Investigating Failure in Polymer-Electrolyte Fuel Cells

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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

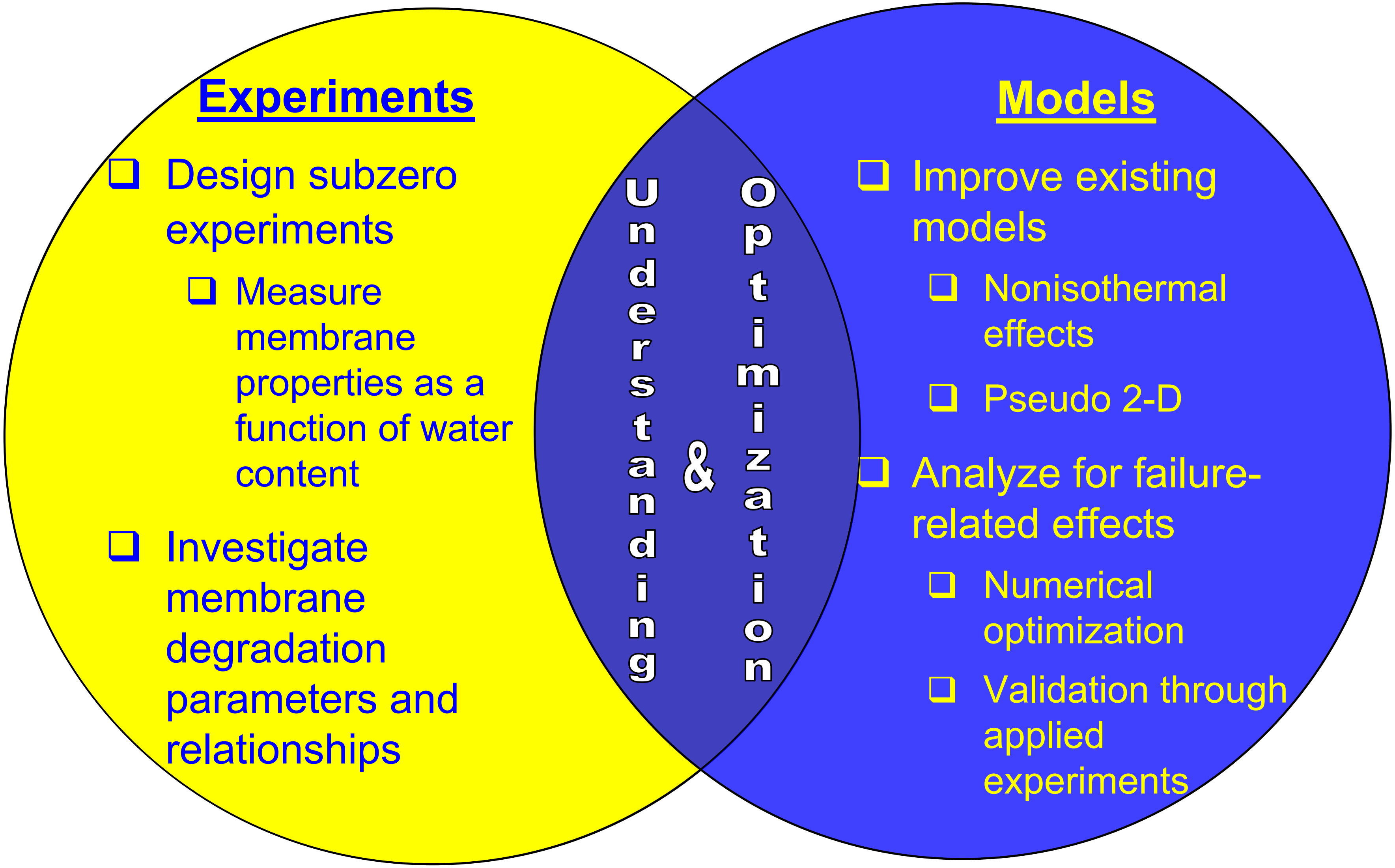
Project Objectives

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

Approach

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



Experiments

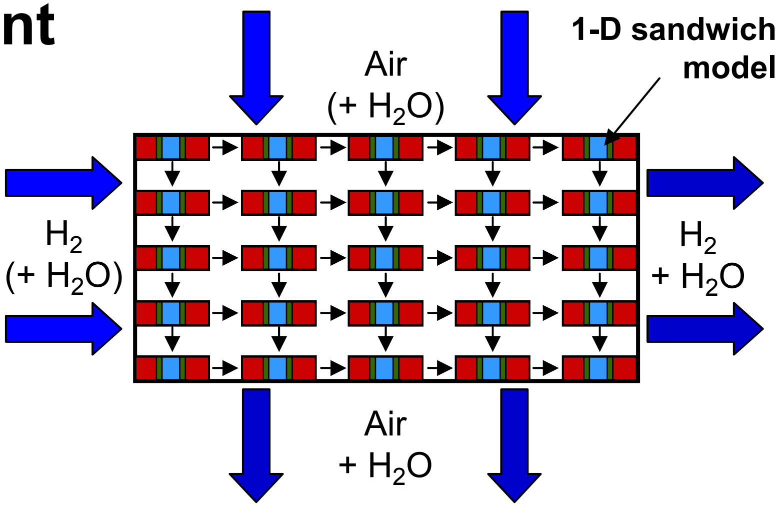
- Design subzero experiments
  - Measure membrane properties as a function of water content
- Investigate membrane degradation parameters and relationships

Understanding & Optimization

Models

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

Technical Achievements



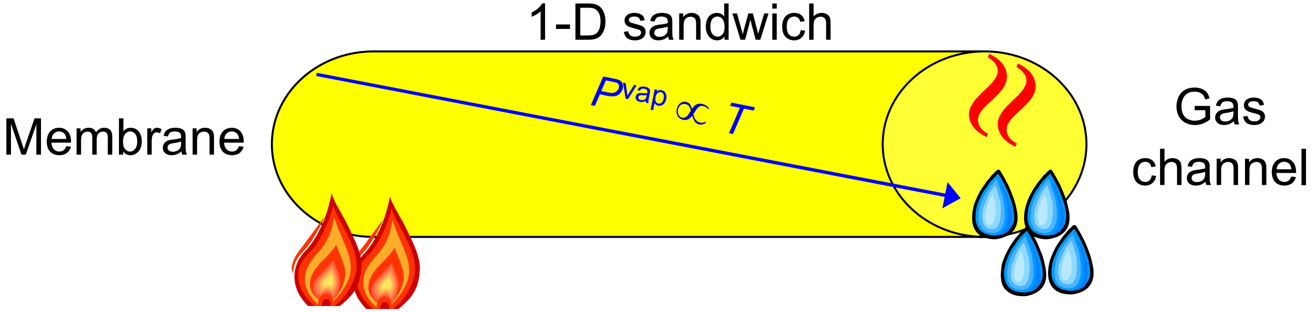
- **Coupled water and thermal management**
  - Developed crossflow model that includes **nonisothermal** effects
    - Heat-pipe effect is significant
  - Explored optimum temperature for **peak power** at given heat-transfer coefficient
- Low-temperature membrane properties
  - In collaboration with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

Coupled Thermal and Water Management

- Increasing temperature has various tradeoffs

<u>Positive aspects</u>	<u>Negative aspects</u>
✓ **Higher kinetic rate constants**	✓ Lower thermodynamic driving force
✓ Higher diffusion coefficients and conductivity	✓ Larger electro-osmotic flow and lower membrane water content
✓ Enhanced gas transport in the catalyst layers	✓ Enhanced gas transport through the membrane
✓ Greater water-vapor capacity	✓ **Reactant dilution by water vapor**

- **Temperature gradients augment heat and water transport**
  - Heat-pipe effect



1-D sandwich

Membrane

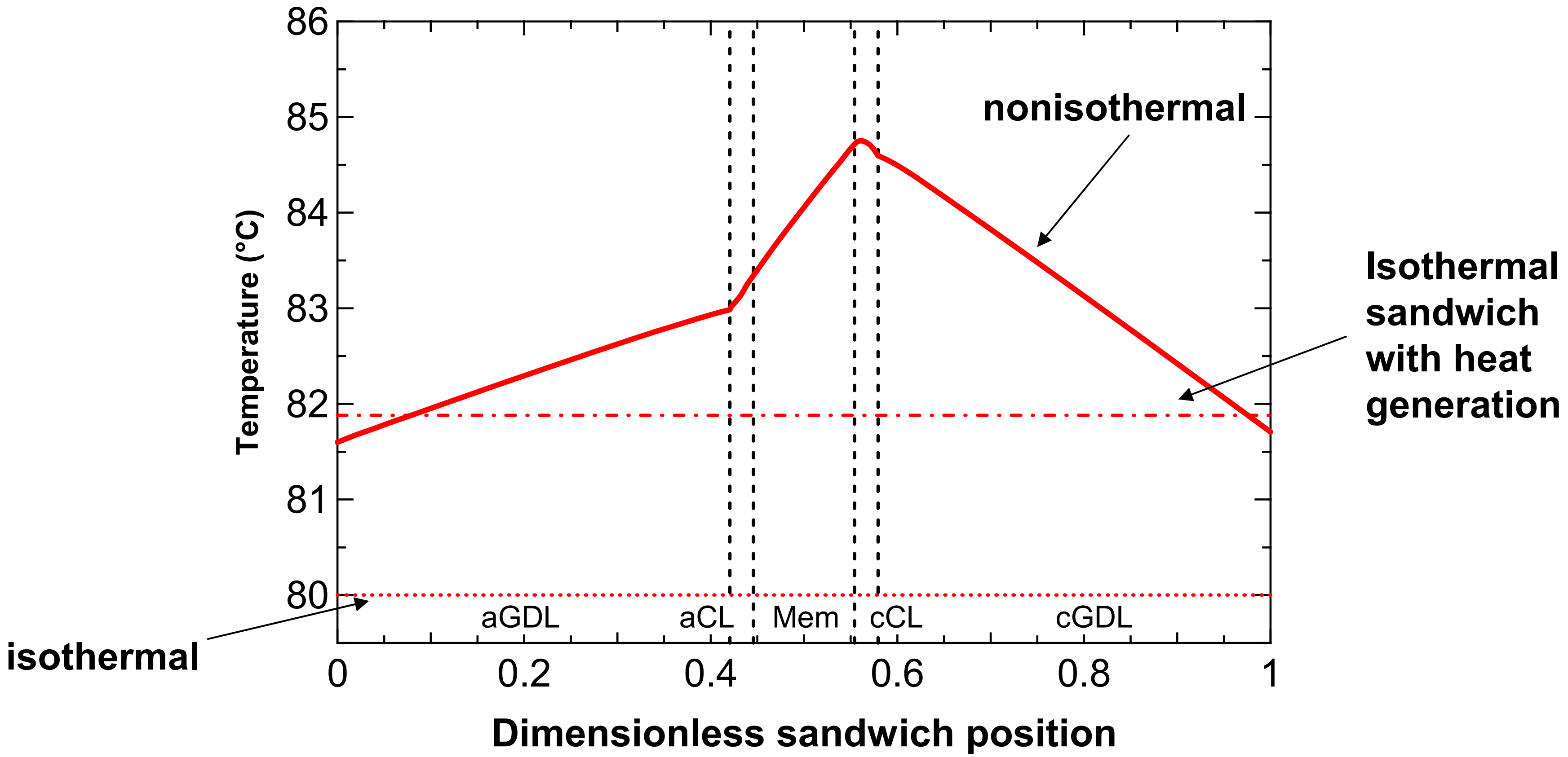
$p_{vap} \propto T$

Gas channel

☞ Temperature gradient causes water vapor-pressure gradient and movement of water by subsequent evaporation and condensation

Coupled Thermal and Water Management (cont'd)

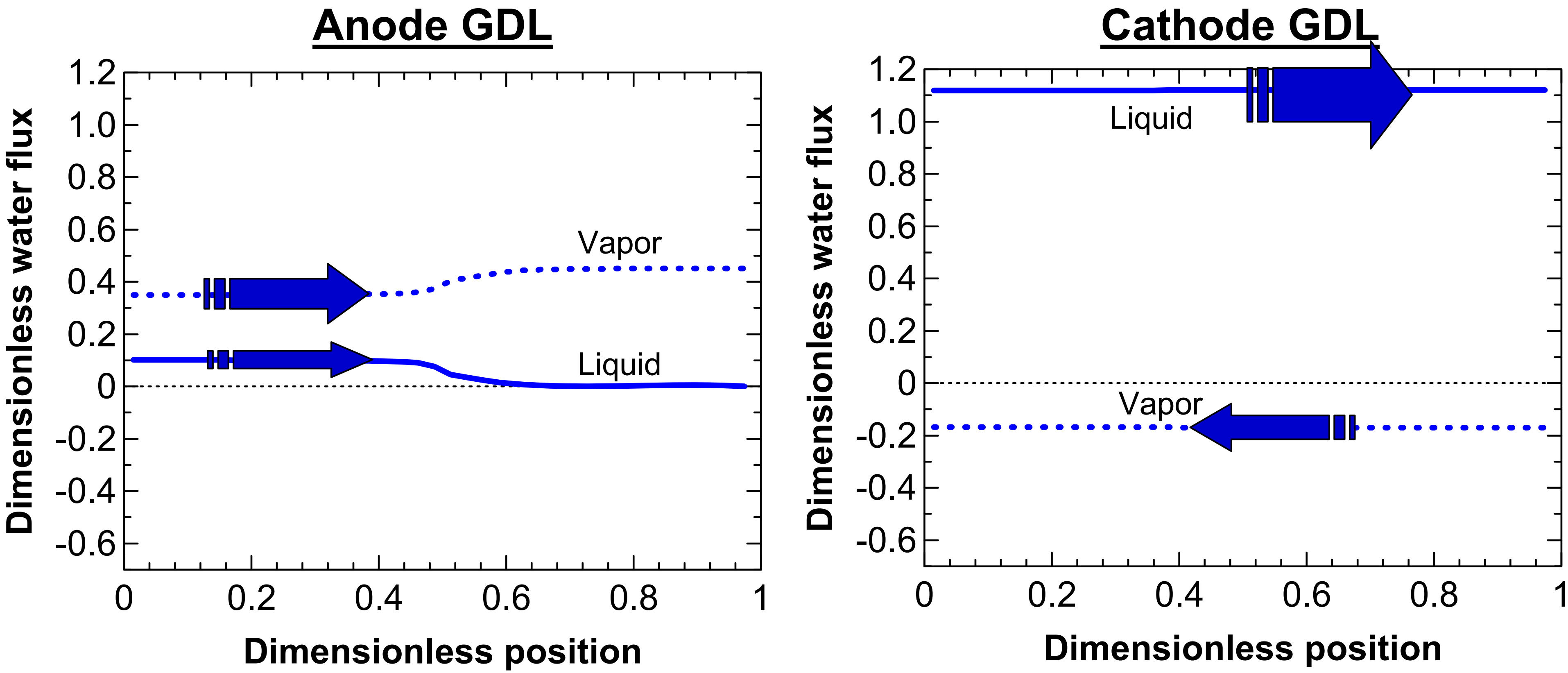
- Temperature profile at 80°C, 0.3 V, 1 bar, saturated feeds



- 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

Coupled Thermal and Water Management (cont'd)

- Examine the vapor- and liquid-water fluxes for the isothermal and nonisothermal cases

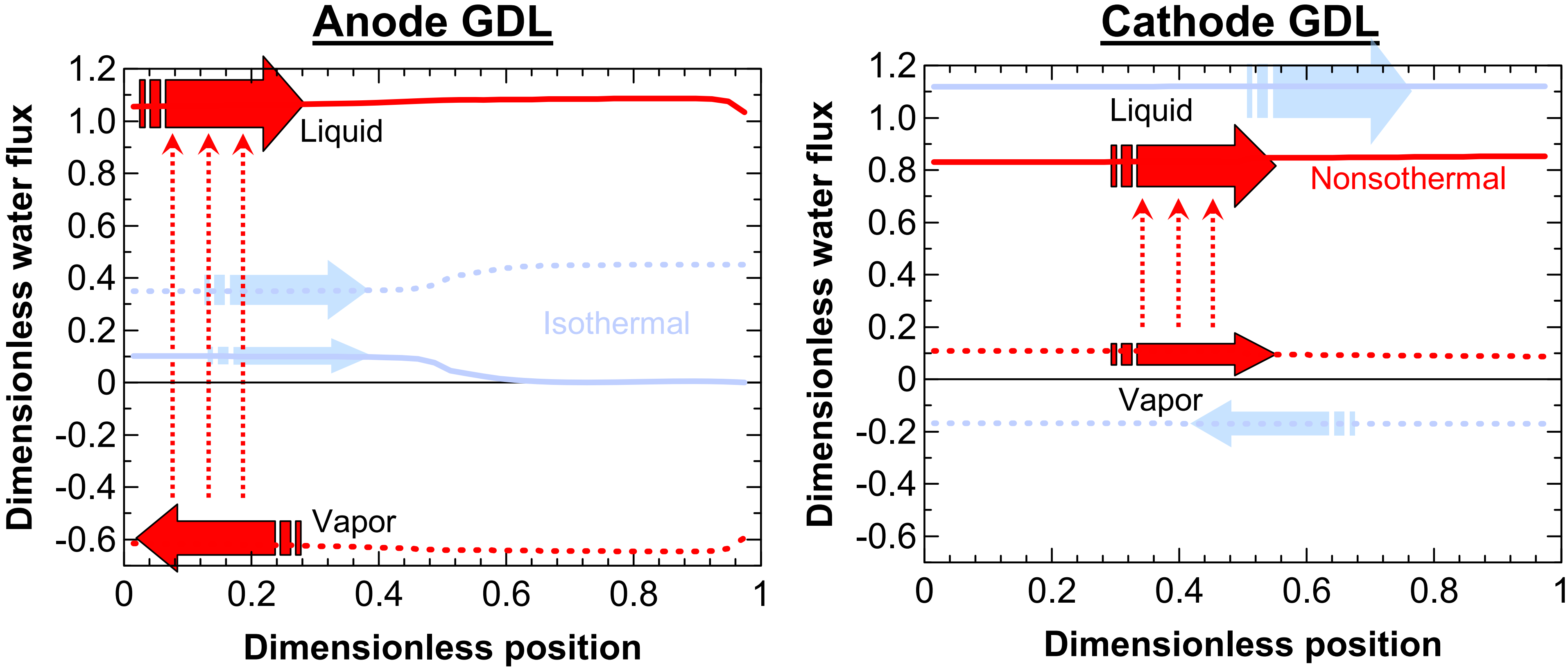


Positive flux signifies water movement from anode to cathode

For isothermal case, water vapor moves *toward* the membrane

Coupled Thermal and Water Management (cont'd)

- Examine the vapor- and liquid-water fluxes for the isothermal and nonisothermal cases

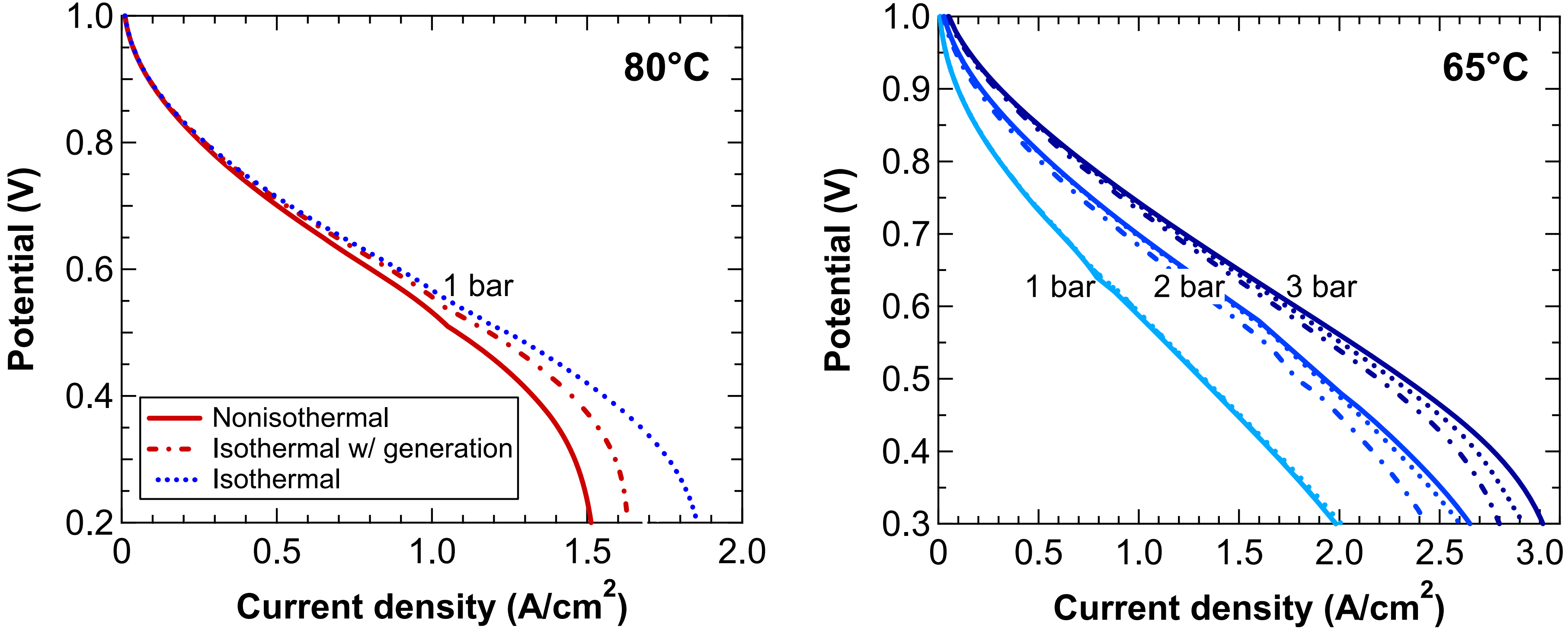


Positive flux signifies water movement from anode to cathode

For nonisothermal case, water vapor moves *away from* the membrane

Coupled Thermal and Water Management (cont'd)

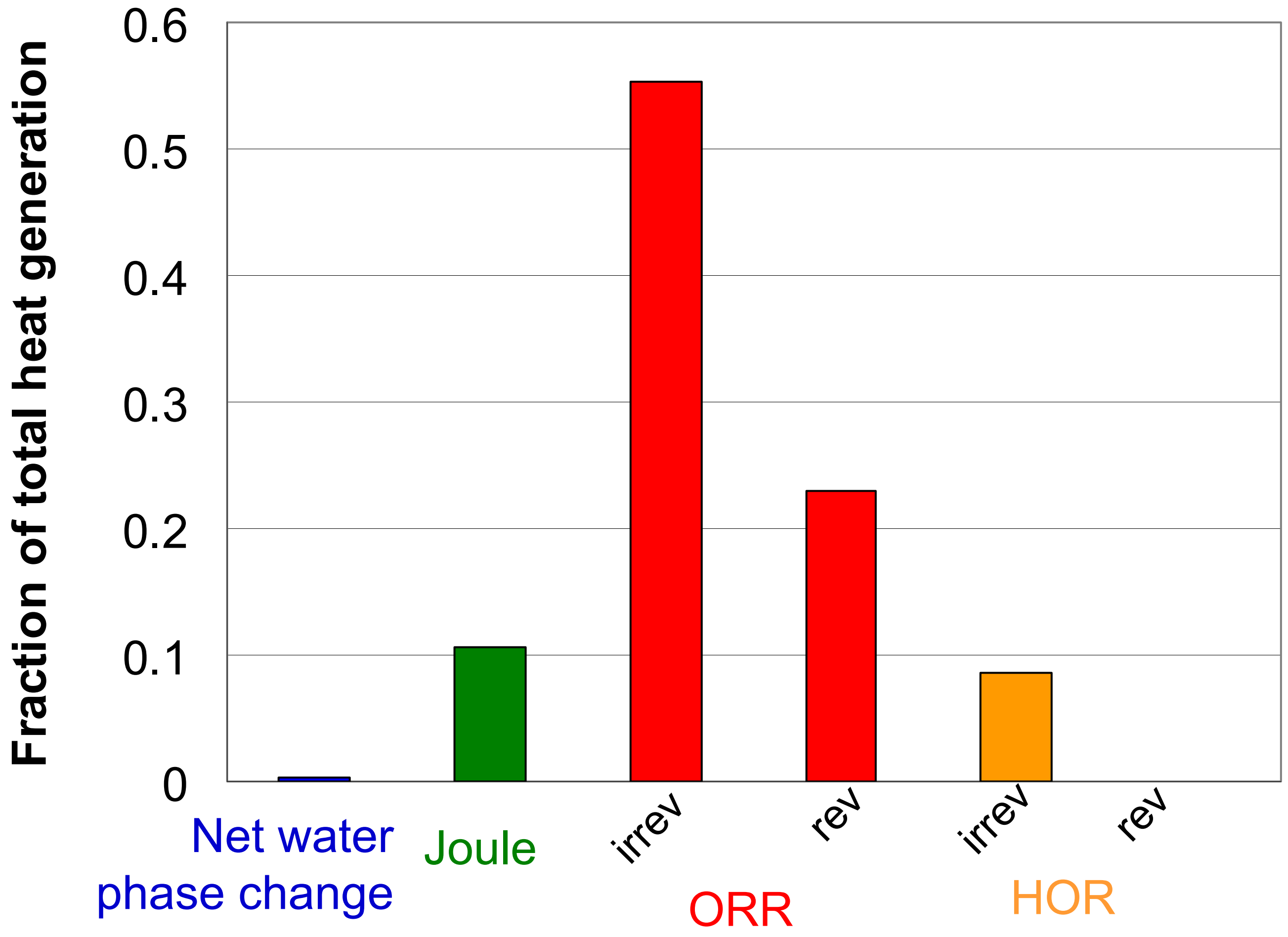
- Inclusion of nonisothermal effects alters polarization performance



- 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

Coupled Thermal and Water Management (cont'd)

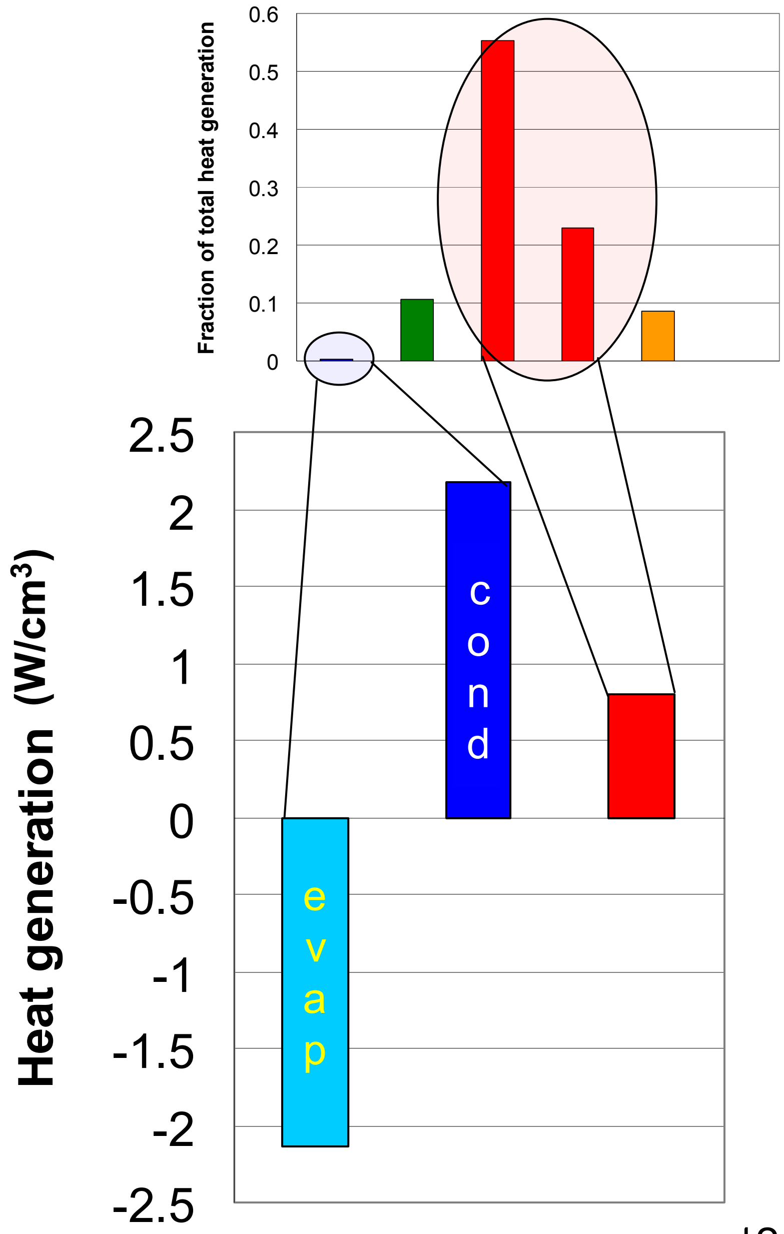
- Breakdown of heat generation



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

Coupled Thermal and Water Management (cont'd)

- 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

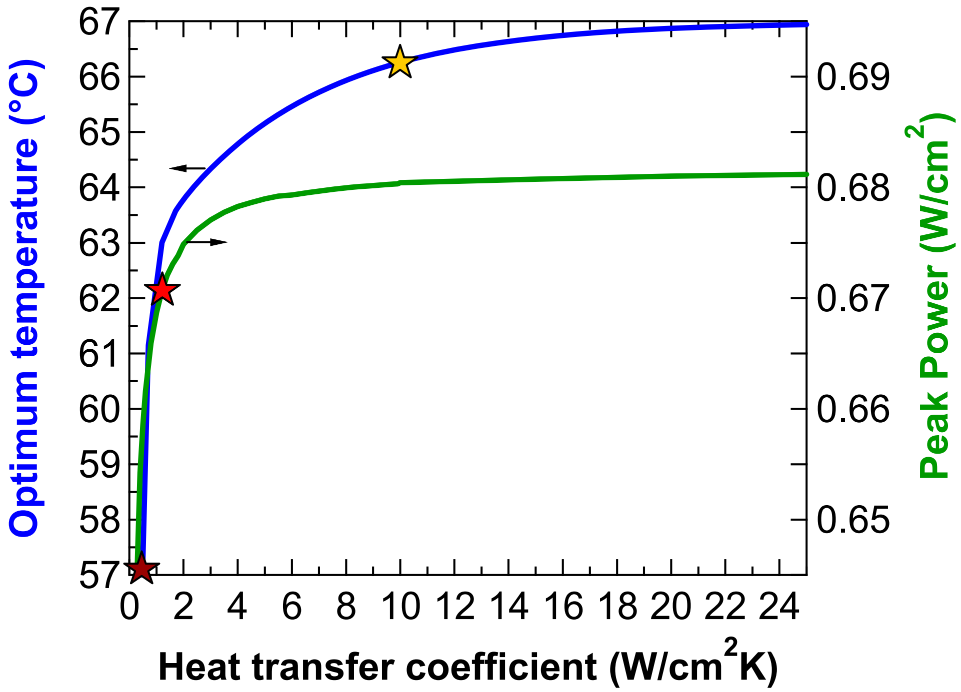


Coupled Thermal and Water Management (cont'd)

- 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

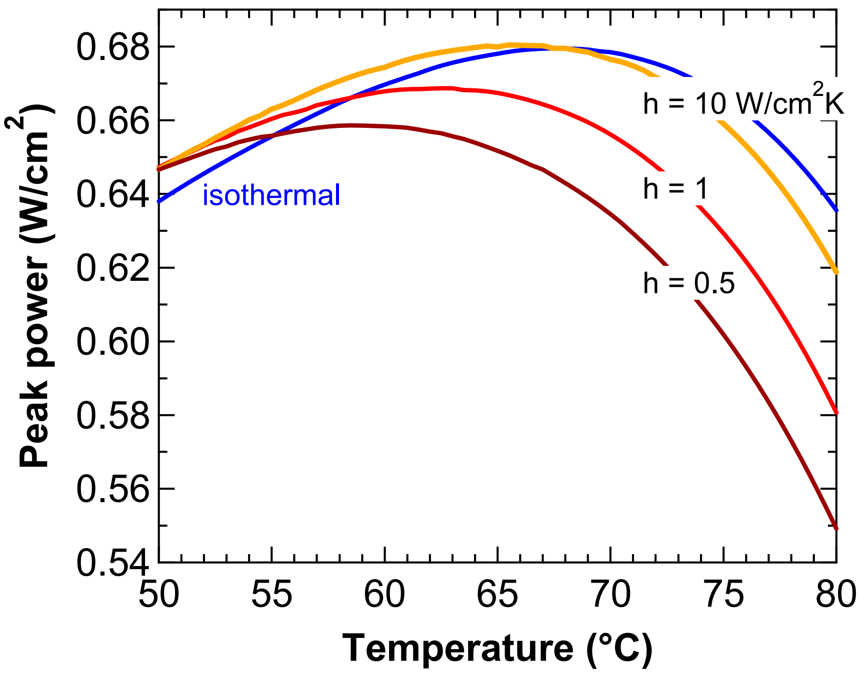
Peak-Power Optimization

- 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

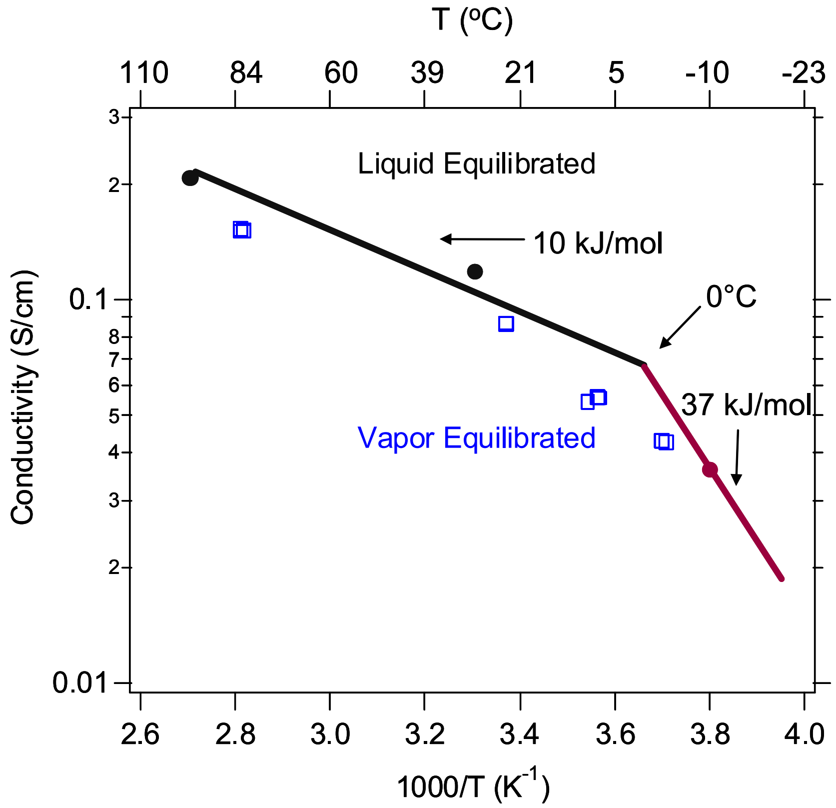
Low-Temperature Membrane Properties

- 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

Cooling Rate	Freezing water*		T_f peak
°C/min	g	λ	°C
1	2.11	11.6	-22.0
10	1.88	10.4	-25.8

*if $\lambda = 22$ and $\Delta H_l = \Delta H_{l,\,water} = 334$ J/g

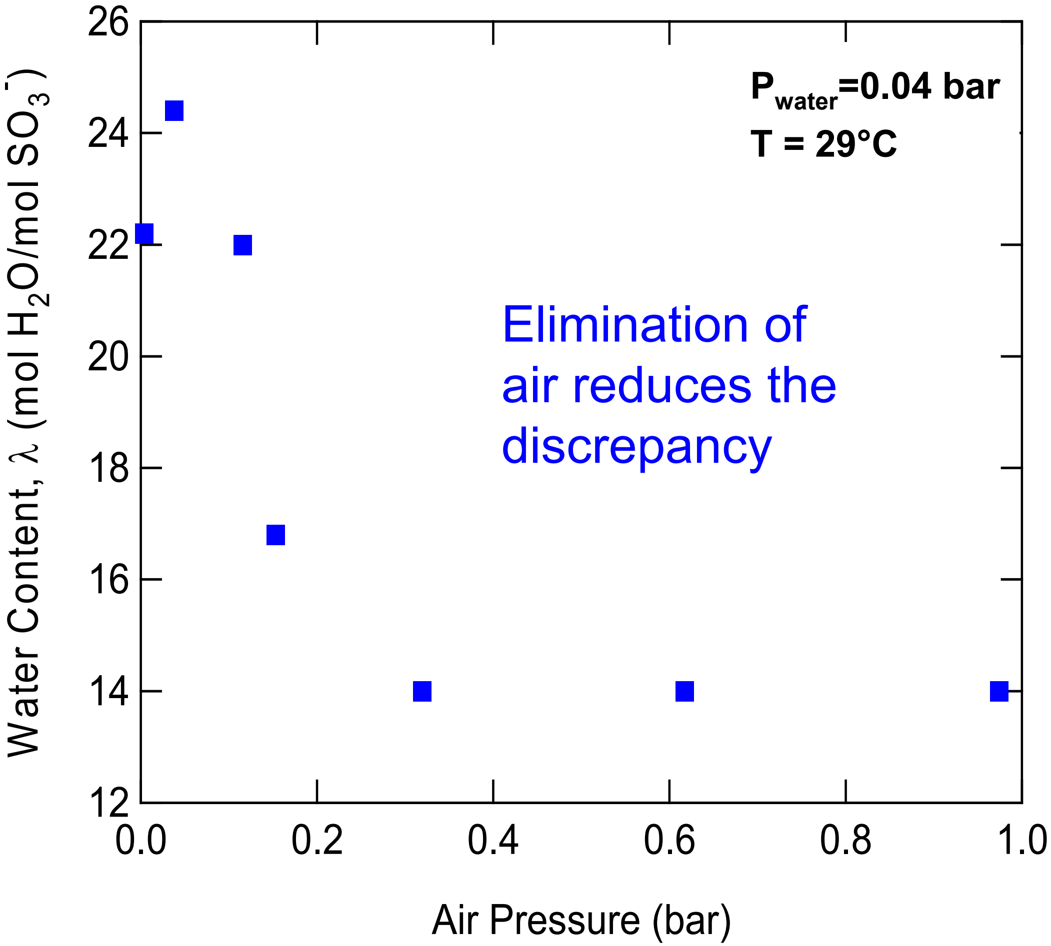
  - More and faster freezing at higher cooling rates
  - **Water diffusion coefficient apparatus designed**
- **Measuring water-uptake isotherms**



L. Onishi and J. Newman, “Low Temperature Membrane Properties”, *ECS Transactions*, accepted (2005).

Membrane Water Content

- Schröder’s paradox: since 1903
  - Water uptake is greater with liquid than saturated vapor
    - Liquid-equilibrated (λ = 22 to 24, 3°C < T < 25°C)
    - Vapor-equilibrated (in air at 1 bar: λ = 14; no air: λ = 22 to 24, 0°C < T < 29°C)

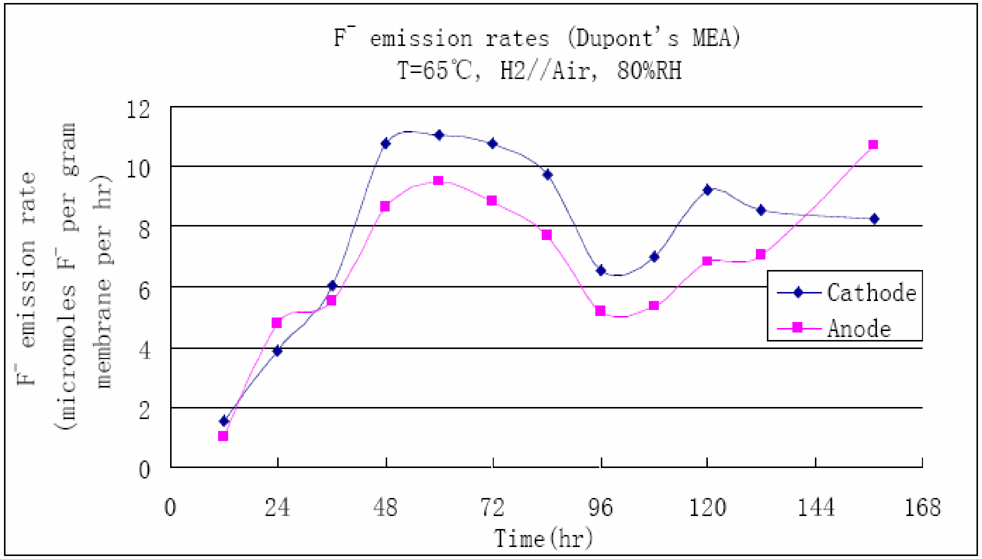


Elimination of air reduces the discrepancy

L. Onishi and J. Newman, “Low Temperature Membrane Properties”, *ECS Transactions*, accepted (2005).

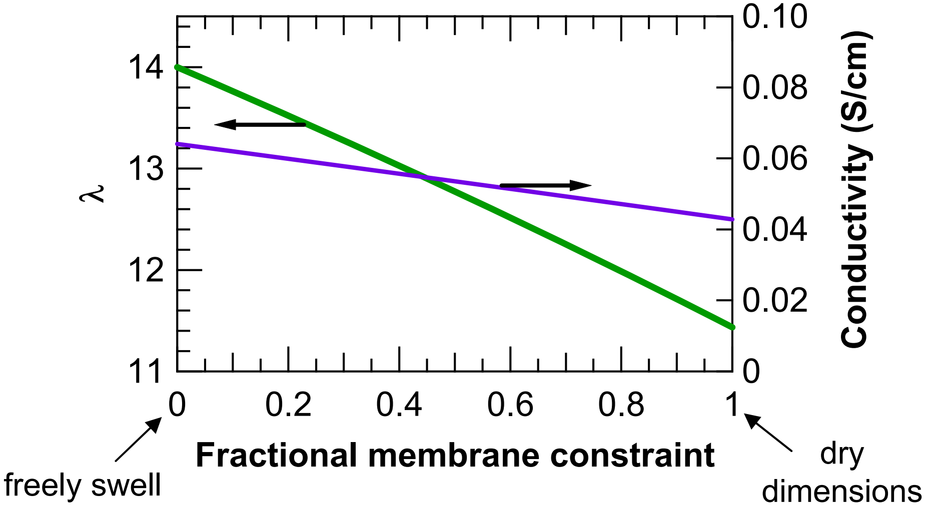
Membrane Degradation

- 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



RH	Membrane fractional constraint	GDL thickness (μm)	Interior stress (MPa)
liquid	0.16	235	4.3
1	0.21	243	3.5
0.9	0.25	245	3.3
0.5	0.45	248	3.1

Simulations with Nafion® 112, 80°C, 0.4 A/cm^2 and various feed RH

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

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

Summary

- **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

Responses to Previous Year Reviewers' Comments

- *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.

Responses to Previous Year Reviewers' Comments (cont'd)

- *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
  - J. Newman, “Trends in Fuel-Cell Modeling,” Fuel Cell Gordon Research Conference, July 2005.
  - A. Z. Weber and J. Newman, “Modeling Gas-Phase Transport in Polymer-Electrolyte Fuel Cells,” 208th Electrochemical Society Meeting, Los Angeles, CA, October 2005.
  - A. Z. Weber and J. Newman, “Modeling Nonisothermal Effects in Polymer-electrolyte Fuel Cells,” 208th Electrochemical Society Meeting, Los Angeles, CA, October 2005.
  - L. Onishi and J. Newman, “Low Temperature Membrane Properties,” 208th Electrochemical Society Meeting, Los Angeles, CA, October 2005.
  - A. Z. Weber and J. Newman, “Effects of Heterogeneities in Polymer-Electrolyte Fuel Cells,” 209th Electrochemical Society Meeting, Denver, CO, May 2006.
- Publications
  - A. Z. Weber and J. Newman, “A Combination Model for Macroscopic Transport in Polymer-Electrolyte Membranes,” in *Device and Materials Modeling of PEM Fuel Cells*, S. Paddison and K. Promislow, editors, Springer, in press (2005).
  - A. Z. Weber and J. Newman, “Macroscopic Modeling of Polymer-Electrolyte Membranes,” in *Advances in Fuel Cells*, T.S. Zhao, editor, in press (2005).
  - L. Onishi and J. Newman, “Low Temperature Membrane Properties”, *ECS Transactions*, accepted (2005).
  - A. Z. Weber and J. Newman, “Modeling Gas-Phase Transport in Polymer-Electrolyte Fuel Cells”, *ECS Transactions*, accepted (2005).
  - A. Z. Weber and J. Newman, “Coupled Thermal and Water Management in Polymer-Electrolyte Fuel Cells,” *J. Electrochem. Soc*., submitted (2006).
  - A. Z. Weber and J. Newman, “Effects of Water-Transfer Plates for Polymer-Electrolyte Fuel Cells,” *J. Power Sources*, in preparation.