Dynamic characterization of partially saturated engineered porous media and gas diffusion layers using hydraulic admittance

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HIGHLIGHTS

► Performed hydraulic admittance on engineered porous sample with over 100 pores.
► Hydraulic admittance of engineered sample matched predicted simulation response.
► Performed hydraulic admittance on 2 GDL samples at different saturation states.
► Hydraulic admittance spectra of GDL samples show expected frequency dependence.
► Distinct resonance peaks show finite number of pores transport liquid water in GDL.

GRAPHICAL ABSTRACT
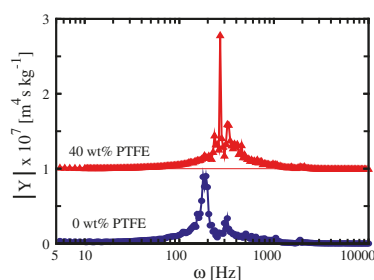
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ABSTRACT

Simple laboratory methods for determining liquid water distribution in polymer electrolyte membrane fuel cell gas diffusion layers (GDLs) are needed to engineer better GDL materials. Capillary pressure vs. liquid saturation measurements are attractive, but lack the ability to probe the hydraulic interconnectivity and distribution within the pore structure. Hydraulic admittance measurements of simple capillary bundles have recently been shown to nicely measure characteristics of the free-interfaces and hydraulic path. Here we examine the use of hydraulic admittance with a succession of increasingly complex porous media, starting with a laser-drilled sample with 154 asymmetric pores and progress to the behavior of Toray TGP-H090 carbon papers. The asymmetric laser-drilled sample clearly shows hydraulic admittance measurements are sensitive to sample orientation, especially when examined as a function of saturation state. Finite element modeling of the hydraulic admittance is consistent with experimental measurements. The hydraulic admittance spectra from GDL samples are complex, so we examine trends in the spectra as a function of wet proofing (0% and 40% Teflon loadings) as well as saturation state of the GDL. The presence of clear peaks in the admittance spectra for both GDL samples suggests a few pore types are largely responsible for transporting liquid water.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are attractive as a power source due to high efficiency, low temperature, and low noise [1,2]. However, at high current densities the generated water condenses within the pores of the catalyst layer and underlying gas diffusion layer (GDL), and reduces the exposed

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catalyst surface area available for the electrochemical reaction [2–7]. To minimize disruption by liquid retention (flooding), the GDL pores must guide the formation of limited water pathways to the gas channels, so that additional liquid can be removed as it forms. GDLs typically have a thin hydrophobic microporous sublayer [8] and are treated with various Teflon loadings to render them hydrophobic [9–11]. The resulting GDL and microporous layer results in a complicated porous material with asymmetric wetting and hydraulic properties [12].

Based on the capillary number (Ca), which relates the viscous forces to surface tension forces, a fuel cell operating at 1 A cm^{-2} is dominated by capillarity with a Ca $\sim 10^{-8}$ [7,13] and falls under the capillary fingering regime (for more details on capillary fingering, refer to [14]). In light of this, there is now a movement toward pore-scale modeling that captures the liquid and gas structure within a pore-lattice network (see review [7]). Additionally, sophisticated imaging techniques (see review [15]) such as neutron radiography [16], magnetic resonance imaging, and synchrotron X-ray radiography [17–21] are continually making advances. Recently, Buchi's [19] group used X-ray tomographic microscopy to reconstruct both the solid GDL as well as the liquid water at different applied liquid water pressures with significantly improved spatial resolution. However, despite the improvement, the technique is still not readily available and currently limited to small GDL sample size of 2.5 mm in diameter, not the large areas normally found in stacks [21–24]. Despite the advances in imaging, sophisticated tools like these are geared toward fundamental understanding, not rapid lab-based materials development and optimization.

Capillary pressure vs. liquid saturation $P_C(S_L)$ measurements have been shown to be an attractive and straightforward characterization approach to quantify the hysteretic wetting of GDL samples during both liquid intrusion (where gas in the pores is displaced by liquid) and gas intrusion (where liquid in the pores is displaced by gas) [25–30]. However, this technique only probes the static interfacial curvature of all the hydraulically connected free-interfaces and lacks the ability to probe the characteristics of the hydraulic network leading to interfaces. Dimon et al. [31] developed a tool that could dynamically probe the interfacial resonance of a pinned free-interface in a single nearly full cylindrical capillary. When a small volumetric oscillation of frequency (ω) is dynamically applied to the pinned free-interface, an oscillatory pressure drop is generated. The complex, frequency dependent ratio of the applied volumetric displacement to this pressure drop is called the hydraulic admittance ($\tilde{Y}_{Hyd}(\omega)$). Using linear theory, the hydraulic admittance is the inverse sum of hydraulic impedances from viscous and inertial fluid forces in the filled part of the capillary ($\tilde{Z}_{V+I}(\omega)$), plus a capillary impedance ($\tilde{Z}_C(\omega)$) derived from the interface state

$$\tilde{Y}_{Hyd}(\omega) = -\frac{1}{\tilde{Z}_{V+I}(\omega) + \tilde{Z}_C(\omega)} \tag{1}$$

where

$$\tilde{Z}_{V+I}(\omega) = -\frac{\mu L(\omega/\omega_c)}{i\pi R^4 \left[1 - \frac{2}{\sqrt{i\omega/\omega_c}} \frac{J_1\left(\sqrt{i\omega/\omega_c}\right)}{J_0\left(\sqrt{i\omega/\omega_c}\right)}\right]} \tag{2}$$

$$\tilde{Z}_C(\omega) = \frac{2\gamma\sin(\theta)(1+\sin(\theta))^2}{i\omega\pi R^4} \tag{3}$$

and μ is dynamic viscosity of the fluid, L is the hydraulic path length, J_1 and J_0 are the 1st and zeroth order Bessel functions of the first kind, respectively, γ is the surface tension, and θ is the contact

angle measured within the liquid. The characteristic frequency ω_c is defined by

$$\omega_c = \frac{\mu}{\rho R^2} \tag{4}$$

where ρ is the density of the fluid. When the magnitude of the hydraulic admittance is plotted against the applied oscillation frequency, resonance peaks are observed for every degenerate combination of fluid path and free-interface. The resonance frequency (ω_o) originates when the viscous and inertial impedances ($\tilde{Z}_{V+I}(\omega)$) are equal in magnitude to the capillary impedance ($\tilde{Z}_C(\omega)$) and 180° out of phase. The resonance frequency scales as

$$\omega_o \sim \sqrt{\frac{\gamma}{\rho R^2 L}} \tag{5}$$

To explore the potential of hydraulic admittance measurements as a probe for the hydraulic properties of complex porous media, we developed a bench-top tool [32] to accommodate porous samples that significantly extended previous studies of single nearly filled capillaries [31,33,34]. In order to accommodate different porous samples easily, the tool was designed to ensure Helmholtz resonances in the cavity did not interfere with the sample interfacial resonances [35–37]. Good agreement was found between theory and experiments for single capillaries and small bundles as a function of their fill state. Briefly, for a constant capillary radius, an increase in hydraulic path length results in a drop in hydraulic admittance magnitude and a shift toward lower frequencies, and for a constant hydraulic path length, an increase in the capillary radius results in an increase in hydraulic admittance magnitude and a shift toward lower frequencies. We further showed that the total hydraulic admittance ($\tilde{Y}_{Total}(\omega)$) of a bundle of M capillaries could be represented by

$$\tilde{Y}_{Total}(\omega) = \sum_{j=1}^{M} \tilde{Y}_{Hyd,j}(\omega) \tag{6}$$

for each individual admittance ($\tilde{Y}_{Hyd,j}(\omega)$). GDL materials are sometimes treated as a bundle of capillaries to approximate their more complex porous structure [4,29].

In this work, we expand our previous work by investigating the hydraulic admittance of more complex porous samples. We start with an engineered material that has hundreds of conical pores. Finite element modeling is included to understand the orientation dependence on the hydraulic admittance as a function of liquid saturations. We then take insights from quantitative measurements done here and previously to qualitatively explore the behavior of hydraulic admittance for two types of GDL samples. We focus on unique features of the measured admittance spectra and describe possible fluid displacement mechanisms that are consistent with the observed spectral features and previous work.

2. Methods

2.1. Materials

An acrylic (TAP plastics, Seattle, WA) porous sample was engineered by laser drilling (300-M Universal Laser Systems, Scottsdale, AZ) 154 pores as shown in Fig. 1. Several passes were necessary to drill all the way through, resulting in oblong-shaped pores instead of a perfect conical pore. Effective major and minor radii were measured from a series of images for both orientations. The effective pore radii reported here were calculated by equating the area of a circle to the area of an ellipse using the measured effective major and minor radii. The average contact angle of DI water on a smooth