V.H.3 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 much 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

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 W/L)
- Specific power (2,000 W/g)
- Cost ($25/kW$_e$)
- 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 at NIST using neutron radiography:

- High resolution (~25 μm) cross-section water profiles
  - Imaging with variation of operating parameters
    - Flow (counter-flow vs. co-flow), simulating anode recycle, gravity effect, cell temperature, inlet relative humidity (RH) variation, current/voltage, gas diffusion layer (GDL) material, membrane material
- Low resolution (150 μm) imaging
  - Imaging of entire 50 cm^2 flowfield area at 1 Hz
- Imaging of water/ice in fuel cells operated at sub-freezing temperatures

Freeze/thaw examination of PEM fuel cells:

- Comparison of backing layers on durability
- Conductivity measurements of membrane materials during cooling/heating cycles from 80 to –40°C at various RHs.

Testing, Evaluation and characterization of GDLs:

- Varying GDL materials and operating conditions
  - GDL substrate and microporous layer (MPL) Teflon® loading
    - Hydrophobicity characterization
  - Microscopic characterization of hydrophobic coating
  - Elemental compositional characterization

Modeling of mass transport losses:

- Delineation of mass transport loss from internal resistance, kinetics, etc.
- Modeling of water-droplet detachment from the GDL/channel interface
- Computational fluid dynamics (CFD) modeling simulates liquid water saturation profiles

Introduction

Effective control of water distribution can be a major impediment to implementation of PEM 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 PEMs 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 (DOE) 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 LANL and includes two other national laboratories (SNL and ORNL), a university (CWRU), a membrane electrode assembly (MEA) supplier (W.L. Gore), a GDL supplier (SGL Technologies), and NIST. This report describes our Fiscal Year 2008 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, and measure the water content and location of water during operation. In situ characterization of water content includes evaluation of the high frequency resistance (HFR), alternating current (AC) impedance 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

Water Profiles by Neutron Imaging

High resolution neutron radiography images of water profiles in operating fuel cells were obtained while varying a number of cell operating conditions. These operating conditions include cell temperature, current density, anode and cathode inlet humidity, polarity of anode and cathode feeds (co-flow vs. counter-flow), and orientation of the cell (effect of gravity). In addition, the anode flow rate was varied in some measurements to simulate the effects of an anode recycle loop. Cell component materials were also varied, including GDL MPL Teflon® loading, membrane material, MEA design and assembly and cathode catalyst layer.

Figure 1 shows the effect of several operating conditions on water profiles for an MEA made of N212 and SGL 24DC GDLs. Note that the membrane/catalyst layer is only about 5 pixels wide for this type of MEA, and less for thinner MEAs. Anode channel/GDL water is significant with constant anode stoich ~1.1, however disappears during operation which simulates anode recycle (3.0 stoich). There is also a noticeable

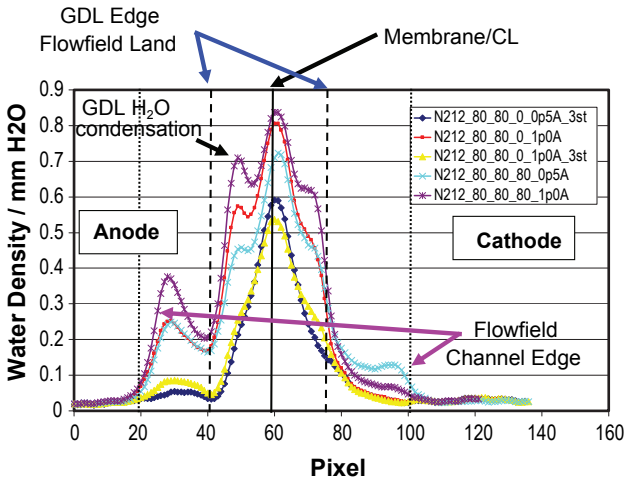

FIGURE 1. Water Profiles Measured by Neutron Imaging (MEA was constructed of N212 with 0.2 mg/cm^2 20% Pt/C. GDLs were both anode/cathode SGL 24DC with 20% substrate and 10% MPL PTFE loading. Cell temperature of 80°C. (a) 3 stoich and 100% RH anode, 2.0 and 0% RH cathode, 0.5 mA/cm^2. (b) 1.2 stoich and 100% RH anode, 2.0 and 0% RH cathode, 1.0 mA/cm^2 (c) 3 stoich and 100% RH anode, 2.0 and 0% RH cathode, 1.0 mA/cm^2 (d) 1.2 stoich and 100% RH anode, 2.0 and 100% RH cathode, 0.5 mA/cm^2 (e) 1.2 stoich and 100% RH anode, 2.0 and 100% RH cathode, 1.0 mA/cm^2.)

increase in the GDL water in the outside portion of the GDL, which may be water condensation due to a heat pipe effect. The measured water content in the Nafion® is lower than expected by equilibrium measurement of Nafion® water uptake. This may be due to the neutron detector spread function and further experiments are planned to resolve this issue.

The effect of co-flow, counter-flow and gravity on MEA water density during operation is illustrated in Figure 2 for a GORE™ PRIMEA® MEA Series 57110. As shown in the Figure 2a, significantly more water is present in the MEA during counter-flow operation than under co-flow. This leads to a lower HFR of 0.064 Ω cm^2 for the counter-flow configuration, vs. 0.10 Ω cm^2 in the case of co-flow, as well as better cell performance for counter-flow (cell voltage of 0.27 V vs. 0.10 V for co-flow at 1A/cm^2). Figure 2b depicts the effect of flipping the cell vertically on water density. The operating conditions were similar to those in Figure 2a. Positioning the anode on top (Figure 2b) decreases the tendency towards flooding, leading to improved performance.

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 transient phenomena, step current transients

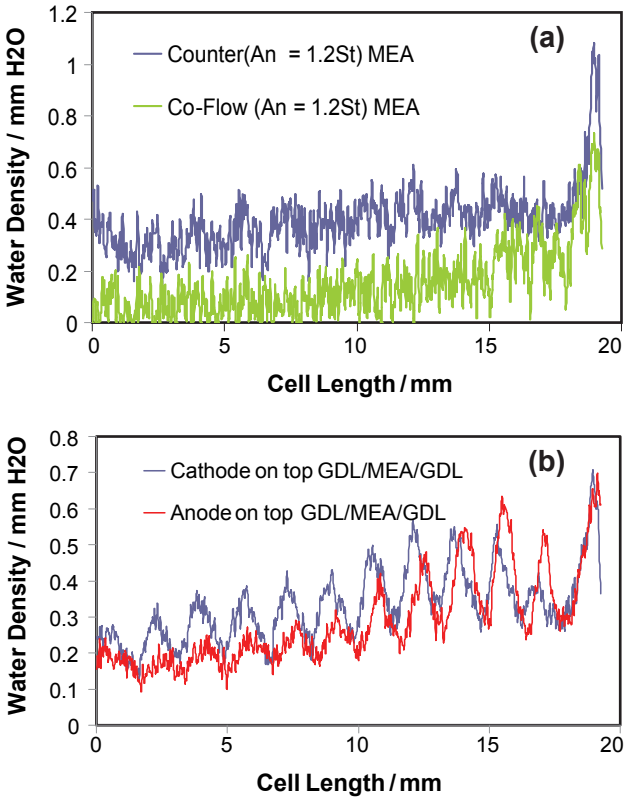

FIGURE 2. GORE™ PRIMEA® MEA Series 57110 with SGL Carbon, cell temperature: 80°C, anode feed: fully humidified H_2, cathode feed: dry air. (a) Effect of flow direction on water content in MEA (Co-flow: I = 1.41 A/cm^2; Counter Flow : I = 1.49 A/cm^2), (b) Effect of gravitational orientation on water content in MEA + GDL layers (Counter Flow: I = 1.49, Counter Flow Inverted: I = 1.39).

were conducted, measuring the in situ response of membrane water content by HFR measurements.

The current step transient from 0.5 to 34.0 amps consistently shows MEA wetting occurs 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 (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. Also, during these transient experiments, there is a larger change in HFR for drier operating conditions, which is likely due to large water content changes. The cell operating temperature also has a large effect on the transient response. Large changes in HFR (MEA water content) for dry operating conditions at 80°C and 50% RH-hydrogen/0% RH-air are reduced at 60°C, and greatly reduced at 40°C. This reflects the much greater drying effect (capacity for water) of the warmer gases.

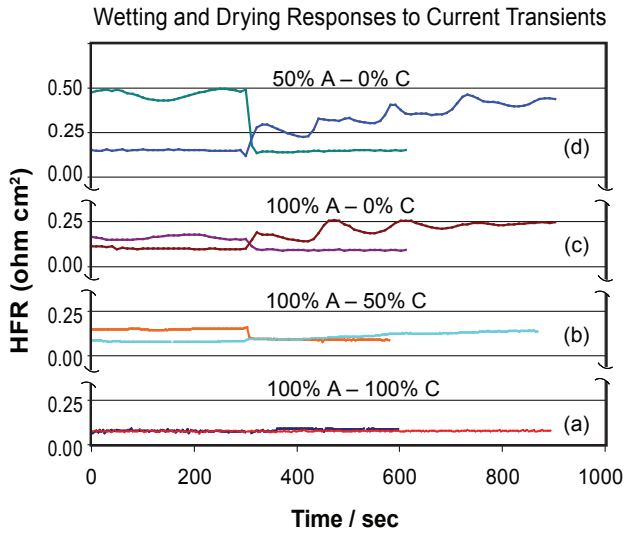

FIGURE 3. MEA wetting responses during 0.5 to 34.0 amp step transient and drying responses during the reverse 34.0 to 0.5 amp step transient for different gas humidification conditions.

Performance and Durability of Sub-Freezing Operations

Special single cells with cooling loops machined in the end plates were used in order to study the start-up behavior of fuel cells at sub-freezing conditions. The cells were first operated at 0.6 V at 80°C with air and H_2 at 100% inlet RH and 30 psi back-pressure. The single cells were then purged using N_2 gas (<5,000 cc/min for <3 minutes) and cooled down to sub-freezing temperatures. Dry H_2 and dry air were then introduced into the anode and cathode of the cells and their performance was monitored isothermally at sub-freezing temperatures at various constant current densities. The voltage exhibited a decay associated with the ice formation resulting in increased mass transport resistance. After the voltage dropped to 0 V, the cell was heated back up to 80°C and cyclic voltammograms were obtained and were used to determine the durability of the catalyst to ice formation. These revealed that the durability of the catalyst layer was strongly dependent on the MEA. While the LANL-prepared MEAs showed little change in surface area (Figure 4a), the commercial MEAs showed a loss in surface area with every cold-start operation (Figure 4b). These latter results are consistent with other studies that have shown catalyst surface area loss due to sub-freezing operations. These results also indicate that catalyst layer ice formation may be controlled and its effects mitigated by careful control of the catalyst layer morphology.

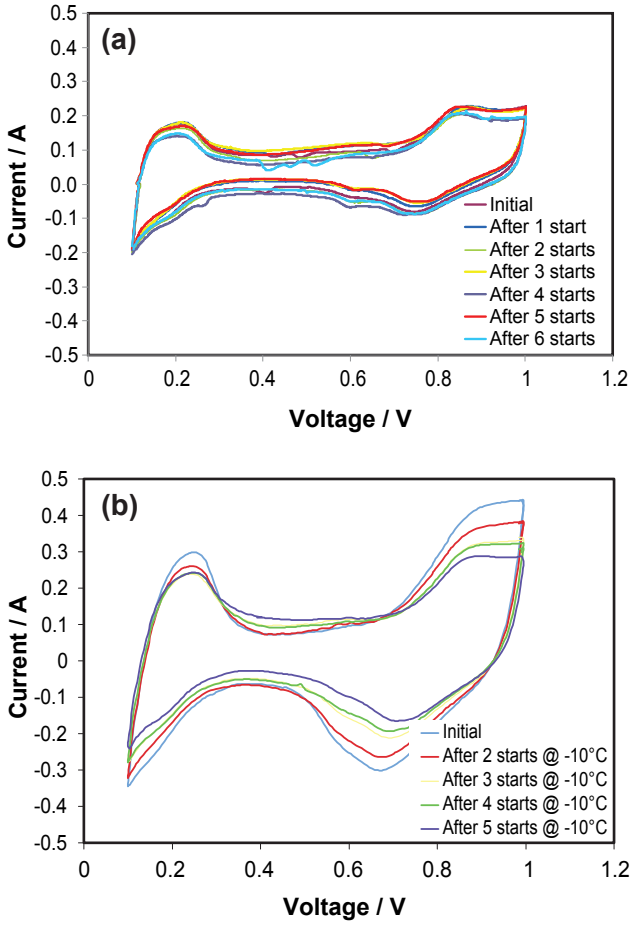

FIGURE 4. Cathode cyclic voltammograms of (a) LANL MEA before and after operation at -10°C and (b) a commercial MEA before and after operation at -10°C.

Model Prediction of Water-Droplet Detachment Onset

Two different mechanisms for water removal from the GDL are being modeled: water droplet detachment from the GDL/channel interface and water migration from the flowfield land to the channel.

CFD simulations of water in the diffusion media show water accumulation above the lands at the channel/land edge. The area of maximum water saturation in this case is in the GDL substrate above the lands. Liquid water streamlines converge towards the channel-land corners where sessile/pendant droplets form and leak down the channel walls. These CFD results agree with neutron images that show the high degree of water saturation above the land, and channel-wall water removal. CFD simulation results also show liquid water accumulating in diffusion media until the liquid pressure at the GDL/channel interface reaches the threshold value (Young-Laplace), after which it exits the GDL into the channel. Once the threshold value

is reached the water forms a droplet that grows and eventually detaches from the GDL.

Elucidating water-droplet detachment from GDL/channel interface and being able to predict the critical air-flow velocity required to detach droplets helps provide critical design and operational guidelines. Modeling of the critical air-flow velocity, U_c has been conducted by making a force balance on water droplets at the onset of detachment. This modeling is based on the force balance between viscous shearing/pressure drag that tends to detach the droplet and surface tension that tends to hold the droplet in place. Simulated 3-dimensional (3D) water-droplet deformation and detachment from GDL/channel interface at various air-flow velocities has been conducted and predicts water detachment at gas velocities approaching 9 m/s.

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
  - Modeling predictions agree with observed water removal mechanisms
- 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
  - Water build-up is observed in flow field of both anode and cathode at constant stoichiometric operation
  - 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
  - Gravity has an effect on water build-up on the cathode with horizontal cell orientation
- GDL surface properties affect water transport
  - Greater mass transfer resistance for GDLs with higher MPL Teflon® loadings
  - Substrate Teflon® 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
  - Ice buildup directly correlates with current density (via neutron imaging)
  - The 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

- NIST Neutron Imaging
  - Start-up of nano-structured thin film catalyst based membranes, understand saturation water content of membrane, high resolution freeze, transients
- Transient Operation
  - Simulate automotive operation, RH transients
- Segmented Cell Operation
  - Measure water transport spatially in cell by HFR
- Freeze Measurement
  - Effect of sub freezing operations on MEA durability
- Characterization
  - Transmission electron microscopy characterization of aged GDL materials, surface spectroscopy of GDL surfaces
- Model Development
  - Develop multi-dimensional (quasi-3D) model of water transport and removal
  - Incorporate sub-models of liquid-water removal via droplet detachment and evaporation

FY 2008 Publications/Presentations

1. R. Mukundan, R. Davey, T. Rockward, J.S. Spendelow, B.S. Pivovar, D.S. Hussey, D.L. Jacobson, M. Arif, and R.L. Borup, "Imaging of Water Profiles in PEM Fuel Cells Using Neutron Radiography: Effect of Operating Conditions and GDL Composition", ECS Transactions, 2007; v.11, no.1, p.403.

2. R. Mukundan, Y.S. Kim, T. Rockward , J.R. Davey, B.S. Pivovar, D.S. Hussey, D.L. Jacobson, M. Arif, and R.L. Borup, "Performance of PEM Fuel Cells at Sub-Freezing Temperatures", ECS Transactions, 2007; v.11, no.1, p.543.

3. K.S. Chen, "Modeling Water-Droplet Detachment from GDL/Channel Interfaces in PEM Fuel Cells", draft paper accepted for publication in the ASME FUELCELL08 Proceedings (in revision).

4. M.A. Hickner, N.P. Siegel, K.S. Chen, D.S. Hussey, D.L. Jacobson, and M. Arif, "In-situ high resolution neutron radiography of cross-sectional liquid water profiles in PEM fuel cells", Journal of the Electrochemical Society, 155 (4) B427 (2008).

5. M.A. Hickner, N.P. Siegel, K.S. Chen, D.S. Hussey, D.L. Jacobson, and M. Arif, "Understanding the liquid water distribution and removal phenomena in an operating PEM fuel cell via neutron radiography", Journal of the Electrochemical Society, 155 (3) B294 (2008).

6. R. Borup, R. Mukundan, J. Davey, D. Wood, T. Rockward, J. Spendelow, D. Jacobson, D. Hussey, A. Muhammad, PEM Fuel Cell Water Transport Exploratory Studies, Abstracts of the 2007 Fuel Cell Seminar, San Antonio, TX, October 15–19, 2007.

7. R. Mukundan, J. Davey, T. Rockward, J. Spendelow, B. Pivovar, D. Hussey, D. Jacobson, M. Arif, and R. Borup, Imaging of Water Profiles in PEM Fuel Cells using Neutron Radiography: Effect of Operating Conditions and GDL Composition, Oct. 9, 2007 212th ECS Meeting, Washington, D.C.

8. R.L. Borup, R. Mukundan, J.R. Davey, D. Wood, Y.S. Kim, J. Spendelow, T. Rockward, D.S. Hussey, D.L. Jacobson, M. Arif, Water Transport Exploratory Studies, Fuel Cell Seminar, San Antonio, TX, Oct. 15–19, 2007.

9. R.L. Borup, R., Mukundan, J.R. Davey, H. Xu, D. Wood, F.H. Garzon, Y.S. Kim, Effect of Water Management on Stack Degradation, International Workshop on Degradation Issues in Fuel Cells, Crete, Greece, September 19 – 21, 2007.

10. R. Mukundan, R.L. Borup, J.R. Davey, Y.S. Kim, B.S. Pivovar , and T. Rockward M. Arif, D.S. Hussey, and D.L. Jacobson Sub-Freezing Effects on Fuel Cell performance and Durability, FC-Cubic Workshop, Tokyo, Japan, Nov. 2007.

11. R. Mukundan, R.L. Borup, J.R. Davey, B.S. Pivovar, T. Rockward, and J. Spendelow, M. Arif, D.S. Hussey, and D.L. Jacobson, Neutron Imaging of Liquid Water in Fuel Cells:Effect of GDL Material and Operating Condition on Fuel Cell Performance, FC-Cubic Workshop, Tokyo, Japan, Nov. 2007.

12. J.R. Davey, R. Mukundan, T. Rockward, J.S. Spendelow, B.S. Pivovar, D.S. Hussey, D.L. Jacobson, M. Arif, and R.L. Borup, "Imaging of Water Profiles in PEM Fuel Cells Using Neutron Radiography: Effect of Operating Conditions and GDL Composition", 212th Electrochemical Society Meeting, Washington, D.C., October 7–12, 2007.

13. R. Mukundan, Y.S. Kim, T. Rockward , J.R. Davey, B.S. Pivovar, D.S. Hussey, D.L. Jacobson, M. Arif, and R.L. Borup, "Performance of PEM Fuel Cells at Sub-Freezing Temperatures", 212th Electrochemical Society Meeting, Washington, D.C., October 7–12, 2007.

14. K.S. Chen and M.A. Hickner, "Elucidating water transport and removal in PEM fuel cells via experiments and modeling", US-Canada Fuel Cell Workshop, National Research Council, Vancouver, Canada, March 17–18, 2008.

15. K.S. Chen, "Predicting water-droplet detachment from GDL/channel interfaces in PEM fuel cells", 212th Electrochemical Society Meeting, Washington Hilton, Washington, D.C., October 7–12, 2007.