Water Transport Exploratory Studies

2008 DOE Hydrogen Program Review
June 9-13, 2008
Presented by: Rod Borup

Solicitation Partners:
Los Alamos National Lab, National Institute of Standards and Technology, Sandia National Lab, Oak Ridge National Lab, SGL Carbon, W.L. Gore, Case Western Reserve University

Additional Partners/Collaborations:
University of Texas-Austin, 3M Company, Nuvera Fuel Cells

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Project Overview

**Timeline**
- New Project for FY07
- 4 year Project Duration

**Barriers**
Water management is critical for optimal operation of PEM Fuel Cells
- Energy efficiency
- Power density
- Specific power
- Cost
- Start up and shut down energy
- Freeze Start Operation

**Budget**
- Total project funding
  - DOE Cost: $6,550,000 (over 4 yrs)
  - Cost Share: $290,811
- Funding for FY08
  - LANL: $1000k
  - Industrial Partners: $300k
  - Other National Labs: $350k
  - FY08 Total: 1650

**Partners**
- Direct collaboration with Industry, Universities and other National Labs (see list)
- Interactions with other interested developers
- Project lead: Los Alamos National Lab
Organizations / Partners

- Los Alamos National Lab: Rod Borup, Rangachary Mukundan, John Davey, Tom Springer, Yu Seung Kim, Jacob Spendelow, Tommy Rockward, Partha Mukherjee
- Sandia National Laboratory: Ken Chen & C.Y Wang (PSU)
- Oak Ridge National Lab: Karren More
- Case Western Reserve University (sub-contract): Tom Zawodzinski, Vladimir Gurau
- SGL Carbon Group (sub-contract in progress): Peter Wilde
- National Institute of Standards and Technology (no-cost): Daniel Hussey, David Jacobson, Muhammad Arif
- W. L. Gore and Associates, Inc. (PR basis): Will Johnson, Simon Cleghorn
- Univ. Texas-Austin (additional sub-contract): Jeremy Meyers
- 3M: Mark Debe (Technical Assistance – providing NSTF materials)
- Nuvera: James Cross, Amedeo Conti, Olga Polevaya, Filippo Gambini (Technical Assistance – low temperature conductivity)
Objectives

• Develop understanding of water transport in PEM Fuel Cells (non-design-specific)
  – 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 operation
  – Develop models which accurately predict cell water content and water distributions
  – Work with developers to better state-of-art
  – Present and publish results
Approach

• Experimentally measure water \textit{in situ} operating fuel cells
  – Neutron Imaging of water
  – HFR, AC impedance measurements
  – Transient responses to water, water balance measurements
  – Freeze measurement / low temperature conductivity
    • Understand the effects of freeze/thaw cycles and operation
    • Help guide mitigation strategies.

• Characterization of materials responsible for water transport
  – Evaluate structural and surface properties of materials affecting water transport
    • Measure/model structural and surface properties of material components
    • Determine how material properties affect water transport (and performance)
    • Evaluate materials properties before/after operation

• Modeling of water transport within fuel cells
  – Water droplet detachment
  – Water profile in membranes, catalyst layers, GDLs
  – Water movement via electro-osmotic drag, diffusion, migration and removal

• Develop (enable) new components and operating methods
  – Evaluate materials effects on water transport
Neutron Imaging
Cross-Section Design for High Resolution Imaging

Design Considerations:
- Maximum field of view is 2 cm X 2 cm for the high resolution neutron detector.
  - Limits X dimension to 2 cm.
  - Outermost edge to image = 3 cm from the detector for good focus.
    - Detector is 0.5 cm inset of the face plate, → 2.5 cm available
- Active area 1.2 cm in width
  - Entire cell is < 3 cm from detector

Design:
- 2.25 cm² active area
- No hydrocarbon materials
- Metal hardware
  - No plate porosity of hardware for water hold-up
- 1 cm linear water imaging length
- Shallow single serpentine flowfield
  - Attempt to simulate pressure drop of real flowfields
GDL Teflon Loading Effect on Water Content
Monitored by Neutron Imaging and AC Impedance

Cross-section Neutron Imaging

AC Impedance

GDL Variation

- GDL A = 5% Substrate 23% MPL PTFE Loading
- GDL B = 5% Substrate 10% MPL PTFE Loading
- GDL C = 20% Substrate 10% MPL PTFE Loading

- Charge transfer resistance
  - Decreases with increasing current
  - Greater for GDL with 23% PTFE in MPL
- Mass transfer resistance
  - Increases with increasing current
  - Greater for GDL with 23% PTFE in MPL

Co-Flow, 80 °C, 172 kPa (abs)
Anode: 1.1 stoich. / 50 % RH
Cathode: 2.0 stoich / 100 % RH

- More PTFE in the MPL results in more water in GDLs and channels
- Mass transport limitations consistent with lower performance of fuel cells with high MPL Teflon loading at high current densities
Water Profiles Nafion 212
Water content comparison for different operating conditions

- Variation of water content as a function of current density/anode stoichiometry
  - Anode stoichi = 3 (simulating anode recycle), dry cathode has lower water content
  - Anode stoichi = 1.2, dry cathode similar water content to fully humidified cell

- Measured Water content in Nafion lower than expected

- Low constant stoich (1.1/2.0)
- Simulating anode recycle (3.0)
- Flowfield co-flow

- Anode channel/GDL water:
  - With const. anode stoich ~ 1.1
  - Disappears with anode recycle
  - Anode GDL water may be water condensation (heat pipe effect)

- Membrane/Catalyst Layer is only ~ 5 pixels wide
- ~ 3 pixels for thinner MEAs
- 1 pixel = 14.7 microns
Water Profiles Delineated in Counter-Flow Orientation

- MEA shows highest water content in middle of cell (land)
- Right Land / Channel (anode out)
- Low water content in cell (compared with other materials)
- Water in channels at outlets

3M NSTF, Counter Flow, 40 °C, 0.59 A/cm², T_a = 28, T_c = 28
Water Content Comparison with Various Materials

- High resolution neutron images of different MEA materials under similar operating conditions.
- N212 high water content, low water content for 3M NSTF materials
- Anode GDL water differs significantly
- Significantly more water in MEA/GDLs at lower temperatures

GORE, and PRIMEA are trademarks of W. L. Gore & Associates, Inc.
Cell Length Water Profiles
Co-flow vs. Counter flow

Co-flow:
- \( I = 1.41 \, \text{A/cm}^2; \, V = 0.095 \, \text{V} \)
- \( \text{HFR} = 0.10 \, \text{Ohm.cm}^2 \)

Counter Flow:
- \( I = 1.49 \, \text{A/cm}^2; \, V = 0.27 \, \text{V} \)
- \( \text{HFR} = 0.064 \, \text{Ohm.cm}^2 \)

- Higher membrane water with counter flow
- Membrane water correlates to lower HFR and higher performance with counter flow

GORE™ PRIMEA® MEA Series 57110
GORE and PRIMEA are trademarks of W. L. Gore & Associates, Inc.
Cell Length Water Profiles
Anode Stoich comparison

- MEA water content ~ same
- Higher anode stoich: lower land water
- Similar Performance

100 / 0 % RH, 1.2 vs. 3.0 st. simulating anode recycle

Counter Flow: 1.2St
I = 1.49; V = 0.27V; HFR = 0.064

Counter Flow: 3.0St
I = 1.49; V = 0.27; HFR = 0.076

GORE™ PRIMEA® MEA Series 57110
GORE, and PRIMEA are trademarks of W. L. Gore & Associates, Inc.
Cell Length Water Profiles
Orientation comparison

Counter Flow
Anode → Cathode

Counter Flow Inverted
Anode → Cathode

100 / 0 % RH
1.2/2.0 St. Orientation inverted

• Membrane water content similar
• Cathode on top shows flooding (gravity effect) and loss of performance
• Cathode on bottom GDL water lower water content

Counter Flow : 1.2St
I = 1.49; V = 0.27V; HFR = 0.064

Counter Flow Inverted: 1.2St
I = 1.39; V = 0.385; HFR = 0.067

The Institute for Hydrogen and Fuel Cell Research

GORE™ PRIMEA® MEA Series 57110
GORE, and PRIMEA are trademarks of W. L. Gore & Associates, Inc.
Freeze Operation

Fuel Cell Start-up at -10 °C

- Little change in HFR
- Steady increase of Charge Transfer Resistance
- Steep increase in Mass Transport Resistance when cell voltage drops

- Performance decays quickly at -10 °C
  - Ice formation leads to mass-transport limitations
  - No change in ECSA at low temperatures
  - As operating time increases, AC Impedance resistance shows mass-transport limitations

- ECSA slightly increases after multiple runs at -10 / 80 °C
  - Possible hydration of membrane or cell break-in

Impedance During Start-up at -10 °C

- T = -10 C
- Anode = H2 (500 sccm)
- Cathode = Air (500 sccm)
- I = 1A (0.02 A/cm²)
- V = 0.87 to 0.89V
- AC Amplitude = 0.1A

ECSA at -10 °C
Neutron imaging of ice formation in a 50 cm² fuel cell operated at 0.5 V at -10 °C.

- Calculated/measured water/ice accumulation from current and neutron imaging in the fuel cells track.
MEA Freezing Conductivity

• At 25%RH @ 70 °C:
  • Hysteresis is seen; Cooling (Lower \( \lambda \)); Heating (higher \( \lambda \))
  • If cell is left at cold temperatures: membrane will rehydrate

• At 100% RH @ 70 °C: Membrane fully hydrated; No hysteresis in conductivity
• At 50% RH @ 70 °C: Membrane \( \lambda \) is lower, Conductivity is lower
• However, membrane hydrates at low temperatures (higher RH)
MEA HFR Response to Transients

80 °C

60 °C

Wilhelmy-Plate Contact Angle
advancing vs. receding

• Advancing more hydrophobic
• Once wet; difficult to ‘de-wet’

• Wetting / dewetting show very different time constants in response to transient inputs
  • MEA quickly hydrates / MEA slowly dehydrates
  • Contact angle characterization shows similar hysteresis

0.1/0.2 GORE™
PRIMEA® MEA
Series 57110
100% RH Anode
50% RH Cathode

GORE, and PRIMEA are trademarks of W. L. Gore & Associates, Inc.

Los Alamos
CFD Modeling of Water Removal from GDL

- Liquid water accumulates above the lands before exiting the GDL in the channel.
- Maximum saturation is above the lands.
- Liquid water streamlines converge towards the channel-land corners.
  - Sessile/pendant droplets form and leak down the channel walls.
- CFD results agree with Neutron Images.
CFD Simulation Results

- Liquid water saturation profiles modeled in the cathode GDL and catalyst layer.
- Liquid water accumulates in diffusion media over time.
  - When liquid pressure at GDL-channel interface reaches a threshold value (Young-Laplace) it exits GDL via channel.

- CFD modeling profiles agree with experimental results (magenta frame above) obtained by neutron imaging.
Motivation: droplet detachment from GDL/channel interface is a key mechanism for liquid-water removal in PEM fuel cells. Elucidating water-droplet detachment from GDL/channel interface and being able to predict the critical air-flow velocity required to detach droplets can provide useful design and operational guidelines.

Channel/droplet/pore dimensions:
Channel height = 1 mm,
Droplet diameter = 0.6 mm,
Pore diameter = 100 μm

Schematic of water-droplet growing and being deformed by flowing air drag at the GDL/flow-channel interface
Simulated 3-D water-droplet deformation and detachment from GDL/channel interface

1 m/s (deformation not yet visible)

5 m/s (deformation visible)

6.3 m/s (moments before detachment)

6.4 m/s (moments after detachment)

Ken S. Chen (kschen@sandia.gov)  Sandia National Lab
Single-phase CFD model explaining neutron imaging patterns on water distribution*

Compared along-channel velocity component and neutron image through a corner of the flow channel

Compared velocity vector plot and neutron image in a corner of the gas flow channel

Regions where liquid water content is reduced corresponds high gas velocity.

Computed velocity field indicates the presence of recirculation zones in the 90° bends.

Low flow speed and circular nature of gas flow lead to reduction in water removal driving force and corresponding increase in water content.

Future Work

- **NIST Neutron Imaging (June 12-18)**
  - NSTF Start-up, 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**
  - *in situ* monitoring of ice formation

- **Characterization**
  - TEM 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
### Milestones

<table>
<thead>
<tr>
<th>Mon Yr</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec 07</td>
<td>Quantify water content by HFR measurements in various cell components under steady-state operation</td>
</tr>
<tr>
<td>Dec 07</td>
<td>Accurate water balance measurements during steady-state operation</td>
</tr>
<tr>
<td>Mar 08</td>
<td>100 freeze/thaw cycles to -40°C on fully humidified cells using paper GDL (completed FY07) New: Performance of fuel cells operated at –10°C</td>
</tr>
<tr>
<td>Jun 08</td>
<td>Report surface properties of GDL and the effect of aging</td>
</tr>
<tr>
<td>Sept 08</td>
<td>Direct observation of ice formation by neutron imaging (completed FY07)</td>
</tr>
</tbody>
</table>

[In progress]
Summary of Technical Accomplishments

• Experimentally measure water *in situ* operating fuel cells
  – Direct water imaging at NIST by neutrons
    • High resolution (25 μm) imaging, Low resolution (150 μm) imaging
  – AC Impedance and HFR measurements
  – Freeze/Thaw
    • Ice results in performance loss associated with increasing low freq. resistance
      – Ice formation limits gas access to the reaction sites

• Characterization
  – Hydrophobicity characterization, microscopic characterization, elemental compositional
  – Varying GDL materials (MPL Teflon loading, GDL substrate Teflon loading)
    • GDL wetting/dewetting properties help explain fuel cell performance hysteresis.

• Modeling of water transport within fuel cells
  – Delineation of mass transport loss from IR, kinetics, etc.
  – Modeling of water-droplet detachment from the GDL/channel interface.
  – CFD modeling simulates liquid water saturation profiles