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Quantifying Percolation Events in PEM Fuel Cell Using Synchrotron Radiography

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ABSTRACT

The distribution of independent water clusters within the gas diffusion layer (GDL) is an important, yet poorly understood, characteristic of polymer electrolyte membrane fuel cells. A better understanding of these water clusters would provide ex-situ invasion experiments and two-phase models with a set of validation criteria that is currently absent from the literature. Synchrotron based X-ray radiography was employed visualize liquid water emerging from the polymer electrolyte membrane fuel cell GDL. Droplet formations, entitled "breakthrough" events originated from either the channel or landing regions of the GDL. The number of breakthrough events in a given area (breakthrough density) provides insight into the size and number of independent water clusters evolving within the GDL. Water clusters were found under the flow field landings more frequently than under the gas channels. Each 1 mm^2 of projected GDL area was found to have 1-2 individual water clusters during most conditions studied, regardless of the GDL substrate or MPL type. The existence of percolating water clusters under flow field channels depended on the combination of GDL type and operating conditions employed.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells may provide hydrogen supplied power to many applications that have traditionally been powered by fossil fuels. PEM fuel cells have been under focused development for decades and have recently reached economic practicality in a number of niche applications, such as material handling and back-up power. Despite the advancements, challenges related to water management hinder the wider adoption of hydrogen paired with renewable energy as an alternative to fossil fuels.

Water is a by-product of the electrochemical reaction of hydrogen and oxygen within the PEM fuel cell, and a certain amount of water is required to keep the PEM ionically conductive. However, condensed water around the electrochemical reaction sites can impede reactions by creating a barrier to the gaseous reactants. A delicate water balance is key for fuel cell performance optimization, but this has often been a black-box type of problem due to the opaque nature of fuel cell components. However, through advancements in X-ray radiography technologies, it has recently become possible to obtain high resolution, in-situ visualizations of water accumulation [1–24].

PEM fuel cells employ an electronically conductive porous material, commonly referred to as the gas diffusion layer (GDL) to allow electrons, heat, and gases to travel to and from electrochemical reaction sites. These porous materials can become partially flooded due to condensation, creating clusters of liquid water, which can continue to grow as long as the local environment favors condensation. Using a pore network model of the GDL, Wu et al. [25] predicted that GDL saturation distributions were highly sensitive to the number of individual water clusters simultaneously percolating through the GDL from the catalyst layer. While the footprint of the combined clusters fully covered the sample area, their study showed that lower overall saturation levels could be predicted when fewer, larger individual water clusters were assumed.

Capillary theory suggests that once a growing water cluster reaches the large pore space within a flow-field channel (point of breakthrough), there can be no further growth by that water cluster throughout the hydrophobic pore-space of the GDL [25–29]. Additional condensed water volume will be capillarily pumped to the channel through this breakthrough pathway. The implication is that individual water clusters within the GDL cannot have multiple, simultaneously active points of breakthrough into the gas channels. Simultaneously active breakthrough locations observed in Refs.

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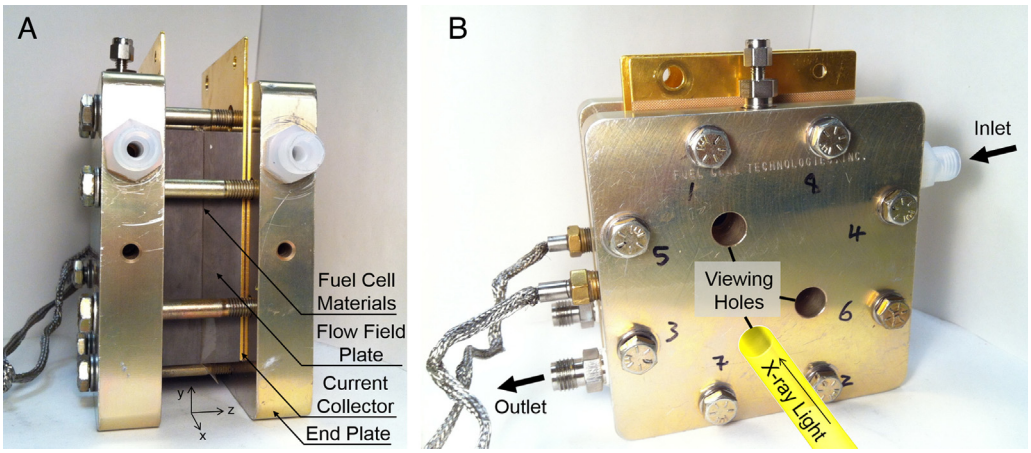

Fig. 1. Images of modified 25 cm^2 Fuel Cell Technologies PEM fuel cell: a) in plane view, and b) through plane view. Note: Although three viewing holes are present, only the lowermost hole was used in this study.

[1,24,30] must arise from multiple, disconnected water clusters within the material. Therefore, a concept entitled "breakthrough density" should be explored. Breakthrough density describes the number of breakthrough locations per unit of projected surface area of the GDL in an operating PEM fuel cell. This information is relevant when developing experiments and models that study the expected distribution of liquid water in the GDL. Examples of such experiments are given in Refs. [31–39], where syringe pumps or water columns were employed to provide the controlled injection of liquid water into a dry GDL material. While these ex-situ experiments provided highly valuable and novel insight into the behaviour of liquid water behaviour in the GDL, ex-situ studies are prone to limitations from inlet source and sample size.

In ex-situ liquid water invasion experiments, GDL materials are invaded from a single liquid water source. With a single liquid water source, only a single percolating water cluster should arise under capillary dominated flow. Also, in such ex-situ experiments, GDL sample size can easily become constrained as a result of experimental requirements. In cases such as microscopy [31–33,36] or X-ray micro-computed tomography (μCT) [39], the optical field of view associated with the desired magnification restricted the sample size. Whereas, in other studies [34,35,37,38], larger sample sizes were convenient for material preparation and apparatus design. As a result of various experimental constraints, studied GDL samples have ranged from 4.9 mm^2 [39] to 20 cm^2 [38]. Despite this large range of sample sizes, only one breakthrough location would be expected in these ex-situ experiments over the entire sample when a single inlet liquid water reservoir was used. In contrast to these ex-situ experiments, high breakthrough densities have been observed during in-situ studies. Breakthrough densities close to 1 mm^{-2} were observed in visualizations provided by Ous and Arcoumanis [30] who employed an air-breathing fuel cell with 5 mm-wide channels to allow for optical observation of gas channels.

Manke et al. [1] demonstrated the ability to visualize in-situ breakthrough events using synchrotron X-ray radiography. They determined that liquid water clusters underneath flow field landings periodically gave rise to breakthrough events at the corners of channel/landing/GDL interfaces. By applying a similar methodology, Lee et al. [24] provided a comparison between GDL materials with and without microporous layer (MPL) coatings. Higher breakthrough densities were displayed for the cell built with MPL-coated GDLs; however, this high breakthrough density did not appear to have a negative effect on cell performance. The MPL was theorized as preventing water clusters near the catalyst layer from spreading laterally and coalescing, thus allowing for more independent water clusters to percolate, while keeping the catalyst layer accessible to oxygen diffusion.

Markötter et al. [15] employed synchrotron based in situ radiography of dynamic liquid water transport. Within the flow field channels, they observed droplets to be collocated with water-filled cracks of the MPL. Upon quantifying the droplet growth rates, they estimated that only 6% of the local electrochemically generated water could be accounted for by the droplets observed emerging under the channel. The apparent breakthrough density displayed in their figures was roughly 1-2 mm^{-2}.

Roth et al. [16] employed synchrotron-based tomography imaging of in-situ liquid water to determine a minimum planar area of the cathode GDL that could provide representative saturation levels. While they found that the dry GDL could be well represented by any 0.5 mm^2 of their image, some saturation configurations required 1.6 mm^2 of area before being generally representative. They attributed the required large representative areas to sparse water clusters throughout the GDL.

During PEM fuel cell operation, breakthrough densities are typically greater than 1 mm^{-2}; therefore, single inlet, ex-situ liquid water invasion experiments with GDL samples larger than 1 mm^2 most likely possess unrealistic saturation levels and spatial distributions. Predictive numerical simulations of GDL invasion that can account for arbitrary numbers and distributions of independent water clusters are vital for understanding the nature of liquid water accumulation at the interfaces and within the bulk of the GDL.

In this work the spatial densities of breakthrough events in 11 operational PEM fuel cells were studied in order to gain insight into the nature of disconnected liquid water clusters within the GDL. Synchrotron X-ray absorption was used to image liquid water droplets dynamically emerging from the GDL. Six GDL types were studied, and their breakthrough densities are presented. The number and sizes of water clusters under the gas channels and under the flow field landings were estimated.

2. Method

2.1. Fuel Cell Materials and Assembly

The fuel cell architecture was based on standard 25 cm^2 assembly produced by Fuel Cell Technologies[1]. It had an active area of 5 cm × 5 cm, a triple serpentine flow field, and 1 mm-wide

[1] http://www.fuelcelltechnologies.com/.