INVESTIGATING FAILURE IN POLYMER-ELECTROLYTE FUEL CELLS

John Newman

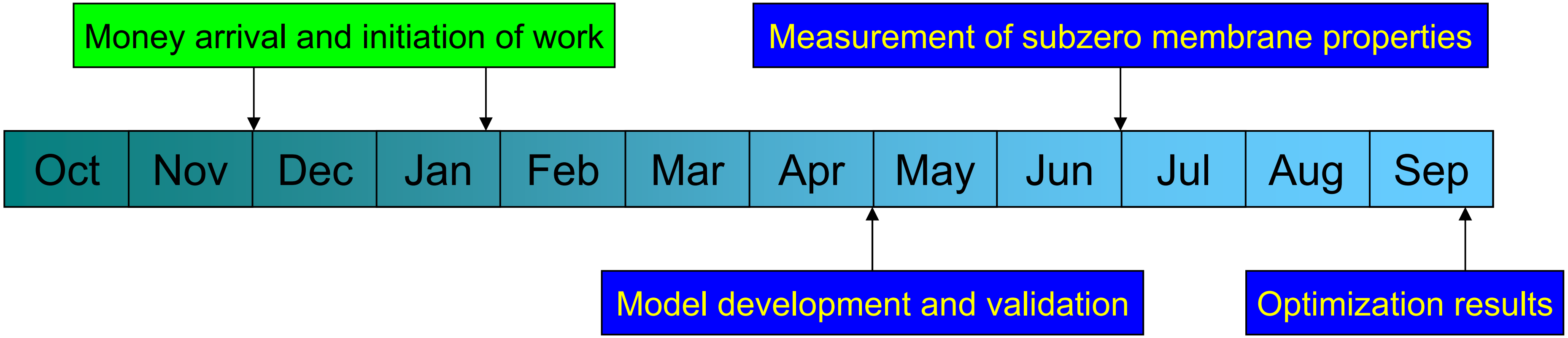
Lawrence Berkeley National Laboratory

May 25, 2005

FC 50

OVERVIEW

- This is a new project that started in FY05



Money arrival and initiation of work

Measurement of subzero membrane properties

Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep

Model development and validation

Optimization results

- 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

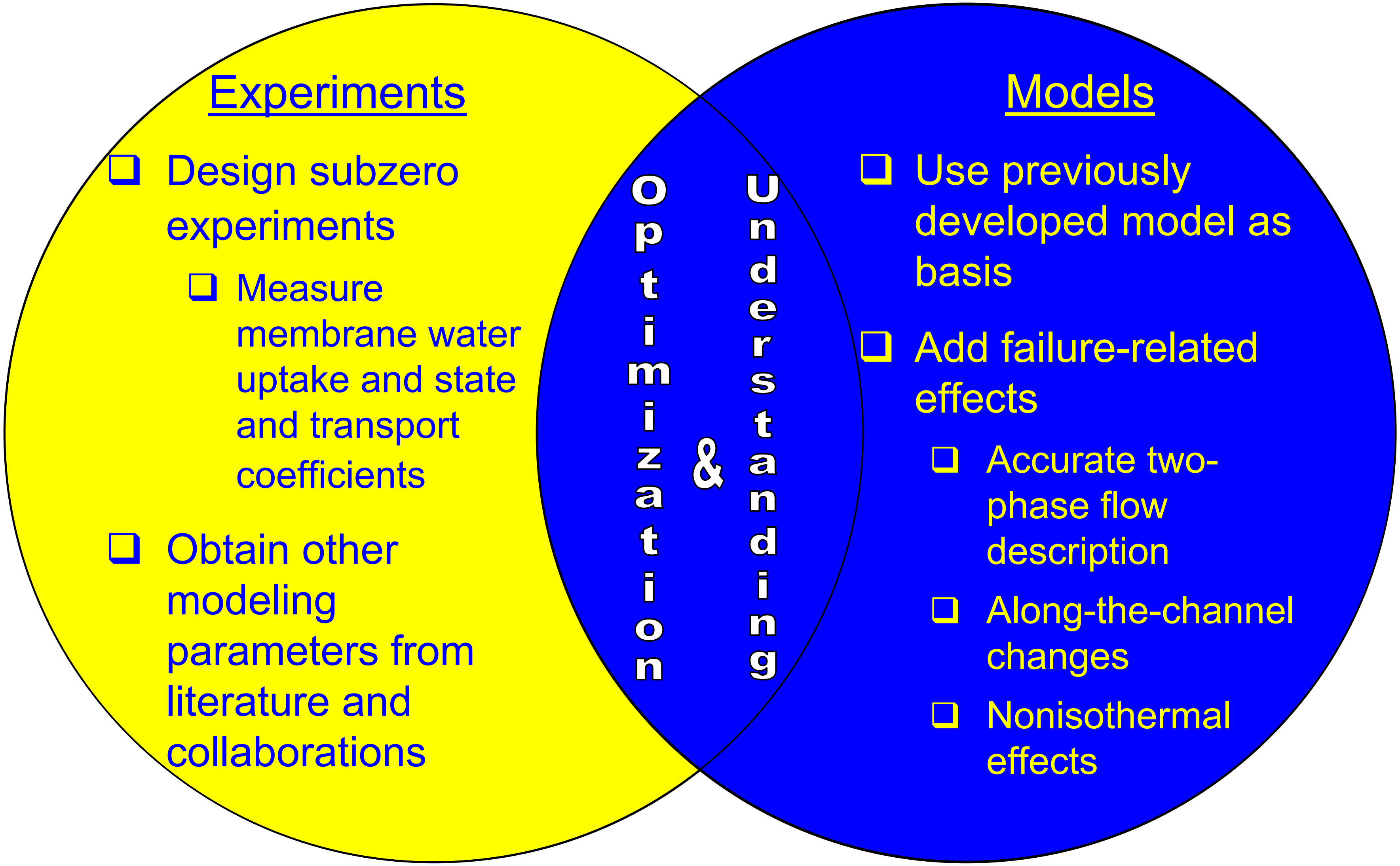
PROJECT OBJECTIVES

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

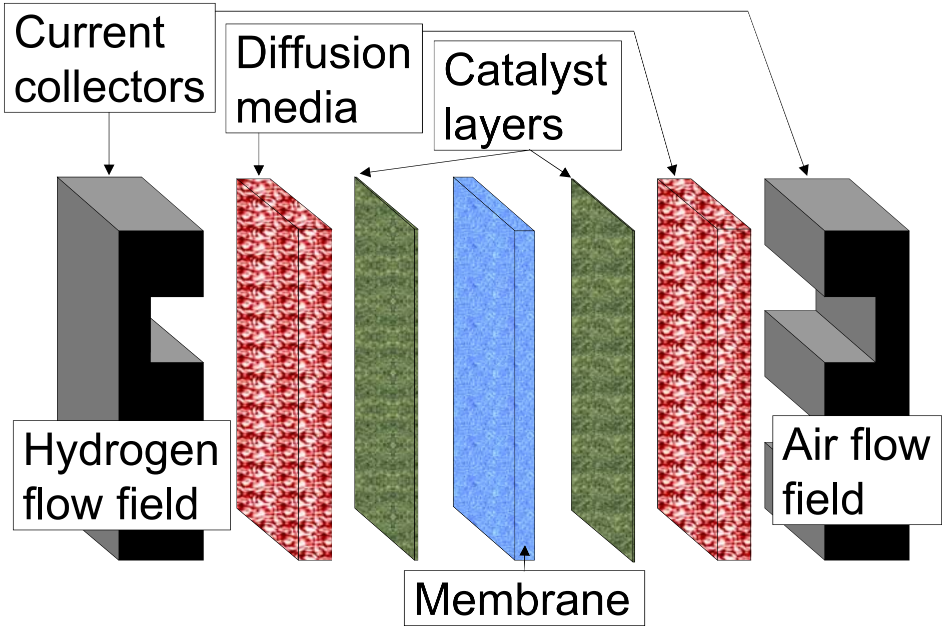
- ☐ Design subzero experiments
  - ☐ Measure membrane water uptake and state and transport coefficients
- ☐ Obtain other modeling parameters from literature and collaborations

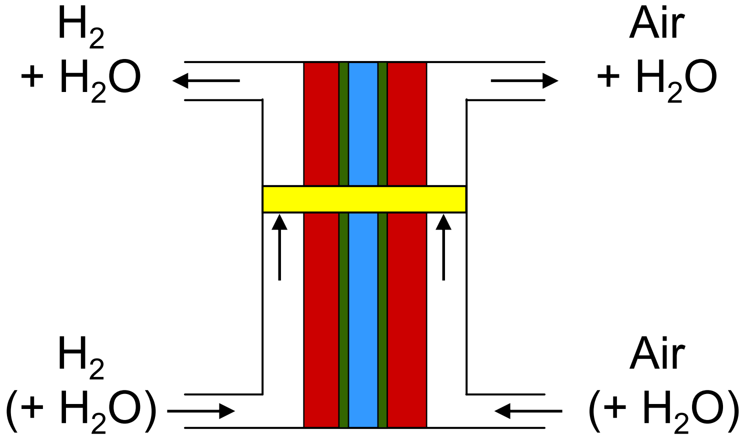
Optimization & Understanding

Models

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

MODELING DOMAIN



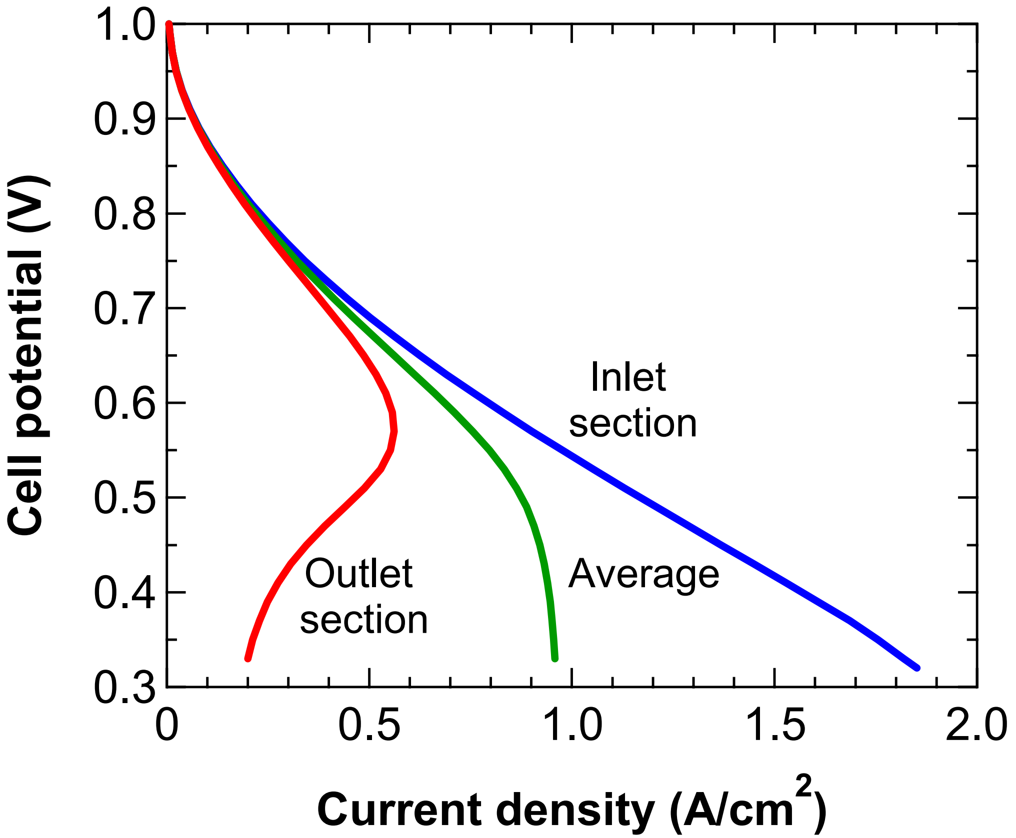


- Developed code to run the sandwich model along the channel
  - Currently adding heat generation and removal along the channel
    - Complications due to temperature exponential in vapor pressure and kinetics
- Completed code allows for analysis and optimization of interplay between water and thermal 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

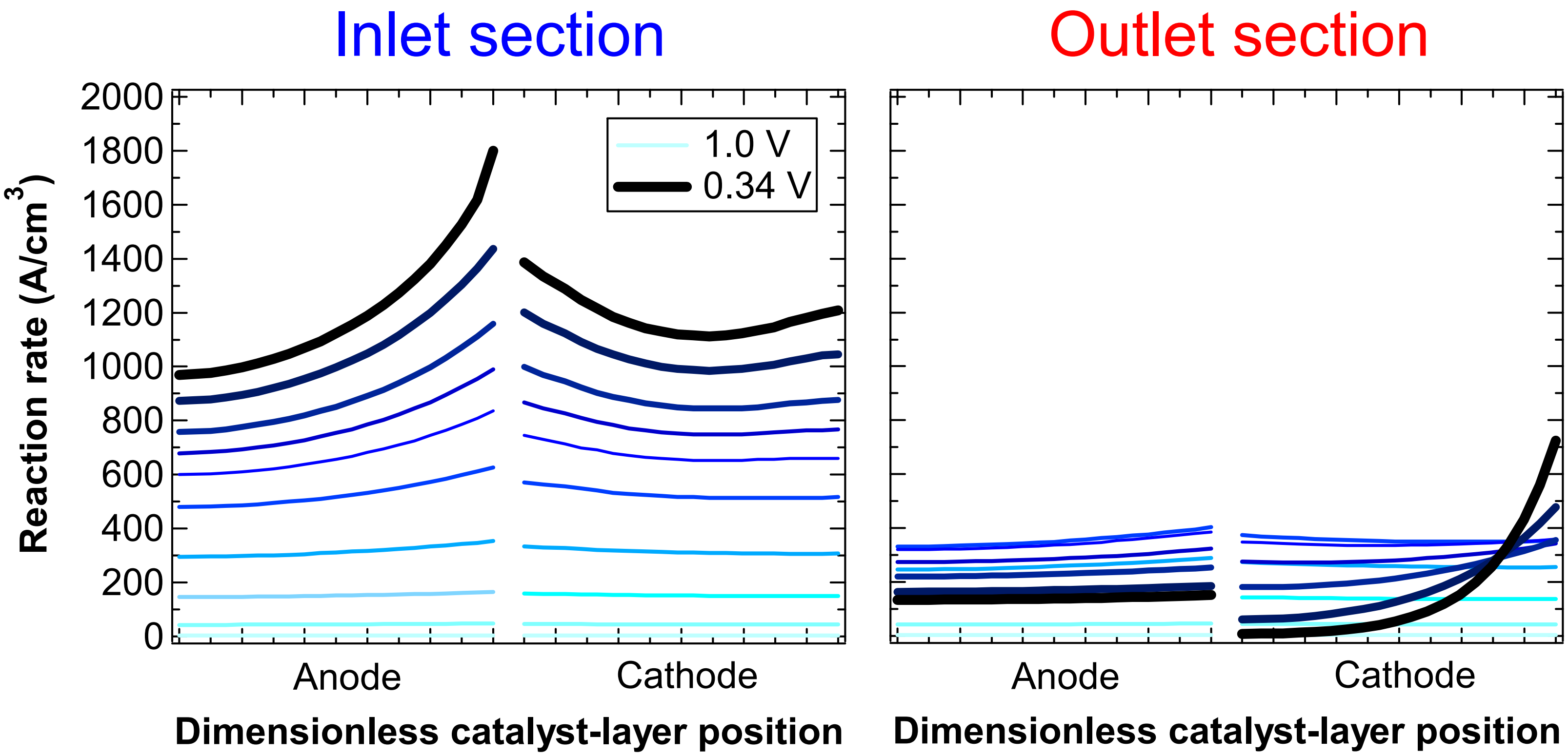
- Different sections show different amounts of mass-transfer effects
  - Qualitatively agrees with segmented-cell results*
  - Need to consider effects along the channel at low stoichiometries
- Green line is what would be measured experimentally
  - Demonstrates that local regions of reactant starvation 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



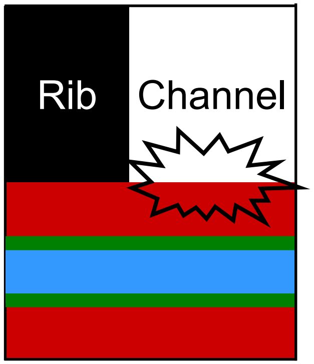
*M. M. Mench, C. Y. Wang, and M. Ishikawa, *J. Electrochem. Soc.*, **150**, A1052 (2003).

ALONG-THE-CHANNEL RESULTS: REACTION-RATE DISTRIBUTION



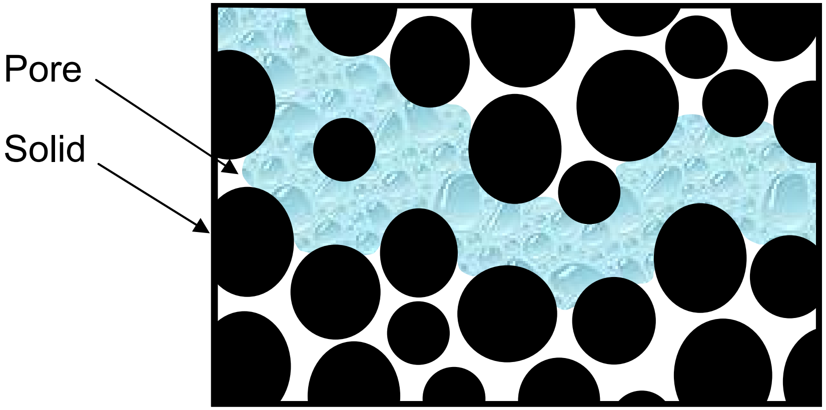
- Outlet section demonstrates depletion of oxygen and dead zones at the cathode catalyst layer whereas the inlet section does not
  - Due to both cathode flooding and oxygen depletion
  - Water-production location and lower current densities alter water balance
    - Outlet section has higher dimensionless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

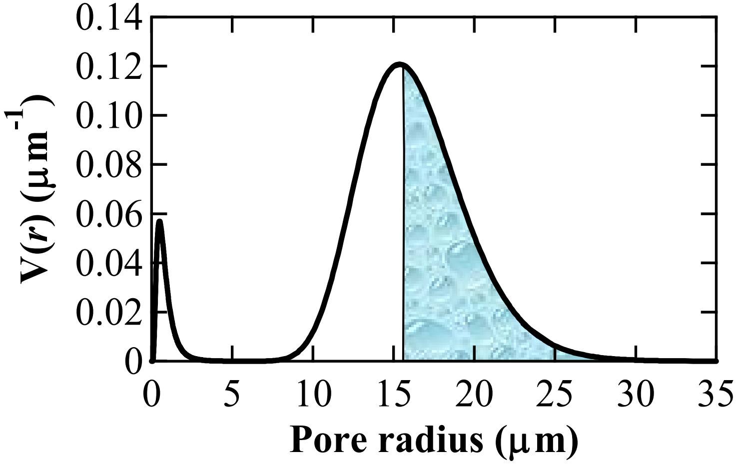
BOUNDARY CONDITION FOR TWO-PHASE FLOW



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





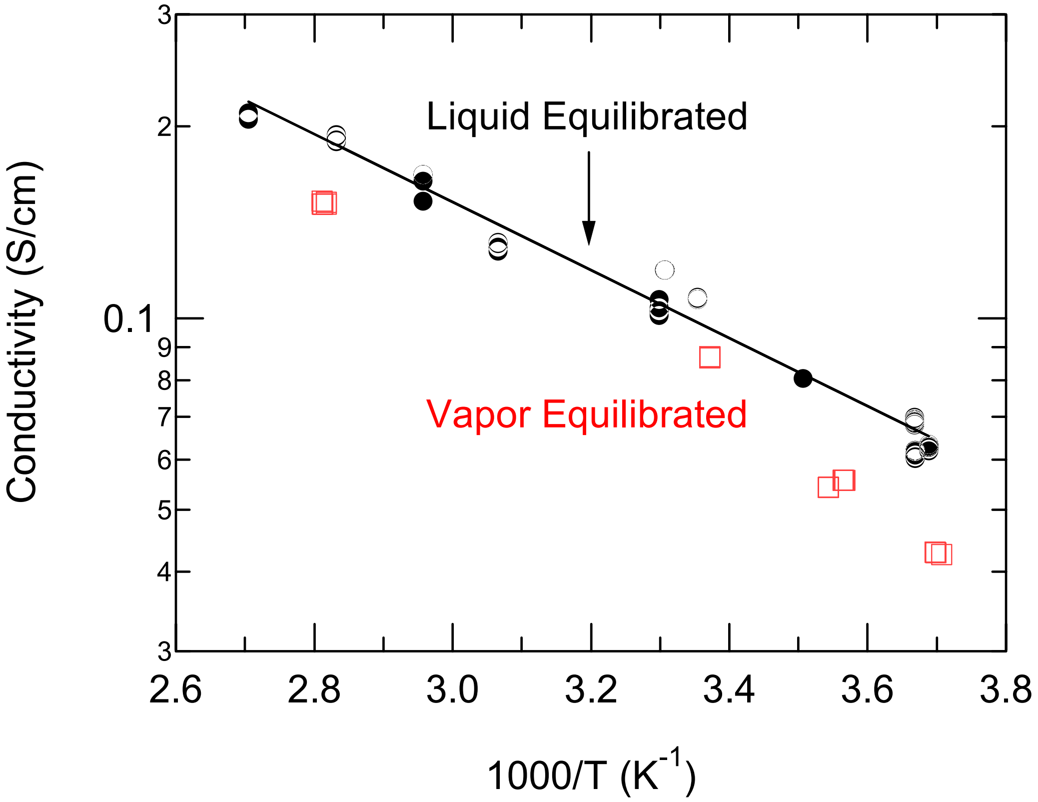
- Question is how to relate the various phases of water and pore properties in a physically consistent and mathematically rigorous fashion

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

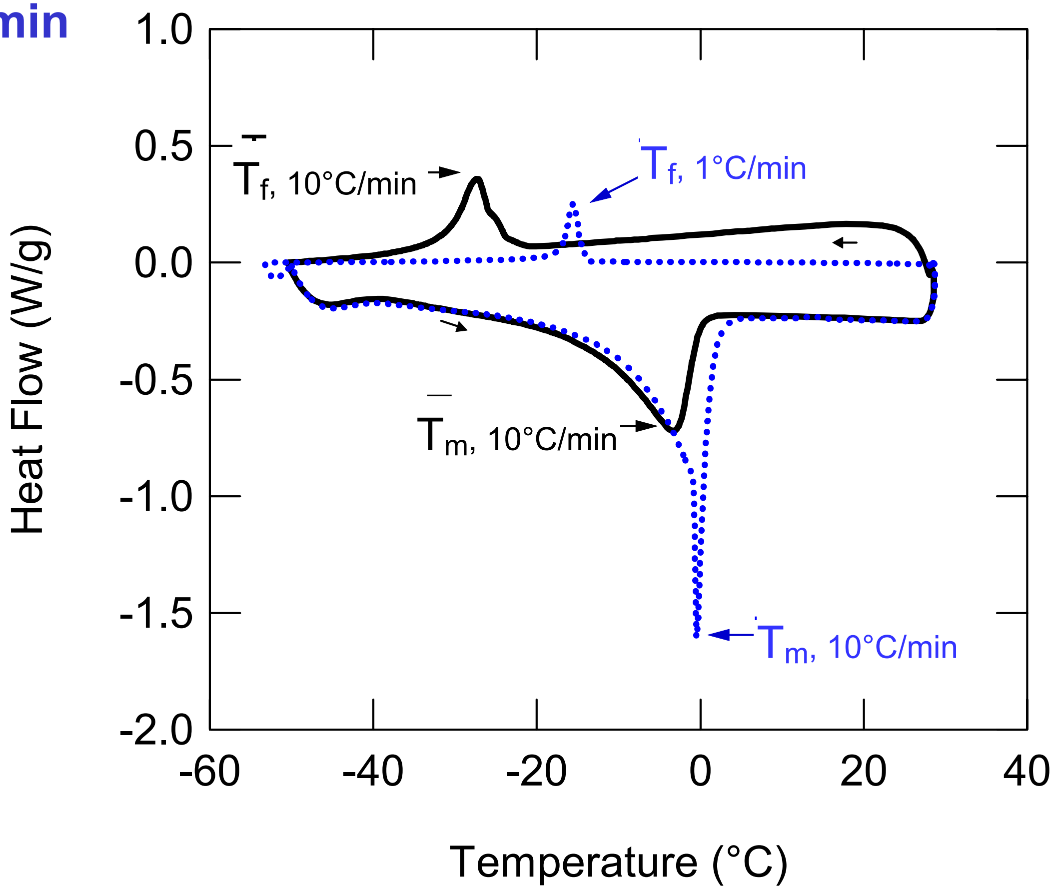
LOW-TEMPERATURE MEMBRANE PROPERTIES

- 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

BERKELEY LAB

FUTURE WORK: FY06

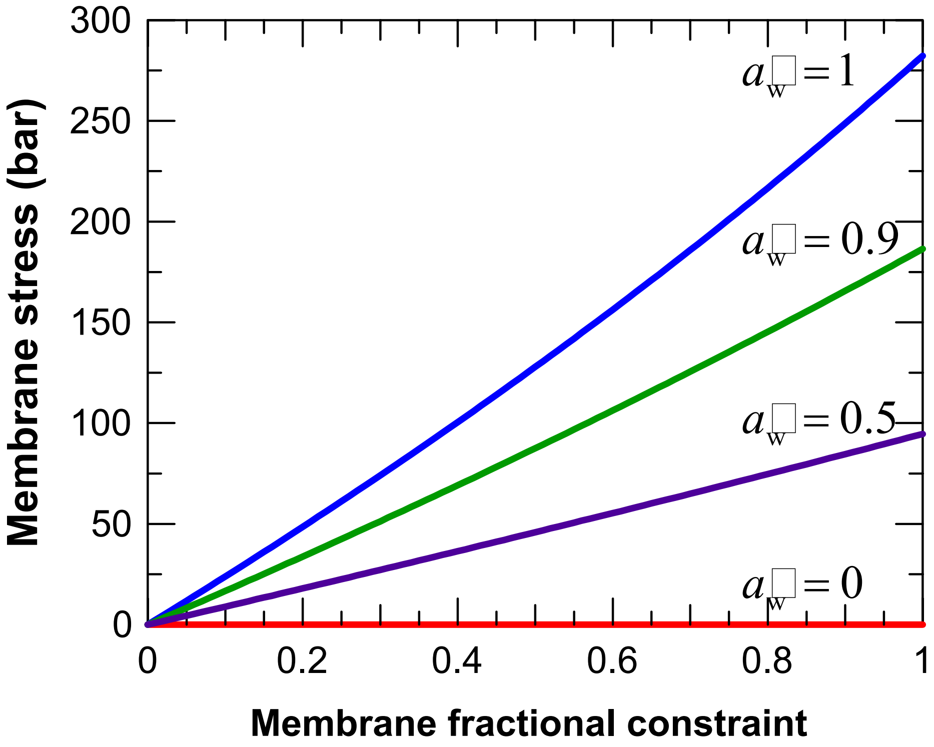
- Use the developed model to help explain experimental observations and optimize and set targets for operating conditions and material properties within realistic constraints
- Examine and develop model for operation at low relative humidity with occasional high-temperature excursions (>100°C)

Positive aspects	**Negative aspects**
✓ Higher kinetic rate constants and poison tolerance	✓ Lower thermodynamic driving force (open-circuit potential)
✓ Reduced barrier to ionic transport	✓ Lower conductivity at drier conditions
✓ Enhanced gas transport in electrodes	✓ Enhanced gas transport through the membrane
✓ No flooding by liquid water	✓ 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).