V.B.1 Water Transport Exploratory Studies

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Objectives

- Develop understanding of water transport in polymer electrolyte membrane (PEM) fuel cells:
    - Non-design-specific (as possible).
- Evaluate structural and surface properties of materials affecting water transport and performance.
- Develop (enable) new components and operating methods.
- Accurately model water transport within the fuel cell.
- Develop a better understanding of the effects of freeze/thaw cycles and sub-freezing operation.
- Present and publish results.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program

Multi-Year Research, Development and Demonstration Plan:

(D) Water Transport within the Stack

Technical Targets

- Energy efficiency (65% at 25% rated power, 55% at 100% rated power)
- Power density (2,000 Watt/L)
- Specific power (2,000 Watt/kg)
- Cost ($25/kWe)
- Start-up time to 50% power (30 seconds from -20°C, 5 seconds from 20°C)
- Freeze start operation (unassisted start from -40°C)
- Durability with cycling: 5,000 hrs

Accomplishments

Direct water imaging by neutron radiography and X-ray tomography

- Measured equilibrium water content in the membrane.
    - Lower water concentrations typically measured for operating membrane electrode assemblies (MEAs) with catalyst layers and gas diffusion layers (GDLs) compared with equilibrium values.
- Imaged water with variation of operating parameters.
- Imaging of water response to transients.
    - Evaluated fast membrane wetting compared with slow GDL de-wetting.

Segmented cell operation

- Measured water variation as a function of GDLs, inlet relative humidity (RH), cell position.

Freeze/thaw examination of PEM fuel cells

- Imaging of water/ice in fuel cells operated at sub-freezing temperatures.
- Monitoring where water freezes as a function of operating variables testing.

Evaluation and characterization of GDLs

- Profiling the GDL in 3-dimensions.
    - Observed water location in the GDL pore structure.

–   Correlated water with Teflon® content in the GDL.

Varied micro porous layer (MPL) and substrate Teflon® loadings and cell operating conditions

•   Neutron imaging and electrochemical impedance spectroscopy (EIS) were used to measure water content and performance.

Modeling of mass transport losses

•   Using characterization data to develop comprehensive GDL water transport model in addition to the existing membrane/electrode model.

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Introduction

Effective control of water distribution can be a major impediment to implementation of polymer electrolyte membrane fuel cells. Several important cell parameters, including membrane conductivity and mass transfer resistance within porous electrodes, are intimately linked to water distribution, requiring effective management of water in order to maximize fuel cell performance. Components such as the membrane and electrode layers require sufficient water to be present in order to allow adequate proton conductivity. Conversely, excess water within the system leads to mass transfer losses and can require additional balance-of-plant costs (extra energy or weight for increased humidification). The range of conditions under which the system is required to operate makes meeting all these requirements at the same time even more difficult. The conditional extremes provide the biggest challenges: maintaining hydration under hot/dry conditions and preventing flooding/dealing with ice formation under cold/wet conditions. Perhaps the most challenging of these conditions is subfreezing temperatures. In order to compete with internal combustion engines, the U.S. Department of Energy has stated goals for fuel cell survivability (-40°C), start-up time (30 seconds to 50% rated power from -20°C), and energy (5 MJ) under subfreezing conditions. In order to address these challenges there is a need for increased understanding of water transport and phase change within fuel cell components. This requires that the structure and properties of fuel cell materials be fully understood. The materials ultimately employed will need durability under normal and transient operations while allowing effective water management under any environmentally-relevant condition.

To achieve a deeper understanding of water transport and performance issues associated with water management, a multi-institutional and multi-disciplinary team with significant experience investigating these phenomena has been assembled. This team is headed by Los Alamos National Laboratory (LANL) and includes Sandia National Laboratories, Oak Ridge National Laboratory, a university (Case Western Reserve University), an MEA supplier (W.L. Gore), a GDL supplier (SGL Carbon Group), and the National Institute of Standards and Technology. This report describes our Fiscal Year 2009 technical progress related to understanding the complex phenomena related to water transport within operating PEM fuel cells.

Approach

Our approach to understanding water transport within fuel cells is structured in three areas: fuel cell studies, characterization of component water transport properties, and modeling of water transport. These areas have aspects that can be considered free-standing, but each benefit greatly from work performed in the other areas. The modeling studies tie together what is learned during component characterization and allow better interpretation of the fuel cell studies. This approach and our team give us the greatest chance to increase the understanding of water transport in fuel cells and to develop and employ materials that will overcome water-related limitations in fuel cell systems.

To help understand the effect of components and operational conditions, we examine water transport in operating fuel cells, measure the water content and location of water during operation. In situ characterization of water content includes evaluation of the high frequency resistance (HFR) and by EIS to quantify the various limiting transport regimes and neutron imaging to visually measure the water content in the individual cell components at various locations. Variation of PEM components helps identify component effects on water management, with characterization of these components providing quantifiable water transport properties.

Results: Equilibrium Water Measurements in Nafion® by Neutron Imaging

Water transport in the ionomeric membrane, typically Nafion®, has profound influence on the performance of the polymer electrolyte fuel cell, in terms of internal resistance and overall water balance. Prior neutron imaging and modeling based off of literature results show large discrepancy; up to a factor of 4 difference in membrane water content [1]. In FY 2009, we conducted high resolution neutron imaging of Nafion® membranes in order to measure water content and through-plane gradients in situ under disparate temperature and humidification conditions.

Several different experimental configurations were used, including 18 micron-thick membranes, N117 (~178 microns), a 3-layer sandwich of N117 (533 microns) and specially cast Nafion® membranes of 500 and 1,000 microns in thickness. 1,000-micron bare membrane exhibited significant swelling and blocked the parallel channels on both sides in a liquid-equilibration mode experiment. The same membrane in the MEA configuration was however sufficiently constrained by the adjoining catalyst layers and GDLs to avoid extensive swelling. High resolution neutron imaging was conducted with the membrane in the MEA configuration in both fuel cell and hydrogen pump modes. Representative water thickness response from neutron scattering data with the membrane in the MEA configuration is shown in Figure 1. The water distribution at the open circuit voltage (OCV) with 175% RH and 80°C temperature shows a distinctive plateau and the average water content, λ, was approximately estimated as 18.7. Furthermore, the water gradient response from such hydrogen pump mode experiments will be used to extract the electro-osmotic drag response of the membrane and correlated to fuel cell water balance. During hydrogen pump operation, the water gradient reverses when the potential is reversed, as expected. For this sample, there appears to be catalyst layer flooding on the anode side of the membrane, as evidenced by the peak at pixel 78.

Figure 2 shows the water profile for a 500 micron Nafion® membrane at OCV, 0.1 and 0.2 A/cm² fuel cell operation. These measurements were made at 40°C and 50% inlet RH. The membrane equilibrium water content at OCV was $\lambda = 5$, which agrees well with literature [2,3]. As the cell is operated under fuel cell mode, water is produced at the cathode catalyst, thus the water
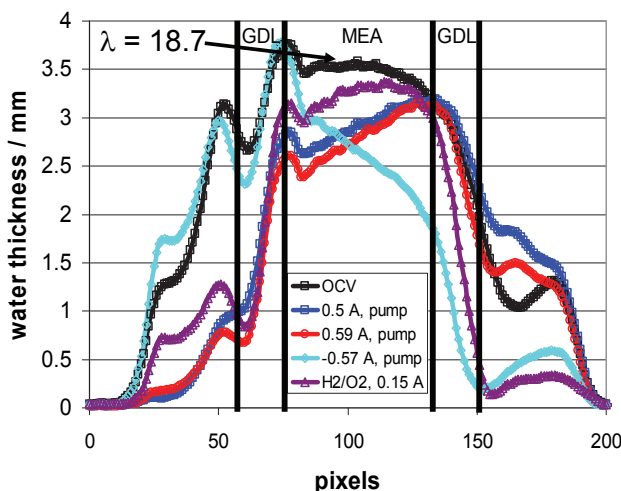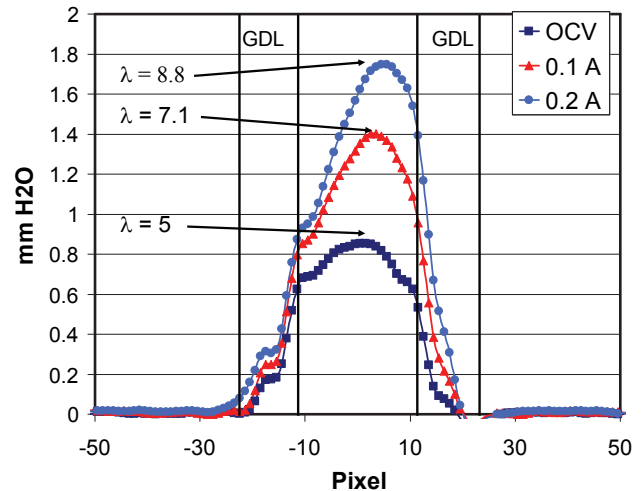

FIGURE 2. Water distribution for a 500-micron cast Nafion® membrane in the MEA configuration at OCV, and operating fuel cell modes. (50/50% RH, 40°C)

content in the membrane increases in concentration to $\lambda = 7.1$ and $\lambda = 8.8$ for 0.1 and 0.2 A/cm² current densities. However, the membrane water content is much lower than often predicted during operation, as it is often assumed that the membrane will equilibrate with the liquid water produced at the cathode catalyst layer.

Results: Water Content Responses to Transient Operation

Fuel cells used in automotive drive cycles experience numerous and varied power transients. The water dynamics in the MEA during these transients can greatly affect performance and perhaps long-term durability. To examine the hydration of the PEM and GDL response to current step-up and step-down transients, water was measured in situ via neutron imaging with simultaneous HFR measurements. Figures 3a and 3b show HFR and water concentrations in the land region and channel regions in response to step transients in current.

Current step transients from 0.5 to 34.0 amps show MEA wetting occurs quickly, within 5 to 20 sec, while MEA drying, during the current transient from 34.0 to 0.5 amps, takes on the order of minutes (see Figure 3). This suggests that the primary wetting effect with increasing current is a fast process of membrane water absorption. The drying effect appears to be a slower diffusion process of water removal from the MEA/GDL.

Higher polytetrafluoroethylene (PTFE) loading in the more open porous structure of the GDL substrates allows for more rapid water movement and facilitates the removal of large amounts of cathode reaction water produced at high current, mitigating mass transport flooding limitations. Such substrates do not hold or retain as much water resulting in cell drying issues at

FIGURE 1. Water distribution for a 1,000-micron cast Nafion® membrane in the MEA configuration at OCV, hydrogen pump and operating fuel cell modes. (80°C 175% RH)
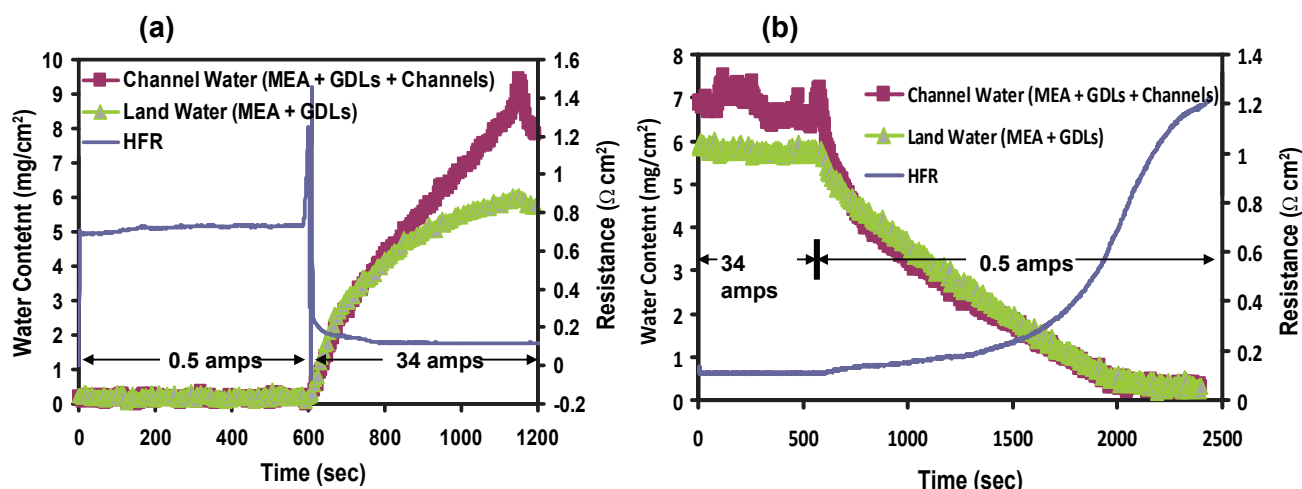
(a)

(b)

FIGURE 3. Integrated Water Content from Neutron Images During Current Transient (a) wetting from 0.5 A to 34 A, 40°C and 0/0 inlet RH (b) drying from 34 A to 0.5 A, 40°C and 0/0 inlet RH.

lower currents with low gas inlet RHs. The opposite effects apply to GDL substrates with low PTFE loadings. MPLs with less open and lower percentage pore structure behave differently with high PTFE loadings. With high loadings the MPLs act as a barrier to water flux. They are likely a barrier to gas flux, although that was not directly studied here. High PTFE MPLs can be used to prevent water loss from the membrane during dry operating conditions but they can also inhibit water moving in to hydrate the membrane. The opposite effects seem to apply to low PTFE MPLs.

Gas counter flow configuration provides more even water distribution throughout the fuel cell compared to co-flow gas configuration. With co-flow configuration, the gases, which are accumulating moisture as they pass down the channels, approach saturation conditions toward the outlet end of the fuel cell that may result in substantial condensation here. Counter flow fuel cells often result in better performance at low inlet RH conditions due to the more even water distribution.

Results: Performance and Durability of Sub-Freezing Operations

The effect of MEA and GDL structure and composition on the performance of single PEM fuel cells operated isothermally at sub-freezing temperatures was studied. The cell performance and durability are dependent on both the MEA/GDL materials used and on their interfaces. When a cell is operated isothermally at sub-freezing temperatures in constant current mode, the water formation due to the current density initially hydrates the membrane/ionomer and then forms ice in the catalyst layer/GDL. An increase in high frequency resistance was also observed in certain MEAs where there is a possibility of ice formation between the catalyst layer and GDL leading to a loss in contact
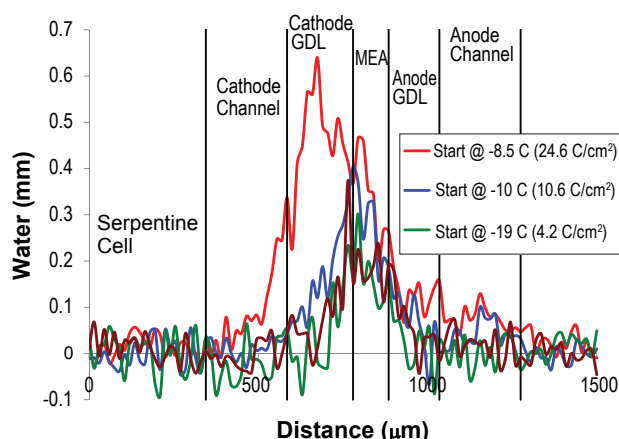
FIGURE 4. Water/ice profiles obtained after various isothermal sub-freezing operations. The profiles indicate only the ice/water formed due to the current flow at the subfreezing temperature and are referenced to the initial water content before the operation.

area. The total water/ice holding capacity for any MEA was lower at lower temperatures and higher current densities. The durability of MEAs subjected to multiple isothermal starts was better for LANL-prepared MEAs as compared to commercial MEAs, and cloth GDLs when compared to paper GDLs.

High-resolution neutron imaging performed on specially designed 2.25 cm² hardware with the Gore MEAs and paper GDLs revealed that the ice formation is concentrated in the cathode catalyst layer (Figure 4). Here the peak in the water profiles is at the MEA/cathode GDL edge for all the isothermal starts where T = -10°C. Moreover, the water capacity in these operations is consistent with the standard 50 cm² cell and there is less capacity to hold water at the lower temperatures (0.99 mg/cm² at -10°C and 0.39 mg/cm² at

-19°C when operated at 0.02 A/cm^2) and higher current densities (0.99 mg/cm^2 at 0.04 A/cm^2 and 0.67 mg/cm^2 at 0.12 A/cm^2 when operated at -10°C). Moreover when the cell is started from -8.5°C, the peak in water content is located within the cathode GDL, well outside of the cathode catalyst layer. Figure 4 shows water/ice profiles obtained after various isothermal sub-freezing operations. The profiles indicate only the ice/water formed due to the current flow at the subfreezing temperature and are referenced to the initial water content before the inside the cathode GDL substrate confirming that there is significant amount of water penetrating into the GDL before freezing. These results help explain the fact that the water holding capacity in these MEAs is greater than that available in the membrane and catalyst layers and why there is more degradation at the lower temperatures when the ice formation is closer to the catalyst layer. Finally the water/ice profile is also narrower at the higher current densities and lower temperatures, consistent with the lower capacity for ice formation under those conditions.

Conclusions

- The ability to measure water in situ during cell operation and relate water profiles to cell operating conditions and performance is invaluable in selecting operating conditions and designing fuel cell components for optimal water management.
    - AC impedance including HFR and neutron imaging in situ measurements correlate water concentration to performance.

- Transient measurements show hysteresis in wetting/dewetting.
    - MEA wetting is a fast process likely related to the hygroscopic nature of the membrane.
    - MEA dewetting appears to be a slower diffusion controlled process.

- Neutron imaging is successful at identifying the effect of operating conditions on water concentrations within the PEM fuel cell.
    - Different materials show different water concentration profiles.
    - More water accumulation in GDL under land area when compared with the GDL under flow channel area.
    - Counter flow keeps membrane well hydrated in comparison with co-flow.

- GDL surface properties affect water transport.
    - Greater mass transfer resistance for GDLs with higher MPL PTFE loadings.
    - Substrate Teflon$^{\circledR}$ content does not have major role in determining water content.

- Sub-freezing operation:
    - Operation at sub-freezing temperatures builds up water (ice) in the cell, which is located primarily on the cathode side, and can penetrate into the cathode GDL depending upon operating conditions.
    - Degradation observed in the amount of active catalyst surface area (H$_2$ adsorption peak) was strongly dependent on the MEA.
    - Catalyst layer ice formation may be controlled and its effects mitigated by careful control of the catalyst layer morphology.

Future Directions

Experimental and Characterization

- Three-dimensional X-ray tomography during operation observing water transport in GDL pores:
    - Identify hydrophobic pores vs. hydrophillic pores.
    - Identify liquid water pathways in GDLs.

- Incorporate 3-dimensional X-ray tomography pore size distribution into capillary pressure simulation.

- Conduct segmented cell measurements varying the GDL PTFE loading as a function of cell location and with counter flow inlets configurations.

- Measure the effect of compression and GDL substrate porosity.

- Better identify GDL loss of hydrophobicity degradation mechanism.
    - Surface characterization (transmission electron microscopy) and surface species identification (diffuse reflectance infrared Fourier transform spectroscopy).

- Measure capillary pressure in GDLs with concurrent flow of water and gas.

FY 2009 Publications/Presentations

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7. Borup, Rod L.; Rangachary Mukundan, John R. Davey, Jacob Spendelow, Daniel S. Hussey, David L. Jacobson, Muhammad Arif, **In Situ PEM Fuel Cell Water Measurements,** Extended Abstracts of the 2008 Fuel Cell Seminar.

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15. S. Basu, C.-Y. Wang, and K.S. Chen, **Predicting phase-change rate in PEFC gas diffusion layer**, in ASME Proceedings of FUELCELL2008, paper #65015 (2008).

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