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Formation of Liquid Water Pathways in PEM Fuel Cells: A 3-D Pore-Scale Perspective

P. Shrestha,* CH. Lee,* K. F. Fahy,* M. Balakrishnan,* N. Ge,* and A. Bazylak**

Thermofluids for Energy and Advanced Materials Laboratory, Department of Mechanical & Industrial Engineering, Institute for Sustainable Energy, Faculty of Applied Science and Engineering, University of Toronto, Toronto, Ontario, Canada

We investigated the 3-D pore-scale liquid water distribution within the cathode GDL via in operando synchrotron X-ray tomography during low current density fuel cell operation to capture the early appearance of liquid water pathways. We found that the invasion of liquid water into the GDL only partially filled certain GDL pores. Liquid water preferentially flowed along some GDL fibers, which was attributed to the hydrophilic nature of carbon fiber and the presence of pore-scale mixed wettability within the GDLs.

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Growing energy use necessitates the adoption of renewable energy sources and sustainable energy conversion devices with low carbon emissions to mitigate anthropogenic climate change.1 Polymer electrolyte membrane (PEM) fuel cells offer a robust solution for on-site energy conversion and utilization without local carbon emissions.2 However, the high cost of the PEM fuel cell has bottlenecked its adoption. Innovative water management strategies aimed at the cathode gas diffusion layer (GDL) have the potential to drastically improve high current density performance of the fuel cell and thereby reduce costs.2 Understanding liquid water transport within the GDL is crucial for driving this much-needed innovation and design. At the pore-scale, most commercial GDLs exhibit a complex heterogeneous structure with mixed wettability due to the non-uniform dispersion14 of a hydrophobic binder, typically polytetrafluoroethylene (PTFE), on the hydrophilic carbon fibers of the GDL. The hydrophobic binder is commonly applied via a dip-coating procedure which results in a heterogeneous coverage of the binder, where the binder may distribute partially on the fibers, deposit as a thin layer along fibers, or preferentially accumulate near the GDL surfaces.3 To implement successful water management strategies, we need to understand the effect of the complex heterogeneous nature of the GDL on the pore-scale transport of liquid water.

Recent advances in pore-scale modeling5–7 and visualization8–11 have shed light on certain water transport mechanisms existing in the complex heterogeneous pore structure of the GDLs. Y. Nagai et al.8 used in operando synchrotron X-ray computed tomography to demonstrate that primary liquid water pathways, which were established in the large micrometer-sized pores of their custom microporous layer (MPL), promoted the efficient removal of liquid water by limiting the number of entry pathways in the GDL substrate. S. J. Normile et al.9 showed that large voids (∼10 μm) at the catalyst layer-MPL interface served as locations for liquid water pooling or membrane swelling. S. Alrwashdeh et al.10 performed pore-scale simulations on experimentally-characterized partially saturated GDLs and showed that hydrophobic treatments on GDLs led to significant improvements in water permeability without impacts on the effective diffusivity of air. Although there has been considerable work on the topic of mixed wettability, the precise nature of how the initial liquid water pathways form in GDLs is not yet known. Initial pathways become established as preferential pathways for liquid water transport, even with increased water generation rates, and hence play an important role in predicting the overall liquid water distribution within the GDL.

In this study, we investigate the three-dimensional (3-D) pore-scale liquid water distribution within the cathode GDL in operando via synchrotron X-ray tomography during low current density fuel cell operation. The goal of the study was to capture the early appearance of liquid water pathways to enhance our understanding of how liquid water pathways form within GDLs and how the pathways are affected by the mixed wettability of the GDL structure.

Experimental

Here, we describe the experimental setup used for in operando fuel cell tomography. Fuel cell electrochemical performance was characterized while acquiring X-ray tomographic projections of the fuel cell. We then describe the image processing and visualization procedures used to convert the tomographic projections into spatially resolved 3-D liquid water distributions.

In operando fuel cell tomography setup.— Fuel cell test setup.— A custom miniature fuel cell was designed and built for electrochemical testing and in operando X-ray computed tomography
The operating fuel cell was imaged using synchrotron X-ray tomography at the Biomedical Imaging and Therapy Wiggler Insertion Device (05ID-2) beamline facility at the Canadian Light Source (CLS) in Saskatoon, Canada. The fuel cell was oriented with the MEA plane horizontal and parallel to the incoming X-ray beam. The X-ray beam was collimated and monochromatic with an energy level of 30 keV. A total of 1500 two-dimensional (2-D) projections were captured at 0.12° rotation increments (total rotation angle of 180°). 2-D images of the incident beam, i.e., flat-field projections, were captured at the beginning and end of each tomography scan. Each projection image was captured with an exposure time of 300 ms, a pixel resolution of 6.5 μm per pixel (as used successfully by L. Battrell et al. to identify GDL pore space), and a field-of-view of 13.3 mm (width) by 1.5 mm (height). Individual GDL fiber diameters range between 1–2 pixels (mean fiber diameter of ~7.6 μm); however, binder and PTFE were not distinguished from the fibers in this scan, hence bundled fibers or fibers coated with binder/PTFE could appear larger than 1–2 pixels wide. A 100 μm thick LuAG scintillator (CRYTUR spol. s r. o.) converted the transmitted X-ray irradiance into visible light which was detected by a digital scientific complementary metal-oxide-semiconductor (scCMOS) camera (ORCA-Flash4.0, Hamamatsu Photonics K.K.). For each current density step, tomographic imaging was conducted for 15 min at steady state after a 10-minute stabilization period which was sufficient to stabilize water distributions within the GDL.

Figure 2. A sample 2-D cross-sectional image slice at the cathode GDL shown at different points in time and under different conditions to highlight image processing procedure after 3-D reconstruction: (a) OCV reference image, (b) in-operando test image aligned with OCV image using the imregister function MATLAB, (c) subtracted image showing liquid water, and (d) overlaid image of OCV reference image (greyscale) and liquid water (cyan) obtained by filtering and segmenting subtracted image (c). White scale bar in (a) represents a length of 0.5 mm. (e) 3-D visualization (perspective view) of liquid water distribution (cyan) overlaid onto contrast-enhanced GDL fibers (translucent brown) and flow-field ribs (orange).
Image processing and liquid water visualization.—The 2-D tomographic projection images were processed to obtain 3-D liquid water and material density distributions. A dark-field image (an average of 10 images taken in the absence of the incident X-ray beam) was subtracted from each projection image to correct for the background noise of the camera. Each projection image was corrected for the non-uniform response of the camera, scintillator screen, and incident X-ray beam using an averaged flat-field image (an average of 20 flat-field projections taken before and after tomographic projections). The corrected projection images were reconstructed into 3-D images using the filtered back-projection algorithm available in the NRecon software (Bruker Corporation). A sample cross-sectional slice of the cathode GDL during operation at OCV and later during the 0.05 A cm\(^{-2}\) step is shown in Figs. 2a and 2b, respectively. The pixel intensities of the image slices represent material density, where darker intensities (black) indicate lower material density (e.g., void space) while brighter intensities (grey) represent solid material (e.g., carbon fiber) and/or liquid water. The 3-D images of the fuel cell during OCV and the 0.05 A cm\(^{-2}\) step were registered for any unwanted translation and rotation using the imregister function in MATLAB (MathWorks). The 3-D image taken at OCV was subtracted from the aligned image taken during the 0.05 A cm\(^{-2}\) step to obtain the liquid water distribution during fuel cell operation (Fig. 2c). The 3-D OCV image represents a dry reference state image where the GDL is devoid of liquid water. The subtracted water distribution image was filtered using a 3-D median filter (width of 2 pixels in each direction) to reduce noise, contrast-enhanced, and segmented into water and background using Otsu’s automatic threshold. Unphysical pixel-wide holes created in the water distribution during the segmentation process were filled in using the Fill Holes function in Fiji. The resulting 3-D liquid water distribution was overlaid onto the 3-D reference OCV image to visualize liquid water with respect to the GDL materials and pores (Fig. 2d). Two software, namely Dragonfly (Object Research Systems) and Fiji, were used to visualize the liquid water distribution in 3-D (Fig. 2e).

Results and Discussion

3-D liquid water pathways were visualized within the fuel cell at a current density of 0.05 A cm\(^{-2}\) (cell potential of 0.43 V; low cell performance was attributed to a high ohmic resistance of 1.3 Ω cm\(^{-2}\) at 0.05 A cm\(^{-2}\), low OCV of 0.81 V, and high kinetic losses at room temperature). In this study, we report and focus on two specific pore-scale phenomena observed within the fuel cell: partial filling of GDL pores and preferential flow of liquid water along GDL fibers and channel boundaries. We then present a discussion of some experimental insights into predicting the formation of liquid water pathways within GDLs.

Partial filling of GDL pores.—We observed that the invasion of liquid water into the GDL only partially filled certain GDL pores. Representative examples are shown in Fig. 3. In the example slice shown in Fig. 3d, the area fraction of invaded pores covered by liquid water was only 85% rather than 100% (fully filled). To better understand the mechanisms for partial filling of GDL pores, we investigate the 3-D distribution of water using cross-sectional orthogonal views. We report two possible explanations for the observed partial filling of pores: a) capillary barrier imposed by narrow constrictions in pore morphology, and b) preferential flow of liquid water along GDL fibers and channel boundaries. It is important to consider the 3-D pore morphology when examining pore-scale liquid water transport. The shape and size of the pore space (pore/throat diameter and connectivity) and the roughness of the pore walls can have significant effects on water transport. Here, we report an effect of the 3-D shape and size of the pore space on water transport. In the representative example...
shown (Fig. 4), the top view shows a partially filled pore space (Fig. 4a). The side and front views (Figs. 4b and 4c, respectively) show that the unfilled void space constricts and narrows towards the edges (outlined for clarity in Fig. 4d). The narrower regions in the apparently hydrophobic pore space would exhibit higher threshold capillary pressures and be unfavorable for liquid water transport compared to the wider (water-filled region) in the pore, and consequently lead to a partially filled pore (Fig. 4a). This pore filling phenomena has also been discussed in the literature through numerical28,29 and experimental30 studies of multiphase flow through porous media.

**Figure 5.** Preferential flow of water along GDL fibers (indicated by red *) and channel boundaries (indicated by red °) shown in 2-D overlaid images (enlarged) of liquid water (cyan) and dry GDL fibers and pores (greyscale) in cross-sectional orthogonal (a) top, (b) side, and (c) front views. Labels II, III, and IV correspond to water clusters shown in Figs. 3(d)–(f). Additional top views of water cluster IV, (g) 3-D isometric view of liquid water cluster IV (cyan), with fibers removed for clarity. Locations of catalyst layer, GDL, and flow-field rib are indicated. The cross-section slices corresponding to the 2-D images in (d)–(f) are taken in locations indicated by dashed lines in (g). II.(c), III.(c), IV.(c), and (g) show preferential liquid water flow around fiber, while II.(b), II.(c), IV.(c), (f), and (g) show liquid water wicking along flow-field rib. White scale bars represent a length of 0.1 mm.
along some GDL fibers and channel boundaries (Fig. 5). In certain locations, water preferentially flowed and surrounded GDL fibers (shown using red * in Fig. 5). This preferential flow of liquid water along GDL fibers is highlighted for the respective regions of interest using cross-sectional orthogonal slices (water clusters II and III in Fig. 6 and cluster IV in Figs. 5d–5f) and 3-D isometric views (water clusters II and III in Fig. 6d and cluster IV in Fig. 5g). This observation was attributed to the hydrophilic nature of the constituent carbon fiber (contact angle of ∼80° for plain single fiber31) and the presence of mixed wettability within the GDLs. Most commercial GDLs, including SGL 25 BC (used in this study), consist of hydrophilic carbon fibers that are hydrophobized with a non-uniform dispersion3,4 of PTFE binder (contact angle of 110°32), where PTFE may cover the fiber partially, as a thin layer, or preferentially near the surface.3 In addition, liquid water was observed to wick along channel boundaries (shown using red ° in Fig. 5), owing to the hydrophilic nature of constituent graphite plates. Due to the mixed wettability in the GDL, a mixed drainage-imbibition process may occur in the GDL, where liquid water preferentially flows along hydrophilic carbon fibers and graphite flow-field boundaries rather than hydrophobic PTFE. This mixed drainage-imbibition process may lead to the partial filling of GDL pores (as seen in Figs. 3 and 5).

**On predicting the formation of liquid water pathways: discussion of experimental insights**—Assuming capillary-dominated liquid water transport (negligible temperature gradient at low current density and negligible vapor transport at low temperature fuel cell operation31), liquid water is transported from the catalyst layer to the flow-field by sequentially filling one pore to the next based on the threshold capillary pressure of the smallest constriction between the pores (i.e., throat). Threshold capillary pressure is affected by a) the morphology of the pore space, which determines the distribution of individual pore/throat diameters and connectivity of pores in the path of liquid water transport (as seen in Fig. 4) and b) the local wettability of the pore (as seen in Fig. 5). The 3-D morphology of the pore space can be accurately modeled when the physical pore space is extracted and segmented into a collection of individual pores/throats, as done in state-of-the-art pore-scale simulations of the GDLs.5,26 However, to accurately predict and model the effects of heterogeneous mixed wettability on the formation of liquid water pathways in GDLs, we recommend to accurately characterize and incorporate the actual 3-D distribution of heterogeneous wettability within the GDL, as also suggested by M. Sabharwal et al.34

**Conclusions**

We visualized initial liquid water pathways in the cathode GDL pores in operando. We found that certain GDL pores invaded by liquid water were partially, rather than completely, filled. Partial pore filling was attributed to the presence of complex 3-D pore morphology and heterogeneous mixed wettability within the GDL. Liquid water was observed to preferentially flow along some GDL fibers and channel boundaries, which was attributed to the hydrophilic nature of the carbon fiber/graphite flow-field and the presence of pore-scale mixed wettability within the GDLs. Our results demonstrate the significance of mixed wettability at the pore-scale for the formation of initial liquid water pathways in the GDL. The phenomena of mixed drainage-imbibition due to mixed wettability should be incorporated and leveraged in GDL modeling and design in order to tailor liquid water transport pathways in next-generation GDLs.

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ORCID

P. Shrestha https://orcid.org/0000-0002-9881-1973
CH. Lee https://orcid.org/0000-0002-8428-1502
K. F. Fahy https://orcid.org/0000-0003-2866-9147
M. Balakrishnan https://orcid.org/0000-0001-7456-8289
N. Ge https://orcid.org/0000-0002-5837-0448
A. Bazylak https://orcid.org/0000-0002-9594-4930

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