Visualization of Fuel Cell Water Transport and Performance Characterization Under Freezing Conditions

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May 21, 2009

Project ID #: fc_37_kandlikar

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Overview

Timeline
• Start date: 03/01/2007
• End date: 02/28/2010
• 70% complete

Budget
• Total project funding
  – DOE: $ 2.68M
  – Contractor: $ 0.8M
• FY08: $ 0.9M
• FY09: $ 0.9M

Barriers
• Barriers addressed
  C. Performance
  D. Water Transport within the Stack
  E. Thermal System and Water Management

Partners
• Interactions/ collaborations
  – Rochester Institute of Technology
  – General Motors Corporation
  – Michigan Technological University

• Project lead:
  Rochester Institute of Technology
Objectives - Relevance

Overall: • Improve fundamental understanding of the water transport processes in the PEMFC stack components under freezing and non-freezing conditions.

• To minimize fuel cell water accumulation while suppressing regions of dehumidification by an optimized combination of new gas diffusion layer (GDL) material and design, new bipolar plate (BPP) design and surface treatment and anode/cathode flow conditions.

• To meet DOE 2010 targets for 80 kWe transportation stacks:

<table>
<thead>
<tr>
<th>Start up and shut down energy from -20°C ambient</th>
<th>Unassisted start temperature</th>
<th>Cold start-up time to 50% of rated power @ –20°C ambient</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 MJ</td>
<td>- 40 °C</td>
<td>30 s</td>
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</table>

FY08: • Implement changes to baseline system and assess the performance:
   ➢ Ex-situ combinatorial performance
   ➢ In-situ combinatorial performance
   ➢ Water distribution and current density distribution
   ➢ Microscopic study and models for water transport in GDL and parallel channels; Component characterization techniques and methods
Plan & Approach

Task 1: Baseline System Definition

Task 2: Baseline Performance Characterization

Task 3: Parametric Studies at Component Level

Task 4: Implement Changes, Combinatorial Assessment on Ex-situ Apparatus

Task 5: In-situ Combinatorial Performance

Task 6: In-situ Performance with Water Distribution and Current Density Measurements

Task 7: Final Recommendations

100% complete

100% complete

50% complete

70% complete

70% complete

50% complete

2/28/2009

5/30/2009

8/30/2009

2/28/2010

Is performance improved over baseline?

Is water distribution acceptable for overall and freeze-thaw operation?

Spatially vary GDL and/or channel properties

Yes

No

Yes

No

No

Yes

Will performance be further improved over baseline?

Is performance further improved over baseline?
Technical Accomplishments (GM)–

Water Accumulation Correlated to Freeze Failure

Precondition: 0.4 A/cm², 150 kPa, 35°C, A/C stoich = 2/2, Dry inlet gas
Purge condition: 0.1 A/cm², 150 kPa, 35°C, A/C stoich = 2/12, Dry inlet gas

Water Accumulation in the Exit Region and Headers

- Ice Distribution
  - Cathode flow
  - Anode flow

- No Start - Complete flow blockage
- Successful Start - Partial flow blockage
- Successful Start - No flow blockage

- Evaporating water from porous layers extends run time while frozen, by providing space for additional ice formation and accumulation

- Water at plate-to-header transition can contribute to flow blockage failure at short shutdown purge times
Technical Accomplishments–

Purge Water Removal Rate Characterization

Ex-situ anode vs. cathode purge characterization

In-situ purge comparison

Comparison of ex-situ and in-situ drying rates provide useful insight into the fuel cell drying performance.

Precondition: 0.4 A/cm², 150 kPa, 35°C, A/C stoich = 2/2, Dry inlet gas

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Technical Accomplishments—Water Location Impacts Purge Dynamics and Duration

The length of the drying front can be predicted based on the parameters measured in the current work independent of flow.

Optimization:
Shutdown Energy - 2010 DOE target of 5 MJ
Start-up characteristics

- Drying rate information is used with purge energy consumption in meeting DOE targets.
Technical Accomplishments—
Ionomer Drying and Temperature Effects During Purge

Steady State

Precondition: 0.4 A/cm², 150 kPa, 35°C, A/C stoich = 2/2, Dry inlet gas

Purge condition: 0.1 A/cm², 150 kPa, 35°C, A/C stoich = 2/12, Dry inlet gas

Water Distribution
HFR Distribution
Temp Distribution

Duration of Purge

cathode flow

anode flow

Linkages between water, HFR and temperature distribution are experimentally verified.
Technical Accomplishments—

GDL Thermal Conductivity Saturation Impact

Baseline GDL \((k = 0.24 \text{ W/mK})\)

- Cathode flow
- Anode flow

Increased Conductivity GDL \((k = 0.49 \text{ W/mK})\)

- Pol Curve Condition:
  - 200 kPa
  - 80°C
  - A/C stoich = 1.5/2 100% RH inlet gas

Lower thermal conductivity GDL leads to reduced water volume.
Technical Accomplishments—

GDL Saturation After 3000 Hours of Operation

Fuel cell performance (as see from the plot) remains essentially the same after 3000 hours of operation.

Fundamental Research Objectives

- In-situ studies indicate that the GDL properties and channel/header configuration affect water saturation.
- To reduce purge energy requirement, water accumulation in the fuel cell should be reduced.
- GDL morphological and channel two-phase flow studies are conducted by MTU and RIT to understand the fundamentals of water transport and accumulation in fuel cell.
Technical Accomplishments (MTU) –
GDL Wettability and Structure

**Wettability**
- method developed for accurate measure of contact angle, $\theta$, on rough surfaces (GDL)
- temperature control (up to 100°C)
- humidity control
- as temperature increases, $\theta$ decreases

**Structure**
- developed calibrated SEM compression fixture
- GDL imaging under incremental compression
- stress-strain relationship for GDLs compressed beneath a channel
  - similar to that found in bipolar plates
- compression range:
  - up to 1600 psi, based on area of four (4) $\frac{1}{2}$ standard samples
  - displacement resolution: +/- 6.5 $\mu$m

- Contact angle dependence on temperature and drop size being studied.
- GDL-bipolar plate interface studied for damage to GDL due to compression.
**Technical Accomplishments—**

**GDL Morphology**

**Morphology**
- statistical analysis from single SEM image of GDL
  - **pore size distribution**
    - Weibull distribution to characterize distribution
    - Weibull coefficients used to generate network for capillary flow model
  - pore depth distribution (stereo SEM imaging)
  - pore roundness distribution
  - pore orientation distribution (Rose plot)
  - nearest neighbor distribution (randomness of pore size distribution)
  - chemistry (x-ray spectrometry)
- assessing relative importance of each parameter

<table>
<thead>
<tr>
<th>GDL sample</th>
<th>Weibull distribution coefficients</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$k$</td>
</tr>
<tr>
<td>MRC 105, 9%(wt)</td>
<td>1.3</td>
</tr>
<tr>
<td>E-Tek LT1200-N</td>
<td>1.5</td>
</tr>
<tr>
<td>Toray T060, 7%(m)</td>
<td>1.65</td>
</tr>
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</table>

- Rapid analysis of important GDL parameters using SEM images.
- Significant advantages over capillary-flow porosimetry and mercury-intrusion porosimetry (MIP).
Technical Accomplishments—
GDL Transport Characterization

**Drainage**

- pseudo-Hele-Shaw experiments
- phase drainage phase map for GDLs
- unique phase drainage diagram for each GDL
- unique capillary pressure curve for each type of displacement and GDL
- provides quantitative input for capillary flow model

**Drainage Phase diagram: Toray T060**

- A novel method developed to represent water transport in GDL
- Captures capillary effects
- Data used to “calibrate” capillary flow model for each GDL
Technical Accomplishments–

Capillary Flow Model

Network Model
• model details presented last year
• model inputs:
  ➢ contact angle (from Wettability studies)
  ➢ pore size distribution (from Morphology studies)
• unique phase drainage diagram for each GDL
• unique capillary pressure curve for each type of displacement and GDL

Capillary Flow Model presents a simple methodology for characterizing capillary effects in GDLs.
Technical Accomplishments—
Channel Characterization

**Single Channel Experiments**

- effect of wettability on 2-phase flow transition presented.
- high speed microscopy shows extreme pressure spikes and density waves in channels at typical reactant purge velocities
- determined critical volume at which static liquid film or drop will spontaneously plug a channel:
  - function of channel and base (GDL) contact angles
  - solution generated via *Surface Evolver*
- use to predict location of channel plugging
- assist with developing channel purge strategies

\[ V_{CR} = 0.244 \]
\[ \theta_{base} = 150^\circ \]
\[ \theta_{wall} = 110^\circ \]

\[ V_{CR} = 0.286 \]
\[ \theta_{base} = 150^\circ \]
\[ \theta_{wall} = 120^\circ \]

Symmetry plane on bend dihedral

- Understanding critical volume for liquid plug formation can assist with flow field purge strategy.
Technical Accomplishments (RIT) –

Water Transport in Channels - Flow Maldistribution

Entrance Region Pressure Drop Method:

Individual pressure taps at the channel entrance

Test section with visual access

Channel maldistribution
Single-phase gas flow

EX-SITU parallel channel flow

IN-SITU parallel channel flow

- Instantaneous flow distribution in individual channels measured.
- In-situ and ex-situ flow maldistribution and two-phase flow interactions in fuel cell gas channels characterized.
Intrusion effects are seen as multiple orifices in series, rather than uniform reduction in channel flow area.

Optical intrusion measurements correlate well with pressure drop predictions and experimental data.

Instantaneous channel flow measurement in individual channels under in-situ and ex-situ conditions.

- Intrusion effects are seen as multiple orifices in series, rather than uniform reduction in channel flow area.
- Optical intrusion measurements correlate well with pressure drop predictions and experimental data.
- Instantaneous channel flow measurement in individual channels under in-situ and ex-situ conditions.
Technical Accomplishments –

Two-Phase Flow Patterns

- Three basic flow patterns observed: Slug Flow, Film Flow and Mist Flow in both in-situ and ex-situ experiments.
- Slug flow is highly undesirable as it leads to severe flow maldistribution.
- Manifold water holdup adversely affects channel flow.
An important trigger for the slug formation in channel is the large stationary droplets on the channel wall.

The critical droplet size is a function of:
- channel contact angle
- channel contact angle hysteresis.

Hydrophilic channels are preferred as they promote film flow rather than slug flow.

Large contact angle hysteresis is not desirable as it promotes slug formation.
Technical Accomplishments—Pressure Drop Signature and Liquid Holdup

Fourier Transform Analysis:

\[ F\{x_i(t)\} = \sum_{i=0}^{n-1} x_i(t) e^{-j2\pi ik/n} \]

\[ F(k) = Re + jIm \]

\[ M = \sqrt{Re^2 + Im^2} \]

Pressure drop signature:

Flow pattern Identification:

Two-phase friction multiplier:

\[ \Phi_g^2 = \frac{\Delta P_{2\phi}}{\Delta P_g} \]

Baseline channel: \( \theta = 60^\circ \)

Hydrophilic channel: \( \theta = 15^\circ \)

- Two-phase multiplier is able to serve as the flow pattern indicator:
  - High \( \Phi_g^2 \) \( \rightarrow \) slug flow; lower \( \Phi_g^2 \) \( \rightarrow \) film flow; \( \Phi_g^2 = 1 \) \( \rightarrow \) mist flow.

- Hydrophilic channel has a lower water holdup in the low gas flow region, and a higher water holdup in the high gas flow region.
Collaborations

RIT:

MTU:
- MTU: Hydrogen Education Curriculum Path at Michigan Technological University, DOE DE-FG36-08GO18108
- MTU: Center for Fundamental and Applied Research in Nanostructured and Lightweight Materials (CNLM), DOE DE-FG36-08GO88104

GM:
Proposed Future Work for FY09

MATERIAL SET for Combinatorial Performance Evaluation

CHANNEL

• Implement changes to flow field channel to incorporate the channel geometries which are representative of high volume manufacturing processes (stamped metal and molded carbon composite):
  (i) sinusoidal, and (ii) trapezoidal cross-section (RIT, GM)
• Further adjust the channel surface treatment and assess its effects on the water transport and holdup in channels. (RIT, GM, MTU)
• Develop predictive tools for water hold-up and two-phase flow in channels. (RIT, MTU).

GDL

• Evaluate the effects of GDL thickness and thermal conductivity on water transport and assess the in-situ combinatorial performance. (RIT, GM, MTU)
• Incorporate GDL compression into network model. (MTU)
• Examine the formation of ice and freeze propagation in GDL. (GM, MTU)

PURGE PERFORMANCE

• Evaluate purge performance of the Phase 2 material set, involving GDL and channel materials which are known to accumulate less liquid water under steady-state conditions (GM).
• Evaluate purge performance of GDL and channel materials with spatially varying properties (GM).
• Combine neutron imaging with printed circuit board measurements of distributed current density, high-frequency resistance and temperature to support pseudo-2D ("down-the-channel") model representation of the shutdown purge process (GM).
• Evaluate freeze start performance of optimized material set, combined with optimized shutdown purge protocol (GM).
Summary – Water Management under Freezing Conditions

Drivers:
- Shutdown Energy: 2010 DOE target of 5 MJ.
- Start-up Time: 30 sec. to 50% of rated power at -20°C.
- Material degradation and performance considerations.

Accomplishments:
- Start-up characteristics:
  - membrane dryout (ionic conductivity), performance
  - ice formation and deposition – amount and location
- Water Transport:
  - location and amount (cathode vs. anode, headers, drying front, purge energy requirements), GDL water holdup, two-phase flow patterns in channels, flow pattern maps, flow maldistribution, water transport models, effect of water holdup on performance
- Material Considerations:
  - Reduced water holdup in GDL
  - Flow pattern and pressure drop characteristics in gas channels
- Identified New material set:
  - GDL thickness
  - GDL thermal conductivity
  - GDL morphology
  - Channel geometry and surface treatment