudenberg H2315 materials are both classified as “felts” where carbon fibres are hydro-entangled during the manufacturing process. In contrast to Toray paper GDLs, felt porosity profiles resulted in saturation profiles that lacked the variations seen for paper.

<table>
<thead>
<tr>
<th>GDL Type</th>
<th>Thickness* (μm)</th>
<th>Bulk Porosity*</th>
<th>Orientation 1 Breakthrough Saturation Level**</th>
<th>Orientation 2 Breakthrough Saturation Level**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toray TGP-H-030</td>
<td>120</td>
<td>0.806</td>
<td>0.46 ± 0.07</td>
<td>0.55 ± 0.08</td>
</tr>
<tr>
<td>Toray TGP-H-060</td>
<td>234</td>
<td>0.788</td>
<td>0.68 ± 0.07</td>
<td>0.69 ± 0.08</td>
</tr>
<tr>
<td>Toray TGP-H-090</td>
<td>300</td>
<td>0.783</td>
<td>0.72 ± 0.07</td>
<td>0.72 ± 0.07</td>
</tr>
<tr>
<td>Toray TGP-H-120</td>
<td>372</td>
<td>0.738</td>
<td>0.71 ± 0.06</td>
<td>0.74 ± 0.06</td>
</tr>
<tr>
<td>SGL Sigracet 10AA</td>
<td>360</td>
<td>0.799</td>
<td>0.65 ± 0.06</td>
<td>0.70 ± 0.06</td>
</tr>
<tr>
<td>Freudenberg H2315</td>
<td>366</td>
<td>0.803</td>
<td>0.61 ± 0.06</td>
<td>0.66 ± 0.05</td>
</tr>
</tbody>
</table>

* Calculated from tomography data [16].
** Simulation result. The average of 70 simulations. A single standard deviation is shown to illustrate the variation obtained from the set of random simulations.
In the literature, typical pore network models of PEMFC GDL invasion result in saturation profiles containing one local maximum (at the CL) and one local minimum (at the FF) [7, 9, 13, 24]. When the inlet condition is modified to allow fewer entry throats at the CL, the single local maximum is seen to shift slightly into the bulk [5, 8, 11]. Peaks in saturation within the GDL bulk can be predicted by a pore network model that includes bulk generation of liquid water due to condensation [14]. Bulk saturation extrema are also witnessed when a wettability gradient is imposed on a mixed-wet pore network model [12]. The model presented in this paper provides an additional explanation to the peaks in saturation within the bulk of the GDL that have been reported in [22, 25, 26]: that water tends accumulate between areas of low porosity.

As shown in Table 1, breakthrough saturation levels vary from 0.46 to 0.71. These are comparatively high predicted saturations with respect to previous pore network studies such as [11, 15]. We believe this difference is primarily caused by the choice of domain size of the present study. In this study computational requirements limited the size and resolution of the domain. However, the choice of domain size has implications on the assumption of transport mechanisms in and around the GDL in a PEMFC. In this study, where a 100 μm × 100 μm cross sectional area is used for all networks, it becomes implicitly assumed that, if this is a representative element of the system, then we expect every 100 μm × 100 μm section of GDL to contain an independent water cluster and breakthrough location, where in actuality, adjacent water clusters likely merge and form only a single breakthrough location, and the spacing of these original water clusters is unknown. Previous works such as [9, 15] have demonstrated the strong relationship between network dimensions and breakthrough saturation levels. Therefore, more data should be collected on breakthrough location density in operational cells, in order to provide insight into the appropriate size of network domains.

**CONCLUSION**

A three-dimensional unstructured pore network model for simulating the liquid water saturation in a PEMFC GDL is presented. Invasion percolation is applied to each generated
Figure 4. Saturation, water thickness, porosity and effective porosity curves associated with six commercially available GDL materials. Subfigures (a-f) represent Toray TGP-H-030, Toray TGP-H-060, Toray TGP-H-090, Toray TGP-H-120, SGL Sigracet 10AA, and Freudenberg H2315, respectively.
network, and breakthrough liquid saturation data is used to compare modelling parameters and specific GDL materials. Using this model, we demonstrate a powerful method of applying porosity profiles to the definition of pore networks. By randomly placing cylindrical fibres in a defined domain, with fibre placement probabilities weighted by a given porosity distribution, x-ray computed tomography data becomes an input to the definition of each generated pore network.

Based on the simulation results presented here, it is found that saturation levels have a large dependence on the porosity gradients in the through-plane direction. The peaks and valleys present in the porosity profiles of thick carbon fibre papers may create highly saturated regions in the bulk of the GDL, with low porosity regions corresponding to high saturation regions. It is recommended that GDLs should be designed to have porosity profiles with few local minimums.

Because this paper applies porosity profiles of uncompressed GDL material with no additional microporous layer (MPL), the above simulations are expected to more closely predict the ex-situ experiment of GDL material invasion [17, 27] than the actual invasion of the GDL within an operating fuel cell. Future work includes applying compressed porosity data of GDL materials with and without MPL layers.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation (CFI), the Bullitt Foundation, and the University of Toronto, as well as scholarships to J. Hinebaugh from the Bert Wasmund Graduate Fellowship in Sustainable Energy Research, the Pierre Rivard Hydrogenics Fellowship, and the Hatch Scholarship for Sustainable Energy Research.

REFERENCES


