Fuel-Cell Fundamentals at Low and Subzero Temperatures

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June 18, 2014

Project ID #
FC 026

Overview

Timeline

- Project started FY09
  - September 2009
- Project end date*
  - September 2014

Barriers

- A. Durability
- C. Performance
  - Cell Issues
  - Stack Water Management
  - System Thermal and Water Management
  - System Start-up and Shut-down Time and Energy/Transient Operation

Budget

- Total Project Funding: $6,057k
  - DOE share: $ 5,600k
  - Contractor share: $ 457k (7.5%)
- Funding Received in FY13: $1,095k
- Planned Funding for FY14: $900k
  - LBNL $596k
  - Partners $304k

*Project continuation and direction determined annually by DOE

Partners

- Project lead**: Lawrence Berkeley NL**
- Direct collaboration with Industry, National Laboratories and University (see list)
- Other collaborations with material suppliers and those with unique diagnostic or modeling capabilities
- Discussion with related project leads and working groups (esp. TMWG)

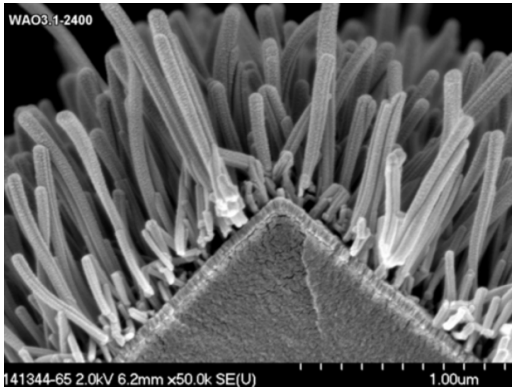
Collaboration: Organizations/Partners

- Lead
  - **Lawrence Berkeley National Laboratory**: Adam Weber, Ahmet Kusoglu, Michael Tucker, Clayton Radke, Dilworth Parkinson, Alexander Hexemer, Frances Allen, Iryna Zenyuk
- Subcontractors
  - **Los Alamos N.L.**: Rod Borup, Rangachary Mukundan, Dusan Spernjak
  - **3M Company**: Andy Steinbach, Michael Yandrasits
  - **United Technology Research Center**: Michael Perry
  - **McGill University**: Jeffrey Gostick
- Other relationships (directly funded through other DOE projects)
  - **Ion Power**: Stephen Grot (membrane and MEAs)
  - **NIST**: Daniel Hussey, David Jacobson (neutron imaging of water)
  - **The Pennsylvania State University**: Michael Hickner (membrane thin films)
- Other relationships (no cost)
  - **UC Berkeley/JCAP**: Rachel Segalman (Membrane scattering, properties, and other studies)
  - **University of Calgary:** Kunal Kuran (Nafion® thin-film data and samples)
  - **NIST**: Kirt Page (Nafion® thin-film studies)
  - **University of Michigan**: Massoud Kaviany (Nafion® MD simulations, ESEM)

Relevance: Objectives

- Understand transport phenomena and water and thermal management at low and subzero temperatures using state-of-the-art materials
  - Examine water management with thin-film catalyst layers
  - Examine water management and key phenomena in the various fuel-cell components
  - Enable optimization strategies to be developed to overcome observed bottlenecks
    - Operational
    - Material

NSTF catalyst layer



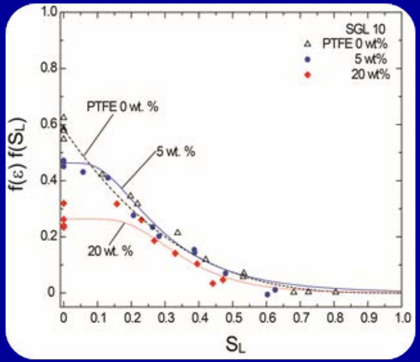
- Elucidate the associated degradation mechanisms due to cold and cool operation
  - Enable mitigation strategies to be developed

Improved understanding will allow for the DOE targets to be met with regard to cold start, survivability, performance, and cost

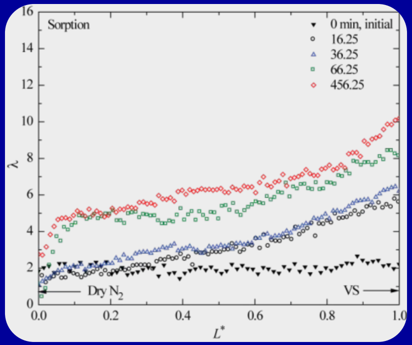
Approach

In/Ex-situ Diagnostics

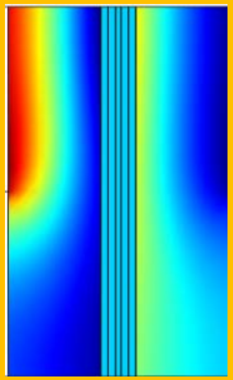
Component properties



Component phenomena

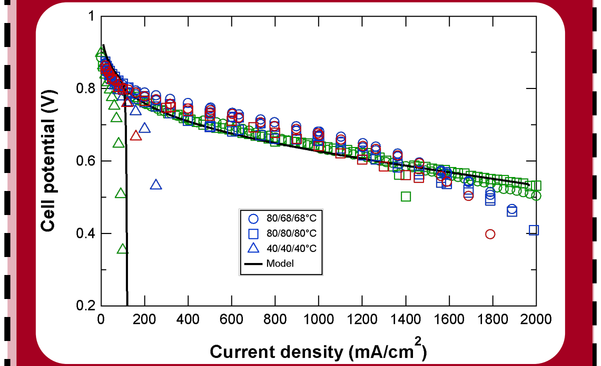


Cell Model

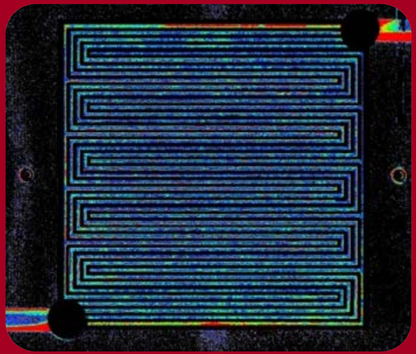


In-operando Studies

Cell performance



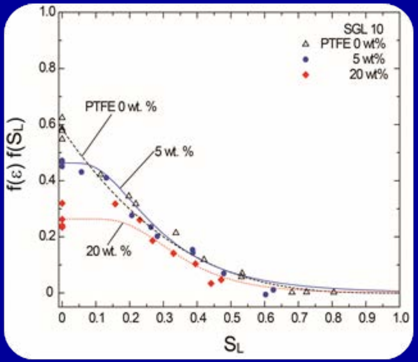
Cell diagnostics



Approach

In/Ex-situ Diagnostics

Component properties

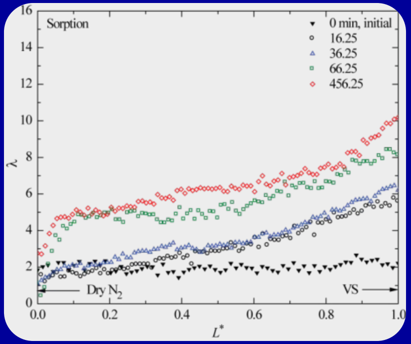


Methods

Properties

Submodels

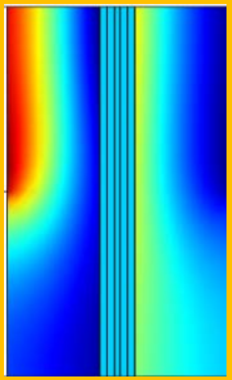
Component phenomena

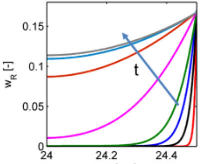


Drives need

Inputs

Cell Model





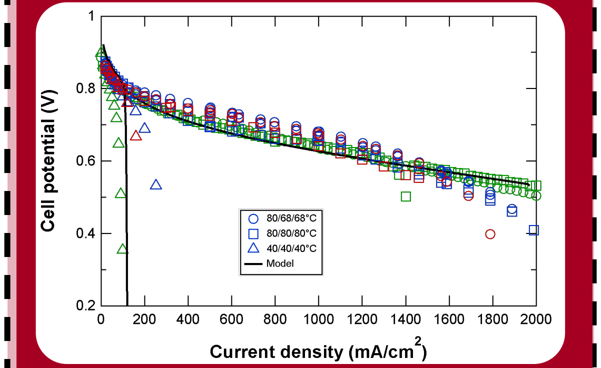
Validate

Validate

Optimization/Mitigation

In-operando Studies

Cell performance

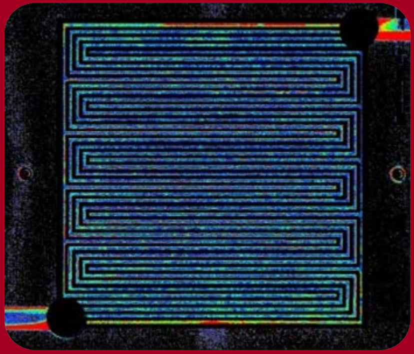


Explain

Validate

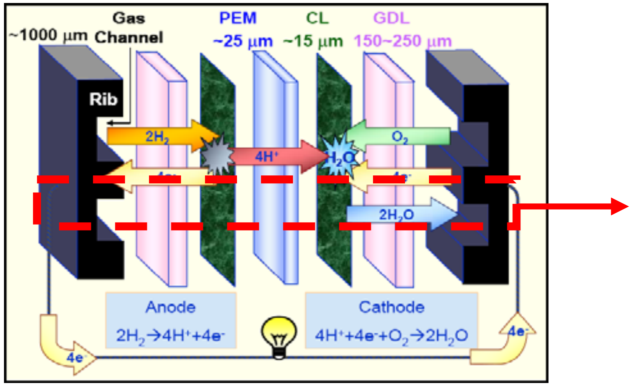
Guidance

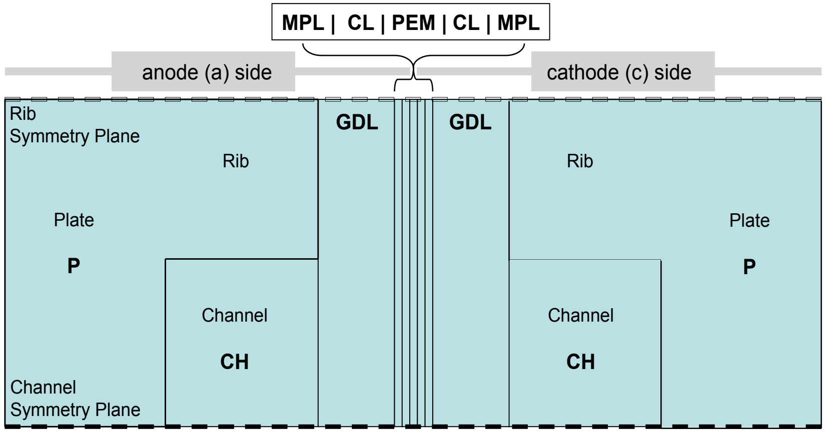
Cell diagnostics



Approach: 2-D Cell Model

- **Model Geometry**





- **Model physics**

Equations (12): 7 2nd-order PDEs; 5 Algebraic equations

Thermodynamics

Standard cell potential
Equilibrium H_2O content
membrane, liquid, vapor, ice

Kinetics

Butler-Volmer for HOR, ORR
H_2O phase change between
ionomer, vapor
liquid, vapor

Transport

Stefan-Maxwell diffusion
for gas-phase components
Darcy's law for liquid, gas phases
Ohm's law for e$^-$ current
Modified Ohm's law for H$^+$ current
H_2O transport by proton drag
H_2O diffusion in membrane

Conserved quantities

Mass; Charge; Energy

Constitutive relations

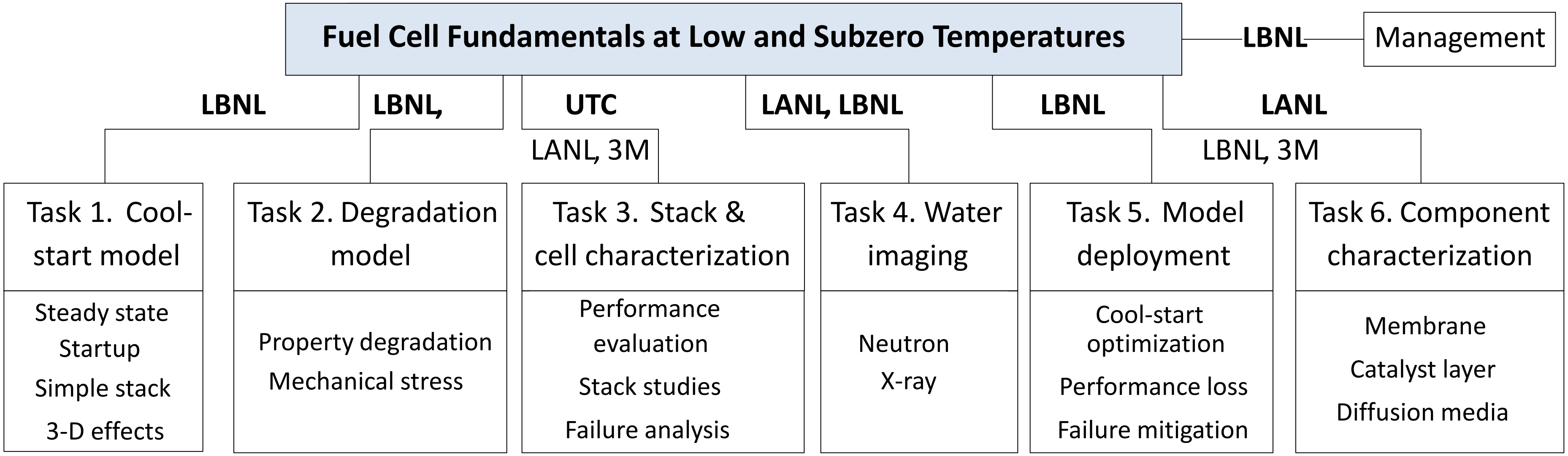
Faraday's law
Ideal-gas law

Properties

Function of *T*
and H_2O content

Key is describing the governing critical phenomena

Approach: Work Plan / Organization



Fuel Cell Fundamentals at Low and Subzero Temperatures

LBNL Management

LBNL

Task 1. Cool-start model

Steady state
Startup
Simple stack
3-D effects

LBNL,

Task 2. Degradation model

Property degradation
Mechanical stress

UTC
LANL, 3M

Task 3. Stack & cell characterization

Performance evaluation
Stack studies
Failure analysis

LANL, LBNL

Task 4. Water imaging

Neutron
X-ray

LBNL

Task 5. Model deployment

Cool-start optimization
Performance loss
Failure mitigation

LANL
LBNL, 3M

Task 6. Component characterization

Membrane
Catalyst layer
Diffusion media

LBNL

- Project management and coordination
- Model development
- GDL and membrane characterization
- Ionomer thin-film diagnostics

LANL

- Ex-situ component characterization
- Single-cell tests
- Neutron imaging

UTRC

- Cell parametric studies
- Identify and characterize failure mechanisms
- Real-world guidance

3M

- Material supplier and testing knowledge including conditioning procedures

Other (McGill)

- Provide unique materials and diagnostics

FY14 Project Timeline

Begin
10/13

M1
12/13

M2,M3,M4
03/14

M5
04/14

M6,M7
09/14

End
09/14

Major Milestones/Deliverables

M1: Measure properties of 2 GDLs with land/channel impacts (*completed with adhesion and droplet detachment measurements for improved and baseline GDLs*)

M2: Quantitative agreement (<10% error) between capillary-pressure – saturation relationship* for GDL/MPLs and GDL/MPL analogues (*completed by understanding droplet dynamics and function of MPL*)

**Changed to droplet dynamics and behavior since deemed more critical*

M3: Data for startup from 4 different thermal boundary conditions using adiabatic cells with two different anode GDLs (*completed both by modeling and experiments showing importance for startup of NSTF*)

M4: Segmented cell measurements to define water concentration by HFR measurements at low temperatures (25 C, 40 C) (*completed for Gore MEAs*)

M5: Obtained lambda – d correlations for 2 different treated ionomer thin films of 4 different thicknesses (*on-track and awaiting beamtime*)

M6: Model agreement of startup from room temperature (<10% deviation) for 2 cells with different diffusion media under 2 different thermal boundary conditions. (*on-track, qualitative agreement accomplished*)

M7: Measurement of water concentration by neutron imaging at low operating temperatures during power transients (30 C with power up 0.1 to 1.2 A/cm^2, power down transients 1.2 to 0.1 A/cm^2). (*on-track*)

Accomplishments

In/Ex-situ Diagnostics

Component properties

- Measured GDL properties
    - Thermal conductivity, effective diffusivity, breakthrough pressure, adhesion force, x-ray tomography
- Measured CL freeze and GDL melting kinetics

Component phenomena

- Examined ionomer thin films
- Investigated membrane structure/function relationships
- Examined phase-change related CL degradation
- Studied role of MPL

Cell Model

- Validated steady-state model
- Developed transient model
- Incorporated properties and diagnostic information
- Explained GDL improvement

In-operando Studies

Cell performance

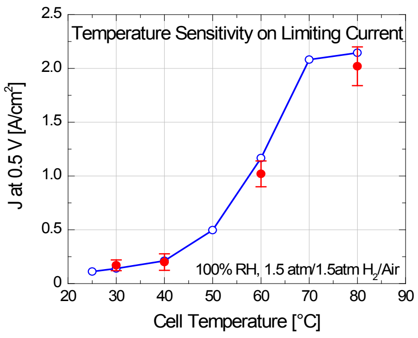
- Understanding and optimizing low-temperature operation with NSTF
- Adiabatic cell studies for startup
- Transient studies

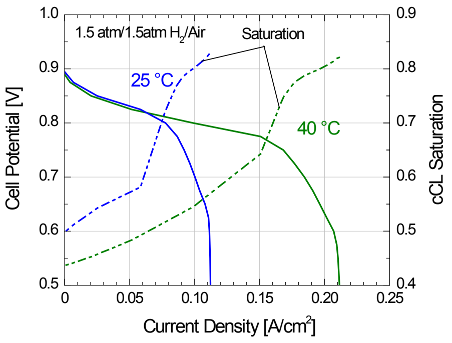
Cell diagnostics

- High and low-res neutron imaging with different GDLs and CLs
- Segmented cell studies
- Water-balance studies

Improving NSTF Temperature Sensitivity

- Model and data show temperature sensitivity of NSTF due to flooding
  - Can improve performance by switching **anode** GDL
    - Different anode GDL decreases cell water amount

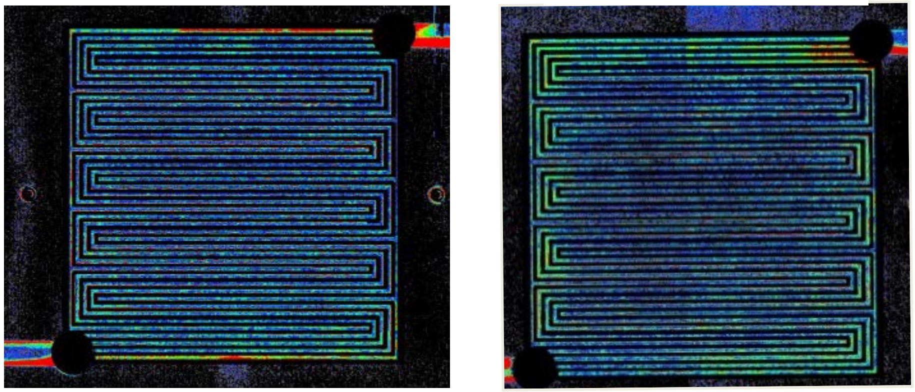




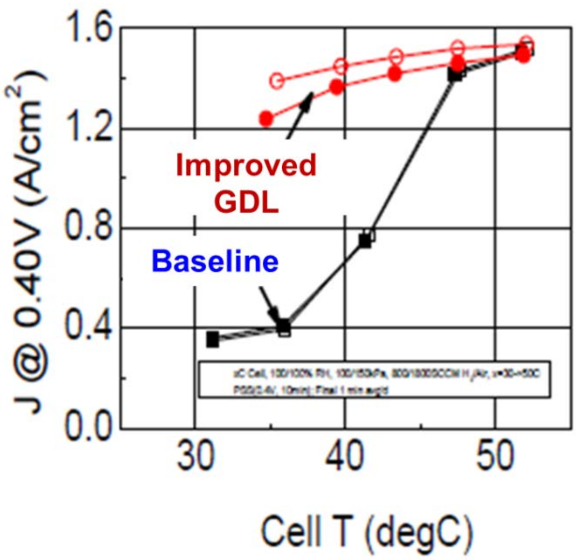
Improved

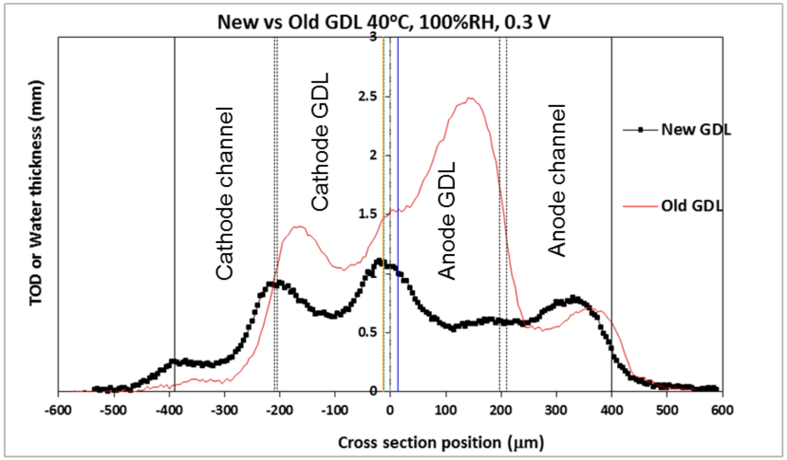
30 C

Baseline



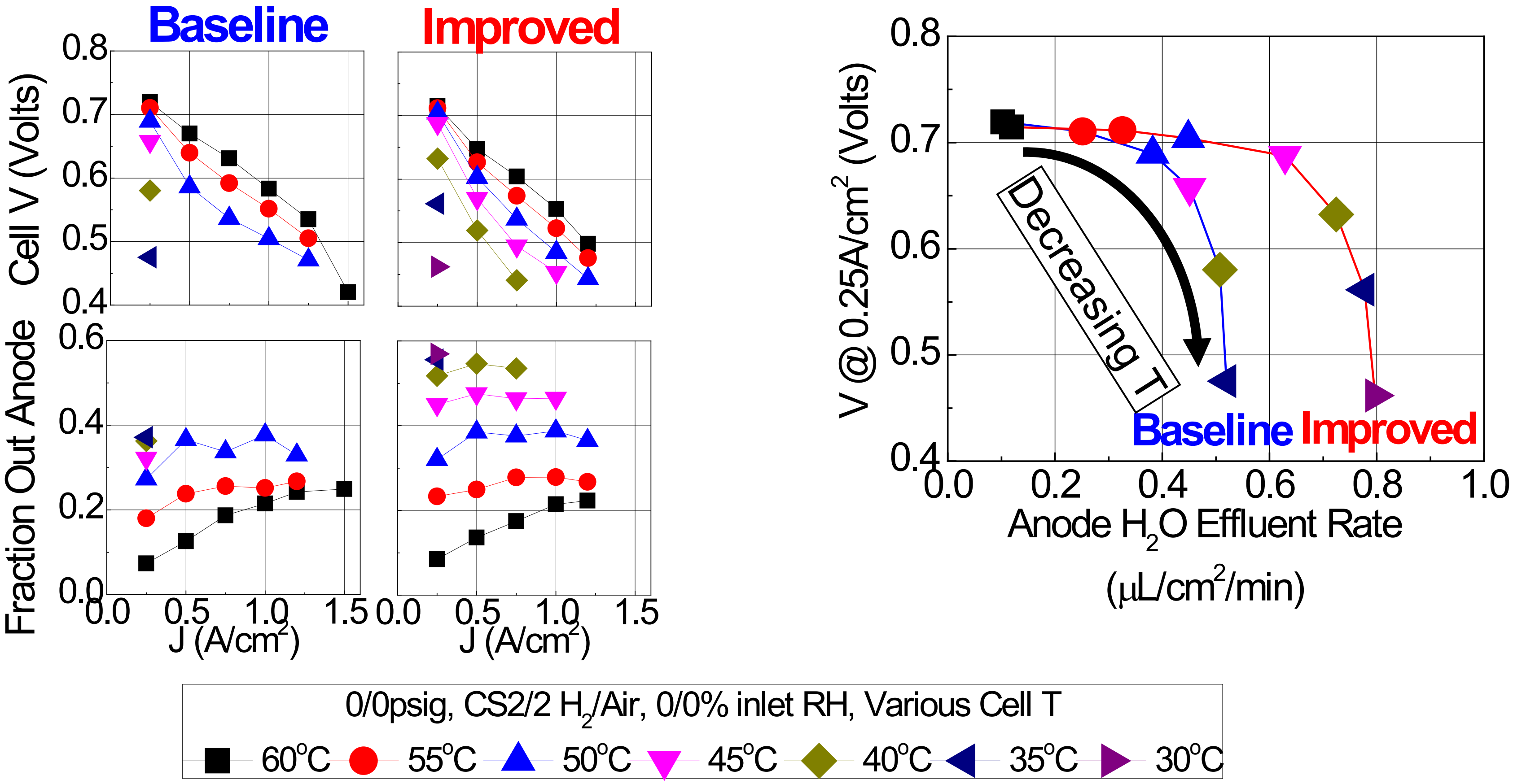
40 C





Water-Balance Results

- As temperature decreases, best performing GDLs move more water out the anode
  - Maximum water removal fraction varies with GDL
  - Performance loss occurs as water removal rate reaches apparent limit

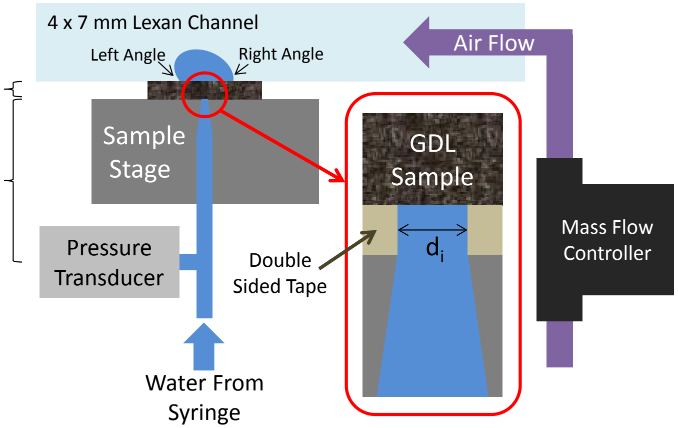


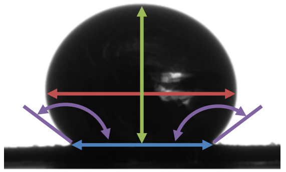
0/0psig, CS2/2 H_2/Air, 0/0% inlet RH, Various Cell T

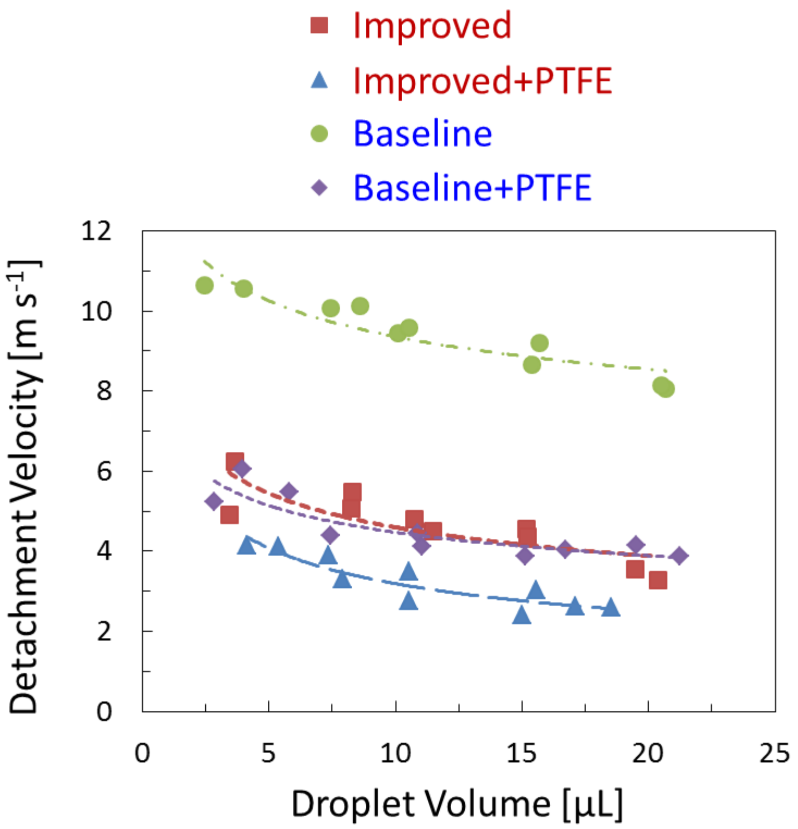
■ 60°C ● 55°C ▲ 50°C ▼ 45°C ◆ 40°C ◀ 35°C ▶ 30°C

GDL Property Comparison

- Examined properties *ex situ* to find correlation for increased low-temperature performance and better water removal
  - Capillary pressure – saturation relationship; Breakthrough pressure; Liquid permeabilities; Electrical and thermal conductivities
- Detachment velocity
  - Improved GDL also shows lower value
    - Correlates to better water removal
  - Can be possible screening tool for new GDLs







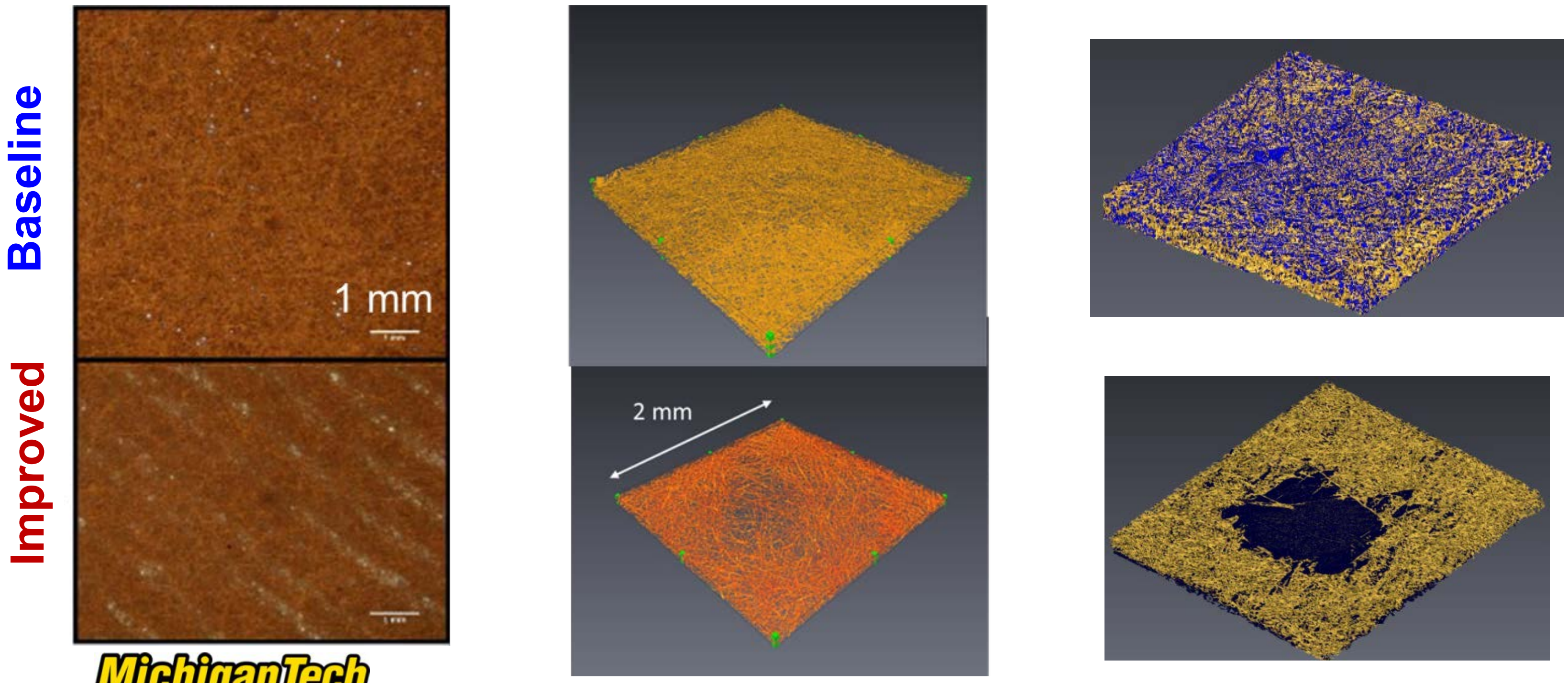
GDL Structure

- Improved seems to have fiber-density modulations
  - ⤷ Cause preferential water pathways and easier droplet detachment

Optical

X-ray tomography (dry)

X-ray tomography (wet)

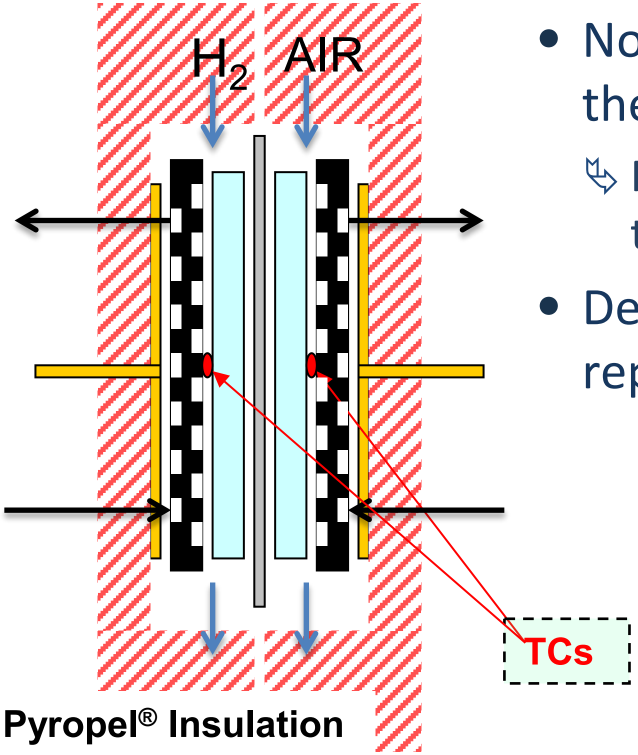


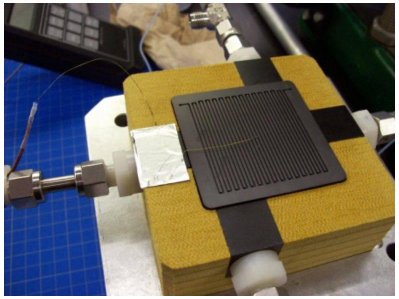
MichiganTech

FC 104

Adiabatic Cell Testing

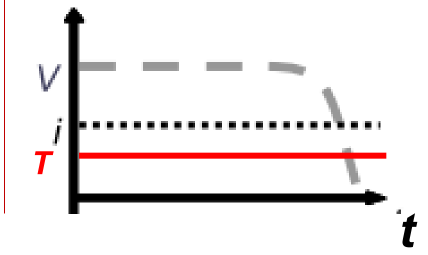
Adiabatic cell is built with low thermal-mass components (closer to situation in a stack)



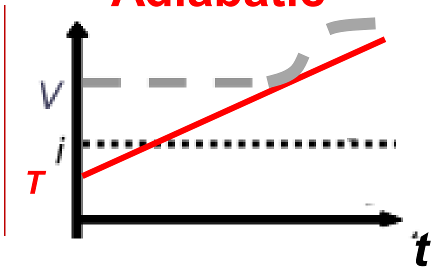


- Normal sub-scale cell hardware have much larger thermal mass per cell relative to cells in actual stacks
  - Results in aggressive condition with respect to temperature transients
- Decreasing thermal mass should allow for startup and replicate stack conditions

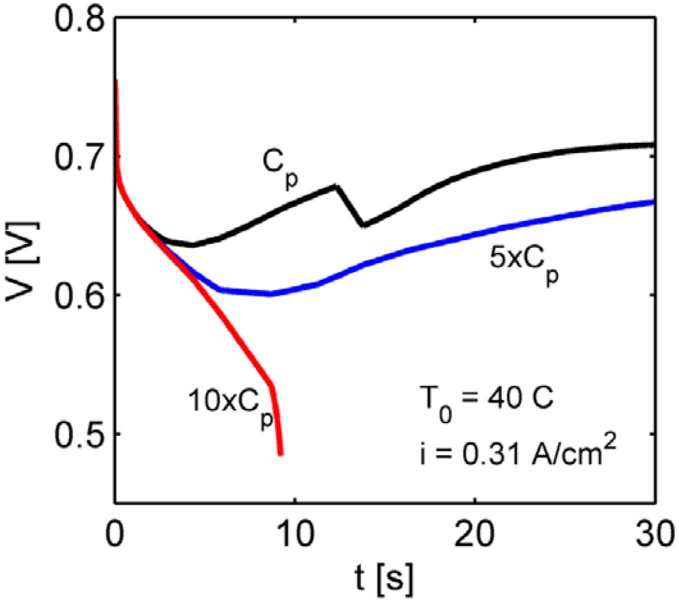
Isothermal



Adiabatic



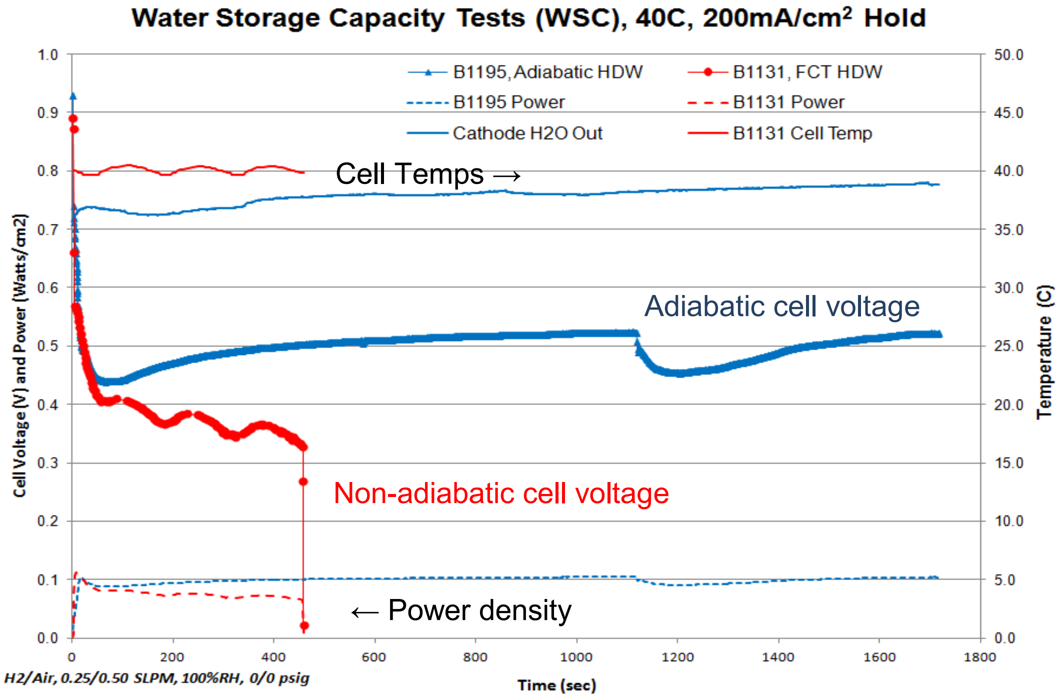
Transient Simulations

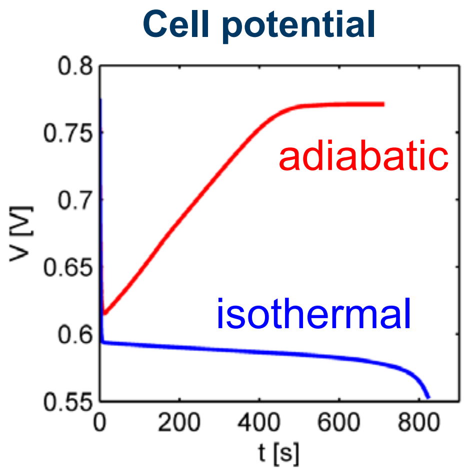


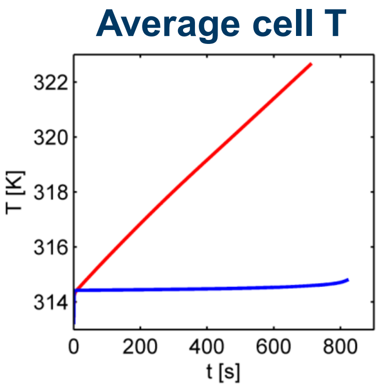
Adiabatic Cell Data and Model

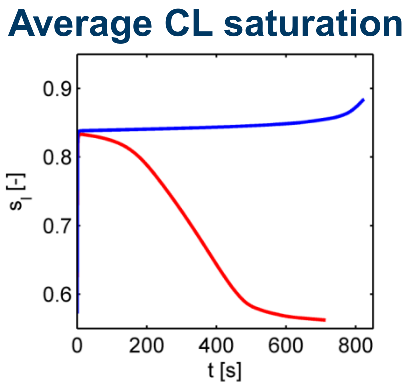
Adiabatic cell is built with low thermal-mass components (closer to situation in a stack)

- NSTF in adiabatic cell hardware demonstrated successful sustained performance during 40°C constant-current hold, whereas it does not in normal hardware
  - Adiabatic cell allows drying out of the catalyst layer
    - Reactant distribution is more uniform for adiabatic in CL





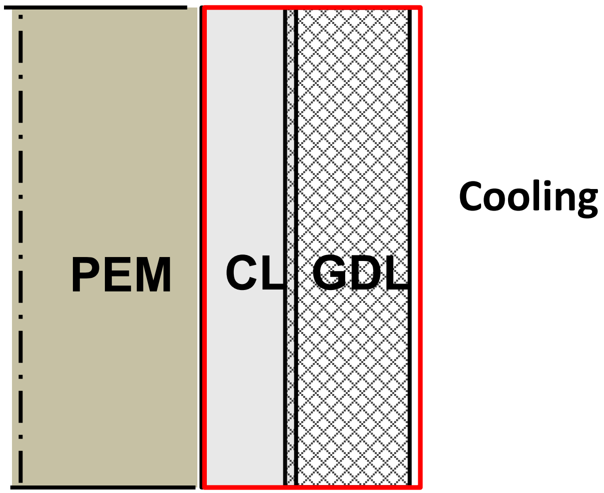




Cold-Start Model and Freeze Kinetics

- Utilize previously developed freeze kinetics to compare to experimental data
  - Ice-crystallization kinetics in PEFC-porous media are important
  - For low subcoolings, freezing is kinetically controlled

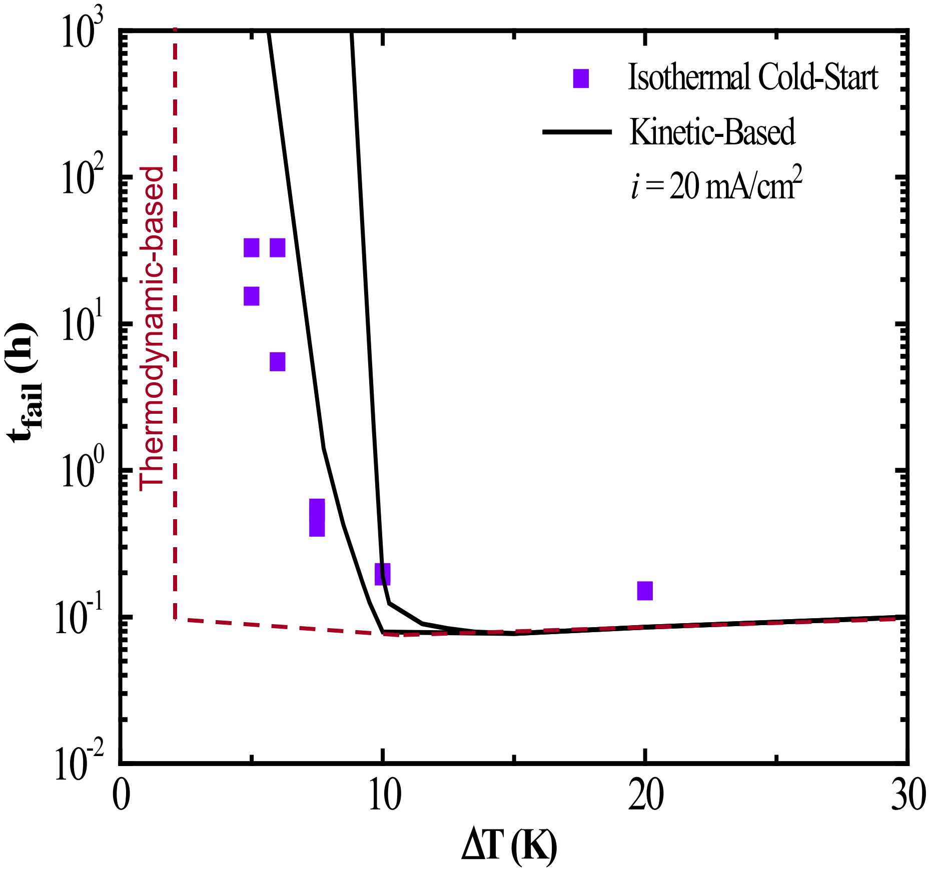
Cathode PEMFC Layers



$$R_i = \rho_i \frac{d\phi}{dt} = k(T)[1-\phi][-\ln(1-\phi)]^{3/5}$$

$$k(T) = 64\pi/15\ \rho_i \alpha_w^{3/2} g(\theta)\, J(T)\, \eta_o^3(T)$$

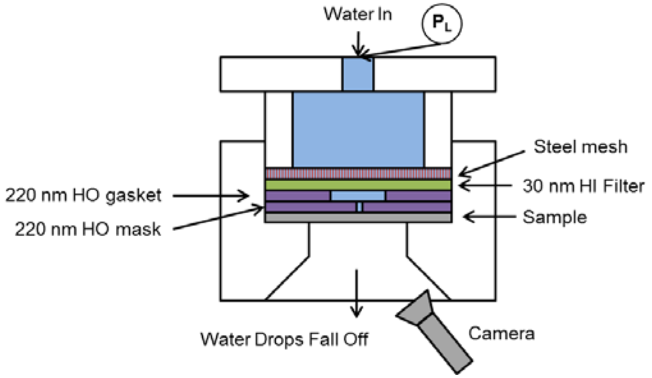
Cell-failure Time, t_{fail}



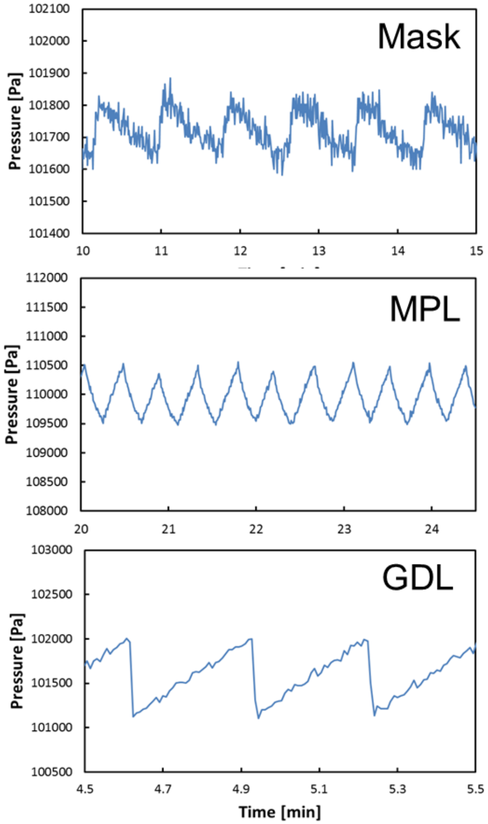
T.J. Dursch *et al. Int. J. Heat Mass Trans.* **2013**, 60, 450-458

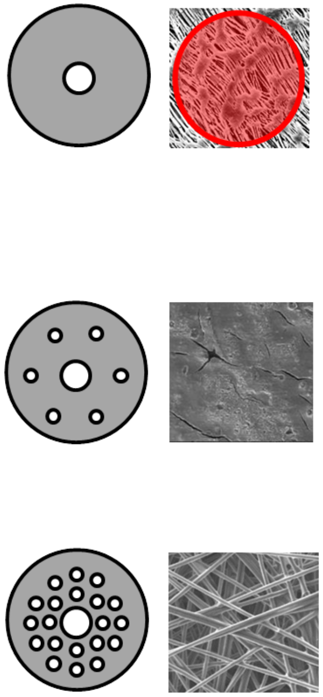
MPL Impact on Water Movement

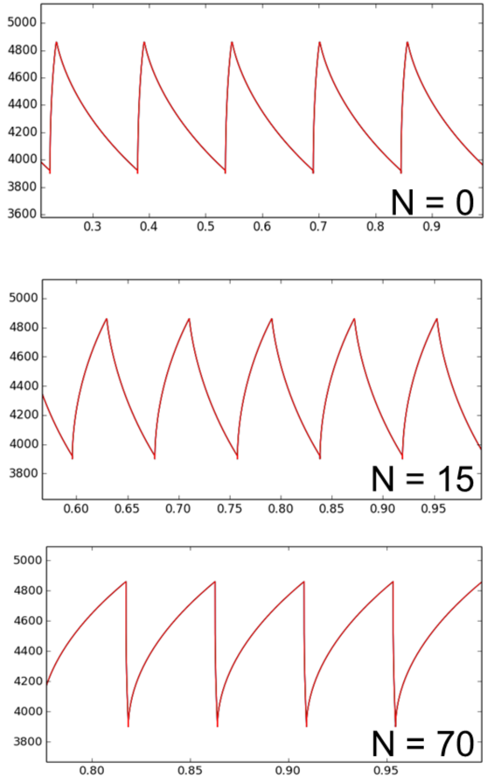
- MPLs provide isolated injection points that impact droplet dynamics as well as total water content
  - Need hydrophobic filter to keep dust from MPL pores
  - Visualize the droplets and monitor pressure
    - Breakthrough pressure can impact cell water holdup



MPLs act to isolate water penetration into GDLs and nonuniform interface and structure provide some small capillary (interface)-driven water capacity



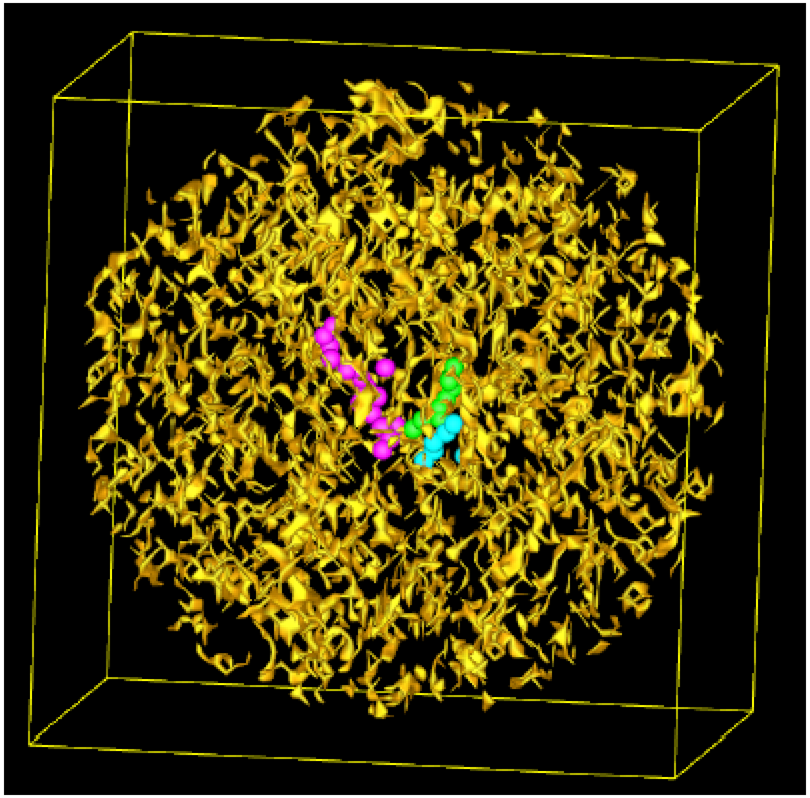


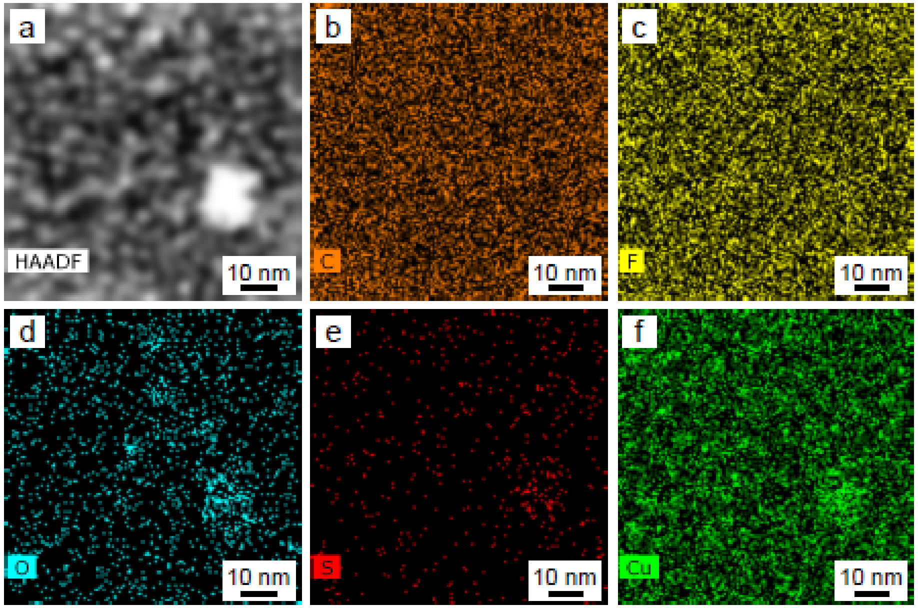


Nafion® Morphology

- Insights into membrane morphology allow for optimization of properties, performance, and durability
  - Water movement into membrane key for thin-film catalyst layers and cold start
  - Knowledge of the morphology can help set design strategies for new membranes

Hydrated morphology as measured by TEM cryo-tomography





Traditional TEM grids and techniques result in membrane contamination

Responses to Previous Year Reviewers' Comments

- It is not clear how all the studies are being tied together and into the final model
  - ⇘ This has hopefully been better articulated in that the diagnostics, submodels, and cell studies, including at all places, provide necessary input or validation to the overall model
- Project is focused on fundamental studies of different MEA components and their assemblies, while less effort is invested in problem solving
  - ⇘ As we try and solve problems, we have found a lack of knowledge of certain key phenomena and parameters, which has necessitated more component-level studies. Future focus is more on solutions and strategies as derived from the integrated model
- The proposed future work is well delineated. However, incorporating transient models and inputs from an automotive company would be further recommended
  - ⇘ We have worked this year on transient modeling, which is being further validated and exercised. In addition, we receive feedback from the Tech Team and are reaching out and interested in dialog with automotive companies
- Since the NSTF catalyst layer was reported about its critical water management problem, it is good to add conventional catalyst later to alternative materials to make knowledge base with respect to water management in cold temperatures (including subzero temperature start-up) more universal
  - ⇘ Throughout the project we have also examined issues and models with traditional Pt/C catalyst layers (e.g., freeze kinetics) and are planning to do more of this in the future, although the main emphasis of the original proposal was NSTF

Remaining Challenges and Barriers

- Still not perfect understanding of how NSTF and ultra-thin catalyst layers conduct protons and their temperature sensitivity

- Need to optimize performance of ultra-thin catalyst layers, especially transient operation
  - Understand stack-location effects

- Water and thermal management at interfaces is poorly characterized and not typically modeled

- Cell model needs refinement

Future Work

- **Cell Performance**
  - UTRC to run cool and cold starts including adiabatic and temperature transients
    - NSTF and low-loaded traditional CLs
  - LANL to run NSTF and Gore cells with different GDLs and operation conditions
    - Segmented cell
    - Power transients
    - NIST high(er)- and low- (transient) resolution imaging
- **Component Characterization**
  - Traditional CLs
    - Examine properties and uptake with low-EW ionomer and ionomer thin-films
  - NSTF CLs
    - Determine proton conductivity on platinum
  - GDLs
    - Impact of lands on liquid-water movement out of the GDL
    - Measurement of effective properties and imaging of liquid water
  - Membrane
    - Interfacial resistance and membrane morphology with different environments
- **Modeling**
  - Use data from all partners to refine transient model
  - Develop bilayer or alternate approach for NSTF CLs
  - Develop down-the-channel model (2-D+1)
- **Understand and increase the operating window with thin-film CLs**
  - Focus on possible solutions and strategies as derived from the integrated model and cell and component studies
- **Solicit input and advice from automotive companies**

Summary

- Relevance/Objective:
  - Help enable, optimize, and mitigate failure in state-of-the-art materials through understanding of operation at low and subzero temperatures
- Approach/Collaborations:
  - Use synergistic combination of cell and component diagnostic studies with advanced mathematical modeling at various locations (national laboratories, industry, and academia)
- Technical Accomplishments:
  - Combined modeling and experiment to understand low-temperature performance of NSTF
    - Examined impact of different anode GDLs through various cell and component diagnostics
    - Increased water out the anode lowers cathode flooding and is driven by morphological features that decrease GDL surface adhesion force
  - Developed transient startup model and showed how it agrees with adiabatic cell startup
    - Mimics cell position in a stack and shows better NSTF startup due to lower thermal mass
  - Investigated role of MPL
    - Provides isolated water injection points with some inherent capacity due to capillary interfaces
  - Examined membrane morphology and thin-film characteristics on various substrates and conditions
- Future Work:
  - Understand liquid-water movement, interactions, and freeze in fuel-cell components
  - Determine optimal materials and engineering solutions for transient and steady-state cell performance using next-generation material sets

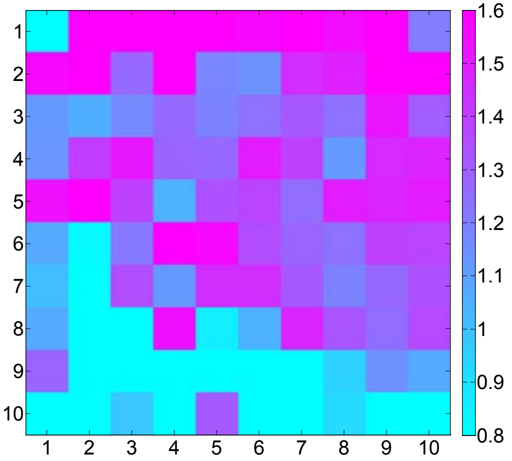
Technical Back-Up Slides

Segmented Cell Studies

- Data extremely helpful for model validation and cell understanding

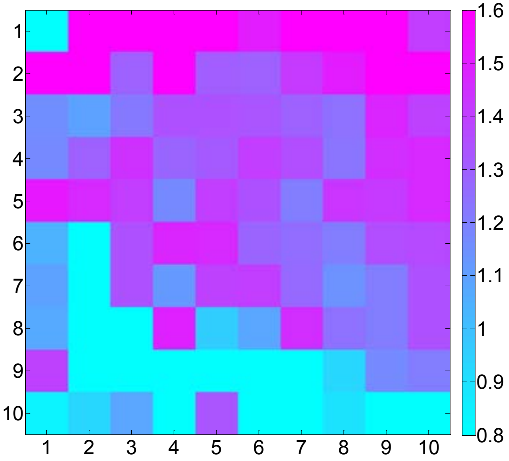
BC 40°C

Current density distribution at 1.2 A/cm^2



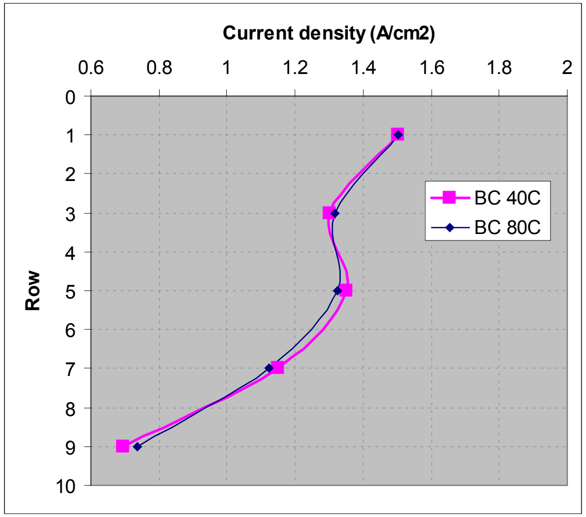
BC 80°C

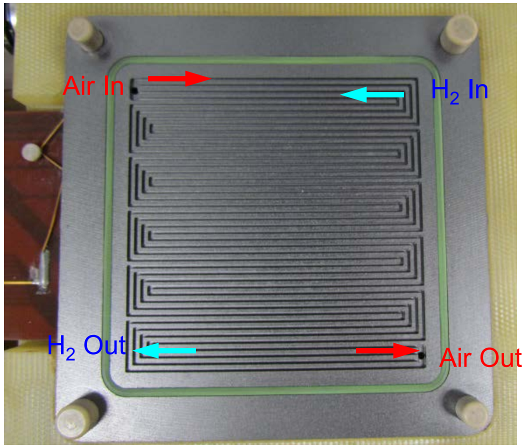
Current density distribution at 1.2 A/cm^2

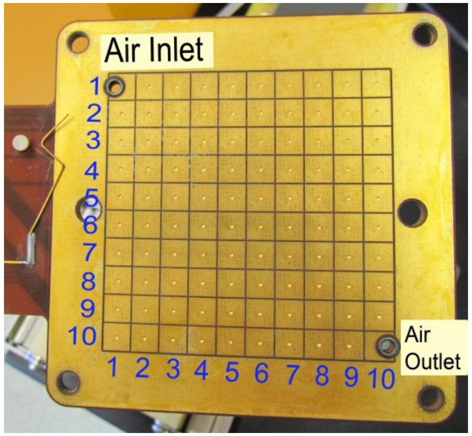


1-D current distribution

(averaged two consecutive rows of segments)







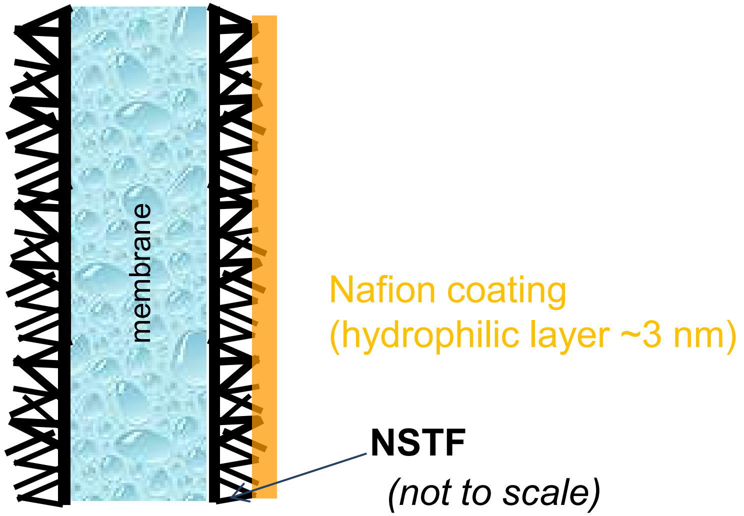
Almost identical current distribution at different cell temperature.

Local current decreases along the flow field, from top to bottom.

Separate aging experiments with BC GDL reveal that current distribution becomes more nonuniform during carbon corrosion AST (potential holds): increase at inlet and decrease at outlet.

PFSA-coated NSTF Summary

Ionomer on cathode of NSTF is beneficial



Key Observations:

Nafion layer on cathode of NSTF cells resulted in:

- Noticeably more stable performance, especially during conditioning
- Reduced temperature sensitivity on Air and Helox (added layer is detrimental with very low O_2 concentration)
- Improved results under constant-current holds at room temperature (not shown here)

UTRC's NSTF *Hypothesis*:

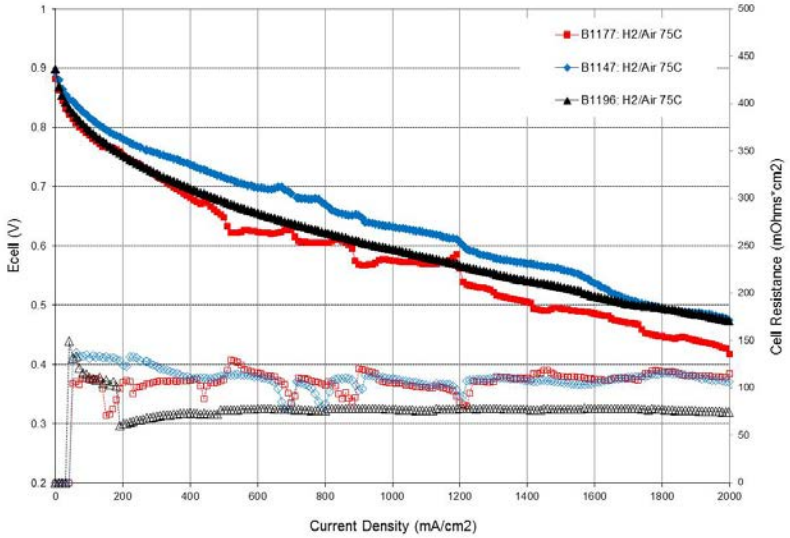
Proton transport in catalyst layer (CL) is primarily via thin-water film:

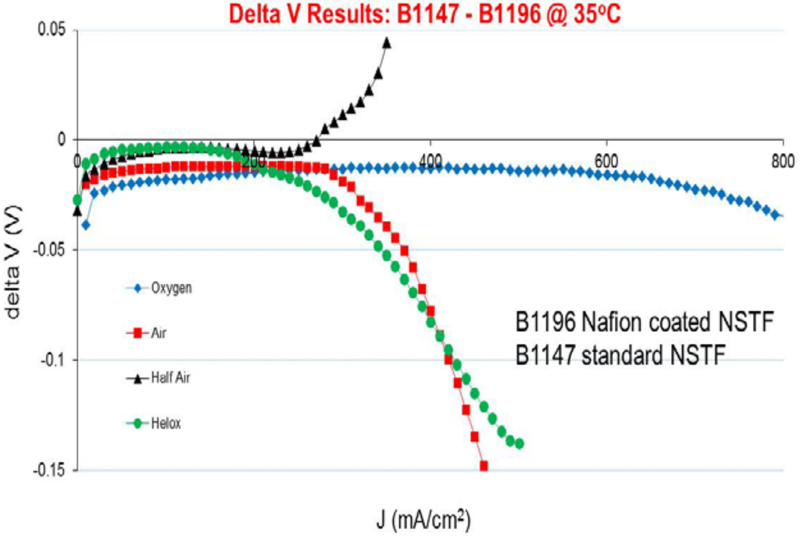
- Water in PEMFC acts as a weak electrolyte (*i.e.*, pH << 7)
- Water-saturation level has major impact on ionic & gas transport of CLs
- Ideal saturation level is sufficient water to form thin film that serves as weak electrolyte; too much dilutes electrolyte and/or results in thicker films
- Extensive NSTF conditioning required to generate weak electrolyte

B1147: Best ever NSTF cell at UTRC

B1177: Typical NSTF cell at UTRC

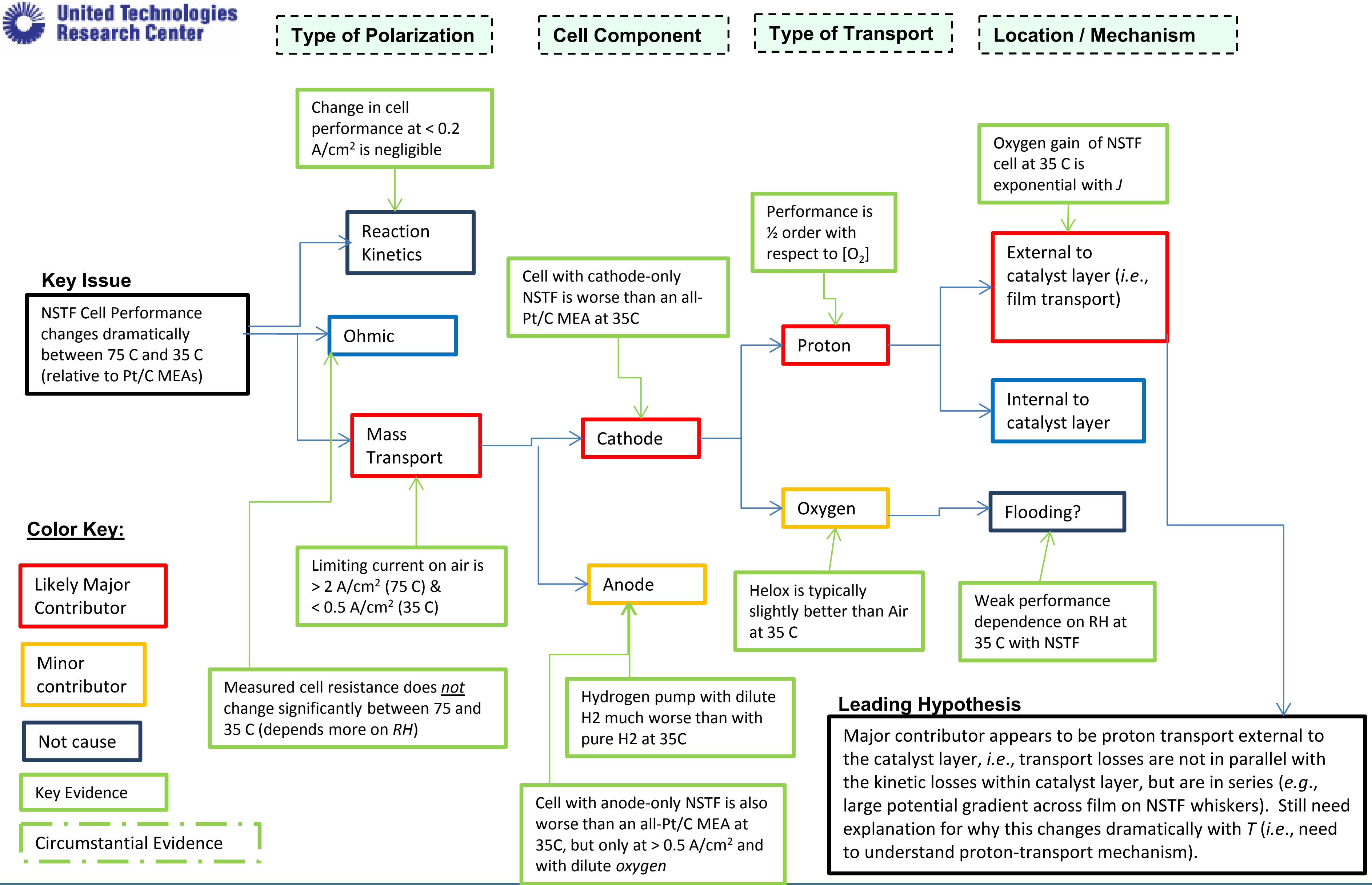
B1196: Nafion-coated cathode NSTF





NSTF Temperature Sensitivity Fault Tree

United Technologies Research Center



Type of Polarization | **Cell Component** | **Type of Transport** | **Location / Mechanism**

Key Issue

NSTF Cell Performance changes dramatically between 75 C and 35 C (relative to Pt/C MEAs)

Change in cell performance at < 0.2 A/cm^2 is negligible

Cell with cathode-only NSTF is worse than an all-Pt/C MEA at 35C

Performance is ½ order with respect to [O$_2$]

Oxygen gain of NSTF cell at 35 C is exponential with *J*

Limiting current on air is > 2 A/cm^2 (75 C) & < 0.5 A/cm^2 (35 C)

Measured cell resistance does *not* change significantly between 75 and 35 C (depends more on *RH*)

Hydrogen pump with dilute H2 much worse than with pure H2 at 35C

Cell with anode-only NSTF is also worse than an all-Pt/C MEA at 35C, but only at > 0.5 A/cm^2 and with dilute *oxygen*

Helox is typically slightly better than Air at 35 C

Weak performance dependence on RH at 35 C with NSTF

Color Key:

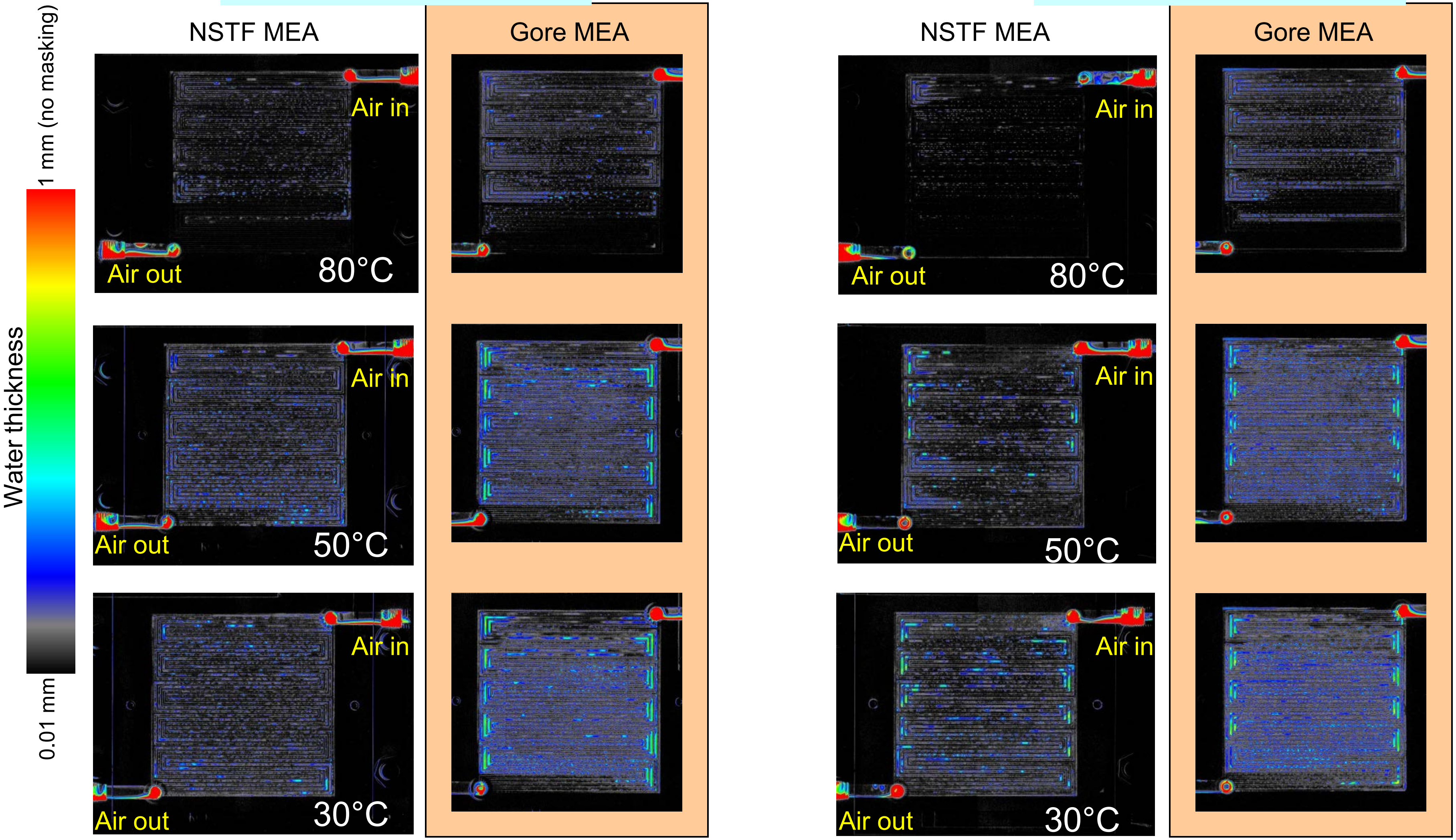
- Likely Major Contributor
- Minor contributor
- Not cause
- Key Evidence
- Circumstantial Evidence

Leading Hypothesis

Major contributor appears to be proton transport external to the catalyst layer, *i.e.*, transport losses are not in parallel with the kinetic losses within catalyst layer, but are in series (*e.g.*, large potential gradient across film on NSTF whiskers). Still need explanation for why this changes dramatically with *T* (*i.e.*, need to understand proton-transport mechanism).

NSTF vs C-Supported Electrodes

Improved Anode GDL no masking Baseline Anode GDL



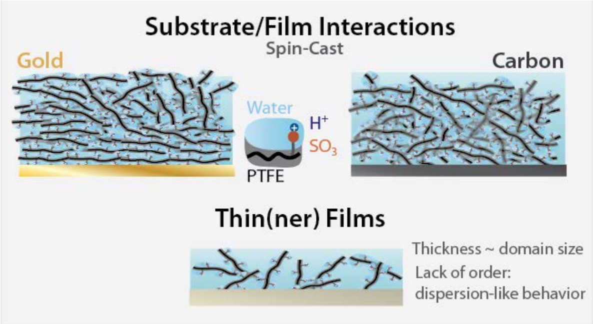
Overall water content higher with Gore over 3M NSTF MEA - steady state data (0.6V)

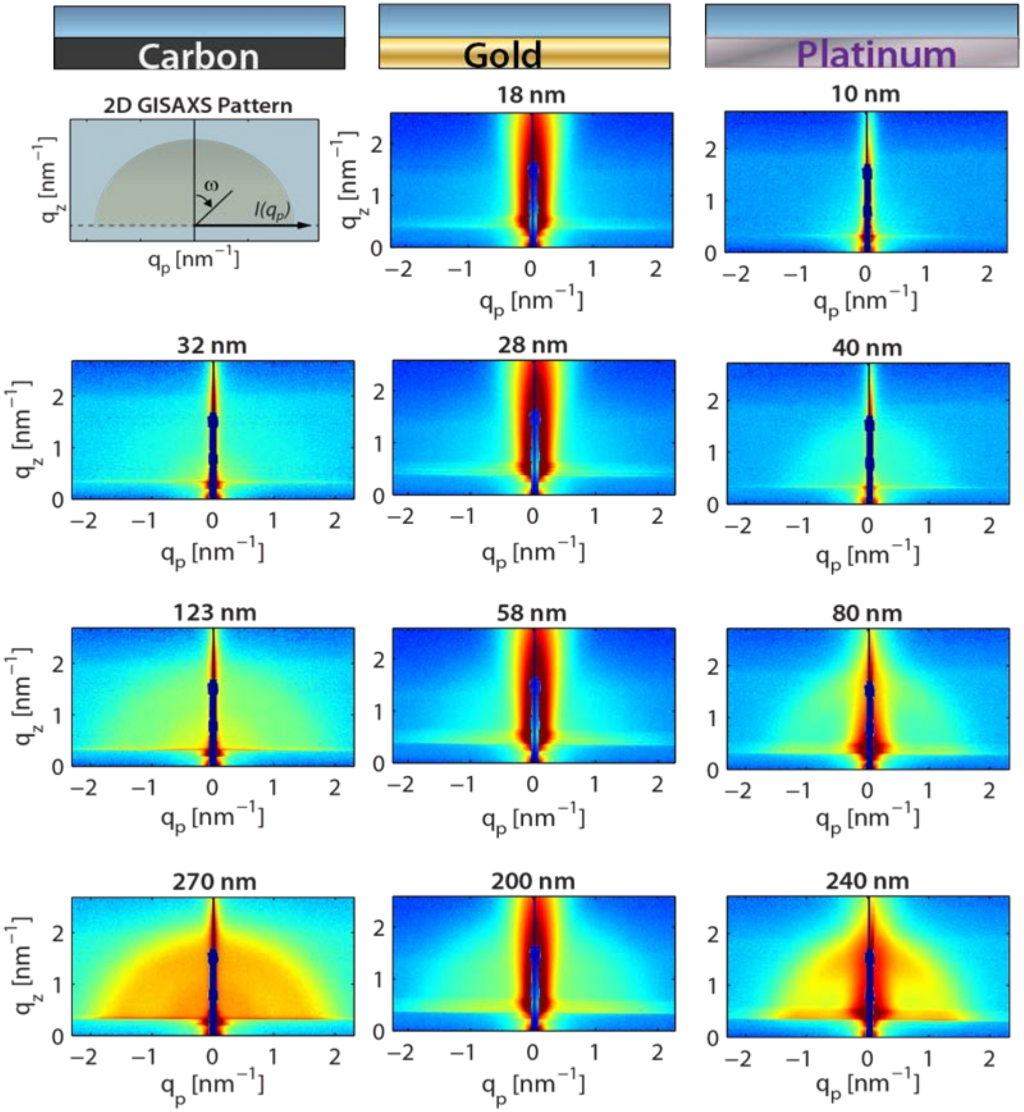
Gore MEA: stable operation at high current, at all cell T. At 30C DPT, Cell T ~38C

Nafion® Thin-Film Studies

Hickner Group (PennState)
Karan Group (U of Calgary)

- Confinement and surface interactions impact PFSA thin-film morphology and uptake behavior
  - Measure with GISAXS, QCM, ellipsometry
  - Complex mechanical/chemical interplay dominated by **substrate** interactions and film **thickness**
    - 50 nm: decrease
    - 20 nm: increase
  - Impact is reduced for:
    - Low IEC, low RH, annealed





Decreasing Film Thickness → Less Structure

A. Kusoglu, et al., ***Adv. Func. Mat.***, in press