Lawrence Berkeley National Laboratory
Recent Work

Title
Understanding Water Transport in Polymer Electrolyte Fuel Cells Using Coupled Continuum and Pore-Network Models

Permalink
https://escholarship.org/uc/item/11q0r77d

Journal
Fuel Cells, 16(6)

ISSN
1615-6846

Authors
Medici, EF
Zenyuk, IV
Parkinson, DY
et al.

Publication Date
2016-12-01

DOI
10.1002/fuce.201500213

Peer reviewed

Understanding Water Transport in Polymer-Electrolyte Fuel Cells Using Coupled Continuum and Pore-Network Models

Ezequiel F. Medici[1], Iryna V. Zenyuk[2], Dilworth Y. Parkinson[3], Adam Z. Weber[4] and Jeffrey S. Allen[1]

[1] Department of Mechanical Engineering-Engineering Mechanics,
Michigan Technological University, Houghton, MI 49931, USA
e-mail: efmedici@mtu.edu, jstallen@mtu.edu

[2]Department of Mechanical Engineering
Tufts University, Medford, MA 02155, USA
e-mail: Iryna.zenyuk@tufts.edu

[3]Advanced Light Source
Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
e-mail: dyparkinson@lbl.gov

[4]Energy Conversion Group, Energy Technologies Area,
Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
e-mail: azweber@lbl.gov

Abstract

Water management remains a critical issue for polymer-electrolyte fuel-cell performance and durability, especially at lower temperatures and with ultrathin electrodes. To understand and explain experimental observations better, water transport in gas-diffusion layers (GDLs) with macroscopically heterogeneous morphologies was simulated using a novel coupling of continuum and pore-network models. X-ray computed tomography was used to extract GDL material parameters for use in the pore-network model. The simulations were conducted to explain experimental observations associated with stacking of anode GDLs, where stacking of the anode GDLs increased the limiting current density. Through imaging, it is shown that the stacked anode GDL exhibited an interfacial region of high porosity. The coupled model shows that this morphology allowed more efficient water movement through the anode and higher temperatures at the cathode compared to the single GDL case. As a result, the cathode exhibited less flooding and hence better low-temperature performance with the stacked anode GDL.

1. Introduction

Optimal water management is essential for the performance and stability of polymer-electrolyte fuel cells (PEFCs), especially with the development of new material sets such as the nanostructured thin-film (NSTF) electrodes developed by 3M [1, 2]. During PEFC operation, water is generated in the cathode electrode and removed to the gas flow-channels in either liquid or vapor phase or a combination of both. PEFCs with NSTF electrodes are susceptible to severe flooding at low temperatures due to their thinness (~0.5 µm thick). In conventional carbon-supported electrodes, water flooding is less of a problem due to their higher water-storage capacity (i.e., thickness) and greater hydrophobicity [3-5]. Water flooding is not as much of a concern at high operating temperatures, since water is generally removed in the vapor phase. However, at low operating temperatures, where phase-change-induced water transport is suppressed, limiting current densities are significantly reduced due to the presence of the liquid water.

Recent experimental studies have suggested that a combination of controlled operating conditions and engineered component morphology may increase the water-removal effectiveness at low temperatures for NSTF PEFCs [6, 7]. Steinbach et al.[6, 7] reported a novel water-management scheme where water removal is directed through the anode by applying extra gas pressure on the cathode side. The increased gas pressure with thin membranes and selected anode gas-diffusion layer (GDL) morphologies that allow high water-permeation rates increased the limiting current density at 40ºC by a factor of four. Various GDL morphologies were tested and the best performing GDL featured a modulated fiber-density morphology with alternating bands of high and low porosity [8]. In addition, when two of these GDLs were stacked on the anode side, effectively doubling the thickness, an unexpected improved low-temperature performance

was observed with NSTF electrodes [8]. The mechanisms behind this improvement are not well understood. To tackle this issue, this paper reports findings from a novel modeling methodology that combines a continuum model for the catalyst layer and membrane and a pore-network (PN) model for the GDL. In addition, analysis of the GDLs from tomographic images and determination of pore-size distribution is also presented.

2. Coupled Continuum and Pore-Network Models

A unique approach to combine the advantages of continuum and PN models, while mitigating the respective disadvantages, was undertaken to help explain observed variations in PEFC performance associated with the use of different GDL materials and morphologies [9]. Continuum models use a volume-averaged approach to model two-phase water transport coupled with electrochemistry [10-12]. These models allow for complex phenomena to be accounted for when describing water transport through GDL morphologies, where effective porous-domain properties are used (e.g., water-retention curves and Darcy's law) [13-15]; however, microstructural information in these models is coarse-grained. Recently, the extent to which these models are applicable when describing thin porous GDLs has been discussed [16, 17]. The main questions are: how well the experimental water-retention curves that use volume-averaged quantities describe the local effective liquid-water permeability, and are they applicable to capillary-driven phenomena. When a significant amount of inhomogeneity is present in the GDLs, continuum models lack the spatial specificity for scalar quantities (temperature, pressure, concentration) to be effective in capturing GDL transport resistances [16-18]. PN models resolve inhomogeneous GDL morphologies and can accurately predict water transport and the appropriate scalar quantities [19-24]. Though implementation of PN models vary widely, all PN models discretize the governing equations across a structured or unstructured grid and use a

4

distribution of material and structural properties to capture the stochastic nature of the material. Incorporation of multiscale electrochemical phenomena has not been widely attempted in a PN modeling framework as it poses severe computational difficulties due to the need for incorporating partial-differential relationships. There have been limited efforts at building a robust electrochemical-transport simulation that takes advantage of both modeling techniques [25, 26]. Herein, the advantage of both techniques is realized in an iterative scheme that utilizes well-established continuum [10] and PN [24] models.

The coupling of the two distinct modeling philosophies for simulating PEFC performance is driven by the desire to understand how a change in GDL material or morphology affects low-temperature PEFC performance. Experimental results indicate a dramatic increase in limiting current density at low temperatures for NSTF electrodes when a specific anode GDL material was doubled in thickness via stacking of two identical GDLs. Details of these experiments can be found in Steinbach et al [6, 7]. Experimental observation related to the GDL materials modeled herein and the improved low-temperature limiting current density can be found in reference [8].

2.1 Model-Coupling Methodology

Salient details of the model formulation are provided here. A more thorough discussion of model coupling techniques can be found in an earlier publication [27]. The continuum model is a steady-state, two-phase, 2-D, nonisothermal, cross-section sandwich PEFC model. The modeled physics include mass and charge transport, heat transfer and electrochemistry of reaction kinetics. The PN model is described in detail by Medici and Allen [24], where physics are simulated on a 2-D regular lattice of cylindrical tubes of constant length. A modified Poiseuille flow describes two-phase fluid-flow transport and capillary-pressure effects. The PN model describes heat transport by conduction between the nodes and latent heat of phase change. The

total heat capacity is computed for each node as the sum of the heat capacity of carbon fibers, liquid water, water vapor, and reactants. In the model, Fick's law describes diffusion of species in the gas phase.

Continuum and PN models are coupled through an iterative scheme wherein the continuum PEFC model passes spatially-resolved current, heat, and mass fluxes to the PN model. Subsequently, the PN model derives a set of effective properties that include thermal conductivity, effective diffusivity, and permeability based on spatially resolved scalar values of temperature, concentration, and liquid-water location. The effective properties are discretized along the electrode-GDL interface and provided as an updated boundary condition for the continuum model. The continuum model computes the next set of fluxes to pass to the PN model and the procedure repeats until convergence is reached. The continuum model is built with Comsol 5.1 Multiphysics (COMSOL, Inc., Burlington, MA), whereas the PN model is coded in Fortran. The two models are integrated using a Matlab interface, which was also used for post-processing and data analysis.

The PEFC domain modeled consists of half land and half channel of 0.5 mm length each. The GDL thicknesses were 150, 300, and 210 µm for the 1x AEX1, 2x AEX1, and U105 GDLs, respectively. The coordinate system in this study used the 'z' direction to be through the GDL thickness (through-plane), whereas the 'x-y' direction was in-plane. The operating conditions used to evaluate PEFC performance were 100% relative humidity, 25 to 60°C, and 0.4 to 0.7 V. Consistent with the experimental tests [8], a gas pressure differential of 50 kPa was applied to the cathode relative to the anode.

3. GDL Characterization for PN Model Realization

Two different GDL materials were simulated. Both the cathode and anode GDLs begin with an uncoated backing that is treated using a 3M proprietary hydrophobization and microporous-layer (MPL) treatments [8, 27]. For the cathode, the GDL is referred to as U105 and for the anode the untreated experimental backing is provided by Freudenberg FFCT SE & Co., and the treated anode GDL is referred to as AEX1. Two variations of AEX1 were studied. The first variation is a single thickness of AEX1 and the second variation is a double thickness of AEX1 generated by stacking two GDLs (without a MPL) for the anode. The simulations of these different anode diffusion media are referred to as 1x and 2x for a single AEX1 and double AEX1, respectively; the cathode GDL was always a single U105.

Discretization of the GDL for use in the PN model is a critical step. The PN version of a GDL, referred to as a realization, requires conversion of an equivalent pore-size distribution (PSD) to a regular grid of thermal and mass-transport resistances. One method to obtain a representative PSD of these highly porous, heterogeneous layers is through micro X-ray computed tomography (CT). This technique is nonintrusive, nondestructive, and has the appropriate spatial resolution (micrometers) and a relatively large field of view (millimeters) [18, 28, 29].

3.1 Determination of PSD from X-ray Computed Micro Tomography

X-ray computed tomography (CT) experiments were conducted at Beamline 8.3.2 at the Advanced Light Source (ALS). Monochromatic X-rays with an energy of 14 keV were used; the detection system consisted of a 0.5 mm LuAG scintillator and 5x lens with a sCMOS PCO.Edge camera, resulting in a pixel dimension of 1.33 µm. Additional details of the experimental setup are provided elsewhere [2]. The working field of view for image analysis was cropped to 2.2 x

2.2 mm from a circular sample of diameter 3.2 mm. To ensure data reproducibility, three 1x and 2x GDL samples cut in different locations of a GDL sheet were imaged.

Image segmentation and analysis was done with Fiji, where the threshold to distinguish fiber from void was selected with the Otsu algorithm. The thickness of the GDL was measured by image inspection, taking an average of thickness at five randomly selected locations. Computation of the spatial distribution of porosity and three-dimensional volume-rendering was done using Avizo Fire 8.1 by importing the threshold image stack from Fiji. A built-in plugin for Fiji – "Local Thickness" was used for extracting PSDs from the X-ray CT image stack; details of the algorithm can be found elsewhere [30-32]. The local thickness is defined as the diameter of the largest sphere that fits inside the object and contains the point:

$$t(p) = 2\max(\{r | p \in sph(x,y) \subseteq \Omega, x \in \Omega\})$$

[1]

The distance map, which is defined as the radius of the largest inscribed sphere centered at x is created first. It is computed over a binary image-stack with the Saito-Toriwaki Euclidean distance transformation. Redundant points are removed with a template algorithm to get a distance ridge, then a scan is performed over the distance ridge to compute local thickness. Finally, a surface clean-up is done, replacing the local thickness value of every surface voxel by an average of its neighbors.

Figure 1(a) shows a schematic of inscribed spherical kernel inside the GDL pore as computed with "Local Thickness" algorithm. Figure 1(b) is a histogram of a PSD for local thickness (diameter) of the inscribed spherical kernels. The size of the kernels is described by the

color-bar and Figure 1c shows the cross-section tomograph of the thresholded 2x GDL and that with inscribed spheres.

Figure 2 shows the through-plane (z-direction) area-averaged porosity distribution for 1x and 2x AEX1 GDLs. The collected images form a 3-D stack, therefore porosity for a given z value in thickness, is area-averaged across the x-y plane. The structure of the GDLs is inhomogeneous as reflected by the porosity distribution, which decreases from 0.81 to 0.65 through the GDL thickness. The porosity distribution for the 2x AEX1 follows similar trend, with 0.86 for z = 0 and a decrease in porosity away from the GDL surface. However, for the stacked GDLs, the interface has large voids and this helps to keep the porosity value near 0.75 for z = 70 µm. There is a porosity increase of 0.25 near the GDL/GDL interface of the 2x AEX1 due to an interfacial void related to the modulated fiber density. The 2x AEX1 cross section is shown as an inset in Figure 2 with the half-channel and half-land domain illustrated. Three morphologies are identified within AEX1. The first morphology is a fiber-density modulation with areas of high and low fiber density. There is also identifiable morphology at one surface of the GDL consisting of high concentration of the 3M non-wetting treatment and/or binder material that reduces the porosity. Finally, there is a bulk morphology between these two surface morphologies with a porosity between the two extremes. The morphology of the second GDL features the same morphologies.

The through-plane porosity variation of the GDLs was examined in order to characterize fiber-density modulations. Figure 3(a) shows the volume-rendered three-dimensional 1x AEX1 GDL and Figure 3(b) shows the porosity as a function of in-plane direction, y, along with a grey-scale cross-section tomographic reconstruction. The bright spots in the grey-scale images are cross sections of fibers within the GDL and the saturated bright spots correspond to PTFE or

binder material. The porosity variation between the peak and valley is about 0.10. The width of high and low-fiber-density regions is about 500 µm each. For the 2x AEX1, the regions of fiber-density modulations for two stacked GDLs were aligned in order to determine whether or not the porosity inhomogeneity was preserved in contrast to Figure 2. As observed in Figure 3(c) and 3(d), these regions were not of a uniform thickness and the porosity variation did not show the same modulation as for the 1x AEX1. In several locations, however, the 2x AEX1 porosity exhibited a similar trend to that of the 1x with a slightly smaller peak-to-valley variation (0.08).

The volume-average porosity varies with thickness as shown in Figure 4(a) and does not differentiate strongly between the GDL morphologies. Therefore, the analysis was extended to mean and maximum radii of these GDLs as shown in Figure 4(b). The maximum radii range for the 1x AEX1 is 55 to 70 µm, whereas the range for 2x AEX1 is 35 to 60 µm. The maximum radius generally describes the large interfacial pores. Both 1x and 2x AEX1 contain large pores at the GDL surface due to the fiber-density modulation morphology. On average, there are more large pores in the 2x AEX1 due to extra interfacial void volume between the two GDLs. The mean PSD radius did not vary and was close to 10 µm for both the 1x and 2x AEX1. The mean and max radii are used to help determine the appropriate PN model realizations. The above similarities of the GDLs in terms of their volume averaged properties highlight the issue and failure that a continuum model alone would have in simulating these GDLs.

3.2 Reconstructed GDL Pore Size Distributions and Realizations

The pore realizations used in the PN model for the 1x and 2x AEX1 anode GDLs and the U105 cathode GDL are based on the PSDs extracted from x-ray CT image stacks. The nondimensional pore volume - probability density function (PDF) versus pore radius were fitted

using a combination of segmented Weibull distributions as shown in Figure 5. The Weibull curves were then used to generate randomized pore realizations for use in the PN model. The U105 PSD from the x-ray tomography data was fitted using three segmented Weibull distributions:

$$\left.\begin{array}{l} Scale\,Factor=1.2 \\ Shape\,Factor=4 \end{array}\right\} for\,0<r<2.4\,\mu m$$

$$\left.\begin{array}{l} Scale\,Factor=2 \\ Shape\,Factor=5.5 \end{array}\right\} for\,2.4<r<3.7\,\mu m$$

$$\left.\begin{array}{l} Scale\,Factor=4 \\ Shape\,Factor=11 \end{array}\right\} for\,3.7<r<20\,\mu m$$

The PSDs and the fitting curves for the 1x and 2x AEX1 GDLs are shown in Figure 5. Two Weibull curves were used for the 1x AEX1. The realization for the 2x AEX1 was divided into three regions, top (gas channel side), center, and bottom (catalyst layer side) and two Weibull distributions were used for each region. The PSD of the center region, shown in Figure 5(c), which is also the interface between the two GDLs, features pores with large sizes (up to 45 µm), whereas the top and bottom regions have largest pores that are only 25 µm in radius. Such a large through-plane inhomogeneity in 2x AEX1 GDLs cannot be properly described with a single GDL realization. Moreover, dividing the GDL into two domains does not capture the interfacial void region accurately. Three layers, however, do exhibit PSDs that are representative. A single realization was generated for the U105, 1x AEX1, and 2x AEX1 for use in the PN model.

Two additional material properties are required for the pore-space realizations; the contact angle and porosity. The contact angle was set to 110 degrees for both anode and cathode sides and is typical of the value measured on the surface of these materials. The porosity was set

to a mean value of 0.65 for the 1x and 2x AEX1 anode GDL and 0.75 for the U105 cathode GDL.

4. Model Simulation Results and Discussion

At high temperatures the simulated PEFC performance was the same for the 1x and 2x AEX1 anode GDLs, which is consistent with the experimental findings [8] and the fact that water is mainly in the vapor phase at these conditions where phase-change-induced flow dominates [33]. The beneficial effect of using the 2x anode GDL was observed at low temperatures and low potentials as shown in the polarization curves in Figure 6a. Figure 6b through 6e are liquid-water profiles in the U105 cathode and 1x and 2x AEX1 anode GDLs, respectively. At 60°C and high potential, the cathode and anode are mostly dry thereby allowing the reactants to flow through both cathode and anode without significant impediment. At 30°C and high potential, the GDLs remain mostly dry due to the low current density. At a potential of 0.55 V, however, a significant shift in current density between the 1x and 2x simulations is apparent with the 1x simulations exhibiting higher potential losses.

A comparison of numerical and experimental temperature dependent performance reveals surprisingly good agreement. Figure 7(a) compares the 1x and 2x AEX1 simulations against limiting current density experiments for a temperature range of 25 to 60°C. The numerical and experimental results for the 1x AEX1 conditions are nearly identical and consistently lower in current density than the 2x AEX1 at the same temperature. The agreement between the 2x AEX1 simulations and experiments is not as good as that for the 1x, with the numerical results demonstrating a less significant performance impact. The fact that the simulated current density is not as high at lower temperatures compared to the experiments is probably due to the fact that

12

the coupled model does not account for the interfacial effects of droplet detachment or other physics that probably play a role [34].

The difference in low-temperature performance between the 1x and 2x AEX1 simulations is easy to discern when looking at the liquid-water profiles in the anode and cathode GDLs. Figure 7(b)-(e) illustrate a significant difference in the liquid-water content at 25°C in the cathode GDL depending upon the anode configuration. With the 1x AEX1 anode, there is significant liquid water present in the cathode GDL: approximately 24% saturation. There is also significant water in the 1x AEX1 anode GDL. When the 2x AEX1 anode GDL is used at 25°C, the predicted liquid-water content in the cathode GDL is nearly zero: approximately 1% saturation (above the irreducible saturation). The 2x AEX1 anode shows significant water content at this temperature; actually greater than that in the 1x AEX1 anode. However, there is no significant effect on hydrogen transport due to the high porosity region in the center of the 2x AEX1 GDL and the use of pure hydrogen. Thus, the increased low-temperature current density using the 2x AEX1 anode GDL can be attributed to less liquid water present in the cathode GDL and catalyst layer since there is more net water movement out of the anode than in the 1x case.

4.1 Effective Transport Properties

Simulations using the combined continuum-PN model indicate that the cathode remains drier at low temperatures when using the 2x AEX1 anode GDL. This explains the experimental results of Steinbach et al. [8], but does not yet reveal the mechanisms by which the cathode remains dry. To investigate the mechanisms responsible, the GDL effective diffusivities and thermal conductivities as determined from the PN model are given in Figure 10.

The effective oxygen and hydrogen diffusivities on the cathode and anode sides,

$D_{eff}^{O2 \vee H2}$, can be calculated from the simulations as

$$D_{eff}^{O2 \vee H2} = \frac{M_{O2 \vee H2} H}{t A_c \Delta C_{O2 \vee H2}}$$ [2]

where $M_{O2 \vee H2}$ is the mass consumption of oxygen or hydrogen, H is the GDL thickness,

t is the elapsed time, A_c is the cross sectional area orthogonal the mass flux, and

$\Delta C_{O2 \vee H2}$ is the concentration difference of oxygen or hydrogen between the gas channel and

catalyst layer. The effective oxygen and hydrogen diffusivities as a function of operating

temperature for the 1x and 2x configurations are shown in Figure 8(a) and 8(b), respectively. The

effective diffusivity of oxygen remains relatively constant for the 2x AEX1 configuration for all

temperatures, which indicates that the cathode GDL is consistently dry for all cell temperatures.

In contrast, the 1x AEX1 configuration at low temperatures has an effective oxygen diffusivity

that is nearly an order of magnitude smaller than for the 2x AEX1 configuration. At higher

temperatures, where there is sufficient heat generation to evaporate the liquid water as

mentioned, the two effective diffusivities converge. This trend mirrors the cathode GDL water

profiles and the numerical and experimental performance.

The effective diffusivity of hydrogen exhibits a slightly different trend. At low

temperatures, the 1x and 2x AEX1 configurations have the same effective hydrogen diffusivity.

At higher temperatures, the 2x AEX1 configuration has approximately four times the effective

diffusivity of the 1x AEX1 configuration. This difference is due to the increase in anode GDL

thickness. At low temperatures, the layer of liquid water shown in Figure 6(c) and 6(e) results in

14

an equivalent resistance to hydrogen transport regardless of the GDL thickness. Even with liquid water in the anode at low temperatures, hydrogen transport is not a limiting factor in PEFC performance due to its high overall diffusivity, inlet concentration, and electrochemical kinetics.

The effective thermal conductivities as determined by the combined model is also indicative of the change in mass- and energy-transport dynamics due to the different anode configurations. The effective cathode or anode thermal conductivities, $K_{eff}^{Cathode \vee Anode}$, is determined for the numerical simulations using

$$K_{eff}^{Cathode \vee Anode} = \frac{\dot{Q}^{Cathode \vee Anode} H}{A_c \Delta T^{Cathode \vee Anode}}$$
[3]

where $\dot{Q}^{Cathode \vee Anode}$ is the heat flux removed through the cathode or anode side, H is the GDL thickness, A_c is the cross sectional area orthogonal the heat flux, and $\Delta T^{Cathode \vee Anode}$ is the temperature difference between the gas channel and catalyst layer. Considering first the anode (Figure 8(d)), the effective thermal conductivity of the 2x AEX1 configuration is 5 times greater than for the 1x AEX1 configuration. Some of the increase in the calculated effective thermal conductivity is due to the increase in GDL thickness. However, this change in thickness is not the complete explanation for the change in the overall heat balance. If the anode-to-cathode heat flux ratio remained constant between the 1x and 2x AEX1 configurations, then the effective thermal conductivity of the 2x AEX1 GDL would nominally be 10 times that of the 1x AEX1 GDL due to the increased thickness and increased heat flux (see eq. 3) caused by the higher current density. For the anode GDLs, the effective thermal conductivity is higher for the 2x case as compared to the 1x case primarily because of the thicker layer and the increased heat flux due to the higher current density. However, the increase in AEX1 thickness alters the resistance to heat transfer through the anode and effectively shunts a greater percentage of the total heat generated to the cathode. If the same percentage of heat transfer between the anode and cathode is maintained for both the 1x and 2x AEX1 configurations, then the effective thermal conductivity of the anode would increase by approximately an order of magnitude. The model captures the shifting in heat transfer from anode to cathode, which results in only a 5x increase in anode thermal conductivity. Liquid water does play a role, but it is a minor one.

The effect of greater heat dissipation through the cathode can be seen in Figure 8(c). At low temperatures, the effective thermal conductivity of the U105 cathode GDL is less in the 2x AEX1 configuration than for the 1x AEX1 configuration by a factor of 1/8. While initially this

may appear to contradict the previous discussion, the calculated thermal conductivity must be considered in conjunction with the liquid-water content. The cathode GDL in the 2x anode configuration is dry even at 25°C despite the increase in water production, which indicates that a significant fraction of the heat flux dissipated through the cathode is due to evaporation. The determination of the effective thermal conductivity does not account for heat transfer by latent heat and phase-change-induced flow, which reduces the temperature gradient in eq. 3. The ratio of heat conduction to evaporative heat transfer via latent heat [24] is lower in the 2x anode configuration than for 1x one. As a result, the temperature difference between the cathode catalyst layer and the gas flow channel is much greater in the 2x configuration resulting in a lower effective thermal conductivity. As the operating temperature increases, the ratios of heat conduction to evaporative heat transfer become comparable for the 1x and 2x AEX1 configurations, and the difference in PEFC performance between the two anode configurations becomes negligible (see Figure 6(a)).

5. Conclusions

The effect of anode GDL configuration on fuel-cell water management was investigated using a unique coupled continuum-PN model. Specifically, the experimentally observed significant increase in low-temperature performance by simply doubling the thickness of the anode GDL was explored. The coupling between the continuum and PN models allows for a comprehensive study of the mass-transport limitations not possible with just the continuum model due to lack of spatial heterogeneities nor with just the PN model due to the absence of electrochemistry and spatially defined membrane and electrode physics. X-ray computed tomography (CT) was used to determine GDL morphology, which was then used to generate the PN realizations for the numerical model.

16

Two anode GDL configurations were modeled each with an identical cathode GDL, membrane, and thin-film catalyst layers. The first configuration was a single (1x) AEX1 GDL. The second anode configuration was two (2x) AEX1 GDLs stacked to form a single layer. Stacking two AEX1 GDLs resulted in a clear pore-size distribution variation through the GDL thickness as shown by X-ray CT. A large interfacial porosity between the stacked GDLs allowed for liquid-water accumulation without affecting hydrogen transport but enabling easier liquid-water transport. The variation in the through-plane pore-size distribution was modeled by dividing the 2x AEX1 GDL into three planar regions; each modeled using two Weibull distributions to fit the PSD data derived from the X-ray CT. The overall effect of doubling the anode GDL thickness with the increase in interior porosity was improved water transport in the anode and a shunting of heat dissipation towards the cathode. These effects ensured that more liquid-water was transported through the membrane and out of the anode and that the cathode oxygen diffusivity remained high due to a lack of flooding, thus explaining the observed higher low-temperature performance with the 2x AEX1 GDL.

References

[1] M.K. Debe, Nature, 486 (2012) 43-51.

[2] M.K. Debe, A.J. Steinbach, K. Noda, ECS Transactions, 3 (2006) 835-853.

[3] I.V. Zenyuk, S. Litster, Electrochimica Acta, 146 (2014) 194-206.

[4] K. Chan, M. Eikerling, J Electrochem Soc, 158 (2011) B18-B28.

[5] P.K. Sinha, W. Gu, A. Kongkanand, E. Thompson, J Electrochem Soc, 158 (2011) B831-B840.

[6] A.J. Steinbach, M.K. Debe, M.J. Pejsa, D.M. Peppin, A.T. Haug, M.J. Kurkowski, S.M. Maier-Hendricks, ECS Transactions, 41 (2011) 449-457.

[7] A.J. Steinbach, M.K. Debe, J. Wong, M.J. Kurkowski, A.T. Haug, D.M. Peppin, S.K. Deppe, S.M. Hendricks, E.M. Fischer, ECS Transactions, 33 (2010) 1179-1188.

[8] A.J. Steinbach, in, 2015 Annual Merit Review Proceedings, 2015.

[9] I.V. Zenyuk, E. Medici, J. Allen, A.Z. Weber, International Journal of Hydrogen Energy, 40 (2015) 16831-16845.

[10] I.V. Zenyuk, R. Taspinar, A.R. Kalidindi, E.C. Kumbur, S. Litster, J Electrochem Soc, 161 (2014) F3091-F3103.

[11] M. Bhaiya, A. Putz, M. Secanell, Electrochimica Acta, 147 (2014) 294-309.

[12] A.Z. Weber, R.L. Borup, R.M. Darling, P.K. Das, T.J. Dursch, W. Gu, D. Harvey, A. Kusoglu, S. Litster, M.M. Mench, R. Mukundan, J.P. Owejan, J.G. Pharoah, M. Secanell, I.V. Zenyuk, J Electrochem Soc, 161 (2014) F1254-F1299.

[13] J.T. Gostick, M.W. Fowler, M.A. Ioannidis, M.D. Pritzker, Y.M. Volfkovich, A. Sakars, Journal of Power Sources, 156 (2006) 375-387.

[14] A.Z. Weber, Journal of Power Sources, 195 (2010) 5292-5304.

[15] P.K. Das, A. Grippin, A. Kwong, A.Z. Weber, J Electrochem Soc, 159 (2012) B489-B496.

[16] P.A. Garcia-Salaberri, Hwang G., Vera, M., Weber A.Z., Gostick J.T. , International Journal of Heat and Mass Transfer, 86 (2015) 319-333.

[17] P.A. Garcia-Salaberri, Gostick J.T., Hwang G., Weber A.Z., Vera, M., Journal of Power Sources, 296 (2015) 440-453.

[18] I.V. Zenyuk, D.Y. Parkinson, G. Hwang, A.Z. Weber, Electrochemistry Communications, 53 (2015) 24-28.

[19] P.P. Mukherjee, Q. Kang, C.-Y. Wang, Energy & Environmental Science, 4 (2011) 346-369.

[20] B. Markicevic, A. Bazylak, N. Djilali, Journal of Power Sources, 171 (2007) 706-717.

[21] A. Bazylak, V. Berejnov, B. Markicevic, D. Sinton, N. Djilali, Electrochimica Acta, 53 (2008) 7630-7637.

[22] J.T. Gostick, M.A. Ioannidis, M.W. Fowler, M.D. Pritzker, Journal of Power Sources, 173 (2007) 277-290.

[23] O. Chapuis, M. Prat, M. Quintard, E. Chane-Kane, O. Guillot, N. Mayer, Journal of Power Sources, 178 (2008) 258-268.

[24] E.F. Médici, J.S. Allen, International Journal of Heat and Mass Transfer, 65 (2013) 779-788.

[25] M.T. Balhoff, K.E. Thompson, M. Hjortsø, Computers & Geosciences, 33 (2007) 393-410.

[26] J. Chu, B. Engquist, M. Prodanovic, R. Tsai, Multiscale Model. Simul., 10 (2012) 515-549.

[27] I.V. Zenyuk, E. Medici, J. Allen, A.Z. Weber, International Journal of Hydrogen Energy.

[28] C. Tötzke, G. Gaiselmann, M. Osenberg, J. Bohner, T. Arlt, H. Markötter, A. Hilger, F. Wieder, A. Kupsch, B.R. Müller, M.P. Hentschel, J. Banhart, V. Schmidt, W. Lehnert, I. Manke, Journal of Power Sources, 253 (2014) 123-131.

[29] N. Khajeh-Hosseini-Dalasm, T. Sasabe, T. Tokumasu, U. Pasaogullari, Journal of Power Sources, 266 (2014) 213-221.

[30] T. Hildebrand, P. Rüegsegger, Journal of Microscopy, 185 (1997) 67-75.

[31] T. Saito, J.-I. Toriwaki, Pattern Recognition, 27 (1994) 1551-1565.

[32] B. Dougherty, in, http://www.optinav.com/Local_Thickness.htm.

[33] A.Z. Weber, J. Newman, J. Electrochem. Soc., 153 (2006) A2205-A2214.

[34] A.D. Santamaria, P.K. Das, J.C. MacDonald, A.Z. Weber, J. Electrochem. Soc., 161 (2014) F1184-F1193.

Captions

Figure 1   (a) A schematic of inscribed spherical kernel inside the pore-space of the GDL as described by the "Local Thickness" algorithm. (b) A histogram of local thickness distribution for the 2x AEX1 GDL, which is shown as (c) a segmented cross-section tomograph (bottom) and corresponding cross-section with inscribed spherical kernels.

Figure 2.   Through-thickness porosity of 1x (dashed) and 2x (solid) AEX1 GDLs, where insets show cross-sectional tomographs at through-thickness z-locations. The regions of 1) fiber-density modulation, 2) PTFE/binder and 3) mixed (PTFE/modulated porosity) are identified.

Figure 3.   Volume-rendered 3D reconstruction of (a) 1x AEX1 and (c) 2x AEX1 GDL. A grey-scale cross-sectional tomograph and area-averaged in-plane porosity are shown for (b) 1x AEX1 and (d) 2x AEX1.

Figure 4.   (a) Volume-averaged porosity as a function of thickness for 1x and 2x AEX1 and U105 GDLs. (b) Mean and maximum radii of PSD as function of GDL thickness.

Figure 5.   (a) Reconstructed PSDs, fitting Weibull curves, and pore realizations for the 1x AEX1 GDL from x-ray CT data. The top, middle and bottom (catalyst layer side) of the 2x AEX1 GDL are modeled separately in (b), (c), and (d), respectfully, in order to capture the through-thickness inhomogeneity of stacked GDLs.

Figure 6.   (a) Polarization curve for two temperatures for the 1x and 2x simulations. Water-distribution profiles for the (b) U105 cathode and (c) 1x AEX1 anode GDLs at $30^{\circ}C$ and 0.4 V, and for the (d) cathode and (e) 2x anode GDLs at $60^{\circ}C$ and 0.7 V.

Figure 7.   a) Numerical and experimental current densities at 0.4 V as a function of temperature for the 1x and 2x AEX1 anode configurations. The experimental data represents the limiting current density [8]. Liquid-water distribution profiles at $25^{\circ}C$ for (b) U105 cathode GDL with 1x AEX1 anode GDL, (c) U105 cathode GDL with 2x AEX1 anode GDL, (d) 1x AEX1 anode GDL, and (e) 2x AEX1 anode GDL.

Figure 8.   Effective diffusivities and thermal conductivities of the U105 cathode GDL and the 1x and 2x AEX1 anode GDLs at various current densities and fuel cell operating temperatures. The potential is set to 0.4 V for all simulations. (a) Effective oxygen diffusivity of the U105 GDL for the 1x and 2x anode configurations. (b) Effective hydrogen diffusivities of the 1x and 2x AEX1 GDLs. (c) Effective thermal conductivity of the U105 GDL for the 1x and 2x anode configurations. (d) Effective thermal conductivities of the 1x and 2x AEX1 GDLs.