Investigating Failure in Polymer-Electrolyte Fuel Cells

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This presentation does not contain any proprietary or confidential information
Overview

- Project started in FY05
- Budget (no cost share)
  - FY05: $228k
  - FY06: $250k
- Project focus areas from DOE multiyear RD&D plan
  - Technical barriers addressed
    - A – Durability
    - D – Thermal, Air, and Water Management
  - Tasks
    - Task 4 – Air, water, and thermal management
    - Task 13 – Advanced membrane R&D
    - Task 14 – MEA materials, components, processes
    - Task 16 – Cold start
- Primary participants and collaborators
  - LBNL
    - Principal investigator: John Newman
    - Scientist: Adam Weber
    - Graduate student: Lisa Onishi
  - Georgia Institute of Technology
    - Principal investigator: Tom Fuller
  - Los Alamos National Laboratory
    - Principal investigator: Bryan Pivovar
- Other interactions
  - UTC Fuel Cells / UTRC
  - General Motors
  - Plug Power
  - Hunter College
**Project Objectives**

**Goal:** To understand and mitigate some of the dominant causes of fuel-cell failure

- To **develop** advanced mathematical models that can predict fuel-cell performance and failure
  - Investigate flooding, material degradation, and thermal issues
- To **understand** the issues related to fuel-cell operation and survivability at low and subzero temperatures
  - Experimentally characterize membrane properties including transport parameters and water content as a function of temperature
- To **optimize** material properties and operating conditions to increase lifetime and durability
  - Understand the effect of heterogeneities and possible conditions that may arise and cause failure
Combination of advanced mathematical model development and necessary fundamental experimentation to understand failure

Experiments
- Design subzero experiments
- Measure membrane properties as a function of water content
- Investigate membrane degradation parameters and relationships

Models
- Improve existing models
- Nonisothermal effects
- Pseudo 2-D
- Analyze for failure-related effects
- Numerical optimization
- Validation through applied experiments
Technical Achievements

**Coupled water and thermal management**
- Developed crossflow model that includes *nonisothermal* effects
  - Heat-pipe effect is significant
- Explored optimum temperature for peak power at given heat-transfer coefficient

**Low-temperature membrane properties**
- In collaboration with LANL, measuring transport properties, water content, and state of water
  - Designed water diffusion coefficient testing apparatus
- Examining existence and cause of Schröder’s paradox

**Membrane-related failure**
- Initiated membrane-*chemical*-degradation subcontract with Georgia Tech.
  - Correlate degradation to relative humidity and gas crossover
- Developing *mechanically related* failure model in collaboration with LANL
Increasing temperature has various tradeoffs

Positive aspects

- Higher kinetic rate constants
- Higher diffusion coefficients and conductivity
- Enhanced gas transport in the catalyst layers
- Greater water-vapor capacity

Negative aspects

- Lower thermodynamic driving force
- Larger electro-osmotic flow and lower membrane water content
- Enhanced gas transport through the membrane
- Reactant dilution by water vapor

Temperature gradients augment heat and water transport

- Heat-pipe effect

Temperature gradient causes water vapor-pressure gradient and movement of water by subsequent evaporation and condensation
Temperature profile at 80°C, 0.3 V, 1 bar, saturated feeds

Maximum temperature rise of around 5°C with gradients of 1 to 3°C

- Significant enough to change performance and water balance
- Gradients depend on material thermal conductivities
Examine the vapor- and liquid-water fluxes for the isothermal and nonisothermal cases.

For isothermal case, water vapor moves toward the membrane.
Examine the vapor- and liquid-water fluxes for the isothermal and nonisothermal cases.

Positive flux signifies water movement from anode to cathode.

For nonisothermal case, water vapor moves away from the membrane.
Inclusion of nonisothermal effects alters polarization performance.

Temperature gradient gives
- Worse performance at high T and low P due mainly to dilution by water vapor and flow-reversal effect
- Better performance at low T and high P due mainly to better kinetics
**Breakdown of heat generation**

- Majority of heat is caused by oxygen reduction reaction
- Water phase change seems small but…

![Bar chart showing heat generation breakdown](image)
Condensation and evaporation are the largest heat interactions, but nearly cancel

- Includes water-vapor to/from membrane phase changes
- Significant amount of water movement due to evaporation/condensation
A small temperature gradient can exist across a fuel-cell sandwich
- Significantly affects fuel-cell performance and water management, especially at higher temperatures and lower pressures

Temperature gradient causes water vapor to move counter to the reactant-gas flow
- Reactant gases have a harder time reaching the catalyst layers

- Anode GDL
  - Water recirculation, resulting in hydrated membrane but also more flooding

- Cathode GDL
  - Lower amount of flooding

Subsaturated feeds exhibit similar, but smaller, nonisothermal effects
Peak-Power Optimization

What is the optimum coolant temperature and how good does the heat transfer need to be?

- Do not need excessive external heat-transfer, although interior places could be problematic
- Results are for 1 bar total pressure

How sharp is the temperature maximum?

- Maximum is broad until higher temperatures
- More dilution by water vapor

Optimum temperature (°C)

Heat transfer coefficient (W/cm$^2$K)

Peak Power (W/cm$^2$)
To understand failure related to subzero operation and freeze, need to measure transport and equilibrium parameters experimentally.

Transport properties (in collaboration with LANL)
- Membrane conductivity and state of water

<table>
<thead>
<tr>
<th>Cooling Rate °C/min</th>
<th>Freezing water g</th>
<th>λ °C</th>
<th>T_f peak °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.11</td>
<td>11.6</td>
<td>-22.0</td>
</tr>
<tr>
<td>10</td>
<td>1.88</td>
<td>10.4</td>
<td>-25.8</td>
</tr>
</tbody>
</table>

*if λ = 22 and ΔH_l = ΔH_l_{water} = 334 J/g

- More and faster freezing at higher cooling rates
- Water diffusion coefficient apparatus designed

Measuring water-uptake isotherms

Schröder’s paradox: since 1903

- Water uptake is greater with liquid than saturated vapor
  - Liquid-equilibrated ($\lambda = 22$ to $24$, $3^\circ C < T < 25^\circ C$)
  - Vapor-equilibrated (in air at 1 bar: $\lambda = 14$; no air: $\lambda = 22$ to $24$, $0^\circ C < T < 29^\circ C$)

Elimination of air reduces the discrepancy

In collaboration with Tom Fuller at Georgia Tech. (started January)

Purpose: correlate and understand how **humidity** and **oxygen crossover** affect membrane **degradation**
- Provide expressions for the modeling effort

Utilize various analyses
- Ion chromatography to detect fluoride-emission rate
- NMR and MS to identify specific fragments
- XPS and Raman to examine degradation
Mechanically Related Failure

- Examine fuel-cell failure mechanisms caused by mechanical properties
  - Requires both experiments and modeling
    - Cell data from collaboration with Los Alamos National Laboratory
  - Initially examine effects related to membrane stress
    - Humidity and freeze/thaw cycling
    - Layer delamination
  - Use our previously developed model* as a starting point

- Membrane water content and properties decrease (RH = 1)
- Membrane swelling compresses the GDLs and affects performance and water management


<table>
<thead>
<tr>
<th>RH</th>
<th>Membrane fractional constraint</th>
<th>GDL thickness (µm)</th>
<th>Interior stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>liquid</td>
<td>0.16</td>
<td>235</td>
<td>4.3</td>
</tr>
<tr>
<td>1</td>
<td>0.21</td>
<td>243</td>
<td>3.5</td>
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<tr>
<td>0.9</td>
<td>0.25</td>
<td>245</td>
<td>3.3</td>
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<tr>
<td>0.5</td>
<td>0.45</td>
<td>248</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Simulations with Nafion® 112, 80°C, 0.4 A/cm² and various feed RH
Future Work: FY06

- Model water and thermal management and their impact on failure
  - Possibly add carbon corrosion and cell reversal to the model
  - Determine impact of higher temperatures and lower humidities
  - Examine the effect of material-property variations on performance

- Correlate humidity and oxygen crossover to membrane degradation
  - Further refine XPS and fluorine measurements techniques

- Determine modeling approach for mechanically related failure

- Continue low-temperature membrane-property experiments
  - Fabricate the water diffusion-coefficient apparatus
  - Design the electro-osmotic coefficient setup
  - Conduct water-uptake and Schröder’s-paradox studies with different temperatures, pressures, and gases
Future Work: FY07

Mathematical modeling
- Incorporate membrane-degradation correlations into the model
- Incorporate low-temperature properties and effects into the model
- Develop models for countercurrent flow and transients
- Validate the model through collaborations
  - Segmented cells, in situ water visualization, testing of optimized designs, etc.
- Optimize and set targets for operating conditions and material properties

Membrane-related failure
- Measure membrane mechanical properties and refine model for mechanically related failure
- Measure low-temperature water uptake and diffusion coefficients
- Investigate the use of photo-acoustic and Raman spectroscopies to examine degradation as a function of position in the membrane
- Detect free OH radicals directly
Purpose: elucidate, explain, and mitigate fuel-cell failure mechanisms from a fundamental perspective

Approach: use both advanced modeling and applied experimentation

Current focus, results, and future work:

- **Water and thermal management**
  - Temperature gradients greatly affect performance
  - A heat-pipe effect exists that causes water movement and can result in mass-transport limitations and convective-flow reversal
  - Water phase changes are significant heat and mass-transport effects
  - Model validation, refinement, extension, and implementation are all planned

- **Membrane-related failure**
  - **Chemical**: correlating degradation to relative humidity and oxygen crossover
  - **Mechanical**: modeling stress distributions and failure due to cycling

- **Low-temperature operation**
  - Determining membrane transport properties, state of water, and water uptake
Focused on only UTC system.
- While we sometimes simulate the UTC water-filled plates, the vast majority of our analysis is on the more traditional solid-plate design.

Some of the membrane related issues may be best accomplished with a partner.
- We have started a subcontract to Georgia Tech. to study some of these issues.

The issues with low RH operation are most important to address.
- This is being examined with the now complete pseudo 2-D, nonisothermal fuel-cell model.

Are there other materials problems that need to be considered, such as freeze related destruction issues ("frost heave") that could be anticipated with a model?
- Planned in the future is a detailed freeze model including such effects but only after the baseline model is complete and the membrane properties are determined.
Consider exploring mal-distribution of temperature and flows (air, hydrogen, coolant, due to channel and cell tolerances).

- This is being planned and will be explored in the upcoming months.

Land effects and co-counter and cross-flow should all be modeled.

- Crossflow has been modeled and counterflow is being worked on as there are difficulties in its numerical implementation.
- Land effects are being considered and will be examined next year with the possibility of either incorporating them into the pseudo 2-D approach or doing a full 2-D model.

Not clear if a dynamic model is planned.

- A dynamic model is planned in the near future; it was decided to focus more on the phenomena at steady-state and getting them correct before moving to the transient simulations.
Critical Assumptions and Issues

In the model, it is assumed that the significant interactions and phenomena occur only in the through-plane direction.

- Time-permitting, we would like to develop a full 2-D model and compare it to our pseudo 2-D model to check this assumption. Such an analysis will also result in better ways to account for the effects of the flow-field rib and material-property anisotropies.

It is inherently assumed that the results of the model are accurate.

- To fix this assumption, more model validation is required both in the treatment of the failure mechanisms as well as the cell results. Further validation is planned through collaborations now being explored in terms of water imaging, cell data, etc.

A problem is that we have a limited amount of resources and there are many different failure mechanisms and a lack of necessary data.

- Discussions with manufacturers will provide assistance in determining the correct phenomena to examine. We also build upon what we have done in order to maximize our effort. We also plan to carry out applied fundamental experiments or collaborate for the necessary data.
Presentations and Publications

Oral presentations


Publications