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Liquid-Water Interactions with Gas-Diffusion-Layer Surfaces

Anthony D. Santamaria,^{a,*} Prodip K. Das,^{b,**} James C. MacDonald,^a
and Adam Z. Weber^{a,*,*,z}

^aEnvironmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

^bSchool of Mechanical and Systems Engineering, Newcastle University, Newcastle-upon-Tyne, NE1 7RU, United Kingdom

Understanding dynamic liquid-water uptake and removal in gas-diffusion layers (GDLs) is essential to improve the performance of polymer-electrolyte fuel cells and related electrochemical technologies. In this work, GDL properties such as breakthrough pressure, droplet adhesion force, and detachment velocity are measured experimentally for commonly used GDLs under a host of test conditions. Specifically, the effects of GDL hydrophobic (PTFE) content, thickness, and water-injection area and rate were studied to identify trends that may be beneficial to the design of liquid-water management strategies and next-generation GDL materials. The results conclude that liquid water moving transversely through or forming at the surface of GDL may be affected by internal capillary structure. Adhesion-force measurements using a bottom-injection method were found to be sensitive to PTFE loading, GDL thickness, and injection area/rate, the latter of which is critical for defining the control-volume limits for modeling and analysis. It was observed that higher PTFE loadings, increased thickness, and smaller injection areas led to elevated breakthrough pressure; meaning there was a greater resistance to forming droplets. The data are used to predict the onset of droplet instability via a simple force-balance model with general trend agreement.

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Polymer-electrolyte fuel-cell (PEFC) and redox flow-battery (RFB) systems have the potential to improve energy efficiency and storage capabilities for mobile and grid-level applications in the near future. In PEFCs, the electrode structure is composed of a catalytic layer supported by porous gas-diffusion layers (GDLs) where multi-phase reactant/product transport and electron conduction occur. Product liquid water can contribute to performance and degradation issues if not properly handled. Numerous studies have shown the importance of water-management strategies during start-up/shutdown and cooler operation where lower cell temperatures may lead to liquid buildup.^{1–15} In RFBs, GDLs serve a similar purpose of effective reactant distribution, especially for gaseous cells,^{16,17} as well as serving as possible catalysts.¹⁸ Understanding multiphase, dynamic GDL water uptake and removal is essential to develop effective liquid-water management schemes as well as next-generation GDL materials for improved PEFC and RFB performance, stability, and component lifetimes.

The influence of the porous-electrode structure on liquid/gas transport and PEFC performance has been studied by several groups focusing on the role of GDL and microporous layer (MPL) effects.^{19–22} Capillary and viscous forces govern two-phase flow through GDLs; the dimensionless parameters that quantify them are the capillary number and viscosity ratio defined as

$$Ca = u\mu_{nw}/\gamma \quad [1]$$

and

$$M = \mu_{nw}/\mu_{wet} \quad [2]$$

respectively, where u is the superficial velocity of the non-wetting phase, γ is the surface tension, and μ is the wetting (wet) and non-wetting (nw) phase viscosities.^{10,23} Under normal PEFC operation, capillary forces dominate, with Ca between 10^{-8} to 10^{-5} and M around 17.5, indicating capillary-fingering flow.^{10,24} The need to understand complex, capillary-driven transport through GDLs and implications for water removal has led to focused efforts to characterize properties such as breakthrough pressure and droplet adhesion force; both of which represent key barriers to liquid-water removal.²⁵

Breakthrough pressure, sometimes referred to as threshold pressure, is related to the capillary pressure and is determined predominantly by the pore structure and the contact angle between a liquid droplet and the GDL. The Young-Laplace equation defines capillary pressure, P_c , as

$$P_c = P_L - P_G = -\frac{2\gamma \cos(\theta)}{r} \quad [3]$$

where θ is the contact angle between water/air and GDL, and r is the radius of a pore.²⁶ Water invasion into a hydrophobic GDL usually follows a path whereby pores with larger connecting throat radii are filled first.²⁷ Breakthrough pressure, P_{BT} , as defined here, refers to the maximum capillary pressure (usually a result of the minimum throat radii) that must be overcome by the reservoir pressure before flow out of a GDL can occur. Benziger et al. studied breakthrough pressure of liquid water through carbon-paper and cloth GDLs and examined the effects of pore sizes and surface treatments. They observed elevated breakthrough pressure with decreased pore size and increased PTFE loading.²⁸ Lu et al. examined the effect of MPL on dynamic water breakthrough and concluded that cracks in the MPL can lead to selective water-transport locations, which may have an effect on breakthrough pressure and overall distribution of GDL water saturation.²⁹ Gostick et al. have completed extensive modeling and experimental studies characterizing transient aspects of transport between the catalyst layer and flow-channel highlighting the potential for drainage improvement via MPL modifications including larger holes for water passage.³⁰

Droplet removal from the GDL/gas-channel interface is highly dependent upon the adhesion force between a liquid droplet and GDL surface. The adhesion force represents the resistance force that a droplet needs to overcome to initiate motion along a surface, which can be correlated with the sliding angle of a droplet by a gravity field.²⁵ At the incipient sliding angle, the adhesion and gravity forces acting on the liquid droplet equal each other. Thus, one can calculate the adhesion force, $F_{adhesion}$, between the liquid droplet and GDL surface from the body force acting along the direction of the slide and the wetted diameter by²⁵

$$F_{adhesion} = \frac{\rho V g \sin \theta_s}{\pi d_w} \quad [4]$$

where ρ is the liquid density, V is the droplet volume, g is the gravitational acceleration constant, θ_s is the sliding angle, and d_w is the wetted diameter. Several studies have examined liquid-water droplet

*Electrochemical Society Student Member.

**Electrochemical Society Active Member.

^zE-mail: azweber@lbl.gov

Figure 1. (left) Rotating-stage goniometer setup used for breakthrough-pressure, adhesion-force, and detachment-velocity testing. (right) Schematic of setup highlighting the bottom-injection method as well as key droplet dimensions.

and slug removal from PEFC flow channels characterizing the effects of channel geometry, GDL material, and gas flowrate.^{31–33} Capillary effects may impact droplet wetting at GDL surfaces, however; no existing studies have analysed explicitly this possibility.

In this study, the influences of GDL thickness and PTFE content as well as injection rate and injection area (analogous to MPL crack size) on breakthrough pressure and liquid-droplet adhesion force are examined. The present work focuses on localized GDL and transport behavior rather than flow-field scale phenomena in order to isolate key effects so far unaccounted for in literature. Throughout, we propose empirical relationships useful for modeling and design of these technologies. The outline of this paper is as follows. First, the experimental setup is discussed. Next, the results are presented for breakthrough pressure, adhesion force, and detachment velocity from the GDL surface due to convective gas flow. The results are followed by an integrated discussion of the underlying interrelated phenomena.

Experimental

The experimental measurements of breakthrough pressure and sliding angles were performed with our previously designed automated rotating-stage goniometer (Ramé-Hart) with a custom-made injection system.²⁵ The setup and key components are shown in Figure 1. A detailed description of the experimental apparatus and measurement procedures are given in the following paragraphs.

Breakthrough Pressure Tests.— GDL samples (3×3 cm) were held in place on the injection port plate using 3M double-sided tape. An Omega PX603 series pressure transducer was used to measure pressure at a sampling rate of 10 Hz. Injection rates were controlled digitally using an automated dispensing system, which was routinely monitored for and purged of air bubbles to ensure consistent results. Injection diameter was changed by using different sample plates and tape hole punches producing diameters of 0.17, 0.22, 0.31, 3.175, 6.0, and 11.11 mm. A reference capillary number was calculated for each case by setting $u = q/\pi r_i^2$, where q is the flow rate of water, r_i is the radius of the injection hole, and μ_{nw} and γ are set to 1.002×10^{-3} N-s/m² and 0.0728 N/m, respectively, similar to the method employed by Medici and Allen.²⁴ In this fashion, the true Ca within the GDL may be somewhat different due to flow and spreading within the GDL. System pressure was measured without the GDL so that the differential breakthrough pressure could be isolated. Toray brand GDL (Fuel Cell Earth) was selected because it tends to be more structurally uniform with changing thickness, and the PTFE coating was applied by the manufacturer using a proprietary method. A list of the GDLs tested is presented in Table I. Multiple trials per data point were conducted for error calculation, and in most cases each trial consisted of a fresh dry sample since hysteresis due to injection damage has been reported.³⁴

Adhesion force tests.— The rotating-stage goniometer allowed for the automated calculation of sliding angles, contact angles, and droplet diameters and volumes using the program DROPImage. The stage rotation was controlled at a rate of 1°/s in order to reduce the ef-

Table I. GDL sample properties.

GDL Series	Thickness [μm]	PTFE [wt-%]
Toray TGP-30	110	5, 10, 20
Toray TGP-60	190	5, 10, 20
Toray TGP-90	280	5, 10, 20
Toray TGP-120	370	0, 5, 10, 20, 30, 40, 50, 60

fects of angular motion on the droplet. Both bottom injection and top placement (droplet deposited with a syringe on the GDL surface) were used to examine differences between the methods. The bottom-injection method more closely simulates the water transport from a catalyst layer in a PEFC. Injection quantities of approximately 20 μL were used for all the sliding-angle results; this was to ensure that even with thicker GDL large enough droplets would form and also that a droplet would detach due to gravity. The liquid-water-droplet profile images were taken using a CCD capable of a frame rate of 60 Hz; droplets were backlit with a diffused 150 W halogen lamp. For each case, three to four trials were conducted to obtain statistically significant results. In some tests, multiple droplets formed on the GDL surface; only cases where a single drop was present at the end of the injection period were used for sliding-angle calculations. Movement of the stage was smooth and it was isolated from vibration using an anti-vibration table to ensure that the liquid-water droplet release was due only to gravity.

Detachment Velocity Tests.— In addition to the adhesion-force study, the detachment velocity was also measured for the GDL samples. Using the same basic setup as the previous tests, a 150 mm long translucent Lexan flow channel with a 4 mm height and 7 mm width was fitted directly over the sample and used to simulate tangential flow within a PEFC gas channel. The flow-channel size was chosen to minimize any contact of the droplet with the wall for the droplet sizes studied. An Omega FMA-2609A series flow controller capable of up to 50 (standard)L/min was used to regulate the 20°C dry air flow rate. Detachment was determined at the point where a droplet moved completely beyond its original wetting area; detachment velocity is defined as the average channel flow velocity at this point. These tests were completed for both bottom-injection and top-placement droplets.

Results

Breakthrough pressure.—PTFE content and GDL thickness effects.— GDLs are typically treated with PTFE to increase hydrophobicity and enhance water-removal capability (see Figure 2). These coatings can affect the GDL pore volumes and throat radii influencing the breakthrough pressure, especially as the coatings are known to be nonuniform.^{35–37} Lim and Wang completed extensive performance testing of GDLs in PEFCs containing different PTFE weight loadings.³⁸ They related the overall porosity, ϵ , of a GDL sample to

Figure 2. Scanning-electron microscope (SEM) images of TGP-120 GDL with various PTFE loadings.

the PTFE weight fraction, x ,

$$\varepsilon = \varepsilon_o - \frac{x}{(1-x)} \frac{\rho_{CP}}{\rho_{HP}} \quad [5]$$

where ε_o is the original porosity of the untreated carbon paper and ρ_{CP} and ρ_{HP} are the densities of carbon paper and PTFE, 0.49 and 2.15 g/cm³, respectively. Figure 3a overlays Eq. 5's predicted porosities with those measured using mercury-intrusion porosimetry (Porous Materials Incorporated, 1 inch (2.54 cm) radius sample, 2 to 3 replicates) of the tested GDLs. The effect of PTFE content on droplet contact angle for these samples was measured and is displayed in Figure 3b. PTFE content increases the surface hydrophobicity at low wt-% and then levels off below 40 wt-% since the PTFE is no longer coating the fibers and is only accumulating; at very high levels (> 40 wt-%), the structure is dominated by PTFE and there is less pore area (see Figure 2 and Figure 3a), thereby resulting again in an increase in observed surface hydrophobicity due to the higher breakthrough pressure.

Breakthrough pressure was determined by examining the maximum pressure achieved during an injection period. Figure 4 displays a few examples of typical raw pressure data recorded over a 2000 s injection period for various GDL thicknesses. Analyzing the 110 μm curve, the initial pressure signal is due to the head from water traveling through system lines and filling void space between the GDL and injection port. At approximately $t = 700$ s, a steep climb begins due to water being forced into GDL pores; the slope is attributable to expansion of the injection system and is similar to behavior reported in other studies.³⁹ At about $t = 1200$ s, the pressure reaches a maximum which is accompanied by droplet formation on the GDL surface. This maximum pressure is recorded as P_{BT} followed by a dramatic fall in signal as the pressure decays to a minimum, P_M , due to reduced resistance. Darcy's law was used to calculate the liquid water effective permeability post breakthrough using P_M for each 5 wt-% PTFE

Figure 4. Time-series data acquired for breakthrough-pressure measurements for GDL with 5 wt-% PTFE and various thicknesses.

Table II. Post breakthrough effective permeability.

GDL Series (5 wt-% PTFE)	TGP-30	TGP-60	TGP-90	TGP-120
Thickness [μm]	110	190	280	370
Permeability [m ²]	4.95e-13	4.99e-13	5.85e-13	5.66e-13

GDL series using the 310 μm injection diameter which are listed in Table II. Dynamic behavior of PEFC, such as during startup, may be effected by P_{BT} since liquid flow from the catalyst layer to the GDL must reach this pressure before steady flow can occur. Likewise it could also be critical if one envisions water movement in GDLs as discontinuous droplets (i.e., transient accumulation and subsequent discrete movement).

Breakthrough pressures were measured as a function of PTFE content in Toray 120 (370 μm thick) samples. The results, displayed in Figure 5, show relatively flat behavior at lower PTFE contents and then dramatic increases for greater than 40 wt-% loadings. The individual contributions of changing porosity and contact angle to capillary pressure trends can be visualized by assuming $r/r_o = (\varepsilon/\varepsilon_o)^{1/3}$, inserting the experimentally measured values of ε and θ into Eq. 3, and then normalizing to the 0 wt-% PTFE values (ε_o and θ_o),

$$\frac{P_c}{P_{0\%}} = \frac{\cos(\theta)}{\cos(\theta_o)} \times \left(\frac{\varepsilon_o}{\varepsilon}\right)^{1/3} \quad [6]$$

Figure 3. Predicted and measured (a) porosity and (b) measured droplet contact angles as a function of PTFE content for TGP-120 GDL samples. The bottom-injection method was used to create the droplets which were approximately 10 μL.

Figure 5. Measured breakthrough pressure of TGP-120 GDL as a function of PTFE content. This testing was completed with injection diameter of 310 μm and rate corresponding to $\text{Log } Ca = -4$.

The individual and combined effects of porosity and contact angle on normalized breakthrough pressure are plotted in Figure 6a using Eq. 6. Figure 6b is a summary of the measured normalized breakthrough pressures overlaid with data of Benziger et al.²⁸ Compared

with previous data, the current results demonstrate reduced breakthrough pressure at lower PTFE weights and an increasing rather than logarithmically plateauing trend at higher loadings. This new data matches more closely with the idealized view of PTFE loading effectively reducing throat sizes and increasing contact angle especially at high PTFE wt.%. The current data trend is described via the 5th order polynomial correlation ($R^2 = 0.999$):

$$\frac{P_{BT}}{P_{0\%}} = 8 \times 10^{-9}x^5 - 7 \times 10^{-7}x^4 - 2.4 \times 10^{-5}x^3 + 6 \times 10^{-4}x^2 + 1.2 \times 10^{-2}x + 1.0 \quad [7]$$

where x is the PTFE wt.%. Eq. 7 is valid for Toray 120 (370 μm), $0\% \leq x \leq 60\%$. The higher breakthrough pressure at elevated PTFE loadings may be amplified by the heterogeneous distribution of PTFE that can reduce the number of pores available to water invasion.^{40,41}

Figure 7a shows the results of breakthrough pressure as a function of GDL sample thickness which agree with trends reported in literature.³⁴ A higher breakthrough pressure is expected as increased GDL thickness, l , usually means longer flow pathways and an increased number of pores liquid water must fill before reaching the surface. Linear correlations were used to fit the three data series:

$$P_{5\%} = 6.617 \times 10^{-3}l + 2.601 \quad (R^2 = 0.996) \quad [8]$$

$$P_{10\%} = 6.717 \times 10^{-3}l + 2.613 \quad (R^2 = 0.817) \quad [9]$$

$$P_{20\%} = 4.767 \times 10^{-3}l + 3.691 \quad (R^2 = 0.734) \quad [10]$$

Figure 6. (a) Breakdown of estimated porosity and measured contact-angle contributions to capillary-pressure trends. The effect of each variable is plotted separately and then as a total effect. (b) Measured breakthrough pressures from this study compared to previous work by Benziger et al.,²⁸ all data is using TGP-120 and normalized to the 0 wt-% PTFE weight case. Results from this work used a $\text{Log } Ca = -4$ and an injection diameter of 310 μm .

Figure 7. (a) Breakthrough pressure as a function of GDL thickness for various PTFE loadings. (b) Difference between breakthrough and minimum pressure normalized to the minimum pressure for two different PTFE loadings. Results for $\text{Log } Ca = -4$ and a 310 μm injection diameter.

Figure 8. (a) Breakthrough-pressure and injection-area trends over a range of capillary numbers (Ca). (b) Effect of $\text{Log } Ca$ on breakthrough pressure for different injection areas. This was completed on TGP-120 5 wt-% PTFE.

where l is in units of μm . These are valid for $110\mu\text{m} \leq l \leq 370\mu\text{m}$. Figure 7b highlights the relationship between breakthrough and the reduced resistance pressure, for thicker GDLs this minimum pressure begins to dominate since there is more Darcy friction due to longer drainage pathways.

Injection area and rate effects.—MPLs have been shown to have a significant effect on liquid-water transport through a GDL.^{29,42,43} The injection pore diameter and injection rate were varied to examine the possible effects of various MPL crack sizes on breakthrough pressure (i.e., the diameter is thought to mimic the impact of an MPL on a bare GDL). In addition, such an analysis can provide the smallest area that is still representative of the GDL, an important experimental and modeling value.

Figure 8a presents the results of breakthrough pressure for various injection areas. The coupling between area and capillary number limits the range of tests possible for a given area; the $170\mu\text{m}$ injection diameter was the smallest used for this testing. Breakthrough pressure rises noticeably as the injection area approaches the GDL thickness. As area increases, the breakthrough pressure levels out asymptotically to a minimum, probably due to an increasing number of pores available for breakthrough as discussed by Nam et al.²⁰ This transition quantifies the minimum domain size to be considered in experiments and models that will still be statistically representative of the larger sample. Raising the injection rate also increased breakthrough pressure (see Figure 8b); although, it appears the majority of the increase was due to the smaller injection pore size. Larger increases were observed over $\text{Log } Ca = -4$; however, these flowrates are beyond the operating threshold of typical PEFCs and may include Darcy effects. In relation to MPLs, smaller cracks may have a localized effect on

liquid-water transport properties that may be magnified at higher current densities. Liquid-water drainage through the GDL from larger MPL cracks may be more effective than from smaller ones.

Droplet emergence behavior is shown in Figure 9 and Figure 10. On average, the injection area and rate have little influence on droplet size and number in the regime of PEFC operation. Larger injection areas and faster injection rates produced smaller and more numerous droplets; this is evidence of the increasing number of pores available for breakthrough. In some cases, droplets emerged beyond the boundary of the injection area, therefore models assuming droplet emergence from a single point may be valid over a wide range of flowrates only for injection diameters below $300\mu\text{m}$. The injection-area effect on droplet size has implications for removal; smaller droplets can be harder to remove from flow channels while large droplets, if they contact channel walls, can lead to slug formation.

Adhesion force.—*PTFE content and injection rate effects.*—Static contact angles for $10\mu\text{L}$ droplets are plotted in Figure 11 for bottom-injection and top-placement methods for the 5 wt-% PTFE-loading GDL series. For bottom injection, even though the reported PTFE loading was unchanged, there is a sharp decrease in hydrophobicity with increasing thickness which was first thought to be due to the GDL manufacturing process and PTFE distribution heterogeneity.^{37,41} However, this trend is far less pronounced in the top-placement data and therefore is probably due to the different wetting processes between the two methods. Figure 12a shows the adhesion force (as calculated by Eq. 4) between a water-droplet and GDL surface as a function of GDL thickness for two different PTFE loadings. It should be noted that the adhesion force is an intrinsic property and thus independent of

Figure 9. Recreated top-view of droplet distribution based on images captured by cameras 1 & 2. Larger injection diameters (shown in red) were more likely to produce multiple, smaller droplets at higher injection rates. Results for TGP-30, 5 wt-% PTFE.

Figure 10. Pictures of droplets at various $\text{Log } Ca$ numbers and injection areas, images reflect the typical outcome. Larger numbers of droplets may be observed when more drainage pores are available due to larger injection area. Results for TGP-30, 5 wt-% PTFE.

Figure 11. GDL contact angle as a function of GDL thickness using top placement and bottom injection. Results for 5 wt-% PTFE, $\text{Log } Ca = -4$ and a 310 μm injection diameter.

droplet volume.²⁵ As expected, the adhesion force for GDL with 5 wt-% PTFE is higher than that of GDL with 20 wt-% PTFE. Therefore, GDLs with low PTFE content will require larger external forces to remove water droplets from their surfaces. However, a thinner GDL shows less difference between adhesion force with PTFE loading. This indicates that the changes in GDL surface hydrophobicity with increased PTFE loading reach a maximum for thinner GDLs at lower loadings. Hence, higher PTFE loading for thinner GDLs may provide less benefit for droplet removal from the GDL surface.

The effects of capillary number on adhesion force are displayed in Figure 12b. At higher Ca and injection areas (see Figure 10) multiple forming droplets would agglomerate into a single droplet by the end of the injection process. Overall, an increasing trend was observed for droplets that were forced through the GDL faster; a slight coupling with injection area was noticed which is addressed in the next section.

GDL thickness and injection area effects.—Results shown in Figure 13a also indicate that the droplet formations on a thinner GDL and on a thicker GDL are not identical. To verify these results were due to internal and not surface GDL structure, measured

Figure 12. (a) Adhesion force between water-droplet and GDL surface as a function of GDL thickness at different PTFE loadings using bottom injection. (b) Adhesion force as a function of $\text{Log } Ca$ for various size injection diameters on TGP-30 5 wt-% PTFE series GDL.

Figure 13. (a) Adhesion force as a function of (a) GDL thickness for various injection diameter sizes and (b) injection areas for each sample type; all GDLs have 5 wt-% PTFE and a Log $Ca = -4$.

top-injection adhesion forces did not change significantly with increasing GDL thickness; therefore, the increases in adhesion force seen in the bottom-injection methods are probably due to internal Ca effects. Figure 13b displays droplet adhesion force as a function of injection area for several GDL thicknesses at log $Ca = -5.12$. Droplets emerging from smaller injection areas were easier to remove and that trend was relatively consistent over varying GDL thickness, which is a benefit of MPLs if they minimize injection area. The data show a gradual change and neither a real plateau nor a strong dependency of adhesion force on injection area, which also could have implications for the determination of representative volumes.

Detachment velocity testing.— Droplet detachment is highly dependent upon the net drag force on a droplet from flow gas interactions; therefore, droplet dimensions have a large influence on detachment behavior. Figure 14a-14c is an overview of the growth process of key

droplet dimensions using bottom injection for each GDL series and 5, 10, and 20 μL droplets. Bottom-injection-method droplets for thinner GDLs are subject to decreased liquid/GDL interface due to fewer feeding pores which leads to smaller contact widths. Detachment velocity, presented in Figure 15a, for the bottom-injected droplets varies with GDL type and is higher for the thicker samples, where the lines are just guides for the eye. Bottom-injection data, normalized for the 22 μL detachment velocities along with droplet height normalized with the channel height (prior to gas flow) are plotted in Figure 15b. The normalized curves reflect the full range of slopes expected for these Toray series.

The use of adhesion force to predict detachment velocity was investigated using the results above (Figure 12). A simple analytical droplet force-balance model was implemented to understand if it can estimate the critical detachment velocity as outlined in the Appendix. Figure 16 overlays the predicted onset of droplet instability with

Figure 14. Bottom-injection method droplet dimensions for each 5 wt-% PTFE GDL sample at varying droplet sizes using a 310 μm injection diameter and Log $Ca = -4$.

Figure 15. (a) Bottom-injection detachment-velocity data. (b) Curves from detachment-velocity data normalized to the 22 μL velocity of each bottom-injection case (left axis) and normalized droplet height (right axis). All data are for 5 wt-% PTFE and a 310 μm injector diameter and the lines are just guides for the eye connecting the data points.

Figure 16. Measured detachment velocity data overlaid with predicted instability curves calculated from a droplet force-balance model. This data was for 5 wt-% PTFE, an injection diameter of 310 μm and $\text{Log } Ca = -4$.

measured detachment velocity values for two different GDL series. The area to the right of these lines represents regions where droplet detachment is expected. The results are within an order of magnitude with predictions most useful for droplets $\geq 15 \mu\text{L}$, and the results demonstrate the ability to use adhesion-force data for detachment-velocity calculations, and the ability to evaluate different channel dimensions and conditions. However, it should be noted that the model used was straightforward and simple, and one can achieve better accuracy by including experimentally measured pressure-drop and shear-force data to the present force-balance model.^{44,45}

Discussion

Several theories exist as to the mechanism of liquid-water transport through the GDL and how a droplet forms on the GDL surface.^{8,19,20,40} For example, Nam and Kaviany¹⁹ proposed an upside-down capillary-tree network using a theoretical approach. Later, Litster et al.⁸ showed experimentally that fingering and channeling are dominant scenarios and an upside-down capillary-tree network is less reasonable for PEFC GDLs. Our results may be evidence of the Litster et al. formulation, which is reinforced by the observed difference between the bottom-injection versus top-placement adhesion behavior.⁸ The higher adhesion forces recorded via bottom-injection methods are probably due to the increased interaction between liquid water and the GDL interface, and, in particular, the cohesion of the water droplet with the underlying water structure. Previous X-ray based imaging studies show this idea as liquid water can be detected in pores within the GDL near its surface, which would not necessarily be present under a top-placement scenario.^{46,47} An illustration of how a droplet might form under various parameters is shown in Figure 17; each is discussed with respect to the testing results.

Flow rate (Figure 17a, 17b).— Earlier work on liquid-water penetration behavior at different Ca numbers showed a transition from sparsely filled liquid-water branches (capillary fingering) to a more even invading liquid-water front (stable placement) at higher Ca numbers.²³ It is postulated, from current results, that higher Ca numbers can, in some cases, result in larger numbers of water-filled branches at the droplet/GDL interface feeding during injection that drive wetting toward a Wenzel state^{48,49} and thus increasing adhesion force.

GDL thickness (Figure 17c, 17d).— For thinner GDLs, liquid water needs to travel a shorter distance to form a droplet on the GDL surface. Therefore, fingering and channeling lack space to spread in

Figure 17. Illustrations of postulated capillary effects on adhesion force, F , blue regions in the GDL denote potential water pathways during injection: (a, b) Injection rate: $q_2 \geq q_1 \rightarrow F_2 \geq F_1$, (c, d) GDL thickness: $l_2 \geq l_1 \rightarrow F_2 \geq F_1$, (e, f) injection area: $a_2 \geq a_1 \rightarrow F_2 \geq F_1$.

the through-plane direction. Whereas for thicker GDLs, the fingering and channeling spreads in the through-plane direction as it moves from the bottom to the top of the GDL and hence the droplet shows more of a front, which can spread significantly beyond the original injection area (see Figure 9). In this case, the wetting area of the droplet may be closer to Wenzel conditions. This may be why we observed a higher adhesion force for the thicker GDL compared with the thinner. Detachment-velocity trends are similar to what are predicted by the adhesion-force results. Taking into account the effects of droplet dimensions, our results are consistent with earlier reported work and highlight how thickness may affect droplet removal into channels.⁵⁰

Injection area (Figure 17e, 17f).— Injection area can impact the number of water-drainage pathways through the GDL. For larger injection areas, where more water-filled branches may feed the GDL surface, droplet adhesion force may shift toward a Wenzel condition. Some of this may be attributed to the behavior observed in Figure 9 and 10, which show increasing water branches reaching the GDL surface to form droplets with increasing injection area. This could lead to wetting conditions closer to a Wenzel approximation if a single droplet is fed by multiple branches. These results may be related to the effects of an MPL, where a distribution of various sized cracks dominates water drainage to the GDL. Based on this work, liquid water emerging from smaller MPL cracks may form droplets that are easier to remove via gas flow compared with droplets originating from larger MPL holes.

Overall, these results elucidate the fact that droplet formation on rough and porous surfaces (like PEFC GDLs) is always complex and beyond the simplified two-phase Wenzel model or the three-phase Cassie–Baxter model.^{48,49,51} For example, comparison of the bottom-injection and top-placement studies demonstrate the differences due perhaps to probing differences between the sampling of the pore space by the various droplets. In this sense, the top-placement method represents an unbiased statistical sampling of GDL surface

whereas bottom placement selectively probes large and low contact angle pores/domains during the buildup of the percolation path and also for the breakthrough position. Such an analysis agrees with the lack of thickness dependency for top placement on measured properties and the smaller contact width for same droplet size compared to bottom injection. Additionally, the structure of the water branches that feed droplets can have an impact on droplet location, size, number, and adhesion force, and this structure is likewise impacted by injection area and operating conditions. Further study is required to link the detailed microstructure and impacts of other factors such as wicking and phase change.

Conclusions

Dynamic liquid-water uptake and removal in fuel-cell gas-diffusion layers (GDLs) was systematically investigated in Toray series GDLs under a host of test conditions. Breakthrough pressure, adhesion force, and detachment velocity were measured experimentally to isolate the effects of PTFE content, thickness, and water-injection area and rate. The following key findings were found:

- i Increasing PTFE content and GDL thickness both resulted in higher breakthrough pressure. The capillary equation was found to fit the data trends reasonably well, when results were normalized for the 0 wt-% case, which highlights the strong dependence of breakthrough pressure on a GDL's porosity and contact angle.
- ii The effects of injection area and rate were found to have an inverse relationship; for very small areas the breakthrough pressure was more variable and tended to be higher while higher flow rates lead to a slightly elevated pressure signal. The area behavior was attributed to the number of drainage pathways which increases with larger injection areas. PEFC modelers should keep in mind these area effects when deciding upon a minimum domain size, as breakthrough pressure may vary significantly as the pore size is approached. The breakthrough pressure sensitivity to Ca number observed is less understood and may benefit from further imaging studies.
- iii Top-placement and bottom-injection methods were observed to produce different adhesion force and detachment results, with bottom-injection droplets being more difficult to remove. This was probably due to increased liquid-water interaction with GDL structure and the droplet, thereby shifting a droplet toward a more hydrophilic condition in the bottom-injection cases. Droplet adhesion force decreased with increased PTFE content and reduced GDL thickness. Increased injection area was observed to increase droplet adhesion force, which may be due to the greater number of pores feeding a single droplet causing a transition closer toward a Wenzel-type droplet interface. This was especially true at higher injection rates where multiple droplets were observed to form during injection.
- iv Adhesion force incorporation into a simplified overall droplet force-balance model was found to predict the onset of droplet instability more-or-less well as the majority of measured detachment velocities occurred beyond the calculated threshold.

The gained understanding and exploration of water management and transport in GDLs, including the identification of key behavioral trends is beneficial to the design of liquid-phase management strategies and next-generation GDL materials for PEFC and flow-battery technologies.

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Appendix

Calculations for the detachment velocity prediction via the adhesion force were performed with a simplified force-balance model accounting for pressure (F_P) and shear effects (F_S):

$$F_T = F_P + F_S \quad [A1]$$

In this case, the net force opposing gas flow was calculated using the adhesion-force measurements by $F_T = \pi d_w F_{adhesion}$. The point at which a droplet becomes unstable is determined when the pressure and shear forces are equal to the net force due to adhesion. Pressure and shear forces can be expressed as a function of gas channel velocity taking into account channel and droplet dimensions:

$$F_P = \Delta P \times 2B \times 2r \quad [A2]$$

$$F_S = \frac{3\mu BU}{(B - h/2)^2} (2r)^2 \quad [A3]$$

where ΔP is the pressure drop over a single droplet, B is half the channel height, U is the average channel gas velocity, r is the droplet radius, μ is the air viscosity and h is the droplet height.⁴⁴ The pressure drop was calculated using a formulation validated with COMSOL,

$$\Delta P = \frac{a\mu QL}{WH^3} \quad [A4]$$

where Q is the volumetric gas flow rate, L is the droplet diameter, W is the channel width and H is the channel height.⁵² The factor a accounts for the square channel geometry and is calculated as

$$a = 12 \left[1 - \frac{192H}{\pi^3 W} \tanh\left(\frac{\pi W}{2H}\right) \right]^{-1} \quad [A5]$$

Substituting equations A2 thru A4 into A1 and setting $Q = HWU$, the critical gas velocity for detachment, U_c , may be estimated by

$$U_c = \frac{F_T H^2 (h - 2B)^2}{4B\mu r(aL(h - 2B)^2 + 12H^2 r)} \quad [A6]$$

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