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Liquid-Water Uptake and Removal in PEM Fuel-Cell Components

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Introduction

Water management in PEM fuel cells is critical for optimum fuel-cell performance. This is especially true at lower temperatures, where water exists as a liquid and phase-change-induced flow is insufficient to remove the product water in the vapor phase.[1] Thus, there is a need to understand liquid-water movement and removal from the various fuel-cell components including the membrane, catalyst layers, and diffusion media. In addition, liquid water in these various materials can limit performance due to blocking either gas transport pathways or reaction sites. In this work, the water properties including capillary pressure – saturation relationships and droplet removal will be discussed. In addition, recent work in understanding membrane water sorption and diffusion will be introduced.
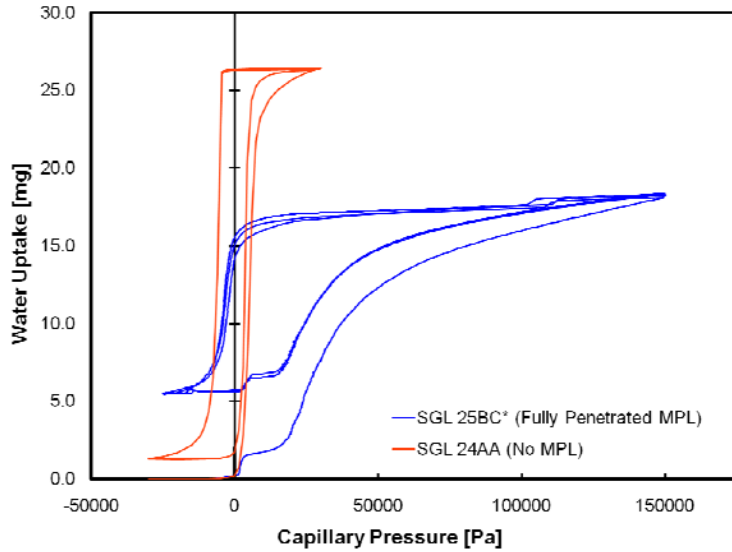
Results

Figure 1. Water uptake as a function of capillary pressure for a GDL and an MPL.

A key characteristic of the presence of liquid water is a change in the effective volume available for transport or reaction. The saturation, or volumetric fraction of empty pore space filled with water, is a good metric to describe the behavior of the various porous fuel-cell materials. Often, this data is measured as a function of the capillary pressure which is the liquid pressure minus the gas pressure.[4] Sample data are shown in Figure 1, where water uptake is used since the total water uptake is unknown in the MPL; the water-uptake value of the GDL ranges from a saturation of 0 to 1. From the curves, one can see that the more hydrophobic and smaller-pore microporous layer requires higher capillary pressure for the same saturation as compared to the SGL gas-diffusion later (GDL). It is also worth noting that the GDL exhibits a strong intermediate wettability, where it takes pressure to push water into the material and requires vacuum to take it out again. This behavior allows for ex-situ tests to be undergone on GDLs after setting the saturation. Tests that can be conducted include the effective gas-phase diffusion coefficient as a function of saturation and freezing-point depression and freeze kinetics.

While the capillary pressure versus saturation profile for diffusion media has been measured, there is still an open question regarding the wettability and subsequent saturation of the catalyst layer. To answer this question, custom catalyst layers of about 30 microns in thickness were fabricated using standard LANL decal fabrication processes. These layers then were used in the capillary pressure fixture; the results are shown in Figure 2. As can be seen, the catalyst layer is mainly hydrophilic as expected due to Nafion and carbon and Pt

particles, but it also contains some hydrophobic character that is probably due to small pores. The curve also exhibits the hysteresis seen in the GDL samples, but not as strong. The data is useful in the modeling of fuel cells and could be important in determining how flooding occurs and how much there is in the catalyst layer. To probe some of these aspects, the catalyst-layer samples were used in an SMS dynamic-vapor-sorption (DVS) apparatus to measure the water uptake of the ionomer in the catalyst layer. As seen in Figure 2, the ionomer exhibits a lower water content for a given relative humidity compared to bulk Nafion. This effect is not entirely unexpected due to the thinner ionomer films within the catalyst layer. In the figure, the impact of having platinum is also shown, which demonstrates higher water contents. While some capillary condensation could be considered at the higher relative humidities, the almost constant shift in the curves demonstrates that the ionomer itself is affected by the platinum. This could be due to specific sulfonic-acid-site absorption by the Nafion side chains on the platinum surface, which may cause the hydrophobic skin of the ionomer to become more hydrophilic and open up the inner morphology for water uptake.
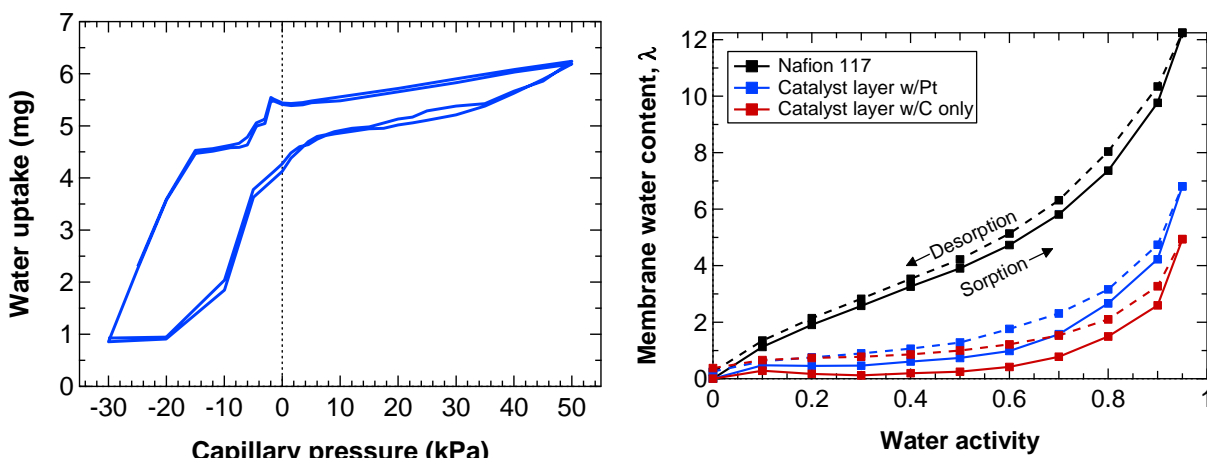

Figure 2. Catalyst-layer (left) water uptake as a function of capillary pressure and (right) ionomer water uptake.

The above experiments and data examine the liquid-water holdup in fuel-cell components, but getting the water out of the cell is critically important. For liquid water, this removal is often through liquid-water droplets from the surface of the cathode GDL. These droplets can also cause water holdup due to increased capillary pressures and through the above water uptake , which we have shown can be related to the material pore-size and contact-angle distributions.[5] A significant amount of experimental work devoted to the study of droplet dynamics in PEM fuel-cell gas flow channels has already highlighted some of the fundamental issues.[2-3,6] Most of these studies,

however, are based on the contact-angle hysteresis and a static force balance on a single droplet,
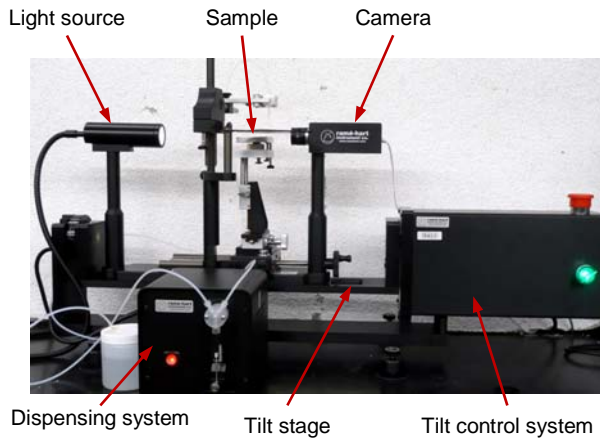
$$F_P + F_G + F_A = 0 \tag{1}$$

Figure 3. Setup used in the tilted-plate experiment to measure sliding angles and adhesion forces for GDL surfaces showing its key components

where P, G, and A, denote the pressure, gravitation, and adhesion or surface-tension force, respectively. The gravitational force has been shown by us and others to not be significant under normal fuel-cell conditions and droplet sizes. While the overall force-balance approach is fine, the contact-angle hysteresis does not provide an accurate estimation of the adhesion force, which is the dominating force holding a droplet on the GDL surface and preventing its detachment. Therefore, we have designed and used a tilted-plate experiment to quantify and directly measure the sliding angles and adhesion forces for liquid -water droplets on the GDL surfaces. The experimental setup used in the tilted-plate experiment to measure the sliding angles and adhesion forces is shown in Figure 3.

In the experiments, two droplet placement methods (placed on a horizontal surface and placed on a tilted surface) and two injection methods (from the top and through the bottom of GDL sample) are investigated. Preliminary data demonstrate that both the placement and injection methods have significant effect on the sliding-angle measurements. For example, Figure 4 shows 20 µL droplets at rest and at incipient inclination where the droplet begins to slide. As seen, while the contact angle of the droplet on the flat surface is similar for both the top and
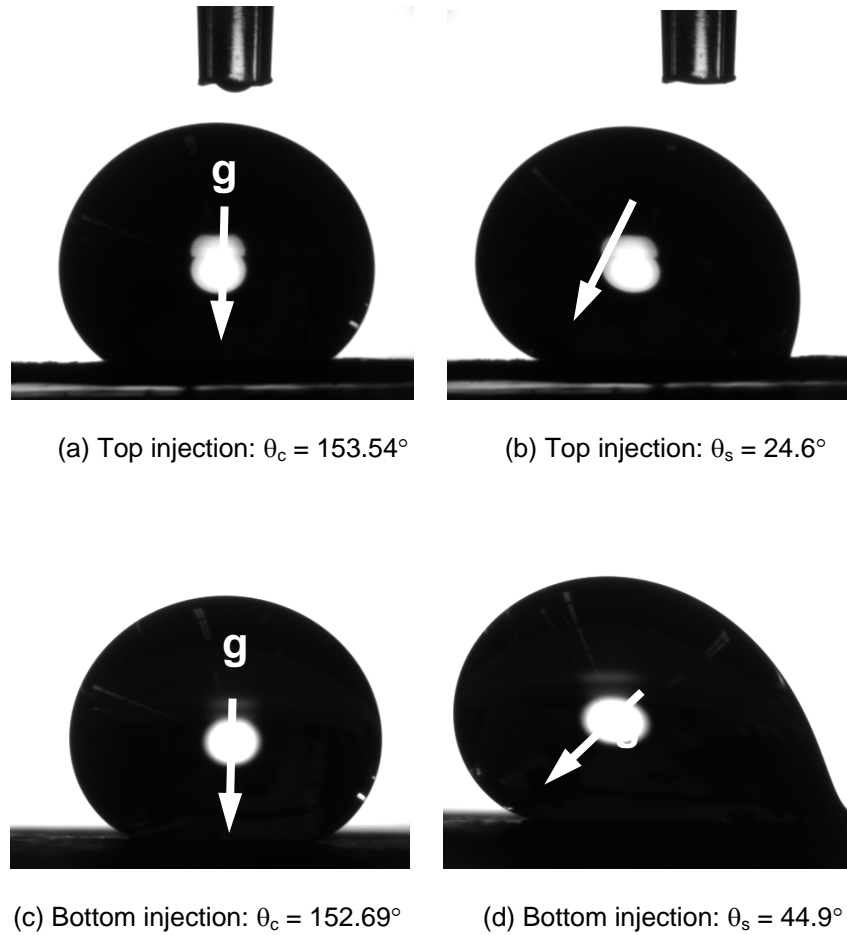
(a) Top injection: $\theta_c = 153.54°$ (b) Top injection: $\theta_s = 24.6°$

(c) Bottom injection: $\theta_c = 152.69°$ (d) Bottom injection: $\theta_s = 44.9°$

Figure 4. Snapshots of 20μL liquid water droplet on SGL 24EA using two injection methods. Parts (a) and (c) show without inclination and the static contact angle, and parts (b) and (d) show with inclination (drop about to slide) and the sliding or inclination angle.
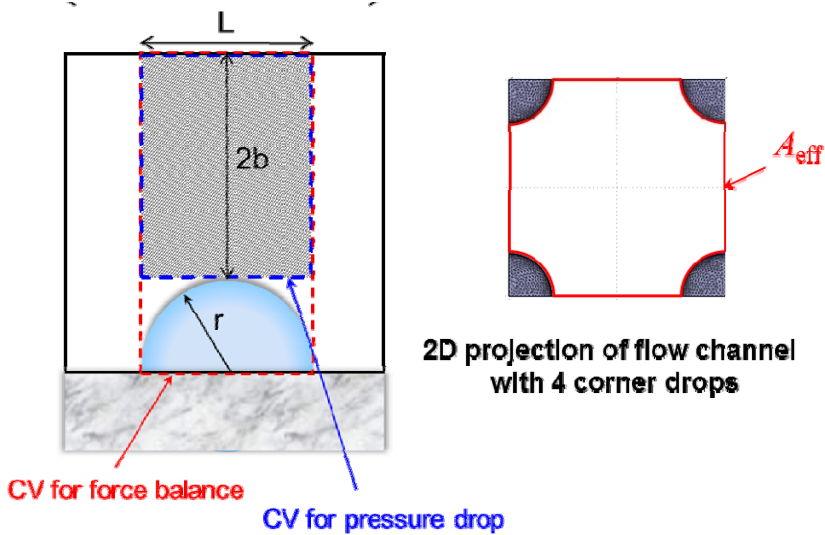

Figure 5. Control volume for the pressure force calculation both for a single droplet and multiple droplets.

bottom injections, the bottom injection requires a much higher inclination angle, which is due to the increased adhesion between the droplet and the underlying water reservoir. This result

highlights the fact that analysis with surface drops is inadequate in capturing the correct underlying physics. Similarly, multiple droplets form when the liquid is pushed through the bottom, and this will be discussed and quantified.

In addition to determining the adhesion force, the pressure or drag force must be determined. This force is determined from the control volume shown in Figure 5. However, one must also consider multiple droplets, including those on the channel that may impact the pressure force, as also shown in Figure 5. The pressure force can be calculated through some relatively straightforward modification of the pressure force derived in the literature.[2] The modifications results in

$$\Delta P = \frac{a\mu U_{\text{eff}} L}{H_{\text{eff}}^2}$$

$$a = 12\left[1 - \frac{192}{\alpha\pi^5}\tanh\left(\frac{\alpha\pi}{2}\right)\right]^{-1}; \ U_{\text{eff}} = \frac{UH}{H_{\text{eff}}}; \ H_{\text{eff}} = \frac{A_{\text{eff}}}{W}; \ A_{\text{eff}} = A_{\text{ch}} - nA_{\text{drop}}$$

(2)

where α is the effective aspect ratio, U_{eff} is the effective gas velocity, H_{eff} is the effective channel dimension, and A_{eff} is the effective x-sectional area. This equation was compared to literature approaches and detailed finite-volume calculation using Comsol Multiphysics as show in Figure 6.
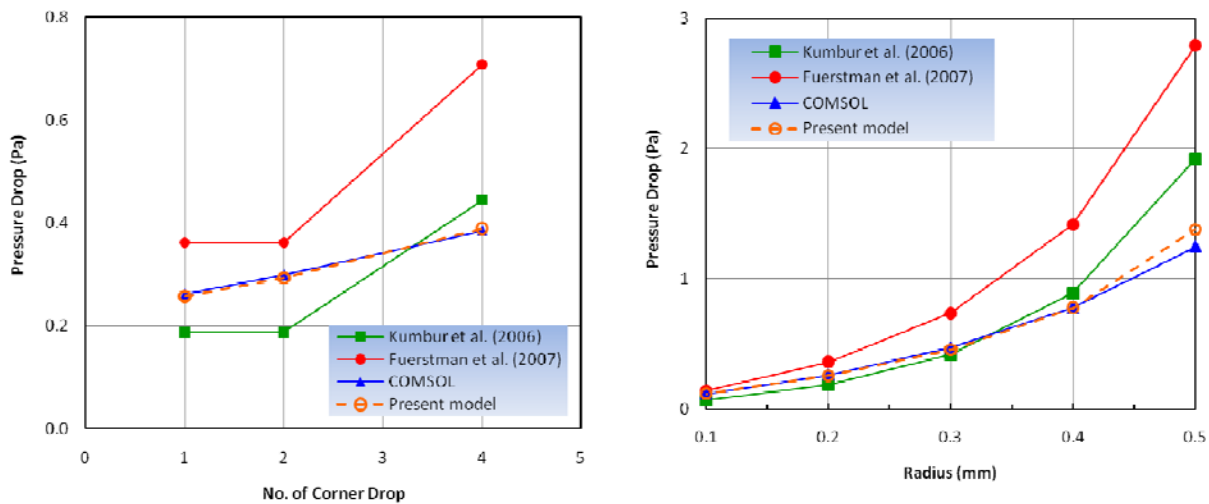
Figure 6. Comparisons of our pressure-drop correlation and those in the literature[2-3] to the detailed numerical one from Comsol.

Using the above values for the adhesion and pressure forces, one can determine the rate and number of droplet detachments or movement from the GDL surface. These can then be related to the capillary pressure in the droplet and hence the saturation of the GDL. In addition, one can also look at where the droplets go in terms of coalescence, wicking into a channel corner, etc.

Summary

Management of liquid water is critical for optimal fuel-cell operation, especially at low temperatures. It is therefore important to understand the wetting properties and water holdup of the various fuel-cell layers. While the gas-diffusion layer is relatively hydrophobic and exhibits a strong intermediate wettability, the catalyst layer is predominantly hydrophilic. In addition, the water content of the ionomer in the catalyst layer is lower than that of the bulk membrane, and is affected by platinum surfaces.

Liquid-water removal occurs through droplets on the surface of the gas-diffusion layer. In order to predict droplet instability and detachment, a force balance is used. While the pressure or drag force on the droplet can be derived, the adhesion or surface-tension force requires measurement using a sliding-angle approach. It is

shown that droplets produced by forcing water through the gas-diffusion layer rather than placing them on top of it show much stronger adhesion forces owing to the contact to the subsurface water.

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