



## Liquid Water Transport in Gas Diffusion Layer of Polymer Electrolyte Fuel Cells

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High-current-density performance of polymer electrolyte fuel cells (PEFCs) is known to be limited by transport of reactants and products. In addition, at high current densities, excessive amount of water is generated and condenses, filling the pores of electrodes with liquid water, and hence limiting the reactant transport to active catalyst. This phenomenon known as "flooding" is an important limiting factor of PEFC performance. In this work, the governing physics of water transport in both hydrophilic and hydrophobic diffusion media is described along with one-dimensional analytical solutions of related transport processes. It is found that liquid water transport across the gas diffusion layer (GDL) is controlled by capillary forces resulting from the gradient in phase saturation. A one-dimensional analytical solution of liquid water transport across the GDL is derived, and liquid saturation in excess of 10% is predicted for a local current density of 1.4 A/cm<sup>2</sup>. Effect of GDL wettability on liquid water transport is explored in detail for the first time. Furthermore, the effect of flooding on oxygen transport and cell performance is investigated and it is seen that flooding diminishes the cell performance as a result of decreased oxygen transport and surface coverage of active catalyst by liquid water.

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Manuscript submitted June 26, 2003; revised manuscript received September 22, 2003. Available electronically February 5, 2004.

Polymer electrolyte fuel cells (PEFCs) have drawn much attention in the last decade as a promising candidate for high-efficiency, low-emission power sources. High-current-density operation of PEFCs, of special interest to vehicle applications, is prone to liquid water formation due to excessive water generation at the cathode. The ensuing two-phase transport of reactant and product species becomes a limiting mechanism for cell performance, particularly at high current densities, *i.e.*, >1 A/cm<sup>2</sup>. Therefore, a fundamental understanding of two-phase transport in porous gas diffusion layers (GDLs) of PEFCs is essential in order to improve performance.

The importance of water management to PEFC performance is repeatedly expressed in the literature.<sup>1-8</sup> A vast majority of currently available polymer electrolytes requires hydration in order to provide higher proton conductivity.<sup>1</sup> When the gas phase is saturated with water vapor, water condensation takes place and resulting liquid water starts to fill the open pores of the GDL and cover the catalyst particles, rendering them electrochemically inactive. This conflicting requirement of membrane hydration and electrode flooding avoidance must be met simultaneously in order to achieve higher performance. Flooding of electrodes is generally linked to high-current-density operation due to higher water production rate; yet, flooding can also be seen even at low current densities under certain operating conditions, such as low temperatures and low gas flow rates, due to faster saturation of gas phase with water vapor. For instance, in automotive fuel cells, cell startup is performed under ambient conditions in which the temperature is lower than the desired operating temperature, commonly referred as "cold start." At cold-start temperatures, the saturation vapor pressure of water is extremely low, therefore saturating the gas phase with water vapor. Hence, flooding may occur even in very low current densities, tremendously affecting the startup characteristics and transient dynamics of PEFC operation.

While numerous studies exist investigating the two-phase transport in PEFCs,<sup>9-17</sup> liquid water transport in hydrophobic GDL has not been explored. Several modeling studies have been published in order to predict PEFC performance at given flooding levels<sup>9-11</sup> without attempting to analyze the transport of liquid water. He *et al.*<sup>13</sup> has proposed a 2D two-phase model for PEFC with interdigitated flowfield, in which they have included capillary transport of liquid water in a completely wetted GDL. Wang *et al.*<sup>14</sup> has developed a two-phase model of the air cathode of PEFC also with a hydrophilic

GDL based on M<sup>2</sup> formulation of Wang and Cheng.<sup>18</sup> Subsequently, You and Liu<sup>15</sup> published a similar work investigating the effects of several operating parameters on two-phase transport. Although these abovementioned studies shed light on the effect of flooding on PEFC performance, they have not investigated and analyzed two-phase transport in hydrophobic GDL. A brief review of this subject was given most recently by Wang.<sup>19</sup>

The objective of this paper is to provide a fundamental understanding of liquid water transport in hydrophobic GDL and the effect of flooding on the PEFC performance. The paper starts with explaining the two-phase transport in hydrophobic porous GDL. Then, we define the onset of the two-phase mixture and derive a set of analytical equations using a control volume analysis of water balance to determine the threshold current density for two-phase occurrence. Finally, we give basic definitions of two-phase transport and provide one-dimensional solutions of liquid water and oxygen transport in GDL, and investigate the effect of liquid water, GDL wettability, and flooding on the performance of PEFC.

### Two-Phase Flow and Transport in Porous GDL

GDL is an essential component of PEFCs. It serves as a support for the polymer electrolyte membrane (PEM), distributes reactant gas over the catalyst layer, and conducts electrons from reaction sites to the outer circuit. Figure 1 shows scanning electron microscopy (SEM) images of commercial carbon-paper and carbon-cloth GDLs.<sup>20</sup> At high current densities, the electrochemical reaction rate is faster than the amount of reactants supplied, specifically oxidizer; therefore, the reaction rate is limited by the transport rate of oxidizer to the reaction sites, which is sandwiched between GDL and PEM. In addition, when the liquid water blocks some pores of GDL, the reactant transport is further limited. As such, PEFC GDL is commonly Teflonized to provide highly hydrophobic surface for easy removal of liquid water.

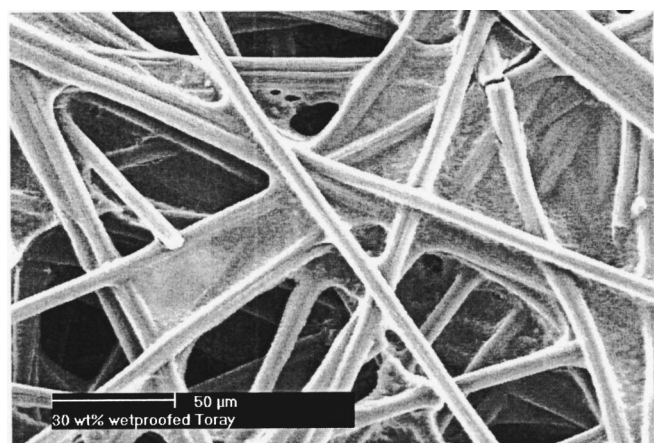
When water vapor pressure exceeds the saturation level, condensation starts, forming a tree-like liquid water percolation in the porous GDL, as illustrated in Fig. 2. The liquid water reaches the interface of porous GDL and open channel, forming liquid droplets. Inside GDL, liquid water is driven by capillary (wicking) action. This capillary action is a result of capillary pressure distribution, which is defined as the difference between gas and liquid-phase pressures. In hydrophobic GDL, the capillary pressure is negative; hence, the liquid pressure is larger than the gas-phase pressure, whereas in hydrophilic media, the gas-phase pressure is higher than that of the liquid phase

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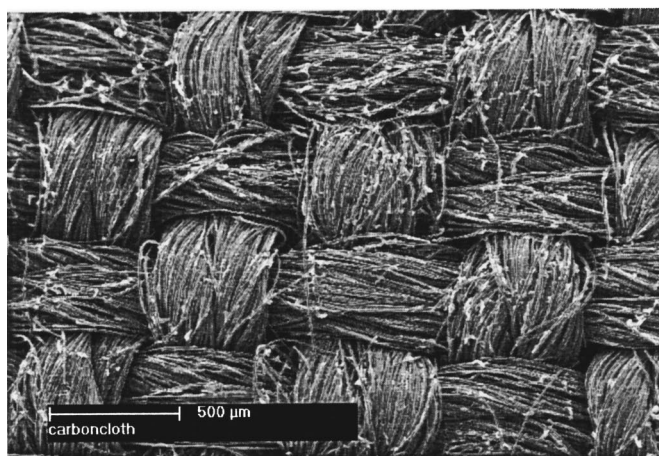
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$$p_c = p_g - p_l$$



(a) SEM of Toray Paper GDL



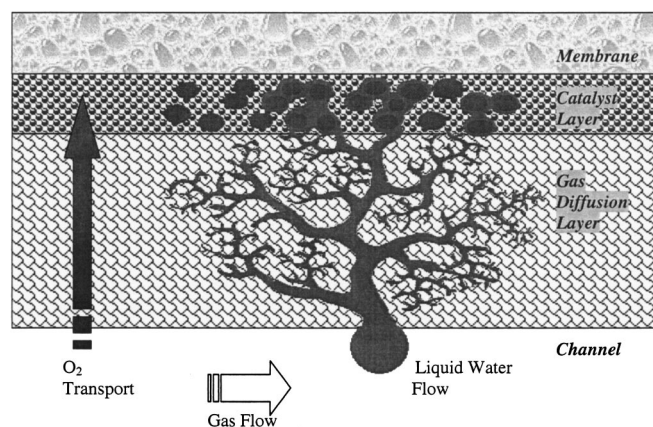
(b) SEM of Carbon Cloth GDL

**Figure 1.** Scanning electron microscopy (SEM) pictures of (a) carbon-paper and (b) carbon-cloth GDL.

$$\begin{aligned}
 p_c &> 0 \therefore p_g > p_l \quad \text{for } \theta_c < 90^\circ (\text{i.e., hydrophilic}) \\
 p_c &< 0 \therefore p_g < p_l \quad \text{for } \theta_c > 90^\circ (\text{i.e., hydrophobic})
 \end{aligned}
 \quad [1]$$

In addition, the liquid pressure increases with the fraction of void spaces occupied by liquid water; therefore, a liquid pressure gradient is formed from higher to lower liquid saturation regions. This pressure gradient becomes the driving force for liquid water flow, as schematically shown in Fig. 3. In PEFCs, the liquid saturation is higher at the catalyst layer, due to water generation and electro-osmotic drag, than the GDL-channel interface. Therefore, the liquid pressure gradient formed in the GDL drives liquid water from the reaction sites toward the open channel. Figure 3 also displays a nearly constant gas pressure profile across the two-phase zone due to much lower gas-phase viscosity. That is, it does not incur much gas pressure drop to drive the gas flow through thin GDLs.

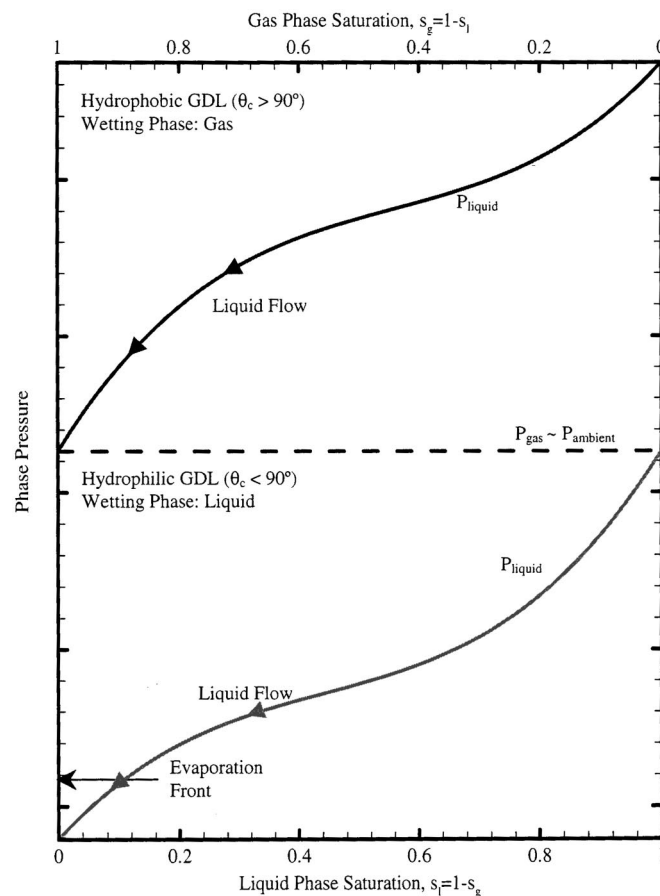
It is interesting to note from Fig. 3 that although the relative magnitude of the liquid to gas pressure is different in hydrophobic GDL than the hydrophilic one, both media provide capillary action to drive liquid water from the inside to its surface. However, the slope of the capillary pressure (i.e., the driving force) is different depending on whether water is the wetting or nonwetting phase. The greater slope of the capillary pressure near the evaporation front (i.e.,  $s \sim 0$ ) in hydrophobic GDL is indicative of more effectiveness of this type of medium for water removal.



**Figure 2.** Transport processes in hydrophobic GDL of PEFC.

The shape of the liquid droplets emerging at the channel—GDL interface is governed by the wetting characteristics of the GDL surface. On a hydrophilic surface, which has a contact angle of less than  $90^\circ$ , liquid spreads over it, whereas on a hydrophobic surface, which has a contact angle greater than  $90^\circ$ , the droplet is more of a sphere-like shape, covering less pore entry, as pictured in Fig. 4.<sup>20</sup>

*Onset of the two-phase regime.*—In this section, an analytical solution predicting the onset of two-phase flow is presented in one-dimension, considering the water transport phenomena in the through-plane direction, i.e., from the anode to cathode. The goal is



**Figure 3.** Schematic illustration of liquid and gas-phase pressure profiles in hydrophilic and hydrophobic porous media.

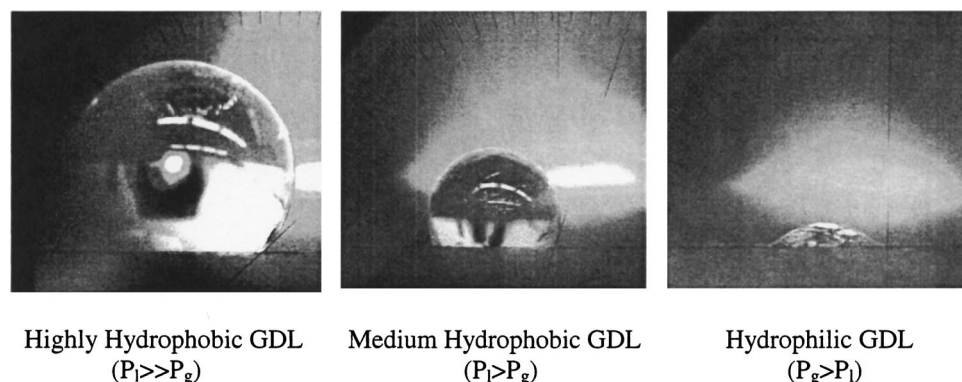


Figure 4. Liquid water droplets on GDL of different wettability at 70°C.<sup>20</sup>

to estimate the threshold local current density under which two-phase conditions start to appear. This onset is defined when the maximum water vapor concentration, occurring at the cathode GDL-membrane interface, becomes equal to the saturation value corresponding to the cell temperature.

Water transport in PEFCs is governed by the following phenomena: generation of water at the cathode due to the oxygen reduction reaction (ORR), forward (*i.e.*, anode to cathode) or backward (*i.e.*, cathode to anode) diffusion of water across the membrane, electro-osmotic drag of water from anode to cathode, and convective removal of water to the gas channel. The considered domain for derivation is sketched in Fig. 5.

The convective mass-transfer coefficient at the channel-GDL interface is calculated using the analogy between heat and mass transfer. It is known that the Nusselt number (*i.e.*, dimensionless heat-transfer coefficient) is constant for laminar flow in ducts and is equal to 4.36 for the constant heat flux condition and 3.66 for the constant surface temperature. Furthermore, using the heat/mass-transfer analogy, the Sherwood number (*i.e.*, dimensionless mass-transfer coefficient) can also be correlated with the Nusselt number with the ratio of Schmidt number to Prandtl number ( $Sc/Pr$ ). This reveals that the Sherwood number, and hence, the mass-transfer coefficient, is independent of flow velocity in the channel. It follows that the convective mass-transfer coefficient can be calculated as

$$Sh_D = Nu_D \frac{Sc}{Pr} \quad [2]$$

$$h_m = \frac{Sh_D D^{H_2O}}{D_h} \quad [3]$$

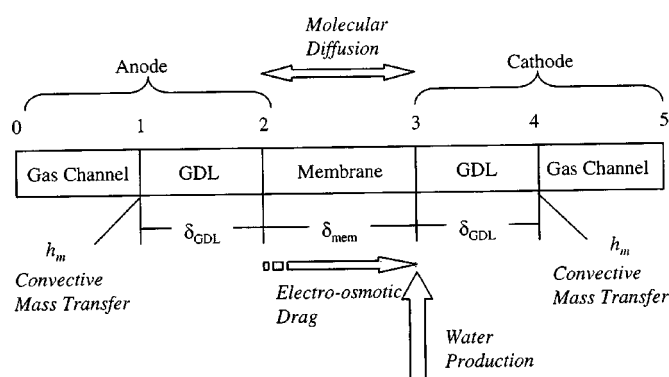


Figure 5. One-dimensional control volume and related transport processes for analysis of the onset of two-phase regime.

A control volume analysis of water balance under steady-state conditions at points 1-4 of Fig. 5 provides a set of linear equations for unknowns of  $C_1^{H_2O}$ ,  $C_2^{H_2O}$ ,  $C_4^{H_2O}$ , and  $I_{onset}$ . These relations are

$$h_{m,a}(C_1^{H_2O} - C_0^{H_2O}) = D_{GDL,a}^{H_2O} \frac{C_2^{H_2O} - C_1^{H_2O}}{\delta_{GDL}} \quad [4]$$

Anode GDL—membrane interface -2-

$$D_{GDL,a}^{H_2O} \frac{C_2^{H_2O} - C_1^{H_2O}}{\delta_{GDL}} - D_{mem}^{H_2O} \frac{C_3^{H_2O} - C_2^{H_2O}}{\delta_{mem}} = -n_d \frac{I}{2F} \quad [5]$$

Membrane—cathode GDL interface -3-

$$D_{GDL,c}^{H_2O} \frac{C_3^{H_2O} - C_4^{H_2O}}{\delta_{GDL}} + D_{mem}^{H_2O} \frac{C_3^{H_2O} - C_2^{H_2O}}{\delta_{mem}} = (2n_d + 1) \frac{1}{2F} \quad [6]$$

Cathode GDL—membrane interface -4-

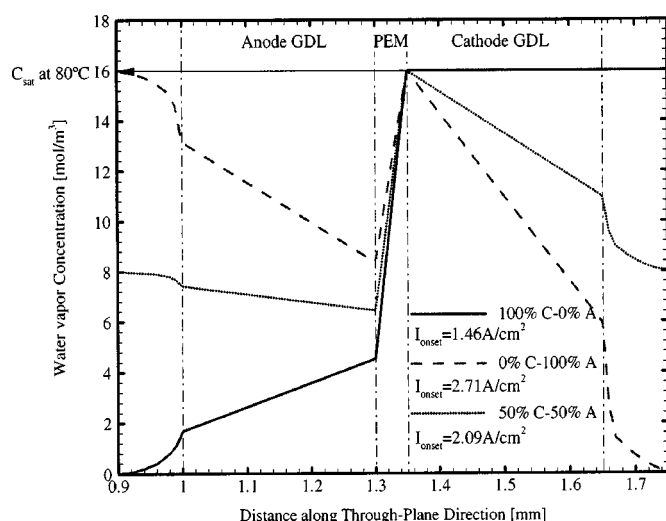
$$h_{m,c}(C_4^{H_2O} - C_5^{H_2O}) = D_{GDL,c}^{H_2O} \frac{C_3^{H_2O} - C_4^{H_2O}}{\delta_{GDL}} \quad [7]$$

For this part of the work, membrane water content is assumed to be constant across its thickness and is calculated from the arithmetic average of water contents on the anode and cathode sides of the membrane. Water diffusion coefficient in the membrane is calculated by an empirical relation<sup>2,3</sup> using this average water content. Water vapor diffusion coefficient in the GDL is corrected for tortuosity effects using the Bruggeman correlation.

Note that the values of  $C_0^{H_2O}$  and  $C_5^{H_2O}$  correspond to the free-stream water concentrations in the anode and cathode channels, respectively. Hence, these values correspond to the humidification levels of channel flow. Setting  $C_3^{H_2O} = C^{H_2O,sat}$ ,  $I_{onset}$  can be found by solving the above set of linear equations. This threshold local current density, characterizing the onset of liquid water, also defines the maximum value of local current density at that corresponding cell location in which the cell operates in the single-gas-phase transport and flow conditions.

Figure 6 shows the water concentrations at the threshold current density at various interfaces across the membrane electrode assembly (MEA) for different humidity levels. It is seen that at the threshold current density, the net water flux is toward the anode when the anode channel is completely dry. However, when the anode and cathode channels have the same humidity, *i.e.*, 50% relative humidity, the net water flux is toward the cathode due to the electro-osmotic drag of water molecules, as signaled by decreasing water concentration through the anode GDL toward the membrane.

The solution shown in Fig. 7 assumes that the in-plane gradients



**Figure 6.** Water concentration at various important locations in the through-plane direction for different anode and cathode relative humidities.

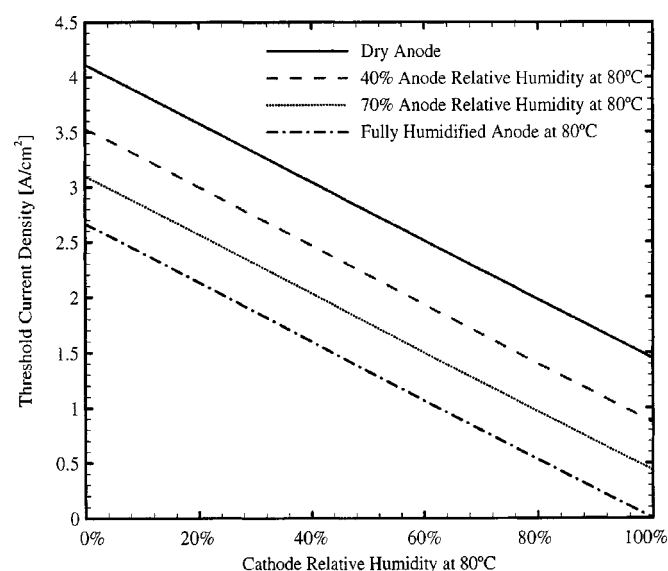
of water concentration, *e.g.*, along the channel or in the channel-to-land direction, are negligibly small and hence considers only the transport of water in anode to cathode (through-plane) direction. However, in low-stoichiometry cases, there are strong in-plane gradients, thereby requiring multidimensional numerical modeling. This is addressed in a companion paper.<sup>21</sup>

**Basic parameters of two-phase flow in GDL.**—**Liquid saturation.**—Liquid saturation,  $s$ , is defined as the volume fraction of the total void space of porous media occupied by the liquid phase. Hence,  $s$  is defined as

$$s = \frac{V_l}{V} \quad [8]$$

Saturation may vary from zero to unity and saturations of all phases add up to unity.

**Relative permeability.**—In liquid-gas two-phase flow in porous media, the available pore space is shared by liquid and gas; thus, the



**Figure 7.** Variation of threshold local current density for onset of two-phase with anode and cathode channel relative humidities.

cross-sectional area available for each fluid is less than the total available pore space. This phenomenon introduces the concept of relative permeability  $k_{rk}$ , which defines the ratio of intrinsic permeability of a phase  $k$  at a given saturation level to the total intrinsic permeability of the porous medium.<sup>18</sup> In this work, GDL is assumed to be a homogeneous porous medium, with relative permeabilities proportional to the cube of phase saturation, *i.e.*

$$k_{rl} = s^3; \quad k_{rg} = (1 - s)^3 \quad [9]$$

**Capillary pressure.**—Capillary pressure between two phases is expressed as

$$p_c = \sigma \cos \theta_c \left( \frac{\varepsilon}{K} \right)^{1/2} J(s) \quad [10]$$

where  $J(s)$  is the Leverette function and is given by the following relation

$$J(s) = \begin{cases} 1.417(1 - s) - 2.120(1 - s)^2 + 1.263(1 - s)^3 & \text{if } \theta_c < 90^\circ \\ 1.417s - 2.120s^2 + 1.263s^3 & \text{if } \theta_c > 90^\circ \end{cases} \quad [11]$$

Note that for a hydrophilic medium, the wetting phase is the liquid phase. Therefore the Leverette function is expressed in the gas-phase saturation, whereas in hydrophobic medium, the gas phase becomes the wetting phase and so the liquid-phase saturation is used. Contact angle,  $\theta_c$ , of the GDL is dependent upon the hydrophilic ( $0^\circ < \theta_c < 90^\circ$ ) or hydrophobic ( $90^\circ < \theta_c < 180^\circ$ ) nature of the GDL, and varies with the Teflon content. Here, the surface tension  $\sigma$ , for the liquid water-air system is taken as 0.0625 N/m.

**One-dimensional solution of liquid water transport across GDL.**—Liquid water flow in GDL is driven by the liquid pressure gradient according to Darcy's law. Once the gas phase in GDL is fully saturated with water vapor, the only mode of water transport across the GDL is then the liquid water flow. At steady state, the mass flux of liquid water is equal to the amount of water generated due to the ORR, if the net transport of water across membrane is assumed to be zero. Therefore

$$\frac{1}{2F} M^{H_2O} = \frac{k_{rl}}{\nu} K [\nabla p_c + (\rho_l - \rho_g) \mathbf{g}] \quad [12]$$

Here use has been made of the assumption that the gas-phase pressure remains constant throughout the GDL and is equal to the ambient pressure in the cathode gas channel. Furthermore, because of the very small dimensional scales in PEFC geometry, the gravity effect can be neglected. Substituting Eq. 10 into the Eq. 12 results in

$$\frac{I}{2F} M^{H_2O} = -\frac{s^3}{\nu} K \sigma \cos \theta_c \left( \frac{\varepsilon}{K} \right)^{1/2} \nabla J(s) \quad [13]$$

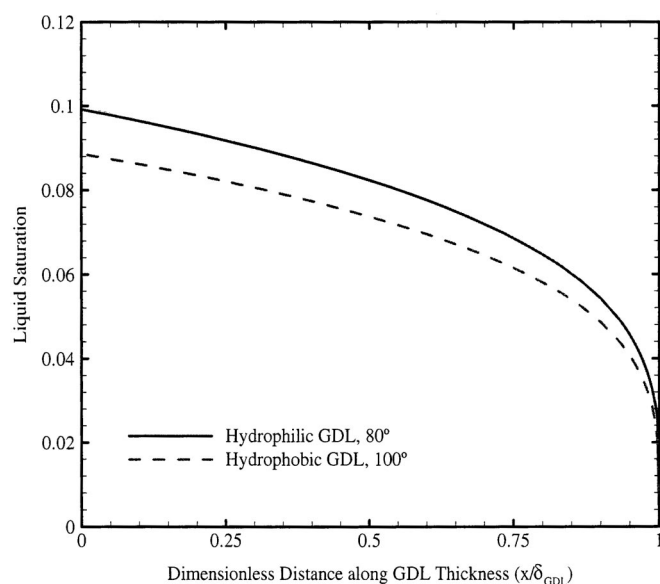
For hydrophobic media, the Leverette function is

$$J(s) = 1.417s - 2.120s^2 + 1.263s^3 \quad [14]$$

Combining Eq. 13 and 14 yields

$$\frac{I}{2F} M^{H_2O} = -\frac{\sigma \cos \theta_c (\varepsilon K)^{1/2}}{\nu} s^3 (1.417 - 4.240s + 3.789s^2) \nabla^2 \quad [15]$$

Considering the one-dimensional transport of liquid water only in the through-plane direction, the Eq. 15 reduces to an ordinary differential equation, which can be solved analytically. For hydrophobic ( $\theta_c > 90^\circ$ ) GDL



**Figure 8.** Liquid saturation profile across GDL predicted by 1D analytical solution of liquid water transport.

$$s^3(1.417 - 4.240s + 3.789s^2) \frac{ds}{dx} = \frac{I}{2F} M^{\text{H}_2\text{O}} \frac{\nu}{\sigma \cos \theta_c (\varepsilon K)^{1/2}} \quad [16]$$

or

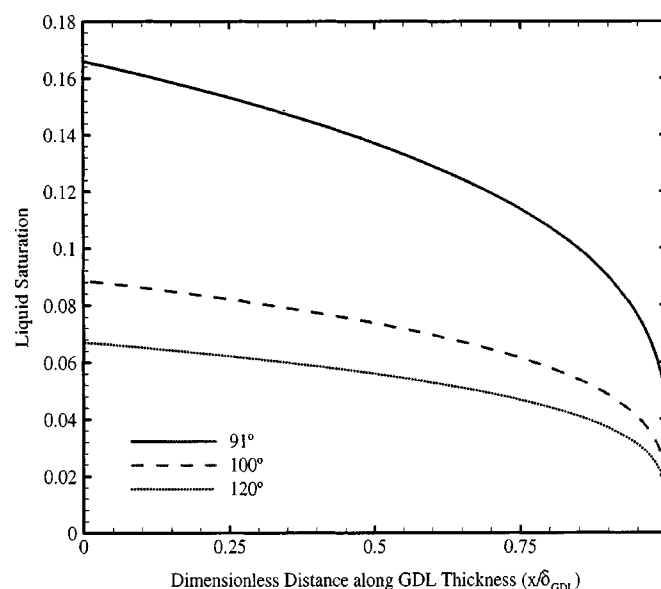
$$s^4(0.35425 - 0.8480s + 0.6135s^2) = \frac{I}{2F} M^{\text{H}_2\text{O}} \frac{\nu}{\sigma \cos \theta_c (\varepsilon K)^{1/2}} x + C_1 \quad [17]$$

Following the same procedure, the following equation is derived for hydrophilic ( $\theta_c < 90^\circ$ ) GDL

$$s^4(-0.2415 + 0.6676s - 0.6135s^2) = \frac{I}{2F} M^{\text{H}_2\text{O}} \frac{\nu}{\sigma \cos \theta_c (\varepsilon K)^{1/2}} x + C_1 \quad [18]$$

In these equations, the integration constant  $C_1$  is governed by the boundary condition, which is the liquid saturation at the GDL-channel interface. Once liquid saturation at this boundary is known,  $C_1$  can be easily calculated. Here, for simplicity, it is assumed that no liquid water is present in the open channel.

For a local current density of  $1.4 \text{ A/cm}^2$ , the saturation profiles obtained from this equation for GDLs having contact angles of 80 and  $100^\circ$  are given in Fig. 8. The results show that the liquid saturation level at the GDL-catalyst layer interface can be as high as 10%, even in the case of no liquid water in the gas channel, which may result in severe flooding. Note that in this case the net water transport across the membrane is neglected; however, in real PEFC operation, there may be a significant water transport from anode to cathode due to electro-osmotic drag, especially if the anode stream is well humidified. In addition, it is also seen that the liquid saturation level near the catalyst layer interface is higher for hydrophilic than hydrophobic media, suggesting a higher water removal rate for hydrophobic ( $\theta_c > 90^\circ$ ) GDL. This is because the liquid water flow is driven by the liquid pressure gradient, and the latter depends on the first derivative of the liquid pressure with respect to liquid saturation. It is seen from Fig. 3 that the slope of liquid pressure curve is steeper for hydrophobic GDL at lower liquid saturations (*i.e.*, up to



**Figure 9.** Liquid saturation profile across GDL predicted by 1D analytical solution of liquid water transport for different contact angles.

20%); therefore, the liquid water removal rate is higher than hydrophilic GDL. This is one distinctive advantage of using hydrophobic GDL in PEFC.

Figure 9 shows the effect of contact angle of hydrophobic GDL on the liquid water distribution. It is seen that the water distribution has a great dependence on contact angle, and the larger the contact angle than  $90^\circ$ , *i.e.*, the more hydrophobic, the lower the liquid saturation at the catalyst layer-GDL interface.

**Effect of flooding on performance.**—As mentioned earlier, flooding reduces the fuel cell performance in two separate manners: (i) by hindering the oxygen transport from the gas channel to the reaction sites and (ii) by covering electrochemically active sites with liquid water. These phenomena can be studied by a simple analysis if the catalyst layer is assumed infinitely thin and the cathode liquid saturation is uniform. Oxygen is transported from the cathode gas channel to the cathode GDL via convection, and then diffuses through the cathode GDL to the catalyst layer. In this derivation, convective transport of oxygen across porous GDL is neglected. When the catalyst layer is assumed infinitely thin, ORR now occurs at the membrane-GDL interface, and the oxygen consumption rate by electrochemical reaction, ORR, is given by

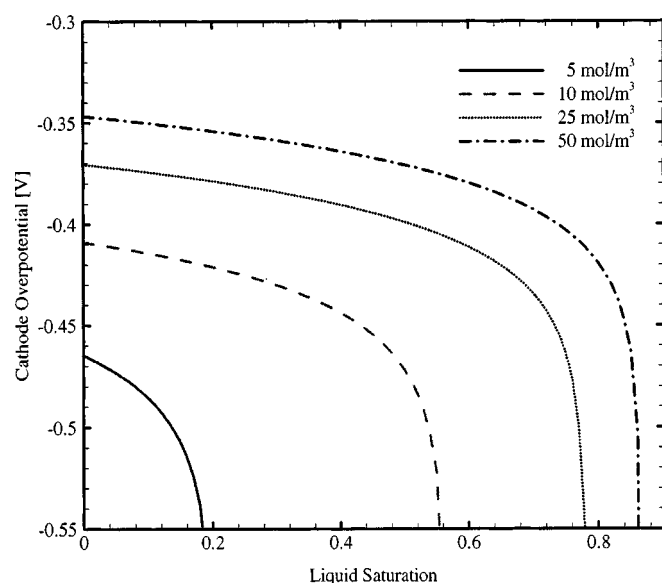
$$j_{\text{rxn}}^{\text{O}_2} = \frac{I}{4F} \quad [19]$$

per unit reaction surface. Electrochemical kinetics is governed by the Butler-Volmer equation, and because the cathode kinetics is sufficiently sluggish, that can be expressed by Tafel kinetics, *i.e.*,

$$I = (1 - s) a_{\text{O}_2}^{\text{ref}} \frac{C_{\text{rxn}}^{\text{O}_2}}{C_{\text{ref}}^{\text{O}_2}} \exp\left(-\frac{\alpha_c F}{RT} \eta\right) \quad [20]$$

In Eq. 20, the factor  $(1 - s)$  represents the active area reduction due to liquid water coverage of catalyst particles.

Oxygen is transported from the channel to the reaction zone via convection in the gas channel and molecular diffusion in the GDL. Therefore, the molar flux of oxygen from the gas channel to the reaction site can be expressed as



**Figure 10.** Cathode overpotential vs. liquid saturation in cathode GDL for different channel oxygen concentrations. Local current density is  $2 \text{ A/cm}^2$ .

$$j_{\text{O}_2} = \frac{C_{\text{ch}}^{\text{O}_2} - C_{\text{rxn}}^{\text{O}_2}}{\frac{\delta_{\text{GDL}}}{D_{\text{O}_2}[\varepsilon(1-s)]^{1.5}} + \frac{1}{h_m}} \quad [21]$$

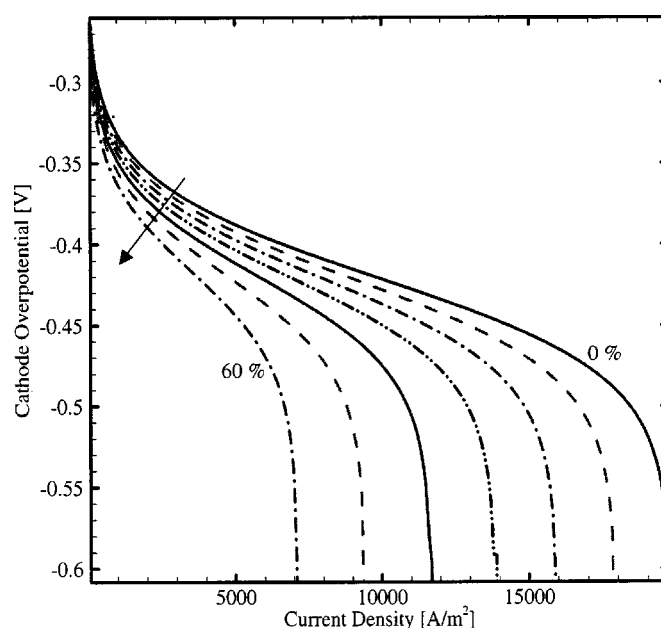
In this equation,  $C_{\text{ch}}^{\text{O}_2}$  and  $C_{\text{rxn}}^{\text{O}_2}$  refers to the oxygen concentration in the gas channel and at the reaction site, respectively, while  $h_m$  represents the convective mass-transfer coefficient at the channel-GDL interface. Convective mass-transfer coefficient is calculated using the same analogy of heat and mass transfer, as explained earlier, and found to be  $0.032 \text{ m/s}$  for a square gas channel of  $1 \text{ mm}$ . The molar flux of oxygen is equal to the consumption rate of oxygen. Therefore, using Eq. 20 and 21, oxygen molar concentration at the reaction surface is calculated as

$$C_{\text{rxn}}^{\text{O}_2} = C_{\text{ch}}^{\text{O}_2} - \frac{I}{4F} \left[ \frac{\delta_{\text{GDL}}}{D_{\text{O}_2}[\varepsilon(1-s)]^{1.5}} + \frac{1}{h_m} \right] \quad [22]$$

Inserting the expression for oxygen concentration at the reaction site from Eq. 22 to the cathode kinetics equation, Eq. 20, one can obtain the cathode overpotential as a function of oxygen concentration in the channel, liquid saturation in the GDL, and the local current density, as follows

$$\eta(s, I, C_{\text{ch}}^{\text{O}_2}) = -\frac{RT}{\alpha_c F} \ln \left[ \frac{IC_{\text{ref}}^{\text{O}_2}}{(1-s)aI_0^{\text{ref}}} \times \frac{1}{C_{\text{ch}}^{\text{O}_2} - \frac{I}{4F} \left[ \frac{\delta_{\text{GDL}}}{D_{\text{O}_2}[\varepsilon(1-s)]^{1.5}} + \frac{1}{h_m} \right]} \right] \quad [23]$$

In Fig. 10, the cathode overpotential is plotted vs. liquid saturation in GDL, using Eq. 23, for a local current density of  $2 \text{ A/cm}^2$  and different channel oxygen concentrations. It is seen that the sharp increase in the cathode overpotential, which identifies the mass-transfer limitation of the cathode reaction, may be seen above 75% liquid saturation when channel oxygen concentration is  $50 \text{ mol/m}^3$ , which approximately corresponds to the oxygen concentration near the inlet of a pure oxygen feed PEFC at  $80^\circ\text{C}$  and  $1.5 \text{ atm}$ . However,



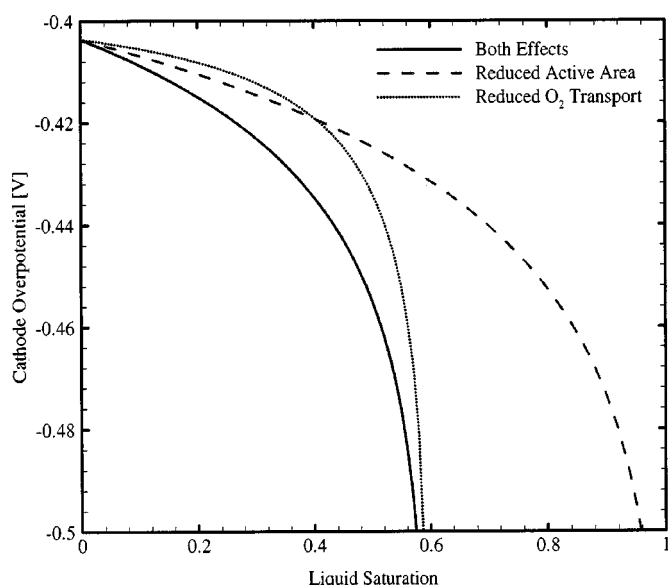
**Figure 11.** Cathode overpotential vs. local current density for different liquid saturations in GDL. Oxygen concentration in the channel is  $4 \text{ mol/m}^3$ .

it is also seen that for a free-stream oxygen concentration of  $5 \text{ mol/m}^3$ , which may correspond to the oxygen concentration near the outlet of an air-feed PEFC operating at a stoichiometric ratio of 2, the mass-transfer limitation starts to appear at as low as 10% liquid saturation.

In Fig. 11, the cathode overpotential vs. local current density is plotted for different liquid saturation values, for an oxygen concentration in the channel of  $4 \text{ mol/m}^3$ . As expected, magnitude of the cathode overpotential increases with increasing local current density. Furthermore, increase in the liquid saturation of GDL results in an increase in cathode overpotential. The increase in the cathode overpotential with increasing liquid saturation is slighter for low current densities and becomes much higher at high current densities. This is attributed to the fact that at higher current densities, the cathode reaction requires more oxygen and the reaction rate is limited by the rate of oxygen transport to the reaction sites. However, in lower current densities the cathode reaction is controlled by activation losses; hence, the change in the cathode overpotential with increasing liquid saturation is not as high as at higher current densities. It is also clearly seen that the limiting current density is controlled by the amount of liquid water present in GDL and catalyst layer.

The analytical expression obtained can be further utilized to separate the two effects of flooding: (i) coverage of active catalyst areas by liquid water and (ii) hindering of oxygen transport by liquid water. In Fig. 12, the hypothetical cases of cathode overpotential are plotted for a local current density of  $2 \text{ A/cm}^2$  near the inlet with a channel oxygen concentration of  $10 \text{ mol/m}^3$ . In the first case, both of the limitations resulting from liquid water are considered. In the second case, it is assumed that liquid water does not cover any active reaction sites; therefore no active area reduction is considered and only the  $\text{O}_2$  transport limitation by liquid water is accounted for. In the last case, it is assumed that the liquid water presence does not interfere with  $\text{O}_2$  transport. Hence, only the effect of coverage of active reaction sites by liquid water is considered. It is seen that the limitation of oxygen transport by liquid water is more dominant over the entire liquid saturation range. Therefore, it is concluded that the primary effect of flooding on the PEFC performance is the reduced effective oxygen diffusivity in GDL due to the filling of pores with liquid water.

The same approach that is used to describe cathode polarization can be used to quantify the anode polarization. In addition, ohmic



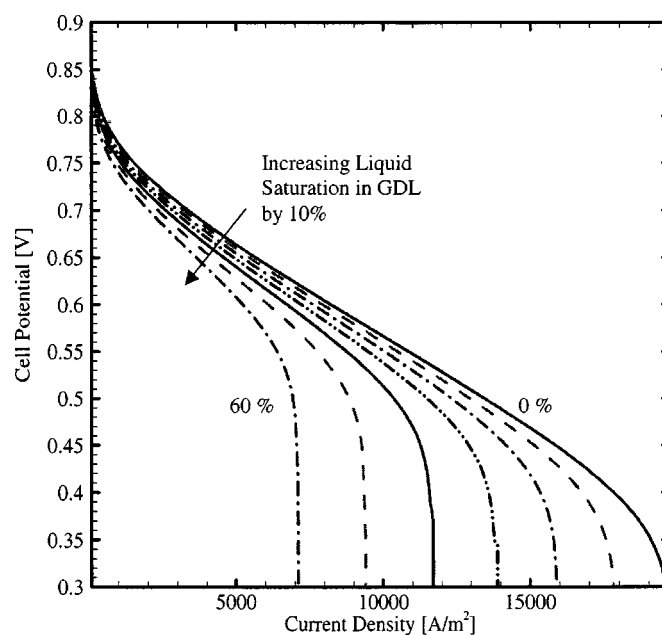
**Figure 12.** Separate flooding effect of reduced oxygen transport and reduced active area on cathode overpotential. Oxygen concentration in the channel is  $10 \text{ mol/m}^3$ .

losses associated with ionic transport can be determined, assuming that the membrane is fully saturated with liquid water. Under these assumptions, the cell potential can be easily determined by

$$V_{\text{cell}} = V_{\text{oc}} - \eta_a - \eta_c - IR \quad [24]$$

The cell dimensions and operating parameters for these calculations are given in Table I. Because the membrane is assumed to be fully hydrated by liquid water, the membrane ionic conductivity is constant and the ionic losses in membrane and catalyst layers can be approximated as

$$IR = I \left( \frac{\delta_{\text{mem}}}{\kappa_{\text{mem}}} + 2 \frac{\delta_{\text{cl}}}{\kappa_{\text{cl}}} \right) \quad [25]$$



**Figure 13.** Local polarization (I-V) curves for different liquid saturations in cathode GDL.

In Fig. 13, the local cell potential is plotted for channel concentrations of 20 and  $4 \text{ mol/m}^3$  of hydrogen and oxygen, respectively, for different liquid saturations in cathode GDL and catalyst layer. The selected values of concentrations correspond to the downstream of an air-feed PEFC operating at  $80^\circ\text{C}$  and 1.5 atm. It is clearly seen that the cell performance is limited by the cathode transport and electrochemical kinetics. As expected, the increasing liquid saturation pulls down the polarization curve, reducing the overall performance of the fuel cell.

The analytical derivations show that the presence of liquid water in porous GDL can dramatically decrease the performance of PEFCs, especially in the cases of low  $\text{O}_2$  concentrations in the channel and higher current density.

**Table I. Electrochemical and transport properties.**

| Description                                                                                            | Unit                       | Value                   |
|--------------------------------------------------------------------------------------------------------|----------------------------|-------------------------|
| Electrochemical kinetics (typical values)                                                              |                            |                         |
| Anode reference exchange current density                                                               | $\text{A/m}^2$             | $1.0 \times 10^9$       |
| Cathode reference exchange current density                                                             | $\text{A/m}^2$             | 20000.0                 |
| Anode transfer coefficient                                                                             |                            | 2                       |
| Cathode transfer coefficient                                                                           |                            | 1                       |
| Faraday constant                                                                                       | $\text{C/mol}$             | 96,487.0                |
| Transport parameters                                                                                   |                            |                         |
| $\text{H}_2$ diffusivity in gas at 353 K and 1.5 atm <sup>22</sup>                                     | $\text{m}^2/\text{s}$      | $3.524 \times 10^{-5}$  |
| $\text{O}_2$ diffusivity in gas at 353 K and 1.5 atm <sup>22</sup>                                     | $\text{m}^2/\text{s}$      | $1.805 \times 10^{-5}$  |
| $\text{H}_2\text{O}$ diffusivity in gas at 353 K and 1.5 atm <sup>22</sup>                             | $\text{m}^2/\text{s}$      | $2.235 \times 10^{-5}$  |
| $\text{H}_2\text{O}$ diffusivity in membrane (at $\lambda_{\text{ave}} = 5.8$ , estimated from Ref. 9) | $\text{m}^2/\text{s}$      | $9.858 \times 10^{-7}$  |
| Liquid water viscosity <sup>22</sup>                                                                   | $\text{Pa} \cdot \text{s}$ | $3.56 \times 10^{-4}$   |
| Surface tension <sup>22</sup>                                                                          | $\text{N/m}$               | 0.0625                  |
| Material properties                                                                                    |                            |                         |
| Anode GDL porosity                                                                                     |                            | 0.5                     |
| Cathode GDL porosity                                                                                   |                            | 0.5                     |
| Anode GDL permeability                                                                                 | $\text{m}^2$               | $6.875 \times 10^{-13}$ |
| Cathode GDL permeability                                                                               | $\text{m}^2$               | $6.875 \times 10^{-13}$ |
| Contact angle of GDL <sup>20</sup>                                                                     | $^\circ$                   | 110                     |
| Volume fraction of ionomer in catalyst layer                                                           |                            | 0.2                     |
| Equivalent weight of membrane (Nafion 112)                                                             | $\text{kg/mol}$            | 1.1                     |
| Dry density of membrane (Nafion 112)                                                                   | $\text{kg/m}^3$            | $1.98 \times 10^3$      |

### Conclusions

The governing physics of liquid water transport in hydrophobic GDL has been presented. It is seen that capillary transport is the dominant transport process to remove water from flooded GDLs. An analytical model was developed to estimate the onset of the two-phase regime in GDLs and the associated threshold current density as a function of various anode and cathode relative humidity combinations. In the two-phase regime, a one-dimensional analytical solution was derived for liquid water transport in both hydrophilic and hydrophobic GDL, and the important role of GDL wettability is elucidated. Finally, the effect of flooding on oxygen transport and cell performance was analyzed, and significant decrease in performance is predicted with increased level of flooding, particularly at high current densities, in accordance with experimental observations. Based on the physics described herein for liquid water transport in hydrophobic GDL, 3D modeling of two-phase transport and flooding in a full PEFC is described in the companion paper.<sup>21</sup>

It is expected that the two-phase transport in PEFCs has different transient characteristics than its single-phase counterpart. Hence, efforts are presently underway to study the effects of liquid water transport and flooding on transient and hysteretic behaviors of PEFCs. In addition, there is a lack of fundamental experiments on water transport in GDLs, and no correlations exist for two-phase transport properties directly relevant to PEFC GDLs, such as relative permeability and capillary pressure. These are the areas of ongoing work in our laboratory.

### Acknowledgments

Funding for this work from Department of Energy under cooperative agreement no. DE-FC26-01NT41098, ConocoPhillips, GM Foundation, and NSF under grant no. CTS-9733662 is gratefully acknowledged.

The Pennsylvania State University assisted in meeting the publication costs of this article.

### List of Symbols

|           |                                                                          |
|-----------|--------------------------------------------------------------------------|
| $ai_o$    | transfer current density $\times$ active catalyst area, A/m <sup>3</sup> |
| $C^i$     | molar concentration of species $i$ , mol/m <sup>3</sup>                  |
| $D_h$     | hydraulic diameter, m                                                    |
| $D^i$     | mass diffusivity of species $i$ , m <sup>2</sup> /s                      |
| $F$       | Faraday's constant, 96,487 C/mol                                         |
| $\bar{g}$ | gravity, m/s <sup>2</sup>                                                |
| $h_m$     | convective mass-transfer coefficient, m/s                                |
| $I$       | local current density, A/m <sup>2</sup>                                  |
| $j$       | molar flux, mol/m <sup>2</sup> s                                         |
| $K$       | permeability, m <sup>2</sup>                                             |
| $k_{rk}$  | relative permeability of phase $k$                                       |
| $M^i$     | molecular weight of species $i$ , kg/mol                                 |
| $n_d$     | electro-osmotic drag coefficient                                         |
| $Nu$      | Nusselt number                                                           |
| $p$       | pressure                                                                 |
| $p_c$     | capillary pressure                                                       |
| $Pr$      | Prandtl number                                                           |
| $R$       | universal gas constant, 8.314 J/mol K                                    |
| $s$       | liquid saturation                                                        |
| $Sc$      | Schmidt number                                                           |
| $Sh$      | Sherwood number                                                          |

|     |                |
|-----|----------------|
| $T$ | Temperature, K |
| $V$ | potential, V   |

### Greek

|               |                                        |
|---------------|----------------------------------------|
| $\delta_i$    | thickness of component $i$             |
| $\varepsilon$ | porosity                               |
| $\eta$        | overpotential, V                       |
| $\theta_c$    | contact angle, °                       |
| $\kappa$      | proton conductivity, S/m               |
| $\nu$         | kinematic viscosity, m <sup>2</sup> /s |
| $\sigma$      | surface tension, N/m                   |

### Subscripts

|      |                     |
|------|---------------------|
| $a$  | anode               |
| $c$  | cathode             |
| $ch$ | channel             |
| $cl$ | catalyst layer      |
| $g$  | gas                 |
| GDL  | gas diffusion layer |
| $l$  | liquid              |
| mem  | membrane            |
| oc   | open circuit        |
| ref  | reference           |
| rxn  | reaction            |
| sat  | saturation          |

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