Investigating Failure in Polymer-Electrolyte Fuel Cells

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May 25, 2005

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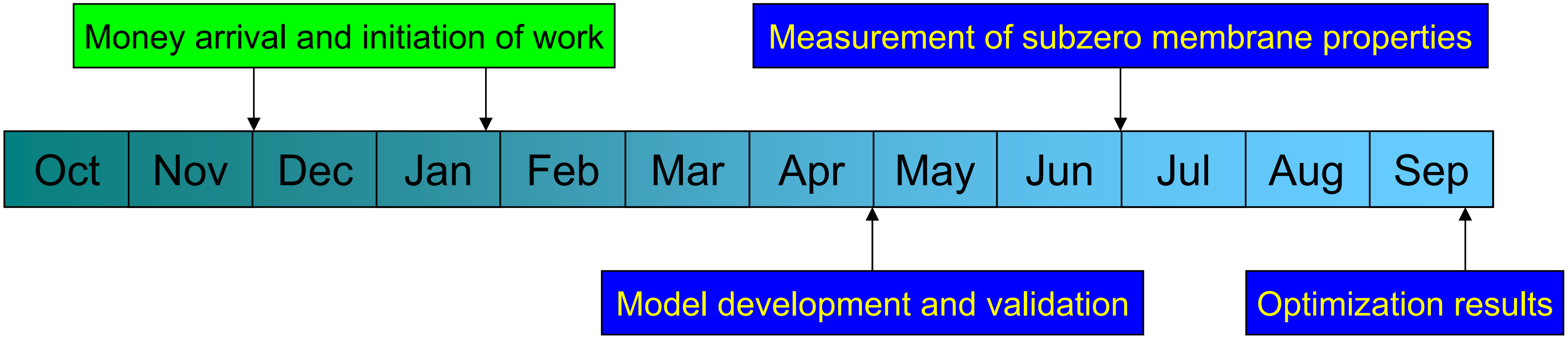
Overview

- This is a new project that started in FY05



- DOE fuel-cell technical barriers addressed
  - A – Durability
  - D – Thermal, Air, and Water Management
- Budget: FY05: $228k (no cost share)
- Collaborators: UTC Fuel Cells, Los Alamos National Laboratory
- Participants
  - Principal investigator: John Newman
  - Postdoctoral fellow: Adam Weber
  - Graduate student: Lisa Onishi

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Project Objectives

Goal: To understand and mitigate fuel-cell failure mechanisms

- 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 develop advanced mathematical models that can predict fuel-cell performance and failure
  - Investigate flooding, membrane degradation, and thermal issues
- 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 (*e.g.*, during transient operation)

Approach

- Combination of advanced mathematical model development and necessary fundamental experimentation to understand failure

Experiments

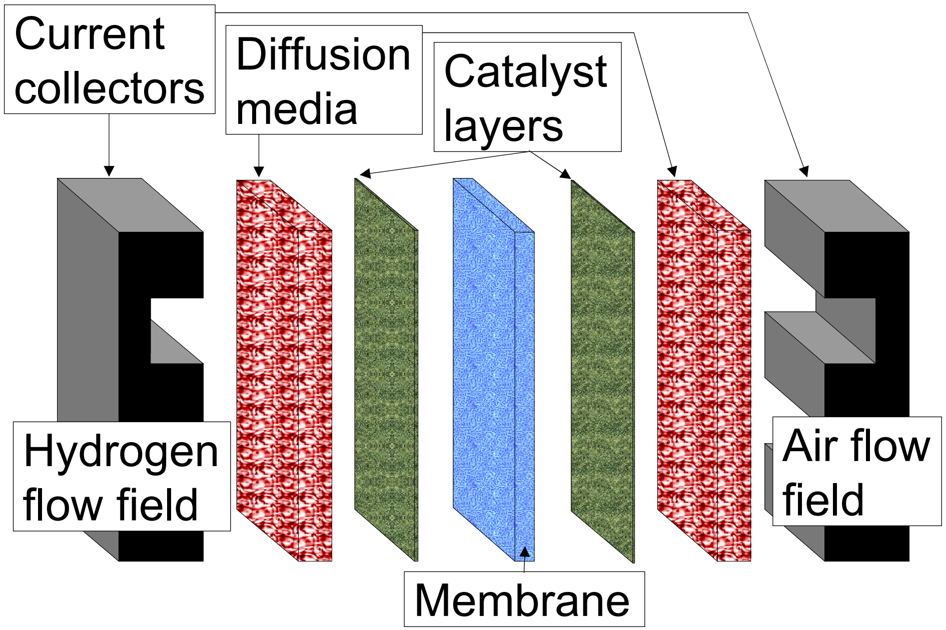
- Design subzero experiments
  - Measure membrane water uptake and state and transport coefficients
- Obtain other modeling parameters from literature and collaborations

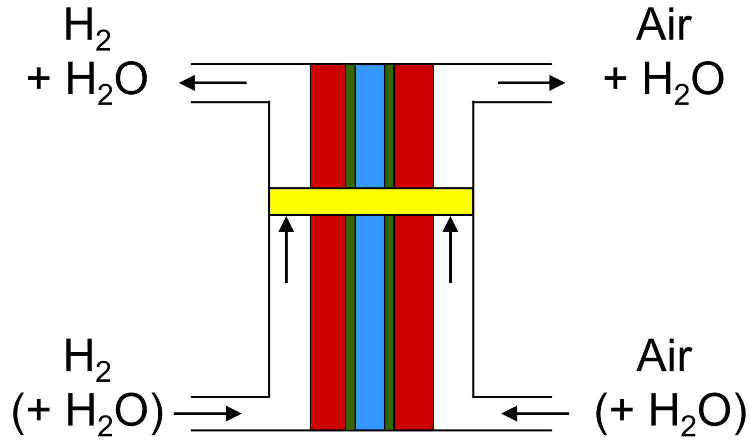
Optimization & Understanding

Models

- Use previously developed model as basis
- Add failure-related effects
  - Accurate two-phase flow description
  - Along-the-channel changes
  - Nonisothermal effects

Modeling Domain



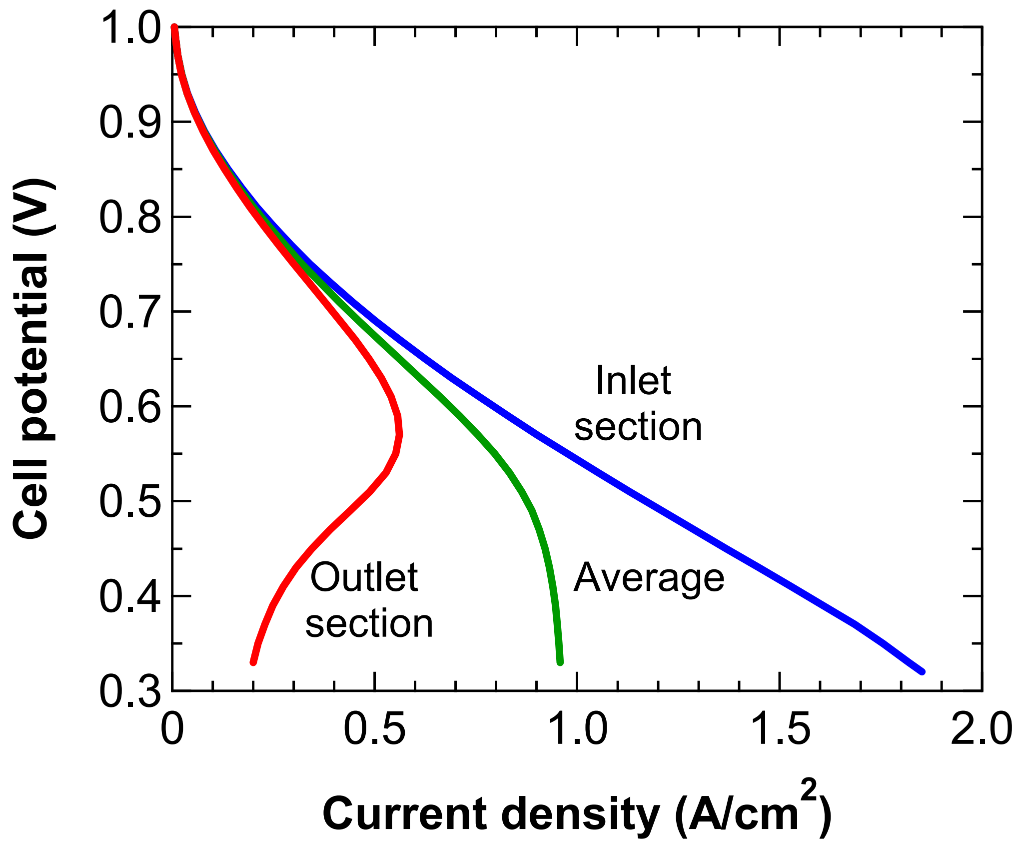


- Developed code to run the sandwich model along the channel
  - Currently adding heat generation and removal along the channel
    - Complications due to temperature exponential in vapor pressure and kinetics
- Completed code allows for analysis and optimization of interplay between water and thermal management and fuel-cell failure
  - Determine what conditions lead to unstable operation, large temperature gradients, low water contents, and fuel and air starvation

Along-the-Channel Results: Polarization Curve

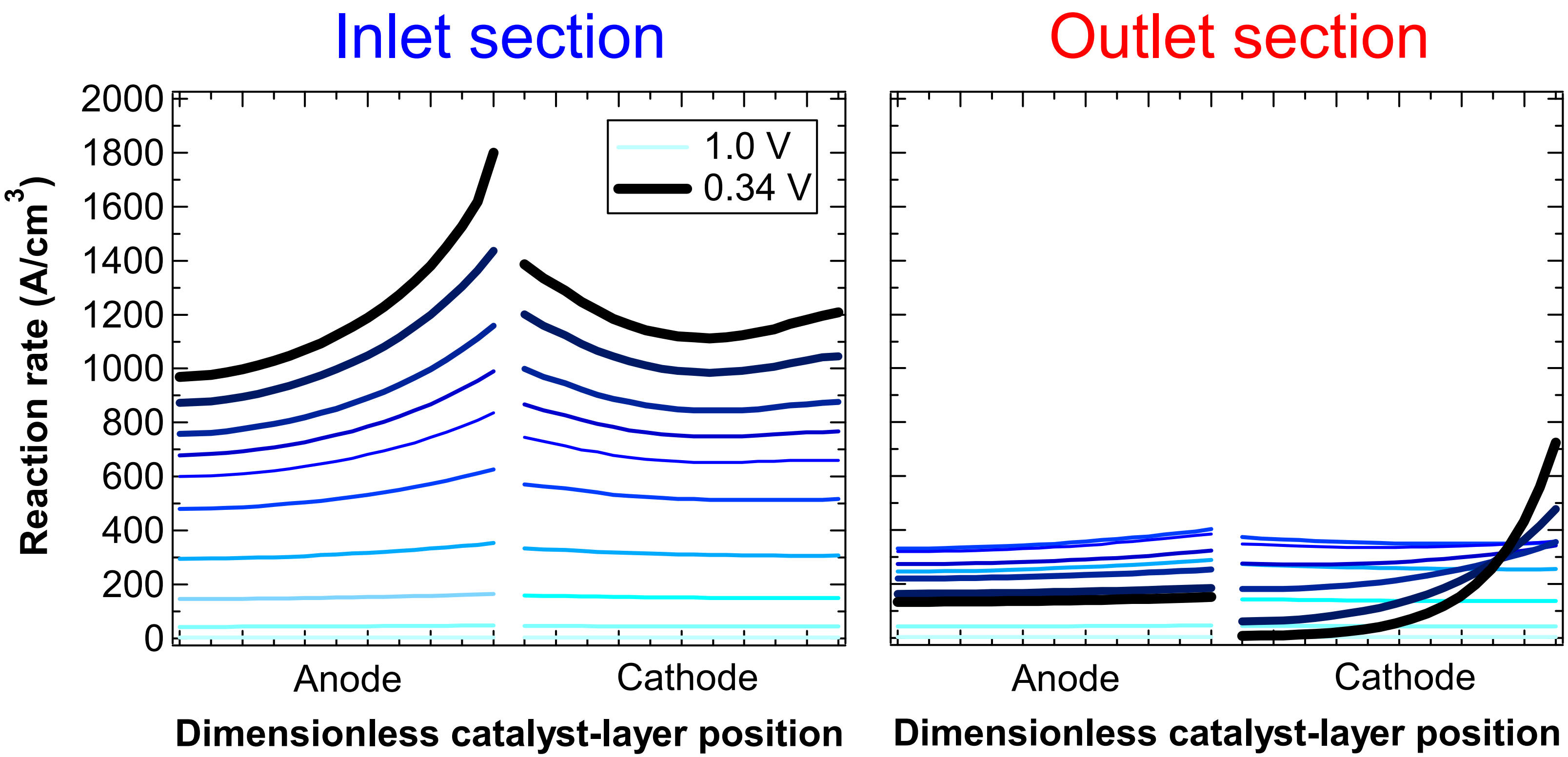
- Different sections show different amounts of mass-transfer effects
  - Qualitatively agrees with segmented-cell results*
  - Need to consider effects along the channel at low stoichiometries
- Green line is what would be measured experimentally
  - Demonstrates that local regions of reactant starvation might exist even if cell performance looks normal
    - May result in lifetime issues due to side reactions

T = 60°C, Nafion® 112, fully humidified feeds at constant flow rates (fuel-to-air ratio of 0.75), channel divided into 20 sections



*M. M. Mench, C. Y. Wang, and M. Ishikawa, *J. Electrochem. Soc.*, **150**, A1052 (2003).

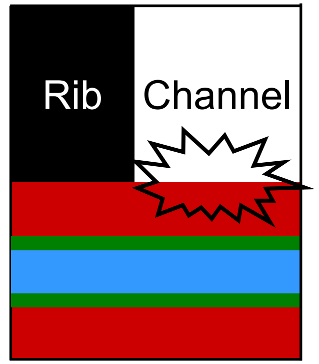
Along-the-Channel Results: Reaction-Rate Distribution



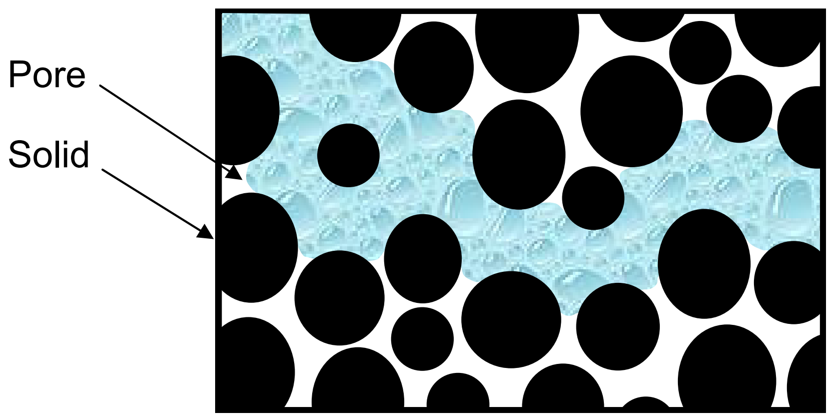
- Outlet section demonstrates depletion of oxygen and dead zones at the cathode catalyst layer whereas the inlet section does not
  - Due to both cathode flooding and oxygen depletion
  - Water-production location and lower current densities alter water balance
    - Outlet section has higher dimensionless water flux from anode to cathode than inlet section

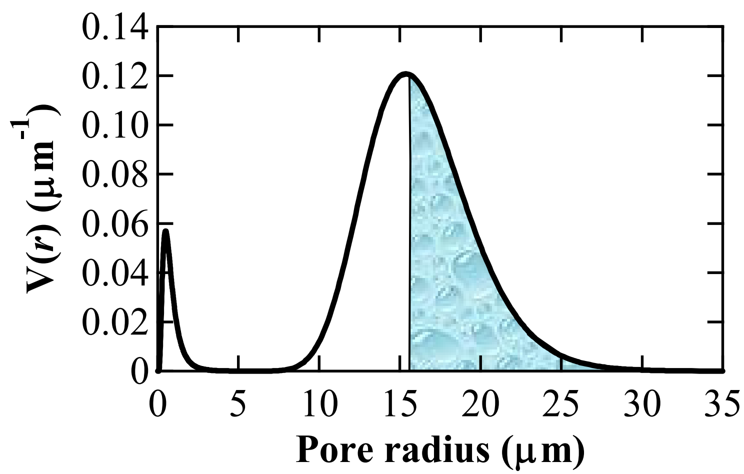
Boundary Condition for Two-Phase Flow

Problem: Need a physically accurate description of liquid and vapor water transfer at the boundary of the gas channel and diffusion medium



- **Boundary condition is crucial for predicting failure due to poor water management (*i.e.*, flooding)**
- Currently, there is no consensus on the proper set of conditions
- Problem deals with the assumption of local equilibrium (pore filling)
  - Example: higher liquid pressure causes the large and then small hydrophobic pores to fill, and also increases the vapor pressure





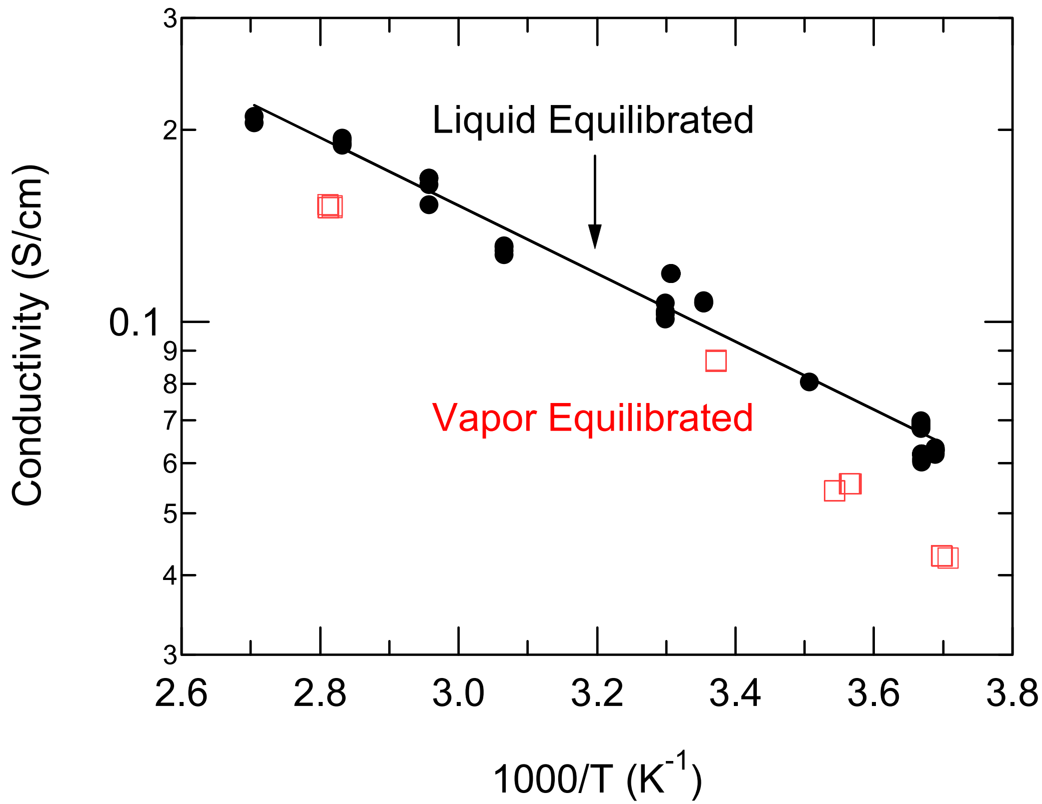
- Question is how to relate the various phases of water and pore properties in a physically consistent and mathematically rigorous fashion

Boundary Condition for Two-Phase Flow (cont'd)

- Need boundary conditions for liquid and vapor water
  - Liquid
    - If the liquid pressure is greater than or equal to the gas pressure, liquid water enters the gas channel with a pressure equal to that of the gas
  - Vapor
    - Problem
      - Cannot set water partial pressure or an *unrealistic* amount of water enters and condenses in the medium
      - Cannot set the water flux to that carried by the incoming gases or there is a mismatch in membrane and diffusion-medium liquid pressures in the catalyst layer
    - Possible solutions
      - Neglect or average differently the capillary pressure – vapor pressure relation
      - Set a saturation at the interface, which basically sets a capillary pressure
    - Need to determine where the water comes from physically
      - Mist flow, bubble formation, annular flow, *etc*., in the gas channel
      - Condensation or membrane back-diffusion in the anode catalyst layer
- May need to account for, or average in, the effects of the rib

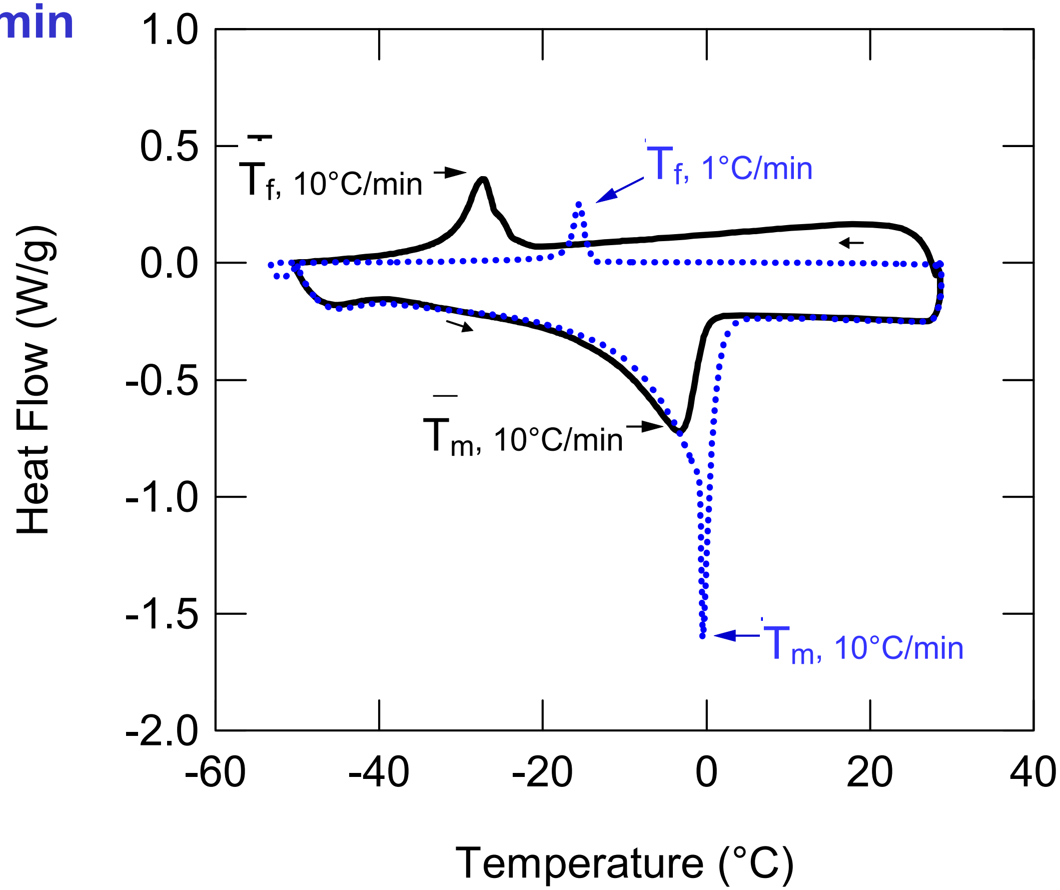
Low-Temperature Membrane Properties

- To understand failure related to subzero operation and freeze, need to measure transport and equilibrium parameters experimentally
- Nafion® conductivity by 4 probe AC impedance
  - Eliminates polarization effects and does not induce concentration gradients
  - Liquid conductivity is greater than vapor conductivity
    - Higher water content in the liquid-equilibrated membrane than the vapor-equilibrated membrane
  - Vapor-conductivity deviates from Arrhenius behavior due to changing water content with temperature
    - Currently measuring water-uptake isotherms



Low-Temperature Membrane Properties (cont'd)

- Investigated the state of water in Nafion® at different temperatures and cooling scan rates using differential-scanning calorimetry
  - Originally immersed in liquid water
    - Scan rate: **10˚C/min** or **1˚C/min**
    - Hold at -50˚C
  - State of water
    - Freezes at **-27˚C**, **-16˚C**
    - Melts at **-3˚C**, **0.4˚C**
  - Shift in peaks may indicate measuring kinetic and not thermodynamic phenomena
  - It is important to consider how a stack freezes
  - Control of membrane water content is crucial and currently being examined



Responses to Previous Year Reviewers' Comments

- This is a new project that started FY05

Future Work: FY05

- Finish the water-and-thermal-management model
  - Resolve boundary condition for two-phase flow
  - Include nonisothermal behavior in the cell sandwich
    - Describe “heat pipe” effects and associated water movement
    - Determine “hot spots” and temperature gradients
  - Quantitatively validate the model further
- Use the model to examine and relate failure to water-and-thermal management issues
  - Understand the dominant failure causes
  - Determine set of guidelines for preventing failure
    - Operating conditions
    - Basic material properties
- Continue the experimental determination of membrane properties at low and subzero temperatures
  - Determine the state and equilibrium uptake of water in the membrane

Future Work: FY06

- Use the developed model to help explain experimental observations and optimize and set targets for operating conditions and material properties within realistic constraints
- Examine and develop model for operation at low relative humidity with occasional high-temperature excursions (>100°C)

Positive aspects

- ✓ Higher kinetic rate constants and poison tolerance
- ✓ Reduced barrier to ionic transport
- ✓ Enhanced gas transport in electrodes
- ✓ No flooding by liquid water

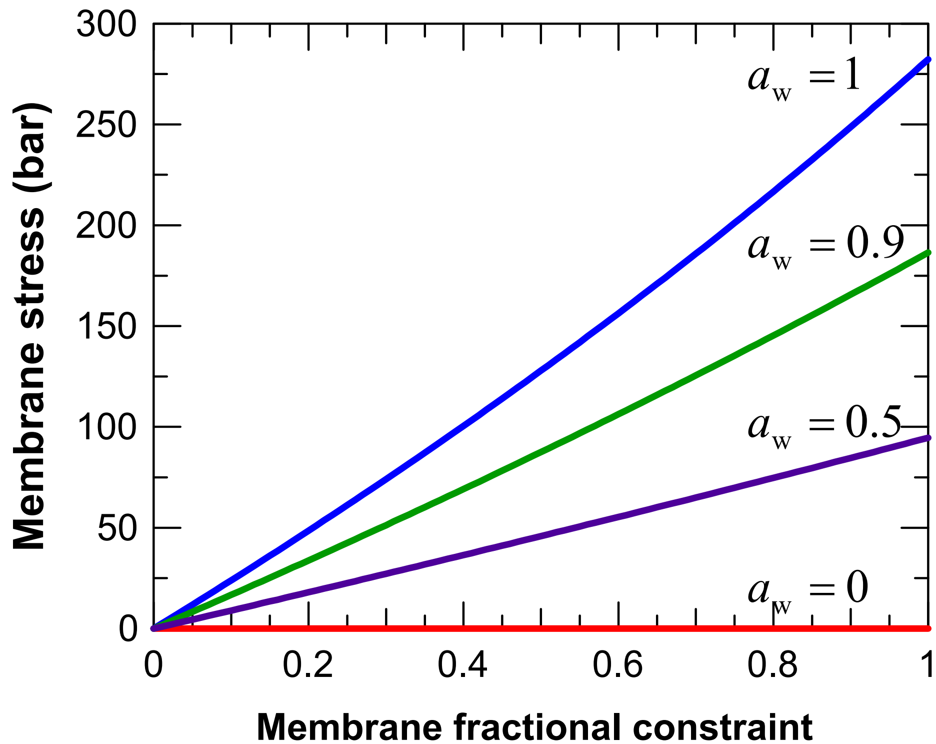
Negative aspects

- ✓ Lower thermodynamic driving force (open-circuit potential)
- ✓ Lower conductivity at drier conditions
- ✓ Enhanced gas transport through the membrane
- ✓ Reactant dilution by water vapor

- Finish determining low-temperature membrane properties
  - Measure water uptake isotherm and dynamic water uptake rates
  - Measure water diffusion coefficients and electroosmotic coefficients
- Investigate hydrogen peroxide formation at low temperatures

Future Work: FY06 (cont'd)

- Examine fuel-cell failure mechanisms caused by mechanical properties
  - May require both experiments and modeling
  - Initially examine effects related to membrane stress
    - Use our previously developed model* as a starting point
      - Membrane swelling compresses the other layers
      - Water balance is changed
      - Membrane water content and properties decrease
    - May lead to failure through
      - Catalyst-layer delamination
      - Pinhole formation
      - Destruction of other layers' morphologies
      - Fatigue during operation with stress buildup and release (*e.g.*, humidity cycling)
    - Relate to freeze/thaw experimental results



*A. Z. Weber and J. Newman, *AIChE J.*, **50**, 3215 (2004)

Hydrogen Safety

The current project does not use hydrogen; thus, there is no hazard associated with it in the project.

Presentations and Publications

- Oral presentations
  - A. Z. Weber, ‘Macroscopic Modeling of Polymer-Electrolyte Membranes,’ Computational Fuel Cell Dynamics III, Banff International Research Station, March 2005.
  - J. Newman, ‘Trends in Fuel-Cell Modeling,’ Fuel Cell Gordon Research Conference, July 2005.
- Publications
  - Sponsored by current project
    - A. Z. Weber and J. Newman, “Effects of Water-Transfer Plates for Polymer-Electrolyte Fuel Cells,” *J. Power Sources*, in preparation.
  - Related to current work
    - A. Z. Weber and J. Newman, ‘Effects of Microporous Layers in Polymer Electrolyte Fuel Cells,’ *J. Electrochem. Soc.*, **152**, A677 (2005).
    - A. Z. Weber and J. Newman, ‘A Theoretical Study of Membrane Constraint in Polymer-Electrolyte Fuel Cells,’ *AIChE J.*, **50**, 3215 (2004).
    - A. Z. Weber and J. Newman, ‘Modeling Transport in Polymer-Electrolyte Fuel Cells,’ *Chem. Rev.*, **104**, 4679 (2004).
    - A. Z. Weber, R. M. Darling, and J. Newman, ‘Modeling Two-Phase Behavior in PEFCs,’ *J. Electrochem. Soc.*, **151**, A1715 (2004).
    - A. Z. Weber and J. Newman, ‘Transport in Polymer-Electrolyte Membranes. II. Mathematical Model,’ *J. Electrochem. Soc.*, **151**, A311 (2004).
    - J. P. Meyers and J. Newman, ‘Simulation of the Direct Methanol Fuel Cell. I. Thermodynamic Framework for a Multicomponent Membrane,’ *J. Electrochem. Soc.*, **149**, A710 (2002).
    - C. M. Gates and J. Newman, ‘Equilibrium and Diffusion of Methanol and Water in a Nafion 117 Membrane,’ *AIChE J.*, **46** 2076 (2000).
    - T. F. Fuller and J. Newman, ‘Water and Thermal Management in Solid-Polymer-Electrolyte Fuel Cells,’ *J. Electrochem. Soc.*, **140**, 1218 (1993).
    - T. F. Fuller and J. Newman, ‘Experimental Determination of the Transport Number of Water in Nafion 117 Membrane,’ *J. Electrochem. Soc.*, **139**, 1332 (1992).
    - J. Newman, ‘Optimization of Potential and Hydrogen Utilization in an Acid Fuel Cell,’ *Electrochim. Acta*, **24**, 223 (1979).