2012 DOE Hydrogen and Fuel Cells Program

MANUFACTURING OF LOW-COST, DURABLE MEMBRANE ELECTRODE ASSEMBLIES ENGINEERED FOR RAPID CONDITIONING

PI: F. Colin Busby
W. L. Gore & Associates, Inc.
5/16/2012

Project ID # MN004

Overview

Budget

- Total Project Funding: $4.2MM
  - $2.7MM DOE Share
  - $1.5MM Contractor Share
- Funding received in FY11: $100k
- Planned Funding for FY12: $400k

Timeline

- Project start: 9/01/08
- Project end: 6/30/14
- 70% Percent Complete as of 3/16/12

Barriers Addressed

- Lack of High-Volume MEA Processes
- Stack Material & Mfg. Cost
- MEA Durability

Partners

- University of Delaware (UD)
  - MEA Mechanical Modeling
- University of Tennessee, Knoxville (UTK)
  - Heat/Water Mgmt.Modeling & Validation
- UTC Power, Inc. (UTCP)
  - Stack Testing
- W. L. Gore & Associates, Inc. (Gore)
  - Project Lead

Table 3.4.3 Technical Targets: 80-kW$_e$ (net) Transportation Fuel Cell Stacks Operating on Direct Hydrogen [a]

Characteristic	Units	2003 Status	2005 Status	2010	2015
Cost[e]	$ / kW$_e$	200	70 [f]	25	15
Durability with cycling	hours	N/A	2,000 [g]	5,000 [h]	5,000 [h]

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Relevance: Overall Objective

The overall objective of this project is to develop unique, high-volume[1] manufacturing processes that will produce low-cost[2], durable[3], high-power density[4] 5-Layer MEAs[5] that minimize stack conditioning[6].

1. Mfg. process scalable to fuel cell industry MEA volumes of at least 500k systems/year
2. Mfg. process consistent with achieving \$15/kW_e DOE 2015 transportation stack cost target
3. The product made in the manufacturing process should be at least as durable as the MEA made in the current process for relevant automotive duty cycling test protocols
4. The product developed using the new process must demonstrate power density greater or equal to that of the MEA made by the current process for relevant automotive operating conditions
5. Product form is designed to be compatible with high-volume stack assembly processes: 3-layer MEA roll-good (Anode Electrode + Membrane + Cathode Electrode) with separate rolls of gas diffusion media
6. The stack break-in time should be reduced to 4 hours or less

Table 3.4.3 Technical Targets: 80-kW_e (net) Transportation Fuel Cell Stacks Operating on Direct Hydrogen [a]

Characteristic	Units	2003 Status	2005 Status	2010	2015
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Durability with cycling	hours	N/A	2,000 [g]	5,000 [h]	5,000 [h]

- **<u>RD&D Plan Section 3.4, Task 3, Milestone 38</u>: Evaluate progress toward 2015 targets. (4Q, 2012)**
- **<u>RD&D Plan Section 3.5, Task 1, Milestone 4</u>: Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2013)**

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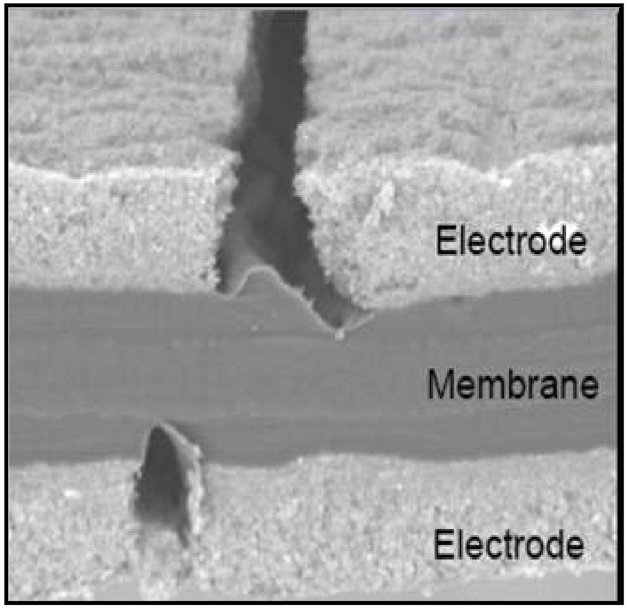
Relevance: Objectives

- Low-cost MEA R&D
  - New 3-Layer (3-L) MEA Process Exploration (Gore)
    - Investigate equipment configuration for MEA production
    - Investigate raw material formulations
    - Map process windows for each layer of the MEA
  - Mechanical Modeling of Reinforced 3-L MEA (UD)
    - Use model to optimize membrane reinforcement for 5,000+ hour durability and maximum performance
  - 5-Layer (5-L) Heat & Water Management Modeling (UTK)
    - Optimization of GDM thermal, thickness, & transport properties to enhance the performance of thin, reinforced membranes and unique properties of direct-coated electrodes using a validated model
  - Optimization (Gore)
    - Execute designed experiments which fully utilize UD and UTK modeling results to improve the new MEA process and achieve the highest possible performance and durability
  - MEA Conditioning (Gore)
  - Evaluate potential for new process to achieve **DOE cost targets** prior to process scale-up (Go / No-Go Decision)
- Scale Up (Gore)
- Stack Validation (UTC)

Approach: Summary

- Reduce MEA & Stack Costs
  - Reduce cost by elimination of intermediate backer materials which are scrapped
  - Reduce number & cost of coating passes
  - Improve safety & reduce process cost by minimizing use of solvents
  - Reduce required conditioning time & costs
- Optimize Durability
  - Balance tradeoffs between mechanical durability and power density of the 3-L construction
- Enabling Technologies:
  - Direct coating: Use coating to form at least one membrane–electrode interface
  - Gore's advanced ePTFE membrane reinforcement & advanced PFSA ionomers enable durable, high-performance MEAs
  - Utilize modeling of mechanical stress and heat / water management to accelerate low-cost MEA optimization
  - Advanced fuel cell testing & diagnostics



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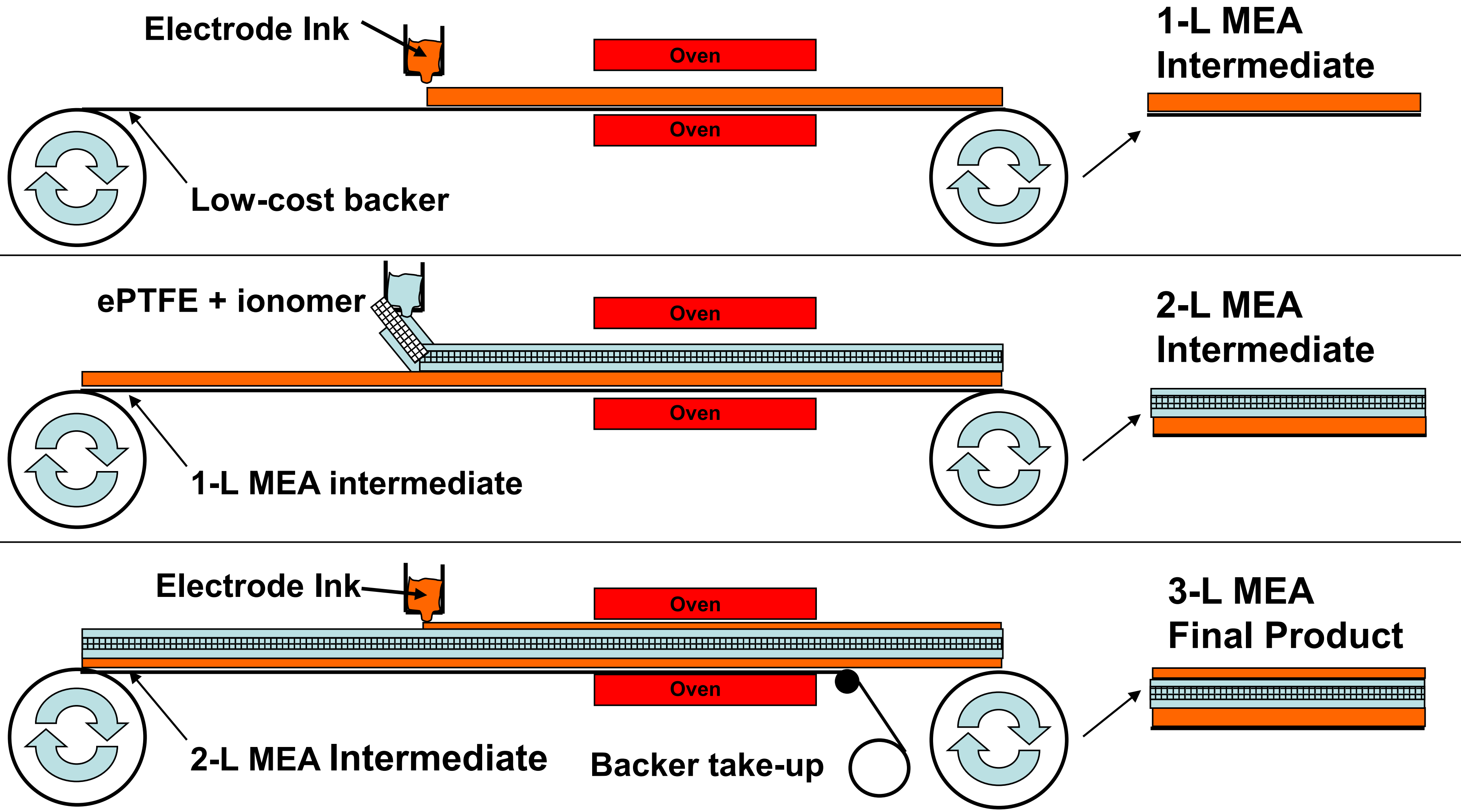
Approach: Low-Cost MEA Mfg Process, Primary Path



Alternate path:

1. Direct coat anode on backer-supported ½ membrane to make 1.5-L MEA intermediate
2. Direct coat cathode on backer-supported ½ membrane to make 1.5-L MEA intermediate
3. Bond membrane-membrane interface of the 1.5-L webs to make a 3-L MEA

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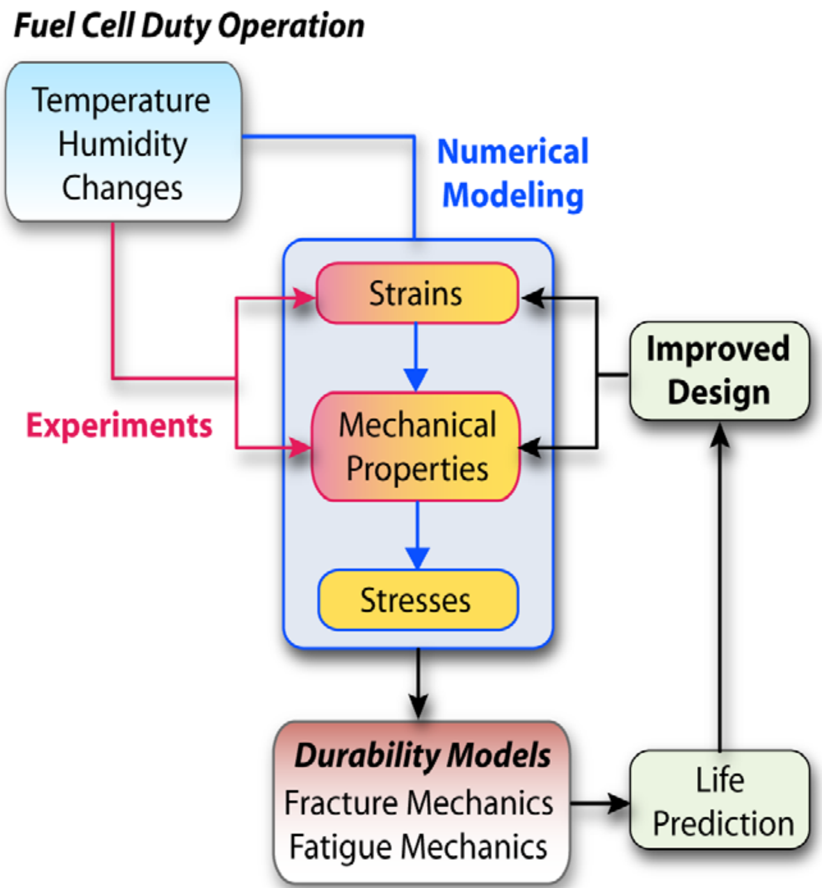
Approach: Mechanical Modeling (UD)

- **Model Concept:**
  Develop a layered structure MEA mechanical model using non-linear (viscoelastic & viscoplastic) membrane and electrode properties to predict MEA stresses for input temperature & relative humidity cycling scenarios

- **Experimental Work:**
  Devise & perform experiments to determine mechanical properties of MEA and reinforced membrane materials as functions of:
  - –Temperature
  - –Humidity
  - –Time

- **Validation Criteria:**
  Model predictions must correlate to in-situ nitrogen RH cycling accelerated mechanical stress test

- **Success Criteria:**
  Use model to optimize membrane reinforcement (5,000+ hour durability and maximum performance) for the MEA that will be made in the new low-cost process



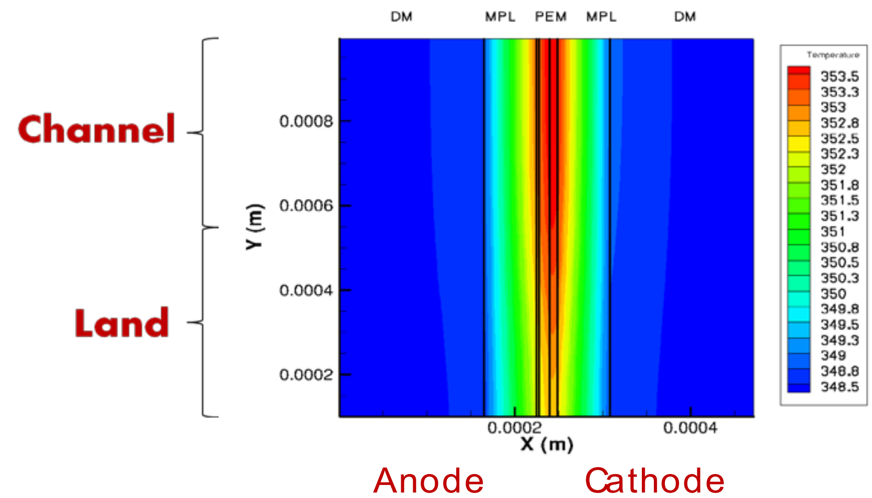
Approach: 5-L Heat & Water Management Modeling (UTK)

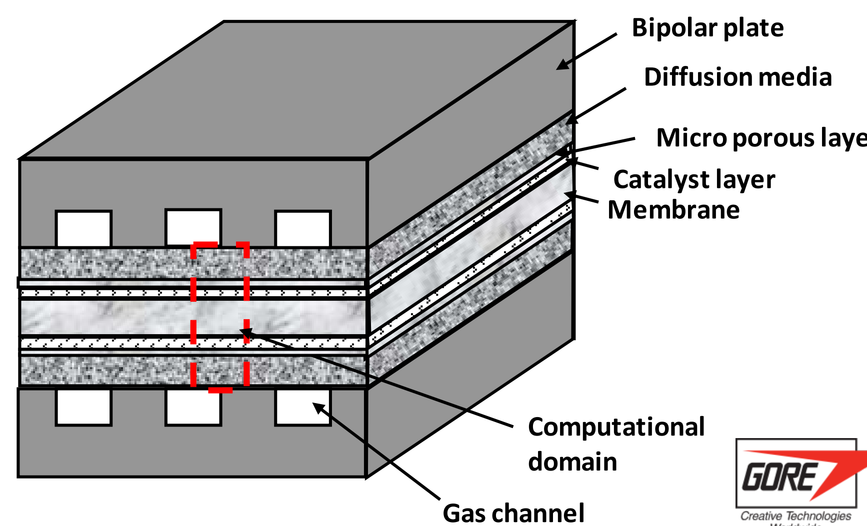
- **Model Concept:**
  Steady state 2D non-isothermal, non-isotropic, performance model. Physics include phase-change induced flow in porous media, condensation/evaporation heat transfer and capillary flow, anode and cathode kinetics with agglomerate based formulation

- **Experimental Work:**
  Determine gas diffusion media properties and perform in-situ 5-L MEA testing (pol curves over a range of targeted operating conditions, EIS, net water balance)

- **Validation Criteria:**
  Model must accurately predict polarization curve and net water transport coefficient for a 5-L structure with a defined range of GDM properties

- **Success Criteria:**
  Optimize GDM thermal, geometric, & transport properties to complement thin, reinforced membranes and unique properties of direct-coated electrodes for the MEA that will be made in the new low-cost process





Technical Accomplishments & Progress: Summary

- Mechanical Modeling of Reinforced 3-L MEA (UD)
  - –Layered model development — 100% Complete
  - –RH & time-dependent mechanical testing — 100% Complete
  - –Parametric analysis of layered structure — 50% Complete

- 5-L Heat & Water Management Modeling (UTK)
  - –Gas diffusion media properties testing — 100% Complete
  - –Performance testing — 100% Complete
  - –Model development — 100% Complete
  - –Computational studies — 100% Complete

- New 3-L MEA Process Exploration (Gore)
  - –Low-cost backer — 90% Complete
  - –Cathode Layer — 90% Complete
    - Power density and robustness BOL testing
    - Electrochemical diagnostics
    - Durability testing
  - –Reinforced Membrane Layer — 85% Complete
    - Power density and robustness BOL testing
  - –Anode Layer — 95% Complete
    - Power density and robustness BOL testing
    - Electrochemical diagnostics

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Technical Accomplishments:

3-L MEA Manufacturing Process Cost Model

2009 cost model results indicate that the modeled process improvements have the potential to reduce MEA cost by 25%

2009 Result

2012 New Process Status Update

2009 Process Waste Map

Membrane Coating

Process Costs	Primary forms of waste	Modeled Process Improvements	2012 Status
Ionomer solution	line losses, edge trim, membrane thickness	Membrane thickness reduction	✓
ePTFE	edge trim		
Backers	all backers	No backers	✓
Solvent/disposables	all		
Process/MOH	time		+
DL	time		+

Electrode Coating

Process Costs	Primary forms of waste	Modeled Process Improvements	2012 Status
Catalyst	line losses, edge trim, electrode residuals	Reduce scrap with better coating process	✓
Backers	all backers	No backers	☆
Solvent/disposables	all		+
Process/MOH	time		+
DL	time		+

3 Layer Roll-Good Finishing Operations

Process Costs	Primary forms of waste	Modeled Process Improvements	2012 Status
Electrode	edge trim	Eliminate this process	✓
Membrane	edge trim	Eliminate this process	✓
Process/MOH	time	Eliminate this process	✓
DL	time	Eliminate this process	✓

✓ = On track to meet expected cost reductions in new process

\+ = Additional cost savings beyond 2009 model assumptions

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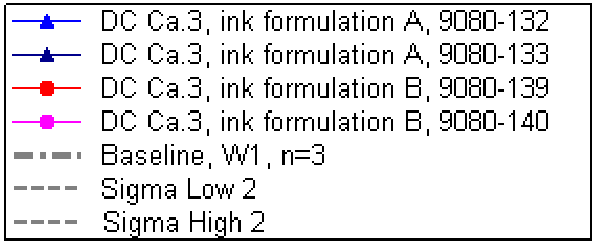
Technical Accomplishments: Excellent Performance of Direct Coated Cathode

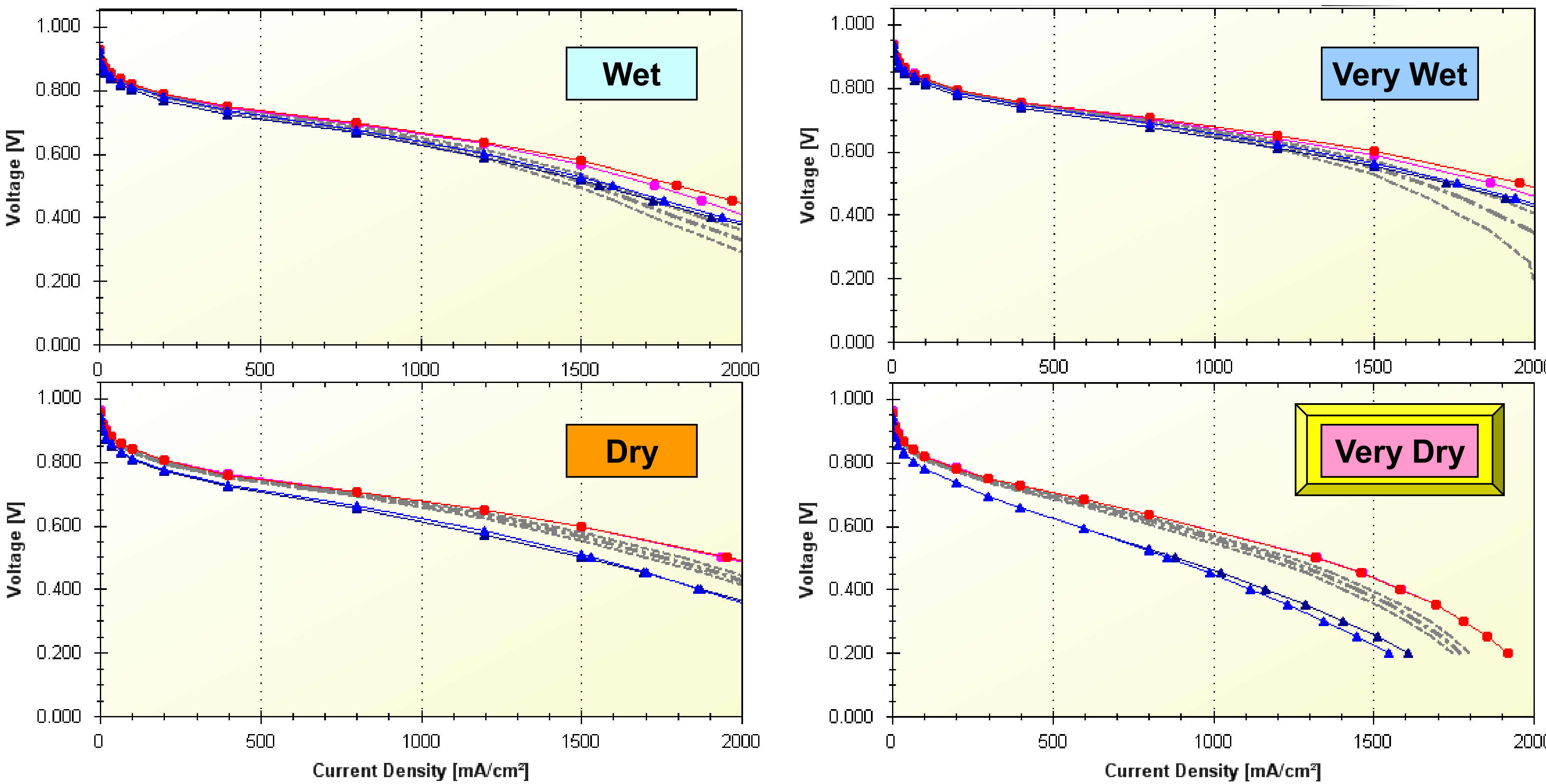


V. Wet: 70°C cell, 80|80°C, S=1.3|2.0, 0 psig, RHavg=170%

Wet: 80°C cell, 80|80°C, S=1.3|2.0, 0 psig, RHavg=112%

Dry: 80°C cell, 55|55°C, S=1.3|2.0, 7.25 psig, RHavg=60%

V. Dry 95°C cell, 55|55°C, S=1.3|2.0, 7.25 psig, RHavg=34%



- 2011 results from small-scale lab coating on previous backer
- Dry high current density performance was significantly increased through direct coating
- Cathode made by primary path process. Control anode & membrane used for all MEAs

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Technical Accomplishments:
New multi-layer low-cost backer

- **Manufacturer of previous backer discontinued the product that had been used for this project**
- **Gore began evaluation of replacement backers in June**
  - **Thickness uniformity**
  - **Mechanical stability up to max drying and piece-part conversion temperatures**
  - **Chemical stability**
  - **Cleanliness**
  - **Electrode release**
  - **Supply chain reliability**
  - **Cost**
- **By August, two promising low-cost multi-layer backer candidates were identified**
- **In December, a non-catalytic test formulation (liquids, ionomer, carbon black) was successfully coated on the most promising backer in a 30 cm wide high-speed-capable roll-to-roll coating/drying process.**
- **Preliminary cost estimate of the low-cost multi-layer back is $2 to $5 per square meter**

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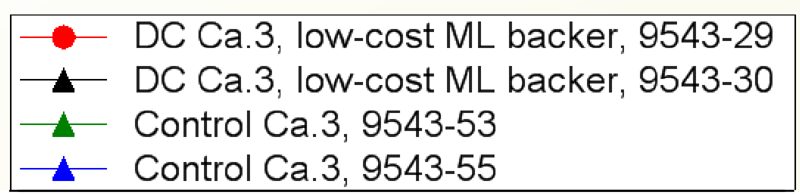
Technical Accomplishments: Excellent Performance of Direct Coated Cathode



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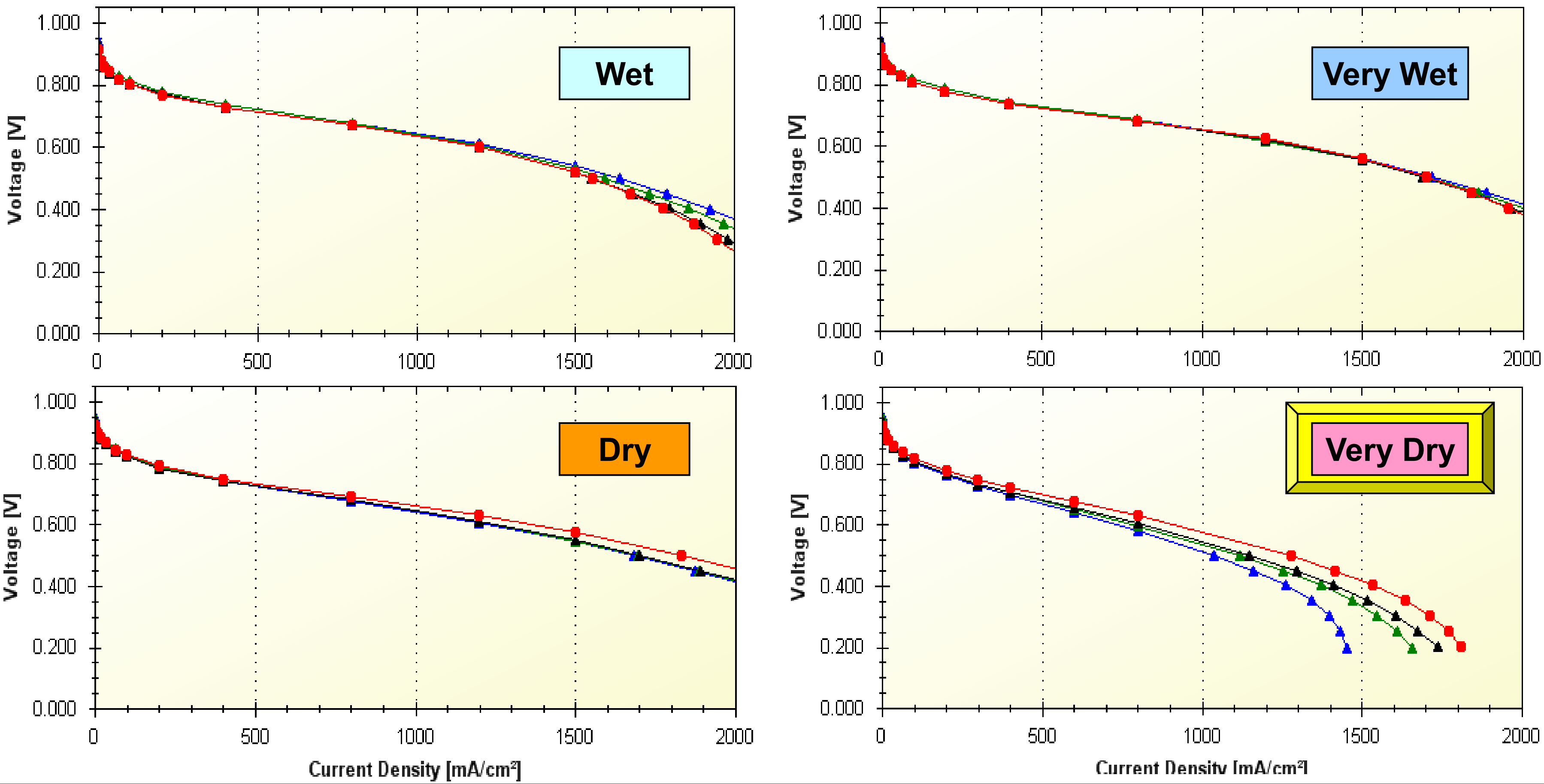

- Ink formulation was modified to optimize performance using new low-cost multi-layer backer
- <u>Cathode made by primary path process</u>. Control anode & membrane used for all MEAs.

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Technical Accomplishments:
DC Cathode Electrochemical Diagnostics

- Standardized protocol that combines BOL robustness testing with key cathode diagnostics at wet and dry conditions
- Test summary
  - **Pre-Conditioning Diagnostics**
    - Cleaning Cyclic Voltammograms (CVs)
    - CV, H_2 Cross-Over, Electrochemical Impedance Spectroscopy (EIS)
  - **Conditioning**
  - **Saturated and Super-Saturated Performance**
    - Polarization Curves, Current Interrupt Resistance, and Stoich Sensitivity
  - **Saturated Diagnostics**
    - He/O_2, O_2 Tafel
    - CV, H_2 Cross-Over, EIS
  - **Sub-Saturated and Hot Sub-Saturated Performance**
    - Polarization Curves, Current Interrupt Resistance, and Stoich Sensitivity
  - **Sub-Saturated Diagnostics**
    - He/O_2, O_2 Tafel
    - CV, H_2 Cross-Over, EIS

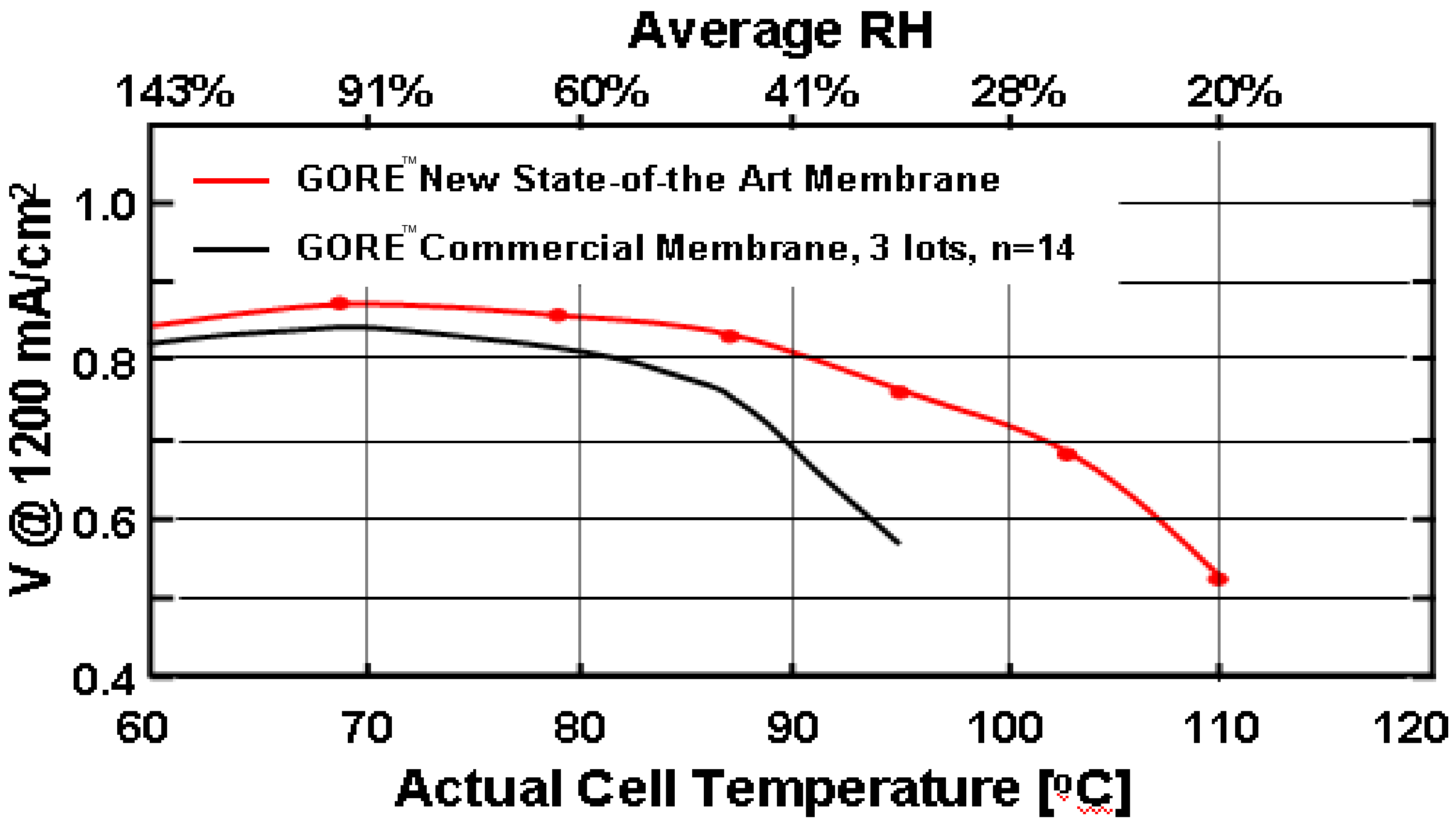
Collected data to quantify oxidized impurities which are associated with conditioning time

Investigated impact of direct-coated electrode structure on molecular diffusion

Quantified ionic conductivity of direct coated cathode

Technical Accomplishments:

Gore's state-of-the-art thin, durable reinforced membrane has been incorporated into the primary path process

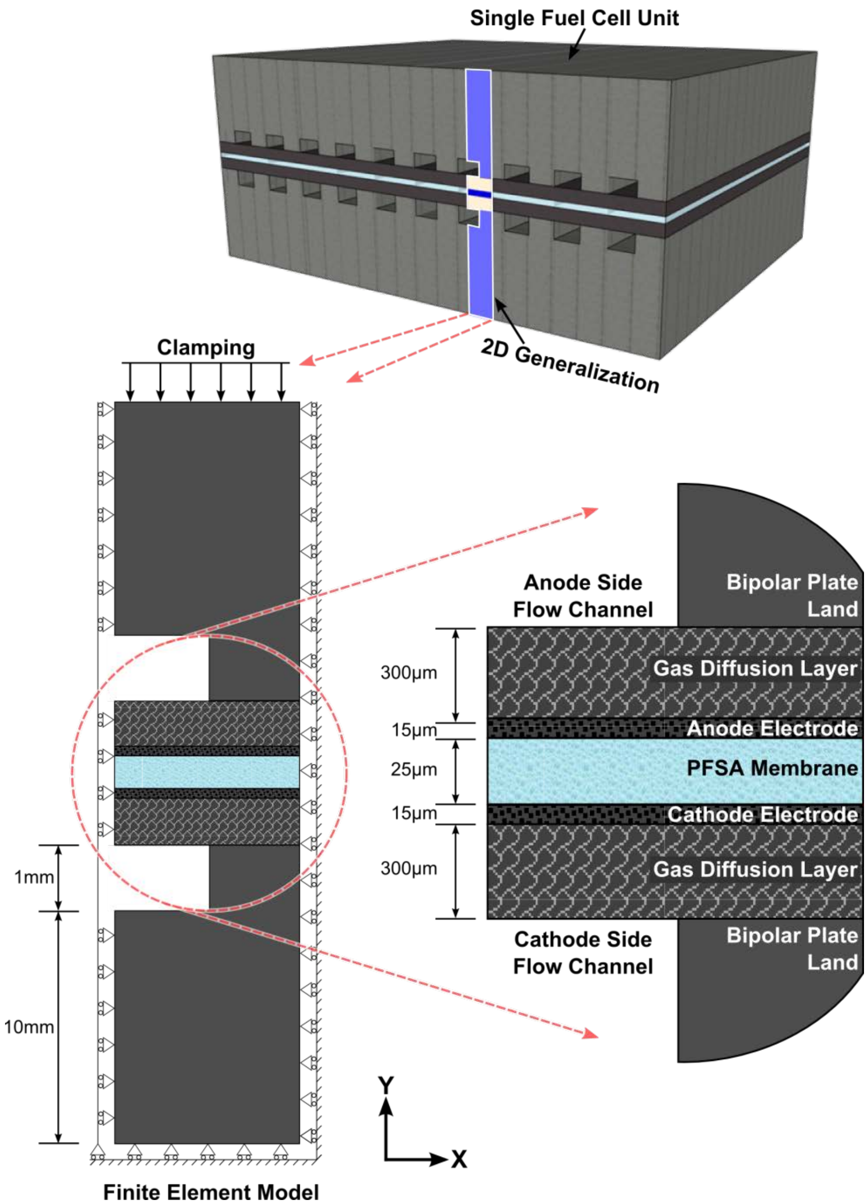


Compared to Gore's current commercial membrane (~20 μm), Gore's thin state-of-the-art membrane (~10 μm) shows greatly enhanced performance at high current density, especially under hot, dry conditions

Note: Membrane Testing Not Funded by DOE

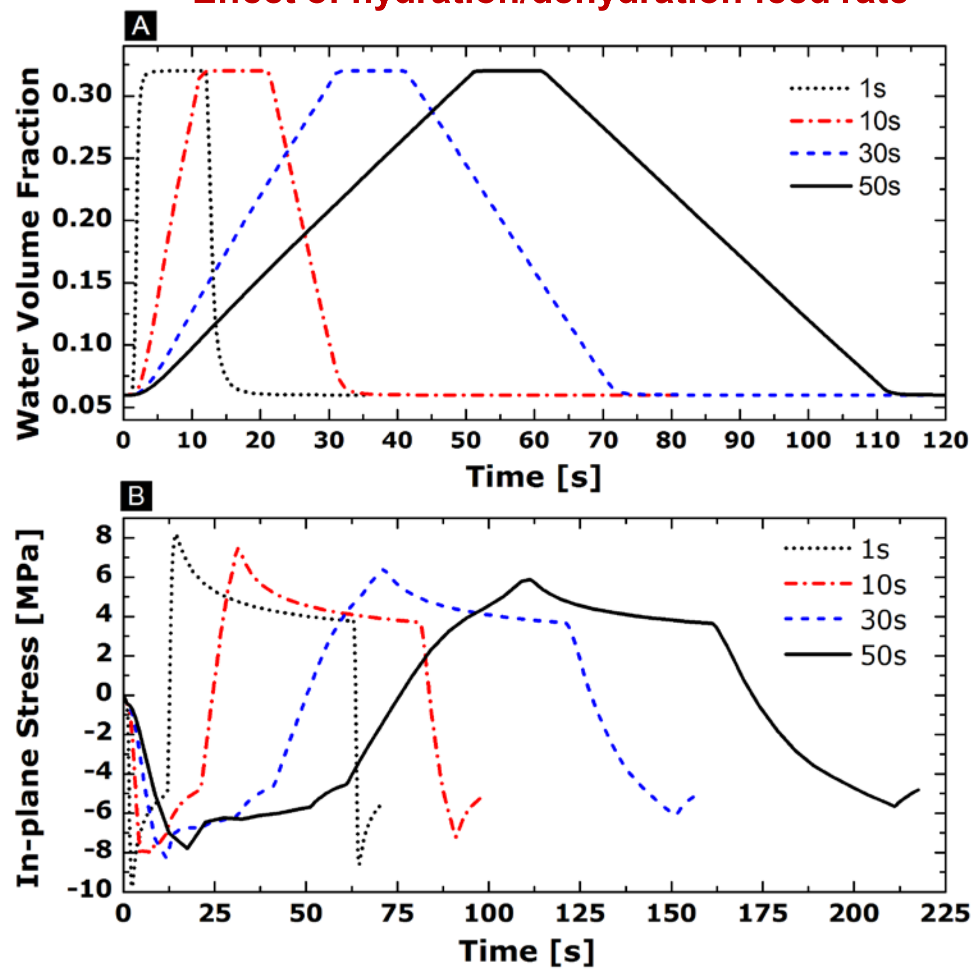
Technical Accomplishments: Mechanical Modeling (UD)

2D Plane Strain Finite Element Model for a Single Cell under RH cycling



Water Volume Fraction	Swelling Strain	Thermal Strain
$\phi_w = \dfrac{18\lambda}{EW/\rho_P + 18\lambda}$	$\varepsilon^{sw} = \left(\dfrac{\theta + 273}{\theta_0 + 273}\right)\ln(1-\phi_w)$	$\varepsilon^{th} = \alpha(\theta - \theta_0)$

Effect of hydration/dehydration feed rate



Technical Accomplishments: Mechanical Modeling (UD)

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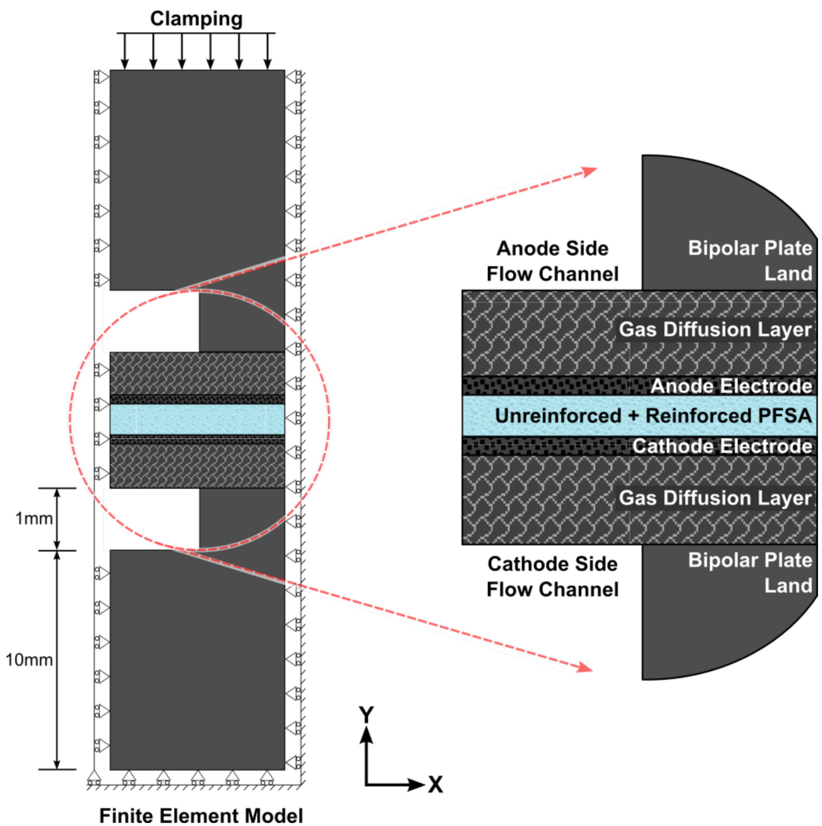
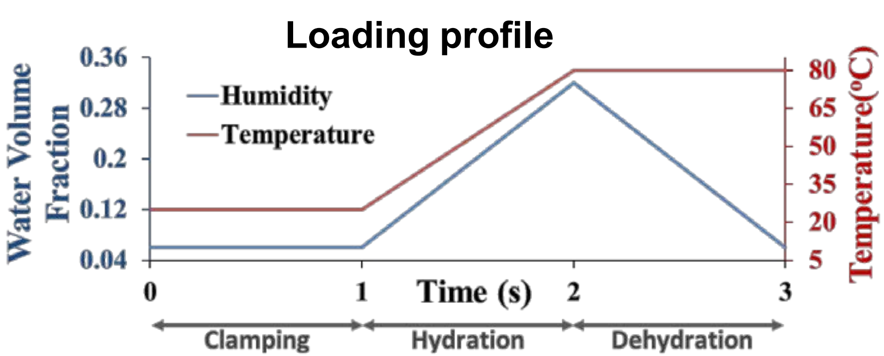
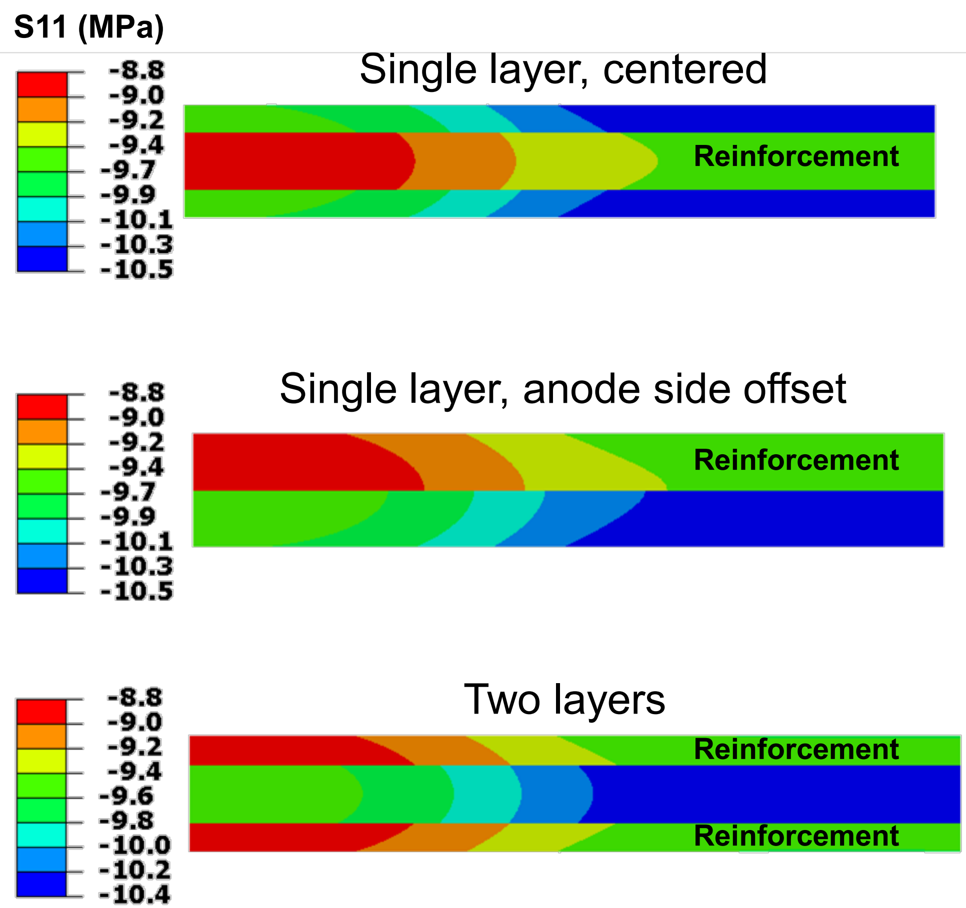




In-plane stress contours after hydration

Total membrane thickness = 10μm

Reinforcement thickness = 5μm



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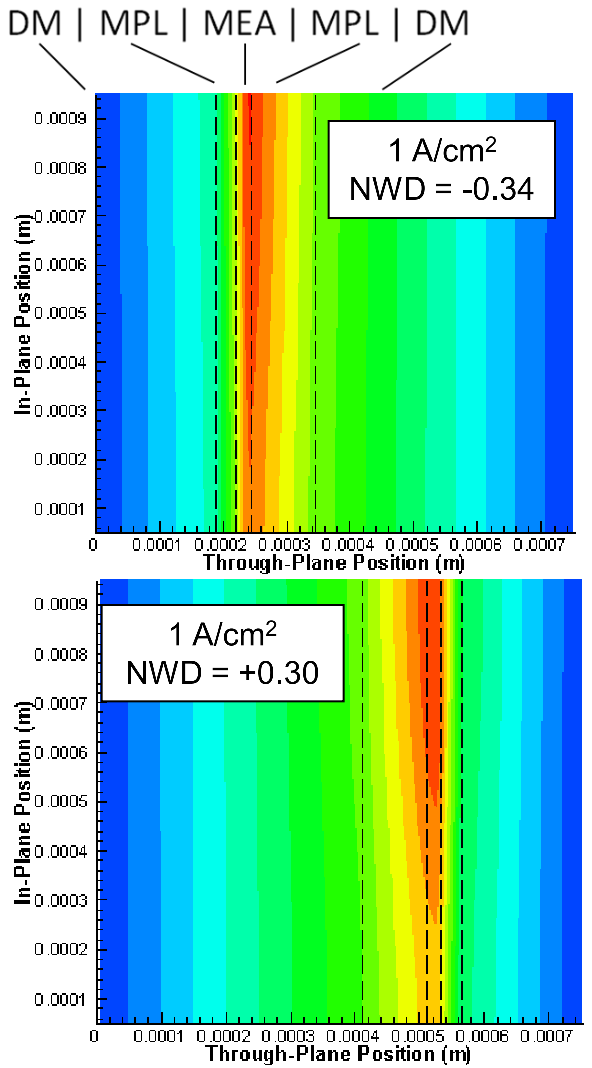
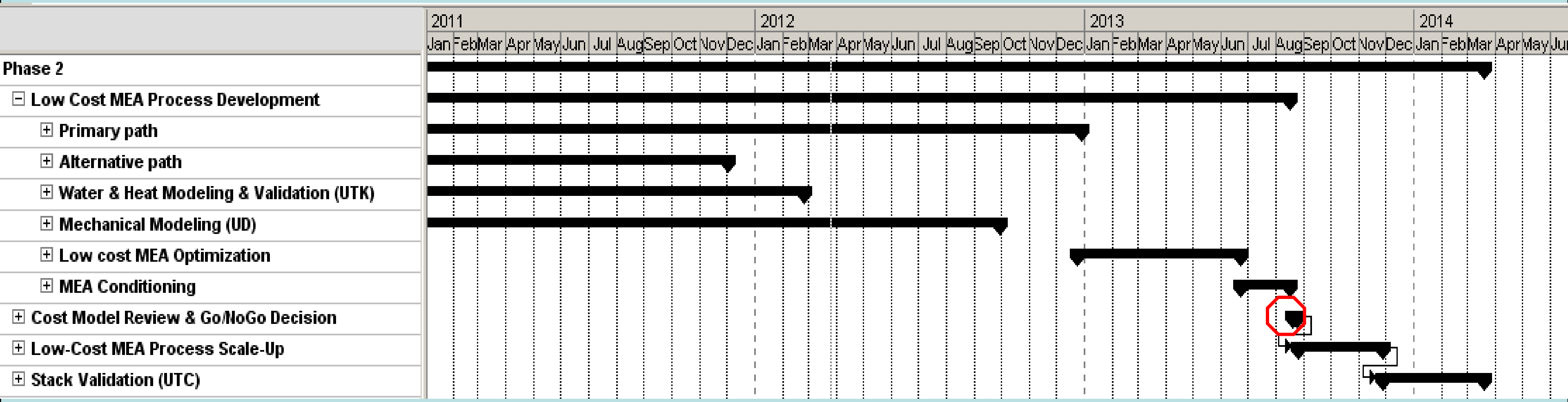
Technical Accomplishments:
5-L Heat & Water Management Modeling (UTK)

- 2-D Model with multi-phase physics, phase-change induced flow, multi-component diffusion, and agglomerate based resistance in electrodes completed.
- As GDL gets thinner and highly conductive, role of MPL in thermal boundary becomes dominant, and ***MPL and CL thermal conductivity are key engineering parameters***.
- Study of impact of porosity, permeability, thickness and conductivity of MPL was conducted.
    - ➢MPL thickness is the strongest parameter. Thinner is better for all cases wet and dry.
    - ➢For high temperature, dry conditions, high thermal conductivity is critical at higher current, but insignificant at low current while in wet conditions, a low MPL thermal conductivity is desired.
    - ➢Porosity and through plane permeability only becomes critical at high current wet conditions.
- Study of asymmetric material combinations was completed to assess maximum thermal redistribution impact with conventional materials.

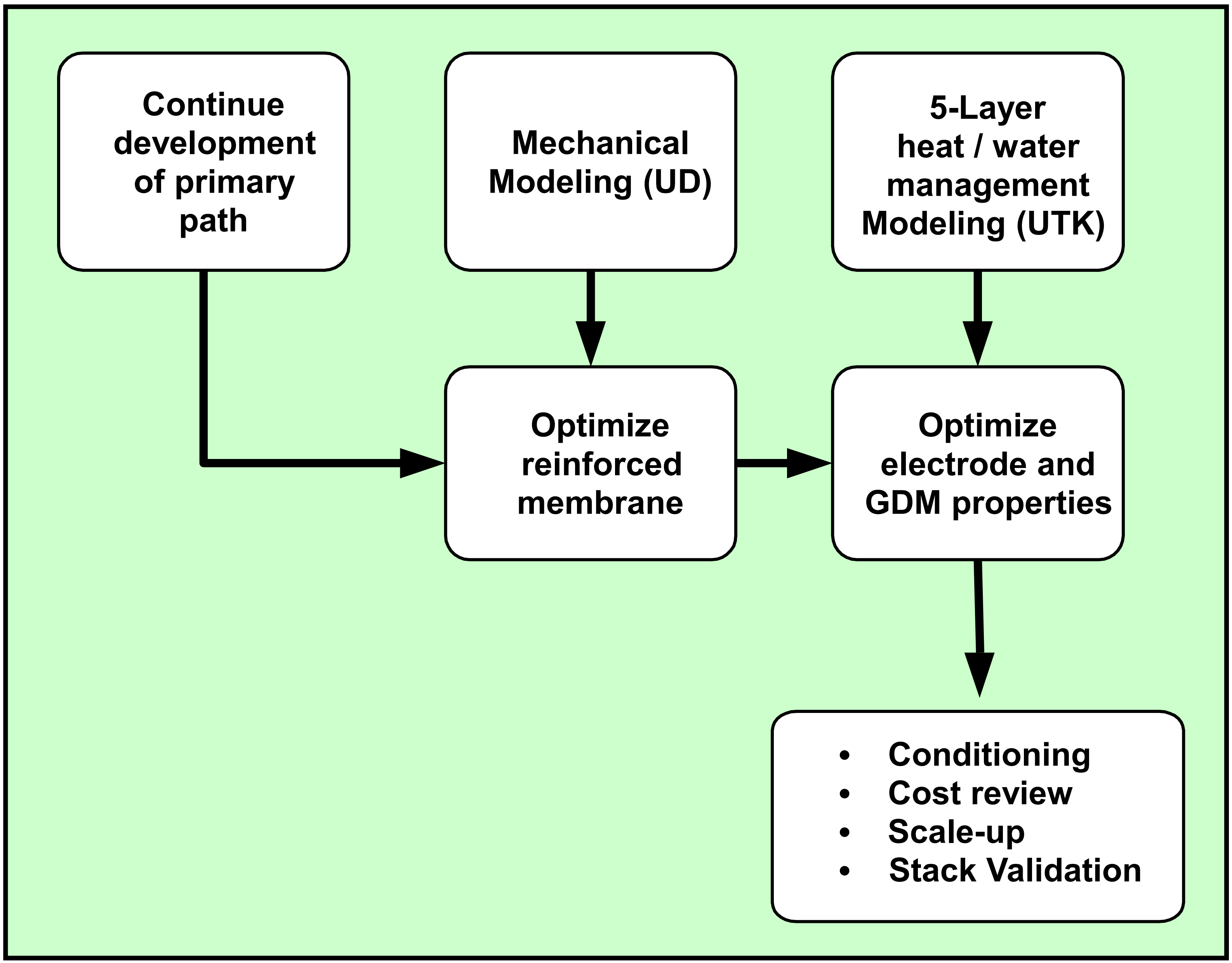


With asymmetric materials, temperature gradient peak and water transport can be shifted considerably to prevent dryout.

Proposed Future Work for FY12: Summary



Proposed Future Work for FY12: Summary



Collaborations

- University of Delaware (academic, sub-contractor)
  - MEA Mechanical Modeling
  - A. Karlsson & M. Santare
- University of Tennessee, Knoxville (academic, sub-contractor)
  - 5-Layer Heat and Water Management Modeling and Validation
  - M. Mench
- UTC Power, Inc. (industry, sub-contractor)
  - Stack Testing
  - T. Skiba
- NREL (federal, collaborator)
  - On-line quality control systems research
  - M. Ulsh
- W. L. Gore & Associates, Inc. (industry, lead)
  - Project Lead
  - F. Busby

Summary (1)

- **The overall objective of this project is to develop unique, high-volume manufacturing processes that will produce low-cost, durable, high-power density 5-Layer MEAs that minimize stack conditioning.**
- **Approach:**
  - **Reduce MEA & Stack Costs**
    - Reduce the cost of intermediate backer materials
    - Reduce number & cost of coating passes
    - Improve safety & reduce process cost by minimizing solvent use
    - Reduce required conditioning time & costs
  - **Optimize Durability**
    - Balance tradeoffs between mechanical durability and power density of the 3-L construction
  - **Unique Enabling Technologies**
    - Develop Direct Coating: To form *at least* one membrane–electrode interface
    - Gore's Advanced ePTFE membrane reinforcement & advanced PFSA ionomers enable durable, high-power density MEAs
    - Utilize modeling of mechanical stress and heat / water management to accelerate low-cost MEA optimization
    - Advanced fuel cell testing & diagnostics

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Summary (2)

- **Key Accomplishments**
  - The primary path for the new 3-L MEA process has succeeded in incorporating the previously modeled process improvements which indicated potential for a **25% reduction in high-volume 3-L MEA cost**
  - Despite a significant timeline extension due to federal funding constraints, lab scale development of the new 3-L MEA process is nearing completion
    - New low-cost multi-layer backer has been proven on a roll-to-roll process and implemented in the primary path
    - Current density of un-optimized direct-coated electrodes is equivalent to or better than current commercial electrodes over a robust range of automotive operating conditions
    - Gore has demonstrated a 10 μm reinforced membrane that is used in the new low-cost process and can meet automotive power density and durability targets
    - Model development at UD and UTK is complete and both partners are on track to enable efficient optimization of the new 3-L MEA process
- The combination of Gore's advanced materials, expertise in MEA manufacturing, & fuel cell testing in partnership with the mechanical modeling experience of UD and the heat and water management experience of UTK enables a robust approach to developing a new low-cost MEA manufacturing process

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Acknowledgements:

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- Feng-Yuan Zhang

University of Delaware
- Anette Karlsson
- Mike Santare
- Narinder Singh
- Zongwen Lu

UTC Power, Inc.
- Tom Skiba

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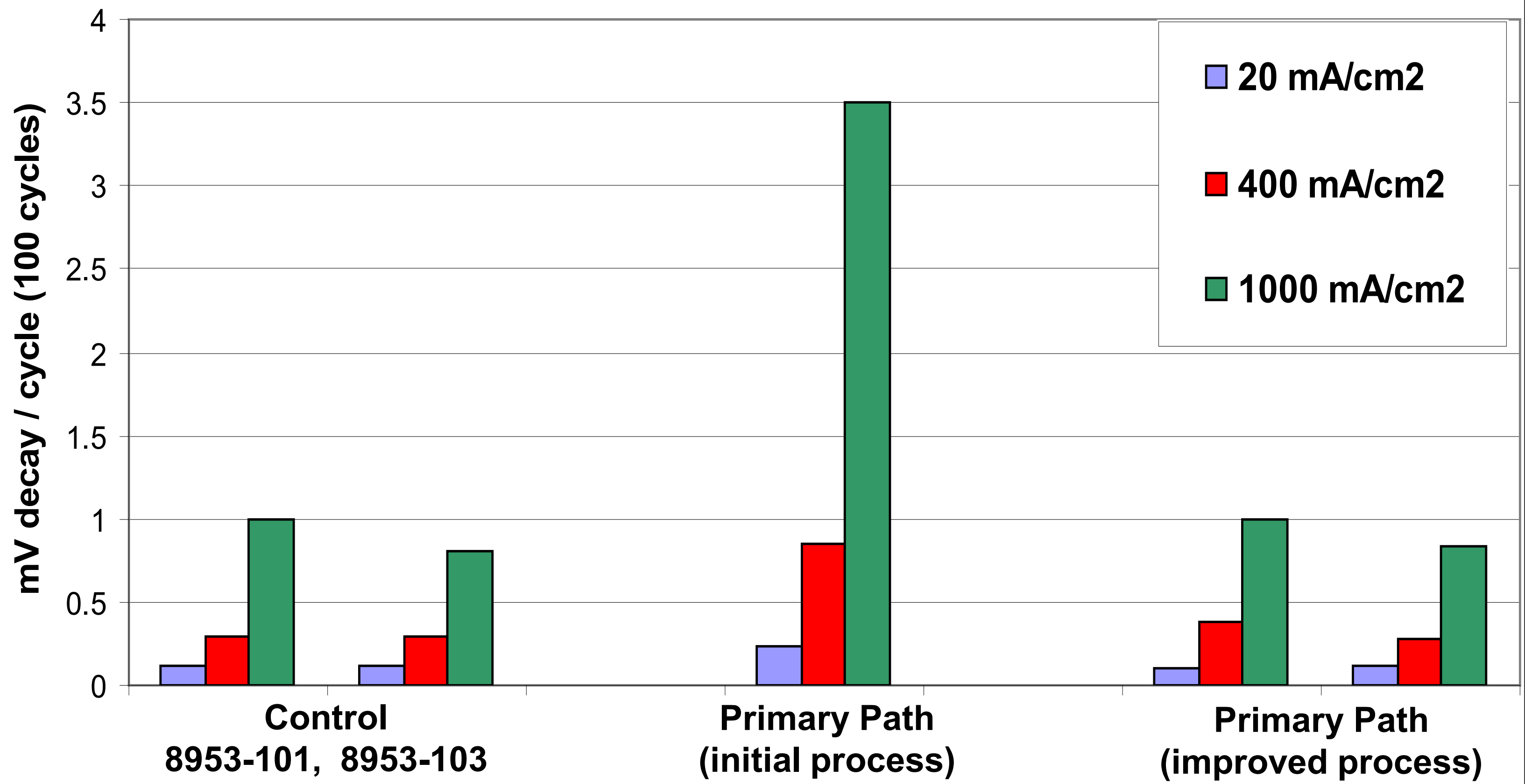
Technical Back Up Slides

Technical Accomplishments:

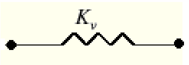
Cathode electrode made by the improved primary path process has demonstrated start/stop durability equivalent to the current commercial control electrode



Data from 2011 AMR

Technical Accomplishments: Mechanical Modeling (UD)

Constitutive Model: Visco-elastic-plastic Model



$$\sigma = K\ \varepsilon$$

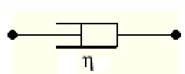
Spring Element
Strain dependence

K_P

(Long-term modulus)

$K_P + K_v$

(Instantaneous modulus)



$$\sigma = \eta \dot{\varepsilon}$$

Dashpot Element
Strain-rate dependence

$$\dot{\varepsilon}_v = A(\sigma_v)^n$$

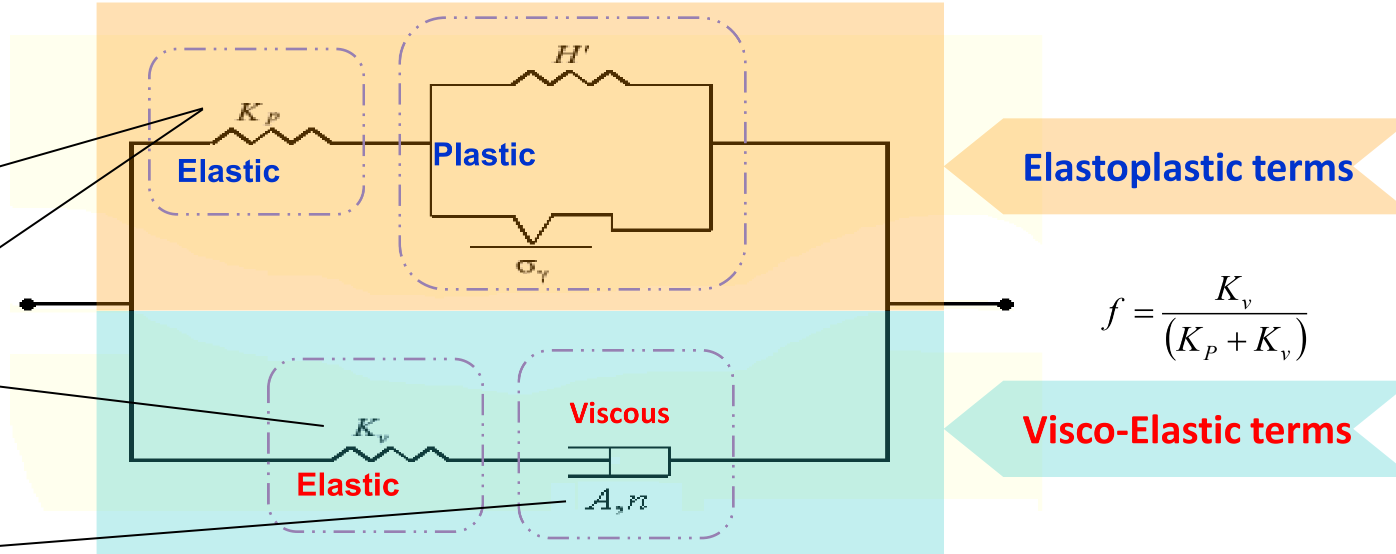
Viscous power law

Parameters

A, n, f, θ, λ

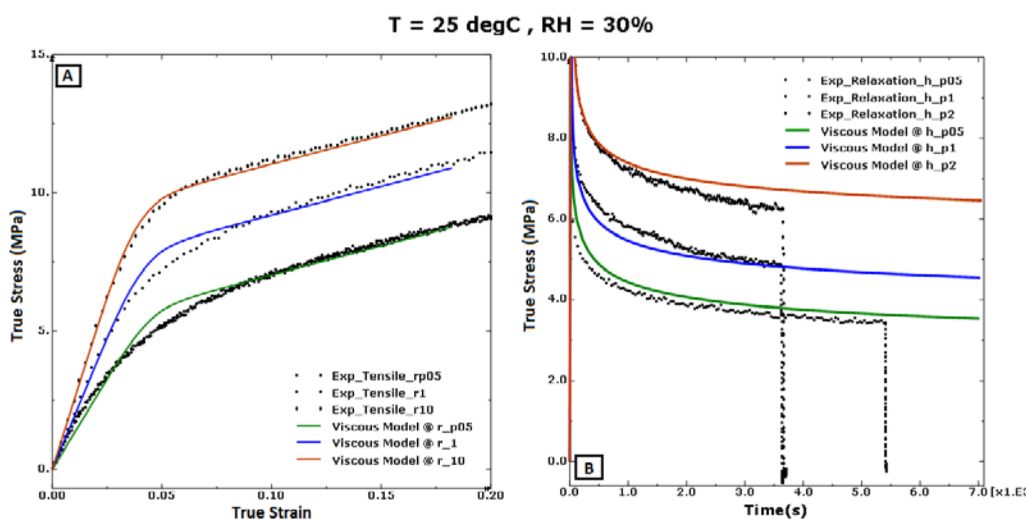
$E(K_P + K_V),$

$\upsilon, \sigma_{yield}, H$



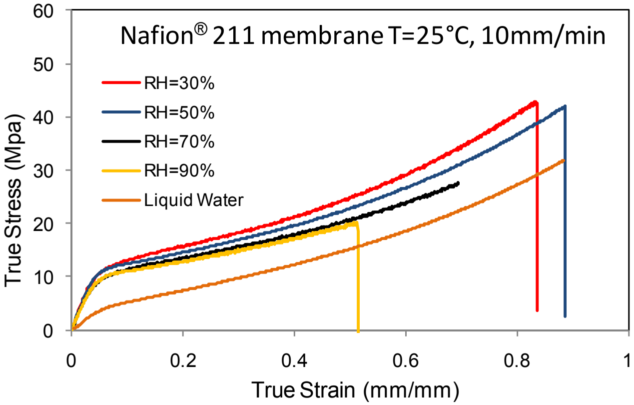
$$f = \frac{K_v}{(K_P + K_v)}$$

Visco-elastic-plastic model is tuned to match measured constitutive responses for MEA materials



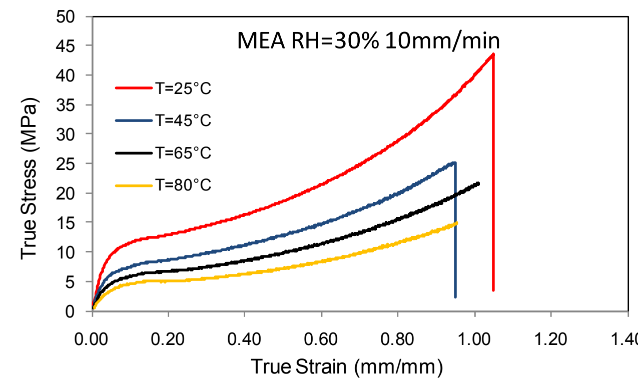
Technical Accomplishments: Mechanical Modeling (UD)

Properties of NAFION® 211 membrane, MEA and Reinforced PFSA measured

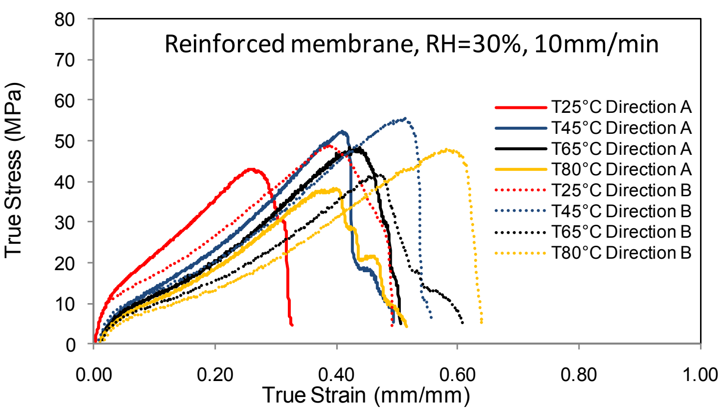


Condition	Rate	K_V [MPa]	K_P [MPa]	A	n	σ_y [MPa]	H [MPa]
T=25, RH=30%	1mm/min	160	31	1.50E-09	6.5	1.55	19.8
	10mm/min	220	31	3.00E-09	6.5		
T=80, RH=30%	10mm/min	80	10.64	1.00E-05	4.5	0.532	7.0
	250mm/min	127	10.64	5.00E-06	4.5		

Visco-elasto-plastic properties of NAFION® 211 membrane determined



Visco-elasto-plastic behavior of MEA determined. Follows trends similar to membrane, but lower stress, indicating electrodes are less stiff than membrane



Visco-elasto-plastic behavior of reinforced membrane determined. Properties anisotropic and much stiffer than homogenous membrane. Visco-elasto-plastic properties nearly independent of humidity

True stresses are instantaneous force (measured) divided by instantaneous cross sectional area (calculated)

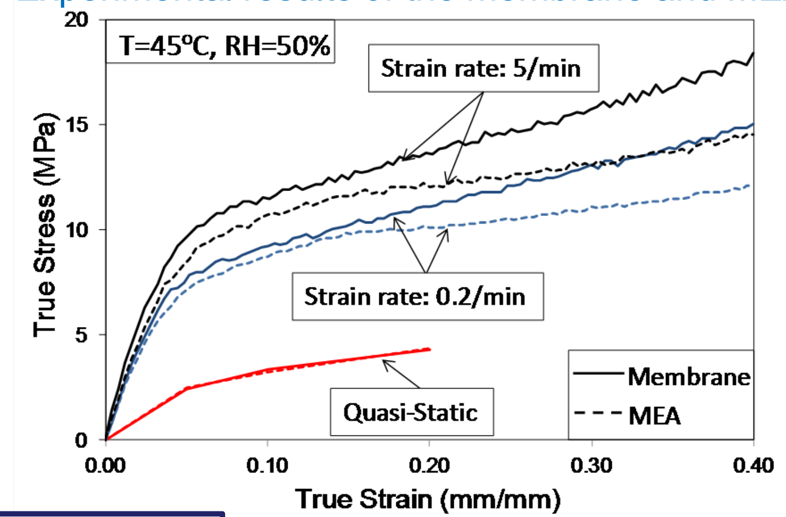
Technical Accomplishments: Mechanical Modeling (UD)

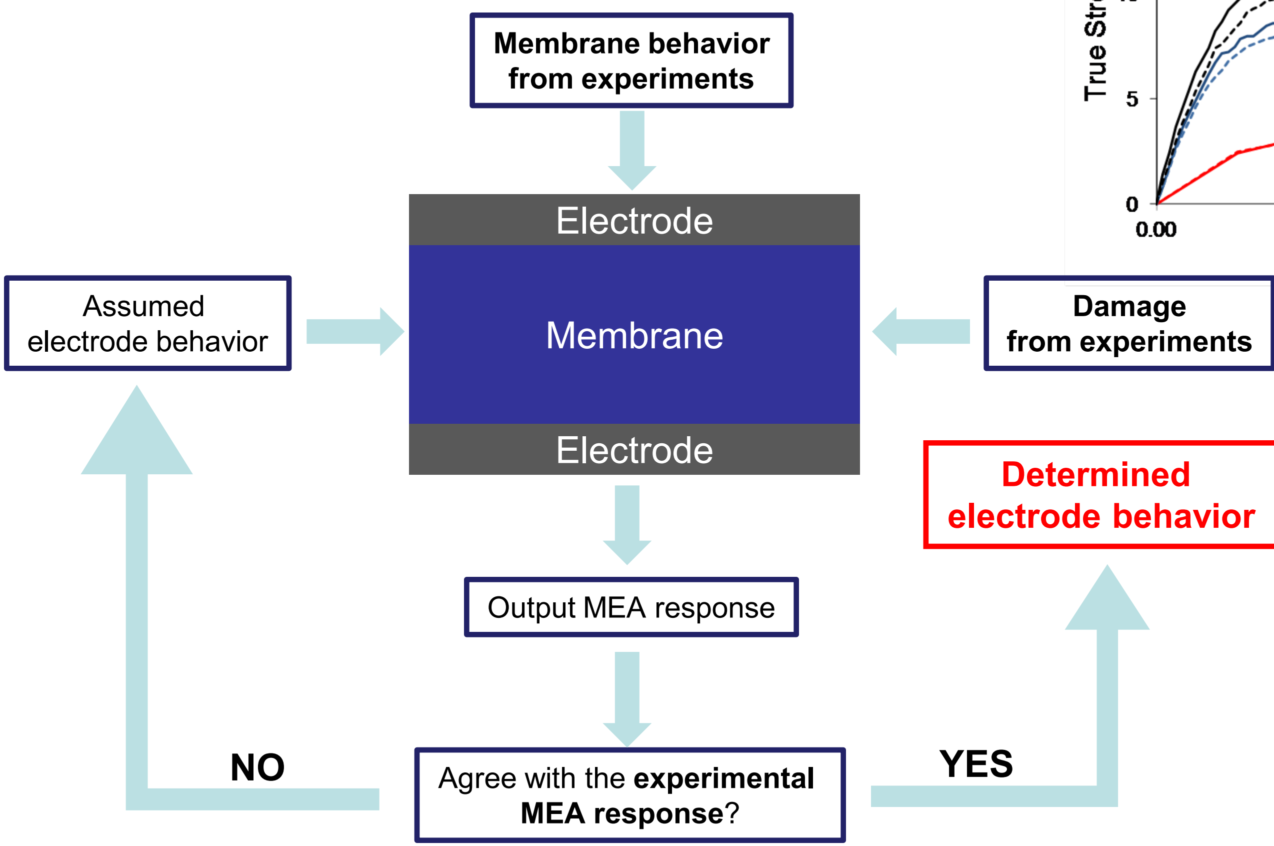
Determination of PEMFC Electrode Mechanical Properties

General methodology

- Within linear elastic region:
  Rule of mixtures
- Beyond linear elastic region:
  Reverse analysis using finite element model (ABAQUS 6.9)

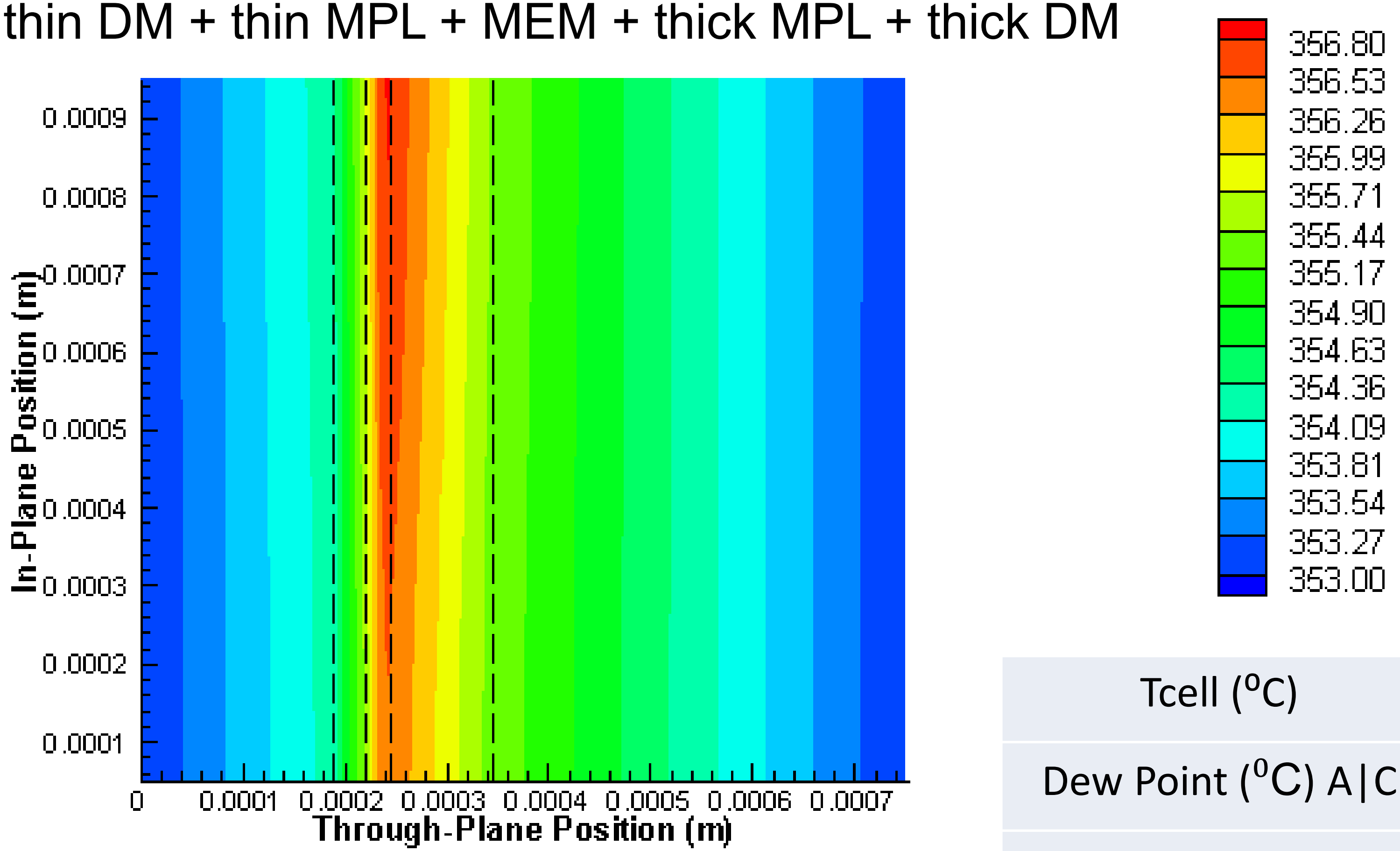
Experimental results of the membrane and MEA





Technical Accomplishments: Asymmetrical GDL modeling thin anode, thick cathode, 1A/cm², V=0.53

thin DM + thin MPL + MEM + thick MPL + thick DM



NWD = -0.345

Tcell (°C)	80
Dew Point (°C) A|C	80 | 80
Back Pressure (kPa)	0
Stoich A|C	1.3 | 2.0