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Interactions between liquid-water and gas-diffusion layers in polymer-electrolyte fuel cells

Prodip K. Das^{a,*}, Anthony D. Santamaria^b, Adam Z. Weber^c

^a*School of Mechanical and Systems Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, United Kingdom*

^b*Department of Mechanical Engineering, Western New England University, Springfield, MA 01119, USA*

^c*Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

Abstract

Over the past few decades, a significant amount of research on polymer-electrolyte fuel cells (PEFCs) has been conducted to improve performance and durability while reducing the cost of fuel cell systems. However, the cost associated with the platinum (Pt) catalyst remains a barrier to their commercialization and PEFC durability standards have yet to be established. An effective path toward reducing PEFC cost is making the catalyst layers (CLs) thinner thus reducing expensive Pt content. The limit of thin CLs is high gas-transport resistance and the performance of these CLs is sensitive to the operating temperature due to their inherent low water uptake capacity, which results in higher sensitivity to liquid-water flooding and reduced durability. Therefore, reducing PEFC's cost by decreasing Pt content and improving PEFC's performance and durability by managing liquid-water are still challenging and open topics of research. An overlooked aspect nowadays of PEFC water management is the gas-diffusion layer (GDL). While it is known that GDL's properties can impact performance, typically it is not seen as a critical component. In this work, we present data showing the importance of GDLs in terms of water removal and management while also exploring the interactions between liquid-water and GDL surfaces. The critical interface of GDL and gas-flow-channel in the presence of liquid-water was examined through systematic studies of adhesion forces as a function of water-injection rate for various GDLs of varying thickness. GDL properties (breakthrough pressure and adhesion force) were measured experimentally under a host of test conditions. Specifically, the effects of GDL hydrophobic (PTFE) content, thickness, and water-injection rate were examined to identify trends that may be beneficial to the design of liquid-water management strategies and next-generation GDL materials for PEFCs.

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* Corresponding author. Tel.: +44-191-208-6170 ; fax: +44-191-208-8600
E-mail address: prodip.das@ncl.ac.uk

1. Introduction

Polymer-electrolyte fuel cell (PEFC) systems are extremely efficient over a wide scale ranging from 1 kW to hundreds of megawatts and some systems can achieve overall efficiencies of 80% or more when heat production is combined with power generation. They are becoming the center of attention as an alternative power source for vehicle and stationary applications due to their ability to produce high power densities under rapid load changes. Although a substantial amount of resources has been devoted over the past several decades to the development of PEFC systems, they are not yet commercially viable due to several technical barriers. Of the many barriers, cost and durability present two of the most significant challenges to achieving reliable, cost-effective PEFC systems. In addition, PEFC performance must meet or exceed that of competing technologies. Therefore, sought after methods to reduce PEFC's cost include: i) reducing expensive Pt loading while maintaining performance ii) improving performance and durability by advanced liquid-water management schemes [1-3].

The United States Department of Energy (DOE) has a target to develop a direct-hydrogen fuel-cell power system for transportation at a cost of \$30/kW by 2017. Paralleling this goal, the DOE's current targeted platinum usage in PEFCs is 0.125 mg/cm² (in combined anode and cathode electrodes) or less, while producing rated stack power densities of 8.0 kW/g_{Pt}. To achieve the DOE's target, a key solution is the design and use of thin catalyst layers (CLs). The limiting factor in thin CL design is believed to be high gas-transport resistance due to the ionomer film covering the catalyst particles as well as issues of tolerance to poisoning [4]. In addition, the performance of thin CLs is sensitive to operating temperatures due to their inherent low water capacity, as the thickness of a CL is often in the range of few microns [3]. At low temperatures, they are prone to severe water flooding, which is problematic since the low-temperature operation is vital for rapid startup and attaining relatively high current densities. Therefore, water management is an especially critical component for PEFC operation with thin CLs, especially at low operating temperatures and during startup/shutdown, where liquid water is present. A balanced liquid-water scheme is therefore essential to achieve the full potential of a thin CL PEFC and to avoid membrane dehydration and porous-media flooding.

A critical issue for optimal water management in PEFCs at lower temperatures is the removal of liquid water from the membrane electrode assembly (MEA). This pathway is intimately linked with the phenomena of water transport (in either gas or liquid phase) and liquid-water droplet removal from surface of the gas-diffusion layer and into the flow channel. Therefore, understanding multiphase, dynamic GDL water uptake and removal is essential to developing effective liquid-water management strategies as well as next-generation GDL materials. To understand the dynamics of GDL and liquid-water interactions, we employed a novel rotating-stage goniometer to quantify and directly measure the sliding angles, adhesion force, and breakthrough pressure for various GDLs. Results of these measurements are presented and analyzed with the aim of finding an optimum pathway for liquid-water removal and designing next-generation GDL materials for PEFCs.

2. Experimental

2.1. Adhesion force

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 and contact angles of a droplet by a gravity field [5]. The contact and sliding angle measurements were done with a custom-made automated rotating-stage goniometer (ramé-hart Model 590) as shown in Fig. 1a. The system utilized a CCD camera (70 fps) of 640 × 480 pixels to capture images every quarter second, with two 150 W halogen lamps used as a backlight. The GDL sample was first placed on the sample-stage and then liquid-water was injected from either above the sample by a needle or the bottom of the sample using an automated dispensing system. The camera was mounted to a stage that was inclined by a rotary motor at a constant angular speed. The rotary motor can operate as low as 0.1°/s. Movement of the stage was vibration-free with no backlash and vibrations from surroundings were isolated from the stage using an anti-

vibration stage to ensure that the liquid-water droplet releases only due to gravity. Several measurements of contact and sliding angles were taken for each sample, while three contact-angle measurements were taken for each droplet within 1 second using DROPImage[®] software.

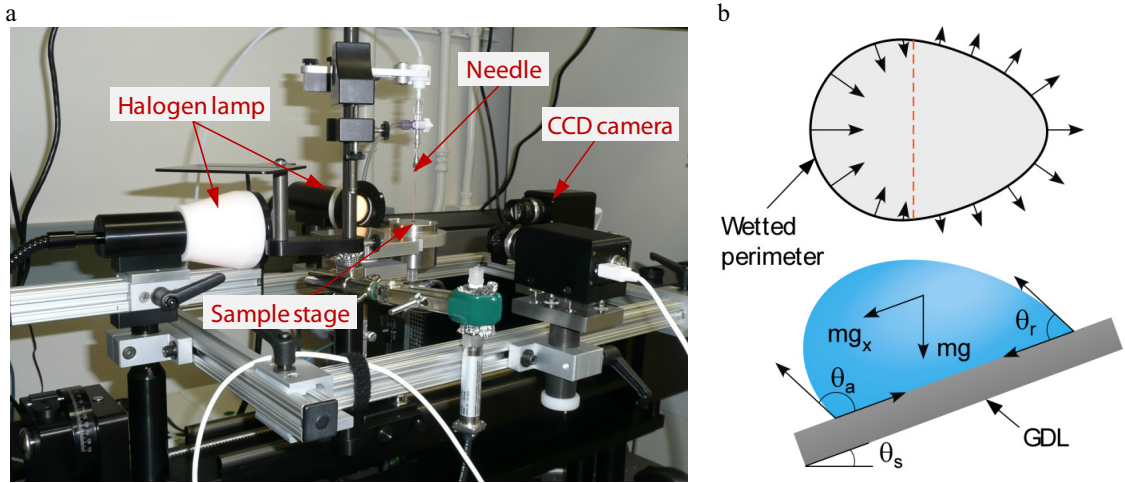


Fig. 1. (a) Rotating-stage goniometer setup used for breakthrough-pressure and adhesion-force measurements. (b) Illustration of contact and sliding angles and forces acting on a liquid-water droplet on a gas-diffusion layer (GDL) surface. Top view of part (b) shows the adhesion force distribution that is preventing the droplet from roll-off (parallel to the GDL surface); dashed line shows contact angle transition through 90°.

As shown in Fig. 1b, at the incipient sliding angle, the adhesion force and the gravity force acting on the liquid-water droplet equal each other. Thus, we can calculate the adhesion force between the liquid-water droplet and GDL surface from the body force acting along the direction of the slide and the wetted diameter,

$$F_{\text{adhesion}} = \frac{\rho V g \sin \theta_s}{\pi d_w} \tag{1}$$

where ρ is the water 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. The wetted diameter represents the equivalent diameter of the wetted area between the droplet and GDL surface as shown in Fig. 1b.

2.2. Breakthrough pressure

Breakthrough pressure is a characteristic parameter for porous material, such as fuel cell GDLs. It is related to the capillary pressure inside the pore and is determined predominately 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

$$P_c = P_L - P_G = \frac{2\gamma \cos \theta}{r} \tag{2}$$

where θ is the contact angle between water/air and GDL pore, r is the radius of a pore, P_L is the liquid-phase pressure, and P_G is the gas-phase pressure [6]. Water invasion into a hydrophobic GDL usually follows a path whereby pores with larger connecting throat radii are filled first. Breakthrough pressure, P_{BT} , 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.

Gas-diffusion layers (GDLs) are typically treated with PTFE to increase hydrophobicity and enhance water-removal capability (see scanning-electron-microscope images in Fig. 2). These coatings can affect the GDL pore volumes and throat radii influencing the breakthrough pressure, especially as the coatings are known to be non-uniform. To measure breakthrough pressure, GDL samples 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. Breakthrough pressure was determined by examining the maximum pressure achieved during an injection period. An example of typical capillary pressure data recorded over a period of time is shown in Fig. 2c. Analyzing Fig. 2c, the initial pressure signal is due to the head from water traveling through system lines (defined as system pressure or P_{sys}) and filling void space between the GDL and injection port and then a steep climb begins due to water being forced into GDL pores. The slope of the curve is attributable to expansion of the injection system before reaching a maximum, which is accompanied by droplet formation on the GDL surface. This maximum pressure is breakthrough pressure (P_{BT}) followed by a dramatic fall in signal as the pressure decays to a minimum due to reduced resistance.

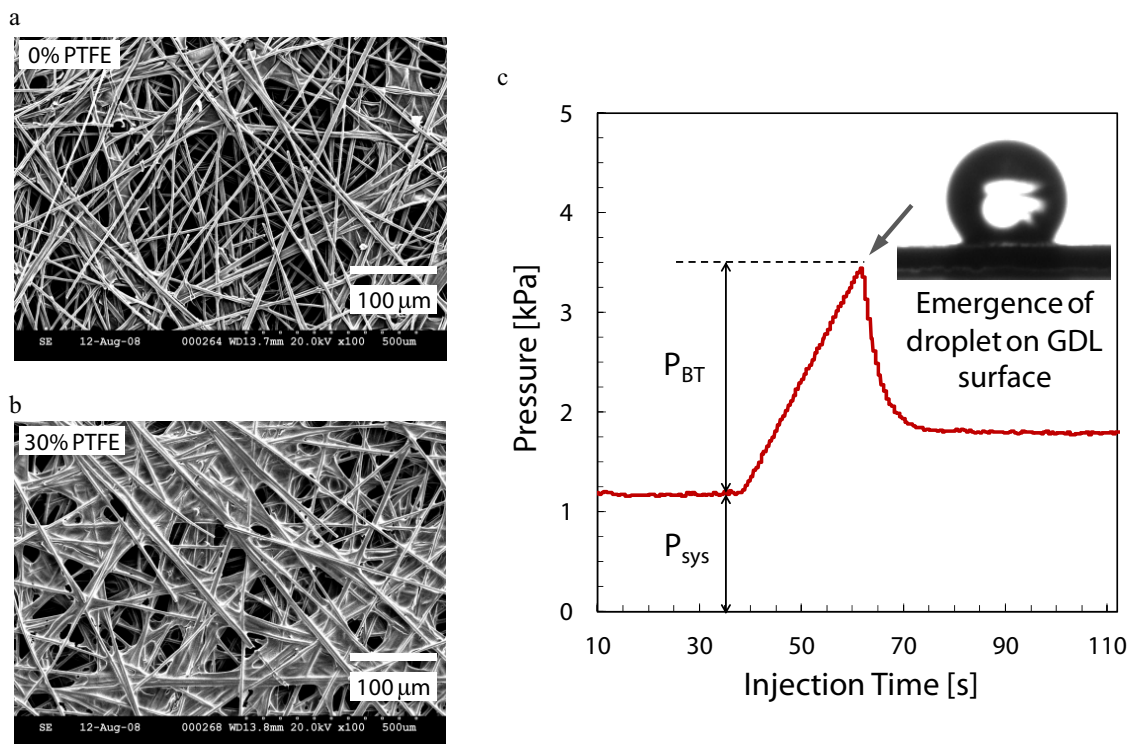


Fig. 2. Scanning-electron-microscope (SEM) images of PEFC gas-diffusion layers showing surface inhomogeneity both without (a) and with (b) PTFE treatment. (c) Time-series data acquired for capillary breakthrough pressure (P_{BT}) measurements, where the maximum capillary pressure represents the breakthrough pressure as droplet forms.

3. Results and Discussions

The interactions between the liquid-water and GDL surface are analyzed through the evaporation of a droplet on GDL surface. The adhesion force between the liquid-water droplet and GDL surface is determined from sliding angle data using Eq. (1). Fig. 3a shows the evaporation of a water droplet on untreated and PTFE treated (20-wt% PTFE loading) GDLs and Fig. 3b shows the effect of water injection rate on adhesion force. The ‘pinning’ effect is

found to be significant for the bottom injection, which assists the droplet adhesion with the GDL surface, whereas both the ‘pinning’ and ‘dewetting’ phenomena are present for a droplet placed on top of a GDL surface using the top injection. Here the pinning represents the scenario when the solid-liquid contact line remains pinned to the GDL surface while the liquid-gas interface shrinks, and the dewetting represents the scenario when the solid-liquid contact line shrinks with the liquid-gas interface.

As observed in Fig. 3a, the change of static contact angle is non-uniform. It initially decreases due to evaporation, and it increases and then again decreases as the droplet size decreases due to evaporation. Here, the adhesion between the droplet and GDL surface changes with the droplet size, which influences the static contact angle. Clearly, the adhesion force dominates over the tension force that prevents the liquid-water droplet from contracting along the wetting line (for times less than 160 s). In other words, the pinning effect is dominant over the dewetting effect. With the decrease of droplet size, the cohesion force eventually helps the droplet to contract, and the droplet exhibits the initial surface wettability again that is indicated between 150 s and 400 s. As droplet size further decreases, the adhesion force eventually regains its dominance, and the pinning effect is again observed after 400 s.

The injection rate is analogous to the operating current density in an operating PEFC. In fact, an injection rate of 1 $\mu\text{L/s}$ corresponds to a water flux derived from a current density of 2.5 A/cm^2 assuming a net water transport coefficient of 0.5 in the membrane of PEFC. The effect of injection rate on the adhesion force is shown for a PTFE treated GDL. As observed in Fig. 3b, the adhesion between the water droplet and GDL surface decreases with injection rate. In other words, faster injection enhances droplet detachment from the GDL surface. Although not shown, the static contact angle decreases with the injection rate, which results in the opposite trend in terms of adhesion force and demonstrates the efficacy of contact angles [5].

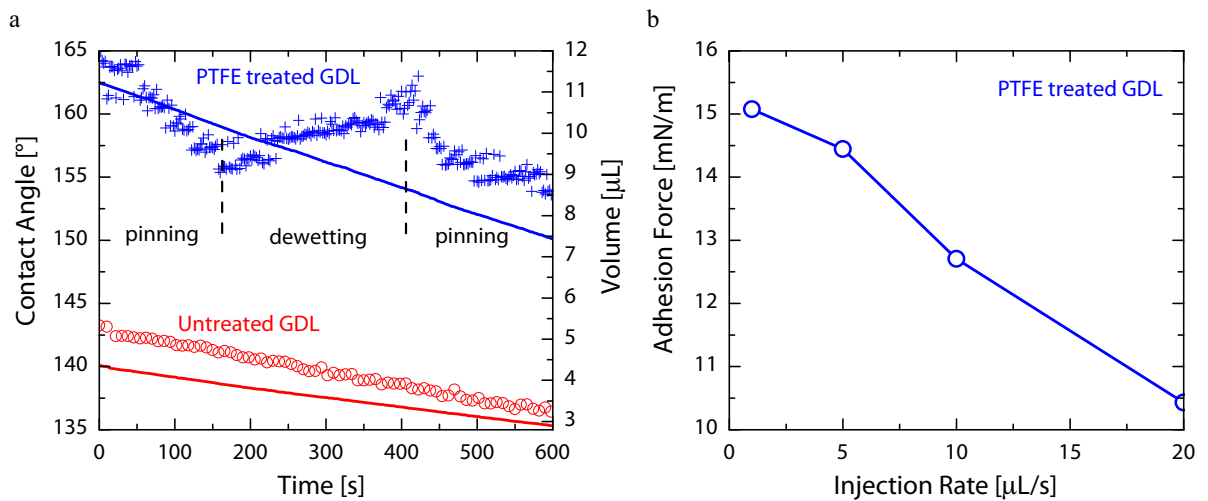


Fig. 3. (a) Interactions between water-droplet and GDL surface are shown through the contraction of the droplet due to the evaporation after 10 min and the pinning-dewetting phenomena. This figure shows the measured droplet volume (solid line) and static contact angle (symbols) as functions of time for PTFE treated and untreated GDLs. (b) Effect of injection rate on adhesion force for PTFE treated GDL [5].

Fig. 4 shows the results of breakthrough pressure as a function of GDL thickness. A higher breakthrough pressure is observed as increased GDL thickness, which implies longer flow pathways and an increased number of pores liquid water must fill before reaching the surface. This result demonstrates reduced breakthrough pressure at lower PTFE weights and an increasing rather than logarithmically plateauing trend at higher loadings. The higher breakthrough pressure at elevated PTFE loadings is due to the heterogeneous distribution of PTFE, as shown in SEM images in Fig. 2, that reduces the number of pores available to water invasion. This result matches with the

idealized view of PTFE loading effectively reducing throat sizes of the porous GDL and increasing contact angle especially at high PTFE content [7].

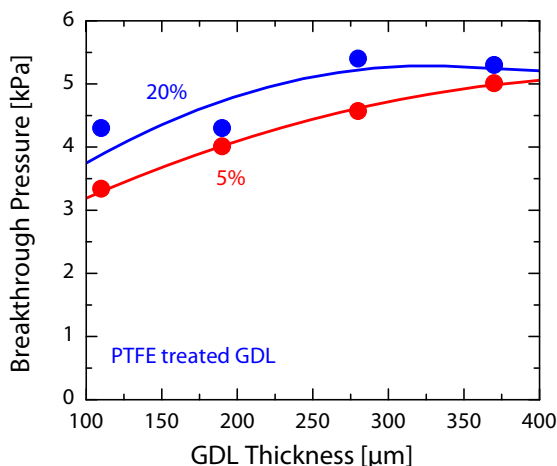


Fig. 4. Breakthrough pressure as a function of GDL thickness for 5% and 20% PTFE loadings [7].

4. Conclusions

The interactions between liquid-water and GDL surface were studied using adhesion force and breakthrough pressure measurements. It has been shown that the direct measurement of sliding angles and adhesion forces is an effective method to accurately predict droplet instability and detachment on and from the GDL surface. It has been observed that both the droplet creation method is important for droplet growth and detachment on a GDL surface. The impact of injection rate showed that higher flow rates results in lower adhesion forces, perhaps due to the kinetic effects and different water-transport pathways. Breakthrough pressure measurements showed that increasing PTFE content and GDL thickness both resulted in higher breakthrough pressure, which highlights the strong dependence of breakthrough pressure on a GDL's porosity and contact angle.

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