Modeling liquid water transport in gas diffusion layers by topologically equivalent pore network

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A B S T R A C T

A topologically equivalent pore network (TEPN) model is developed for the first time to extract pore networks directly from gas diffusion layer (GDL) microstructures and thus account for all structural features of a GDL material. A generic framework of TEPN modeling is presented to design GDL structures that enable improved water management. With TEPNs used as input to a two-phase flow simulator, constitutive relations and steady-state liquid saturation profiles for carbon paper and carbon cloth are obtained and reported in this work. The results indicate a strong influence of the GDL morphology on water transport characteristics, which helps unravel the structure–performance relationship for GDLs.

1. Introduction

A key performance/durability limitation in polymer electrolyte fuel cells (PEFC) centers on liquid water transport and resulting flooding in constituent components. The gas diffusion layer (GDL), being a gateway for reactant and product water transport between gas channel and catalyst layer (CL), plays a crucial role in water management which requires a delicate balance between membrane hydration and water removal from CL and GDL. While considerable research [1,2] has been conducted on water transport in PEFCs, fundamental understanding of liquid water dynamics addressing the role of GDL microstructure and surface wettability remains largely absent. Recently, use of pore network (PN) models to elucidate the pore-scale physics of liquid water transport in GDL was pioneered by Sinha and Wang [3–5] and Gostick et al. [6] and later followed by Djilali and co-workers [7,8], Koido et al. [9], Nam and co-workers [10,11], and Prat and co-workers [12–14]. Detailed investigations have revealed the role of capillary fingering in liquid water transport for the first time [3]. Additionally, the effect of GDL mixed-wettability on liquid water transport is investigated in detail, highlighting the existence of an optimum GDL hydrophobic fraction enabling least mass transport limitations to PEFC operation [4,5].

While the PN models developed to date provided substantial insight into the pore-scale liquid water transport in GDL, they [3–14] have been employing randomly generated pore-network structures which are created to merely match average properties of GDL materials, such as porosity and permeability. These average GDL properties are insufficient to define a unique pore structure since different porous media with totally different microstructures can have the same porosity and permeability. The essential function of PN modeling to include the characteristics of microstructure is grossly approximated in random pore networks, thus preventing achievement of full potential to delineate the role of various carbon paper- or cloth-based GDL materials in liquid water transport. In this work, we shall introduce, for the first time, a topologically equivalent pore network (TEPN) modeling approach in which the pore network is extracted directly from high-resolution, three-dimensional microstructures of GDL materials. A method will be described that deploys computer models to generate a three-dimensional GDL microstructure [15] and its structure-equivalent pore network [16]. Such a generic TEPN modeling framework is instrumental not only to elucidate physical differences in the liquid water behavior in carbon paper- and cloth-based GDL materials but also to design novel GDL materials and structures for optimal PEFC operation. Herein we shall discuss the characteristics of liquid water transport in carbon paper- and cloth-based GDL materials comparatively, and link the differences to their respective microstructural features.
Table 1
Input parameters for microstructure generation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Carbon paper</th>
<th>Published</th>
<th>Carbon cloth</th>
<th>Published</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber diameter (μm)</td>
<td>6</td>
<td>7 [21]</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.80</td>
<td>0.7–0.8 [21]</td>
<td>0.78</td>
<td>0.7–0.8</td>
</tr>
<tr>
<td>Voxel size (μm)</td>
<td>3</td>
<td>-</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Thru-plane permeability (×10⁻¹² m²)</td>
<td>6.5</td>
<td>5–10 [21]</td>
<td>75.6</td>
<td>69.4</td>
</tr>
<tr>
<td>In-plane permeability (×10⁻¹² m²)</td>
<td>9.0</td>
<td>5–12 [21]</td>
<td>51.3</td>
<td>50–60</td>
</tr>
</tbody>
</table>

2. Topologically equivalent pore network

In PN models, a porous medium is represented by a network of pores connected by narrower regions called throats. Complex morphology of pore structures is incorporated through network parameters, such as pore- and throat-size distribution and their connectivity. Macroscopic properties related to network parameters can be inferred from percolation theory.

The construction of a realistic GDL pore morphology is the essential prerequisite for unveiling the influence of an underlying structure on the two-phase behavior. This can be achieved either by three-dimensional (3D) volume imaging or by constructing a digital microstructure based on stochastic models. Noninvasive experimental techniques, such as X-ray and magnetic resonance computed microtomography are the popular methods for 3D imaging of pore structures. Another alternative is reconstruction of a microstructure using stochastic simulation techniques. The low cost and high speed of data generation makes stochastic generation methods the preferred choice over the experimental imaging techniques. Moreover, computer methods can not only construct TEPN of existing GDLs but also virtually design new GDLs by varying porosity, texture, fiber diameter, etc. The latter advantage is particularly useful in the search for optimal GDL pore structures for future generations of PEFCs. As such, we have developed a systematic approach to design a virtual GDL and test its performance, consisting of the following steps:

1. A stochastic modeling method [15] is used to generate high-resolution pore-scale 3D images of GDL.
2. An extensive imaging analysis [16] is employed to extract the computer-generated microstructure in the form of a network of pores and throats. During this process, properties such as volume, radius, and cross-sectional shape of each pore and throat in the network are determined. The coordination number, i.e. the number of independent throats linked to a pore, is assigned accordingly.
3. The extracted pore network is used as input to a pore-network flow simulator to compute macroscopic properties, such as capillary pressure and relative permeability.
4. Further, these macroscopic correlations can be plugged into a two-phase continuum model, such as M2 model [17], to forecast the performance of a virtual GDL in an operational fuel cell.

In the present study, computer models of Toray-060 carbon paper and E-Tek carbon cloth GDLs are reconstructed using a stochastic generation method [15] with structural inputs obtained from the literature and/or manufacturers. Relevant input parameters and intrinsic permeability obtained from the generated microstructures are summarized along with the values of real GDLs in Table 1. The input parameters, i.e. fiber diameter, fiber orientation and porosity, are chosen such that absolute permeability values in both in-plane and thru-plane directions match closely with those measured experimentally in the literature. Representative scanning electron microscopy (SEM) images of carbon paper and carbon cloth are shown in Figs. 1 and 2 respectively. Figs. 3 and 4 display SEM-like images of carbon paper and carbon cloth generated by computers. The striking similarity between original SEM and virtual images confirms that the characteristics of the original microstructures are well represented in reconstructed computer models.

Through extensive imaging analysis of computer-constructed microstructure models, extracted pore networks are stored in data files and then used as a direct input to a two-phase flow simulator. It should be noted that pores and throats are irregular in shape in our extracted pore networks. However, for clarity of presentation pores and throats are depicted in Figs. 5 and 6 by spheres and cylinders, respectively, with radii of their inscribed spheres. The carbon paper network represents a domain of 192 μm × 750 μm × 750 μm, containing 2537 pores and 16,501 throats. The carbon cloth network represents a domain of 360 μm × 1000 μm × 1000 μm, containing 1067 pores and 5200 throats. The pore-size distributions of the extracted pore networks are shown in Fig. 7(a). A vast difference in the pore-size distributions of carbon paper and carbon cloth can be
clearly seen. For carbon paper, the distribution is unimodal with a peak pore size of $\sim 20 \, \mu m$. For carbon cloth, a bimodal pore-size distribution spanning over a few orders of magnitude is observed. The primary mode associated with large pores (i.e. inter-thread pores) among the fiber bundles occurs between $31 \, \mu m$ and $145 \, \mu m$ with peak value at $100 \, \mu m$. The secondary mode associated with small pores (i.e. intra-thread pores) between individual fibers appears between $1 \, \mu m$ and $31 \, \mu m$ with the peak value at $20 \, \mu m$. The distribution patterns, peak values of pore diameters of the extracted pore networks are in accordance with the measured data shown in
Fig. 7. Pore-size distributions of carbon paper and carbon cloth from: (a) topologically equivalent pore networks, and (b) measurements [18]. Note: the unit of pore diameter should be μm instead of mm in (b).

Fig. 7(b) [18], confirming the validity of the generated TEPN structures. Large spread in throat diameters, especially for carbon cloth with narrow throats linking small intra-thread pores and with wide throats linking large inter-thread pores, can be readily observed (Figs. 5 and 6). As shown in Fig. 8, the throat diameter distribution for carbon cloth is also bimodal. Large pores and throats of the primary mode distribute quite uniformly through the sample and form major flow paths. Small pores and throats are localized between neighboring large pores and form local minor flow paths.

Fig. 9 contains images of throat distribution for carbon paper and carbon cloth, viewed from the thru-plane direction. Together with 3D views (Figs. 1–6), it shows that carbon paper and carbon cloth have distinctive fibrous structures. The microstructure of carbon paper is shown to be high topology layers formed by randomly arranged fibers along the in-plane direction. The throats are densely arranged in a highly random order. Its coordination number varies from 2 to 51, with the averaged value of 13. On the other hand, the carbon cloth shows the well organized plain-weave structures. The throats are coarsely distributed in a highly ordered and structured manner. Its coordination number varies from 2 to 102, with the averaged value of 10. Both carbon paper and carbon cloth have very complex microstructures, such as wide distributions of pore and throat size and high coordination numbers, implying that the ability of cubic or randomly generated pore networks to incorporate structural attributes of real GDLs is quite limited. It is difficult to generate random structures with high porosity and anisotropy as well as pore-size distribution with large span and average coordination number higher than 6.
In summary, because TEPN has an accurate description of size and position of pores and throats and interconnectedness of pores and throats and eliminates all the aforementioned limitations of the random pore networks, it becomes finally possible to predict structure-specific macroscopic transport properties pertinent to liquid water transport in fuel cell GDLs.

3. Modeling of fluid flow

3.1. Model assumptions

Two-phase flow in a pore network is modeled under the following assumptions:

1. Wetting properties are assumed to be constant in the network. Contact angle between liquid water (non-wetting phase for hydrophobic GDL) and carbon fibers is fixed at 110°.
2. While the radius of a throat serves to define its hydraulic conductance, the volume contributed by all throats is assumed to be negligible. The small throat/pore volume ratios of reconstructed samples, 6.14% for carbon paper and 8.64% for carbon cloth, confirm the validity of this assumption.
3. Fluid pressures are only defined in pores.
4. A pore can only have single occupancy by liquid or gas. Physically, the non-wetting fluid is the bulk fluid and the wetting fluid stays as wetting films in corners, but only bulk fluid is considered for simplicity.
5. The flow is laminar everywhere and governed by Hagen–Poiseuille law.
6. The fluids are Newtonian, incompressible, and immiscible.
7. The injecting fluid is the non-wetting fluid.
8. The resistance offered by a pore to flow is assumed negligible.
9. Water enters GDL and flows through GDL in the liquid phase without phase change (evaporation and condensation).

3.2. Invasion

The invading non-wetting fluid located in a pore is flowing into a throat filled with wetting fluid. Due to the surface tension at the interface, the capillary force exists as resistance preventing the non-wetting fluid from freely entering the throat. For invasion of non-wetting fluid into the throat, the pressure difference between non-wetting and wetting phases must exceed the throat entry pressure. Once the throat is open and the non-wetting liquid will fill the entire throat and the pore that is on the other end of the throat, because pores typically have much greater radius than throats.

In real porous media, pores and throats have complex and irregular shapes. In the network extraction algorithm used herein [16], pores and throats are approximated as arbitrary cross-sections, which is regarded as the local saturation, which is used in plotting saturation profiles. Notice from the flow assumptions that each pore can only be occupied by one fluid. Thus $S_i$ is an integer that equals either 0 or 1.

To compute the capillary pressure curve, it is assumed that air pressure throughout the network is uniform. Initially, all the pores and throats are completely filled with air and the inlet throats are connected to a reservoir of liquid water. For liquid water to invade into a throat, the pressure difference across the liquid–gas meniscus must exceed the throat entry capillary pressure as calculated from Eq. (2). During each step of quasi-static displacement, a search is performed over all the interfacial positions to determine the minimum capillary pressure that will allow water to invade further into the GDL. After increasing the capillary pressure to this critical value, liquid water is allowed to invade the connecting pore and any subsequent throats and pores that can be invaded at this capillary pressure. At this time, total volume-averaged saturation is updated based on the liquid water distribution in each pore. Once no further invasion can occur, the capillary pressure is increased by a next minimum increment.

To compute the absolute permeability and relative permeability, Hagen–Poiseuille flow through throats is assumed. The volume flow rate of phase $\alpha$ between two neighboring pores $i$ and $j$ can thus be expressed as:

$$Q_{ij}^\alpha = g_{ij}^\alpha (P_i - P_j)$$

3.3. Two-phase flow algorithms

In pore network simulations two algorithms are commonly used. The first one is the quasi-static algorithm, which is conceptually simple and computationally efficient. It neglects the viscous and dynamic effects. The second one is dynamic algorithm, which accounts for all the relevant physics. The trade-off is a large increase in complexity and computational requirement for the dynamic algorithm.

The quasi-static algorithm is applicable to flow through porous media at an infinitesimal flow rate ($Ca < 10^{-4}$) where the viscous pressure drop across the network is negligible and capillary forces completely control the fluid configuration. For a typical fuel cell application, the capillary number is of the order of $10^{-8}$. Thus the quasi-static algorithm is used here to compute the constitutive relations: capillary pressure and relative permeability as functions of liquid water saturation.

3.4. Constitutive relations

Capillary pressure curve $P_c(S)$ and relative permeability curve $K_r(S)$ are two key relations entering into a continuum model for PEFCs. Both relations depend strongly on the pore-level distributions of the phases as well as the complexity of pore structures. The volume averaged liquid water saturation is defined as

$$S = \frac{1}{V} \sum_{i \in RV} V_i S_i$$

where $V_i$ and $S_i$ represent volume and liquid water saturation of pore $i$ respectively, and $RV$ the representative volume. If $RV$ represents the whole modeling sample, $S$ will be the total average saturation, which serves as a key parameter $P_c(S)$ and $K_r(S)$ curves. Otherwise, if the representative volume contains only a portion of pores, $S$ is regarded as the local saturation, which is used in plotting saturation profiles. Notice from the flow assumptions that each pore can only be occupied by one fluid. Thus $S_i$ is an integer that equals either 0 or 1.

Capillary pressure curve $P_c(S)$ is a dimensionless shape factor

$$G = \frac{A}{P^2}$$

where $A$ is the cross-sectional area and $P$ is the corresponding perimeter. In the present work, cross-sections of most throats are of triangular shape in the TEPN of carbon paper and carbon cloth. For a triangular throat connected with pores $i$ and $j$, the entry pressure, $P_{ij}^c$, is given by

$$P_{ij}^c = \sigma \cos \theta \left( 1 + \frac{2\sqrt{\pi c_{ij}}}{r_{ij}} \right)$$

where $\theta$ is the contact angle of wetting phase and $r_{ij}$ the minimum inscribed radius of the throat.
non-wetting phases is given by [20]

\[ A_{ij}^w = \frac{r_{ij}^2}{4G_{ij}} \left( 1 - \left( \frac{\sigma}{\gamma_{ij}P_{ij}} \right)^2 (1 - 4\pi G_{ij}) \right) \] (5)

\[ A_{ij}^{nw} = \frac{r_{ij}^2}{4G_{ij}} \left( \frac{\sigma}{\gamma_{ij}P_{ij}} \right)^2 (1 - 4\pi G_{ij}) \] (6)

where \( nw \) and \( w \) stand for the non-wetting and wetting phases, respectively.

The conductance of the non-wetting phase through a throat between pore \( i \) and pore \( j \) is given by Poiseuille’s law:

\[ g_{ij}^w = \frac{r_{ij}^3}{8\mu nw l_{ij}} \] (9)

where \( \mu \) is the viscosity and \( l_{ij} \) is the length of the throat.

For the wetting phase, it follows that [20],

\[ g_{ij}^w = \frac{r_{ij}^3}{8\beta \mu^w l_{ij}} \] (10)

where \( \beta \) is a dimensionless flow resistance factor which accounts for the reduced conductance of the wetting phase close to the pore wall. \( \beta = 2.5 \) is used for a no stress interfacial boundary condition [20].

Since the fluids are assumed to be incompressible, volume conservation applies at each pore:

\[ \sum_j Q_{ij}^w = 0 \] (11)

where \( j \) runs over all the pores connected to pore \( i \). Eqs. (4) and (11), together with the appropriate boundary conditions, form a system of linear algebraic equations to determine the pressure at each pore:

\[ \mathbf{GP} = \mathbf{b} \] (12)

where \( \mathbf{G} \) is a \( n \times n \) conductance matrix (\( n \) is the number of pores being solved), \( \mathbf{P} \) is a \( n \times 1 \) column vector storing pore pressures, and \( \mathbf{b} \) is a \( n \times 1 \) source vector accounting for boundary conditions and sources.

Liquid water distribution inside pores and throats is determined by quasi-static displacement and the corresponding capillary pressure is applied at all the inlet throats. Thus Eq. (12) is solved numerically at each pore with pressure boundary conditions at the inlet and outlet faces of the network.

To compute absolute permeability, the network is forced to be fully saturated with a single fluid (liquid or air). By specifying a pressure drop across the GDL, Eq. (12) is solved and the volume flow rate \( Q \) at the inlet or outlet surface is calculated. The absolute permeability \( K \) is determined from Darcy’s law:

\[ K = \frac{Q\mu^w L}{A_s \Delta P} \] (13)

where \( A_s \) is the area of inlet or outlet surface and \( L \) is the thickness along the direction where pressure drop occurs.

Similarly, relative permeability is calculated by specify a pressure drop across the GDL for phase \( \alpha \), but at various saturation levels of the invasion process. Calculate the volume flow rate of phase \( \alpha \),

\[ \left( \begin{array}{c} u_{i,j}^\alpha \\ u_{i,j}^w \end{array} \right) = -\frac{1}{\mu^\alpha} \left[ k_{r,x}^\alpha K_x \right. \left. K_{r,y}^\alpha K_y \right] \nabla p_{\alpha} \] (16)

For typical fuel cell applications where the GDL is very thin, it is reasonable to assume a constant gas-phase pressure. Thus the following expression can be derived for liquid water,

\[ \left( \begin{array}{c} u_{i,j}^\alpha \\ u_{i,j}^w \end{array} \right) = \frac{1}{\mu^\alpha} \left[ k_{r,x}^\alpha K_x \right. \left. K_{r,y}^\alpha K_y \right] \frac{dp}{ds} \nabla s \] (17)

![Fig. 10. Capillary pressure curves of carbon paper and carbon cloth predicted by TEPN.](image-url)
Eq. (17) implies that the liquid water flux is proportional to the liquid relative permeability, the absolute permeability, and the slope of capillary pressure curve. All these three parameters are strongly tied to the GDL microstructure. With the detailed microstructure described by TEPN, two groups of simulations, “thru-plane flow” and “in-plane flow”, are carried out to investigate the impact of different pore structures of carbon paper and carbon cloth on their macroscopic transport properties.

4.1. Absolute permeability

Calculated values of thru-plane and in-plane absolute permeabilities based on the extracted pore networks of carbon paper and cloth are listed in Table 2. Both absolute permeabilities of carbon paper and carbon cloth are in a good agreement with those obtained directly from the microstructures (Table 1). For carbon paper, the thru-plane absolute permeability is $6.31 \times 10^{-12}$ m$^2$, whereas the large throats in the bimodal distribution for carbon cloth increase its value to $70.9 \times 10^{-12}$ m$^2$.

4.2. Capillary pressure

For comparison, capillary pressure curves (primary drainage curves) of both carbon paper and carbon cloth are plotted in Fig. 10. Capillary pressure plays an important role in the description of water flow in GDLs. For a given capillary pressure the amount of liquid water entering inside GDLs depends on the slope of capillary pressure curve. Liquid water being the non-wetting phase preferentially invades larger throats in the pore structure. Hence, characteristics of capillary pressure curve are strongly determined by both throat- and pore-size distributions. The liquid water invasion starts with larger throats and pores and then moves toward smaller ones in the pore- and throat-size distributions. Entry pres-

<table>
<thead>
<tr>
<th>Material</th>
<th>Thru-plane</th>
<th>In-plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon paper</td>
<td>6.31</td>
<td>7.68</td>
</tr>
<tr>
<td>Carbon cloth</td>
<td>70.9</td>
<td>52.7</td>
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</table>
Predicted critical saturation at the first breakthrough.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thru-plane flow</th>
<th>In-plane flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon paper</td>
<td>0.15</td>
<td>0.42</td>
</tr>
<tr>
<td>Carbon cloth</td>
<td>0.295</td>
<td>0.39</td>
</tr>
</tbody>
</table>

The slope of the capillary pressure curve is also determined by pore- and throat-size distributions and how these two distributions are associated. The capillary pressure curve of carbon paper has a flat slope between saturation of 0.05 and 0.8. At saturation of 0.05 and 0.8 the capillary pressures are 4.5 kPa and 6.0 kPa, corresponding to 16.5 μm and 12.4 μm diameter throats respectively. This means that the dominant throat diameter is in a very narrow range between 12.4 μm and 16.5 μm. 75% pore volume is connected by dominant throats. The small decrease in throat diameter from 16.5 μm to 12.4 μm leads to the small increase in capillary pressure, thus the flat slope of capillary pressure curve between saturation of 0.05 and 0.8. In the region beyond the saturation of 0.8, capillary pressure for carbon paper increases rapidly as liquid water invades further into smaller pores.

With a bimodal throat- and pore-size distribution, capillary pressure curve of carbon cloth differs significantly from that of carbon paper. The capillary pressure curve exhibits a bimodal ramp increase: a flat slope and slow increase of capillary pressure between the saturation of zero and 0.8, and a steep slope and fast rise beyond that. At the saturation of 0.8 the capillary pressure is 2.0 kPa, corresponding to 37.5 μm diameter throats. This means that the dominant throat diameter is in a wide range between 37.5 μm and 81.5 μm. The flat slope region is associated with the primary mode in the pore-size distribution of carbon cloth. The pore volume in this mode represents about 80% of the total volume of all pores. The sharp sloped region is associated with the secondary mode. Abrupt slope change around saturation 0.8 indicates that the peaks in the bimodal pore and throat distributions are well separated.

4.3. Liquid water distribution

In Fig. 11, liquid-saturated pores at the first breakthrough are plotted. All throats are depicted by straight lines. All pores are plotted proportionally to the real dimensions of the GDL structure as the inscribed spheres of the pore spaces for simplicity. The liquid pore cluster in blue color represents the connected cluster with a liquid breakthrough point at the outlet surface. Others in green color are all dead-end liquid pore clusters. Blue surfaces represent the inlet plane or reservoir. Grey surfaces represent the outlet plane. Carbon paper has much larger pore number density than that of carbon cloth owing to their distinctive pore structure and thickness.

The total volume saturations at the first breakthrough for both carbon paper and carbon cloth structures are listed in Table 3. The liquid saturation marking breakthrough in the thru-plane direction is lower than that in the in-plane direction, as expected. All of the breakthrough saturation values are in the range of 0.1–0.4, a range highly relevant to typical fuel cell operation. As shown in Fig. 11, the size of open and dead-end clusters for in-plane flow is much larger than those for thru-plane flow. This is due to the fact that liquid in the in-plane flow needs to travel over a greater length and invade many more pores to reach the outlet plane compared to the thru-plane flow.

Saturation profiles at the first breakthrough for different structures are plotted in Fig. 12. In order to calculate the local saturation using Eq. (3), the total GDL is equally divided into \( n \) representative volumes between inlet and outlet surfaces. The number \( n \) is chosen such that enough number of pores falls into each \( RV \) to obtain a meaningful averaged saturation. If \( n \) is too large, a representative volume without any pores may exist, giving rise to zero local saturation. Based on this rule, carbon cloth in the thru-plane direction can have at most 3 RVs.

Distribution of liquid-saturated pores at the first breakthrough shows fractal fingering flow: among all clusters connected with the inlet plane, only one cluster breaks through (Fig. 11). This fractal nature of capillary fingering gives the saturation profile an overall decreasing concave trend toward the outlet. However, local saturation does not monotonically decrease toward the outlet in some cases. The complex shape of local saturation profiles can be explained by scrutinizing the 3D liquid water distribution shown in Fig. 11. For instance, for in-plane flow through carbon cloth, the local saturation increases from 0.05 to 0.15 near the outlet region. This is due to the fact that the representative volume near the outlet contains two large liquid-saturated pores, whereas the representative volume next to it has only one liquid-saturated pore. The shape of the saturation profile is strongly linked to the characteristics of
the GDL microstructure. As a result, the saturation profile locally may have a decreasing convex trend or even an increasing trend.

4.4. Relative permeability

In Fig. 13, the predicted thru-plane and in-plane relative permeabilities are compared for both carbon paper and carbon cloth respectively. Relative permeability is determined by the conductance matrix of phase \( \sigma \) flowing in throats. As such, it is influenced by the throat length, throat-size distribution, and connectivity of neighboring throats.

At the same liquid saturation, the connectivity of throats flown by a specific phase is strongly direction-dependent, caused by the anisotropy of the structures of carbon paper and carbon cloth. This leads to a significant difference between the in-plane and thru-plane relative permeability curves. As shown in Fig. 11, liquid water cannot penetrate in the GDLs to form a continuous flow path until a critical water saturation is attained where water breaks through on the outlet surface. Hence, the liquid relative permeability is zero below the breakthrough saturation in Fig. 13.

As shown in Fig. 13, the liquid relative permeability in the in-plane direction is much smaller than in the thru-plane direction. For carbon paper, below liquid saturation of 0.72, the in-plane liquid relative permeability is very small (<0.04), thereby exacerbating flooding under the land region. Hence, for high-humidity operation, carbon paper is not the best choice. However, under the low-humidity operation, carbon paper has the advantage of retaining product water and hence improving membrane hydration.

Between the breakthrough saturation and saturation of 0.8, the liquid relative permeability curves for carbon cloth are not smooth, exhibiting step-wise variations. This is reflective of the unique topological structure of carbon cloth. In the saturation range, the liquid relative permeability is associated with the primary mode in the bimodal pore-size distribution. Although merely 8% in number, pores in this mode are very large and occupy 80% of the total volume of all pores. Liquid volume saturation can jump by a few percent even when only one large pore is invaded. Flat regions of the curves indicate that a large change in liquid saturation hardly impacts the relative permeability. This happens when invasion proceeds in the dead end clusters consisting of large pores. Since those clusters have no connection with the outlet, there is no contribution to the liquid permeability despite the liquid volume saturation increases appreciably. Abrupt-change regions of the curves, where a slight increase in liquid saturation causing rapid rise in relative permeability, happen when a dead-end cluster with large pores finally breaks through or connects with an open cluster. This dramatically changes the total conductance of the entire network, with a little change in the saturation. Beyond the saturation of 0.8, both thru-plane and in-plane liquid relative permeability curves are seen to be very flat. This is because major liquid flow paths are already established throughout the network at the high saturation of 0.8. Adding minor liquid flow paths by invading smaller throats in the secondary mode hardly increases the total conductance of the network. Thus, beyond saturation of 0.8 the liquid relative permeability stays very close to unity.

The absolute permeability of carbon cloth is almost 15 times of carbon paper. At the same saturation, both thru-plane and in-plane relative permeabilities of carbon cloth are much higher than those of carbon paper. As indicated by Eq. (17), the absolute and relative permeability, together with the slope of capillary pressure–saturation curve determine the water flux across the GDL. Hence, carbon cloth has a much higher capability to transport liquid water than carbon paper, leading to less retention of liquid water in carbon cloth and hence making it more suitable for high-humidity operation. For the same reason, carbon cloth GDL is inferior to carbon paper under low-humidity operation.

The gas relative permeability is calculated under the assumption that liquid-filled pores offer no conductivity to gas flow. For carbon paper, the predicted gas relative permeability in the in-plane direction is much smaller than that in the thru-plane direction, which could cause severe mass transport limitation under the land region. For carbon cloth, once the liquid saturation exceeds 0.55, the thru-plane and in-plane gas relative permeabilities reduce to nearly zero. This means that gas transport can be effectively blocked by filling a few large pores along the main flow path. For carbon paper, the saturation needs to reach 0.7 to block the gas transport.

It should be noted that the predicted correlations are based on a single computer reconstructed sample of carbon paper and carbon cloth. They are not as accurate and smooth as statistically averaged relative permeability, for which more stochastic generated samples are required. However, the predicted results still reveal the dramatic impact of the GDL microstructure on their macroscopic properties, and the relative permeability correlations presented herein exhibit

![Fig. 13. Predicted relative permeability curves of (a) carbon paper, and (b) carbon cloth.](image-url)
new characteristics that have not been captured by random pore networks.

5. Conclusion

In this work we have developed a topologically equivalent pore network (TEPN) method to describe the dramatic impact of GDL pore morphology on water transport properties. A virtual GDL design approach is described through generation of TEPNs of two commonly used GDLs, carbon paper and carbon cloth. With a detailed representation of the complex porous structure, macroscopic properties are distinguished between carbon paper and carbon cloth and linked to their respective microstructural features. Bimodal pore- and throat-size distributions characteristic of carbon cloth lead to two distinctive regions in capillary pressure and relative permeability curves, while only one region is observed for carbon paper owing to its unimodal pore- and throat-size distributions. It is found that concave-shaped saturation profiles, typical of capillary fingering, are representative for homogenously hydrophobic paper and cloth GDLs. Virtual GDL design by TEPN method described in this paper will help explore new GDL structures for optimal water removal.

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