2013 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.
5/15/2013

Project ID # MN004

Overview

Budget

- Total Project Funding: $4.2MM
  - $2.7MM DOE Share
  - $1.5MM Contractor Share
- Funding received in FY12: $ 400k
- Funding for FY13: $ 502k

Timeline

- Project start: 9/01/08
- Project end: 6/30/14
- 80% complete as of 4/11/13

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 Management Modeling
- UTC Power
  - Stack Testing
- W. L. Gore & Associates, Inc. (Gore)
  - Project Lead

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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 $9/kW DOE 2017 automotive MEA 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 3.4.14 Technical Targets: Membrane Electrode Assemblies

Characteristic	Units	2011 Status [a]	2017 Targets	2020 Targets
Cost[c]	$ / kW	13 (without frame and gasket) 16 (including frame and gasket)[d]	9	7
Durability with cycling	hours	9,000[e]	5,000[f]	5,000[f]

- **RD&D Plan Section 3.4, Task 10.1: Test and evaluate fuel cell systems and components such as MEAs, short stacks, bipolar plates, catalysts, membranes, etc. and compare to targets. (3Q, 2011 thru 3Q, 2020)**
- **RD&D Plan Section 3.4, Task 10.2: Update fuel cell technology cost estimate for 80 kW transportation systems and compare it to targeted values. (3Q, 2011 thru 3Q, 2020)**

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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)

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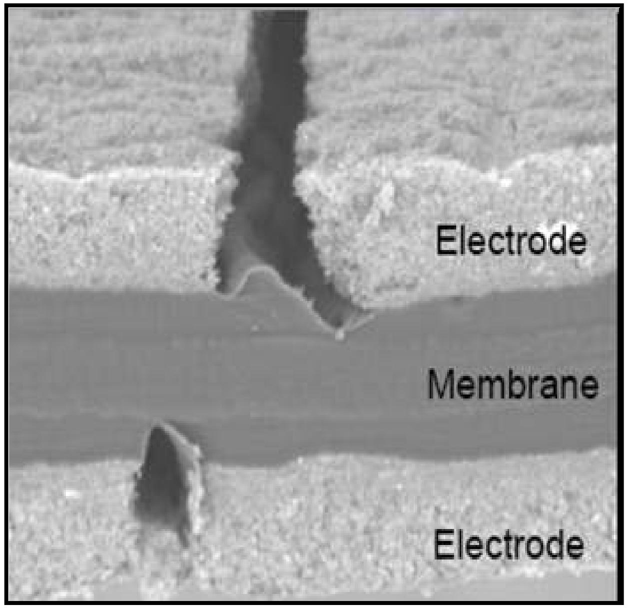
Approach: Summary

- 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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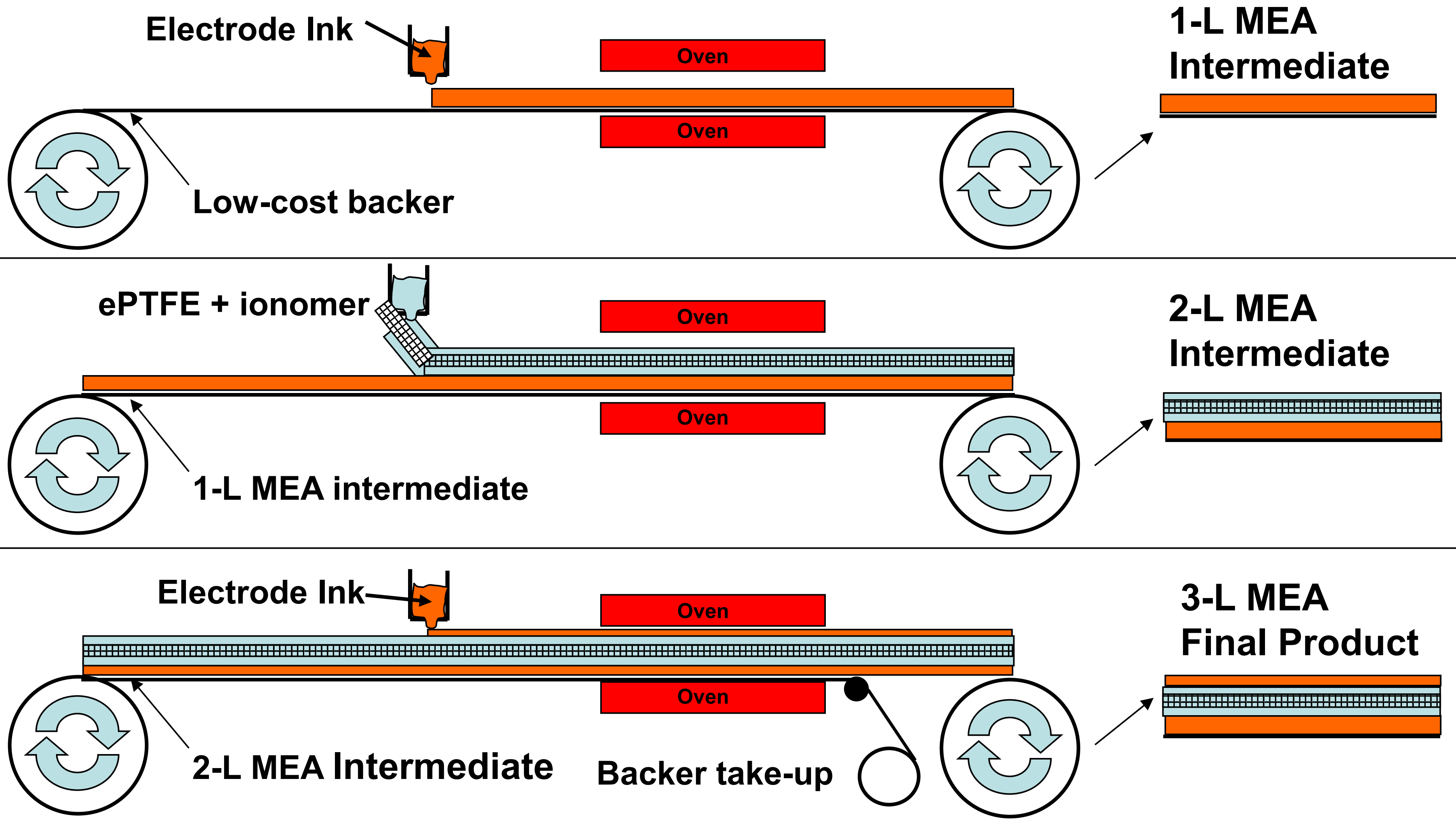
Approach: Low-Cost MEA Mfg Process, Primary Path



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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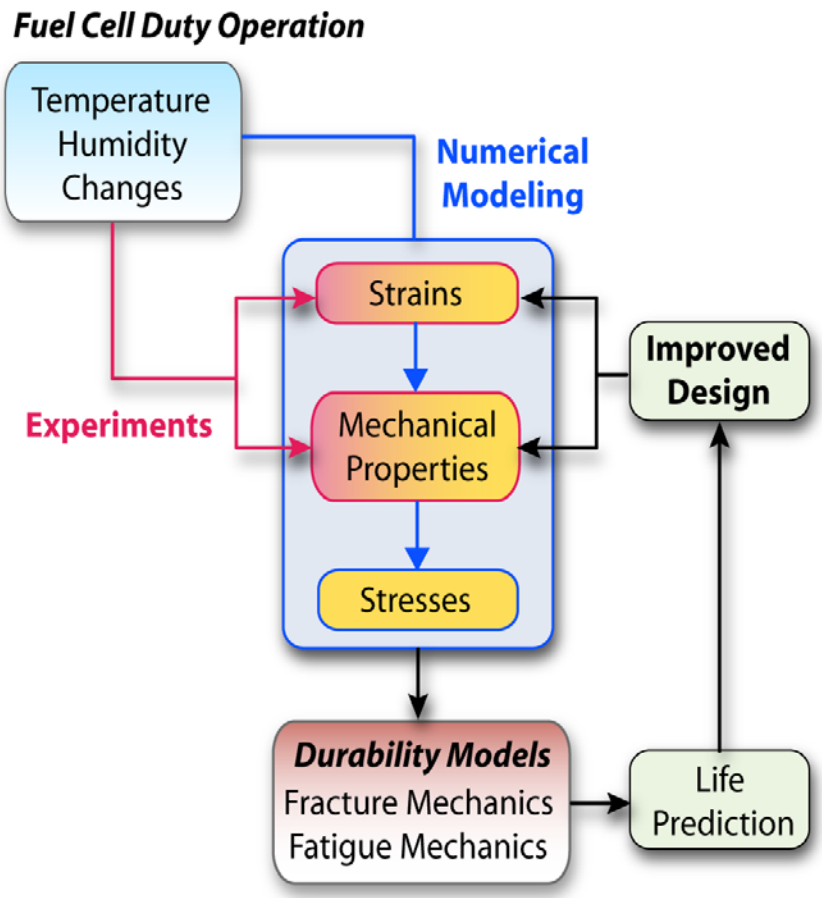
Approach: Mechanical Modeling (UD)

- **Model Concept:**
  Develop a layered structure MEA mechanical model using non-linear (viscoelastic & viscoplastic) membrane and electrode properties to predict MEA stresses and fatigue failure 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



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 80% Complete
  - –Fatigue analysis of layered structure 30% Complete

- New 3-L MEA Process Exploration (Gore)
  - –Low-cost backer 100% Complete
  - –Cathode Layer 95% Complete
    - Power density and robustness beginning of life (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
  - –Cost analysis (Gore and SA collaboration) 100% Complete

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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

2013 New Process Status Update

2009 Process Waste Map

Membrane Coating

Process Costs	Primary forms of waste	Modeled Process Improvements	2013 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	2013 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	2013 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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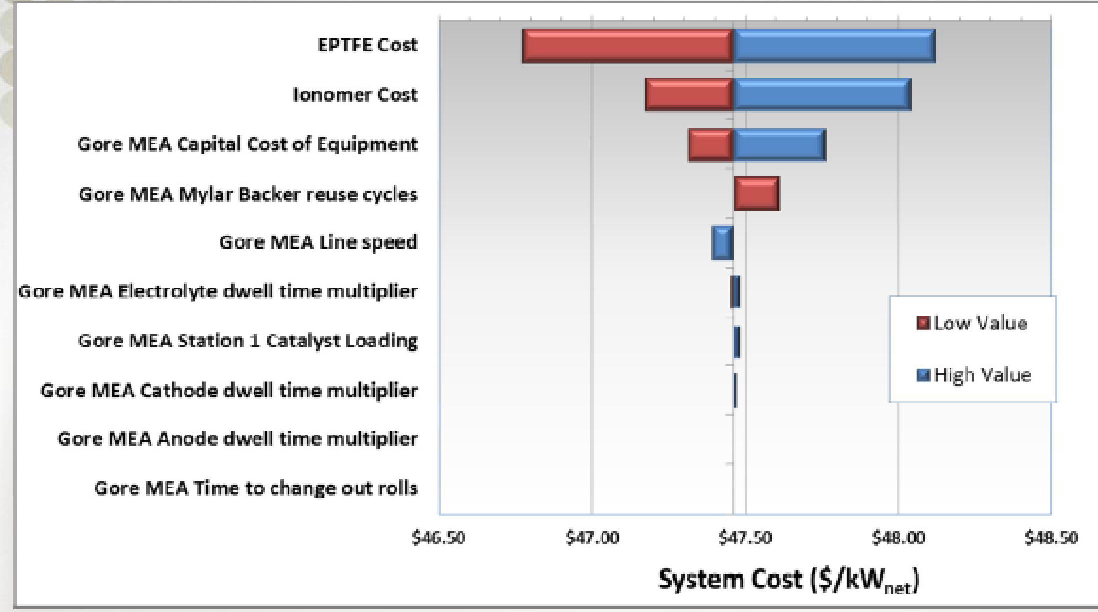
Technical Accomplishments:
Gore and SA Cost Model Collaboration

MEA Sensitivity



System Cost ($/kWnet), 500,000 sys/year				
Parameter	Units	Low Value	Base Value	High Value
EPTFE Cost	$/m^2	1.82	6	10
Ionomer Cost	Multiplier	0.5	1	2
Gore MEA Capital Cost of Equipment	Multiplier	0.5	1	2
Gore MEA Mylar Backer reuse cycles	cycles	1	5	10
Gore MEA Line speed	m/min	3	10	300
Gore MEA Electrolyte dwell time multiplier	multiplier	0.5	1	2
Gore MEA Station 1 Catalyst Loading	mg/cm2	-	0.05	0.146
Gore MEA Cathode dwell time multiplier	multiplier	0.5	1	2
Gore MEA Anode dwell time multiplier	multiplier	0.5	1	2
Gore MEA Time to change out rolls	min	1	10	-
2013 Auto System Cost			$47.46	

- Top three cost uncertainties:
  - ePTFE cost
  - Maximum coating speed
  - Ionomer cost
- None the less, MEA uncertainty is still only~ +/-2% for each variable.
- Caveat: MEA performance assumed to equal that of modeled 3M NSTF MEA

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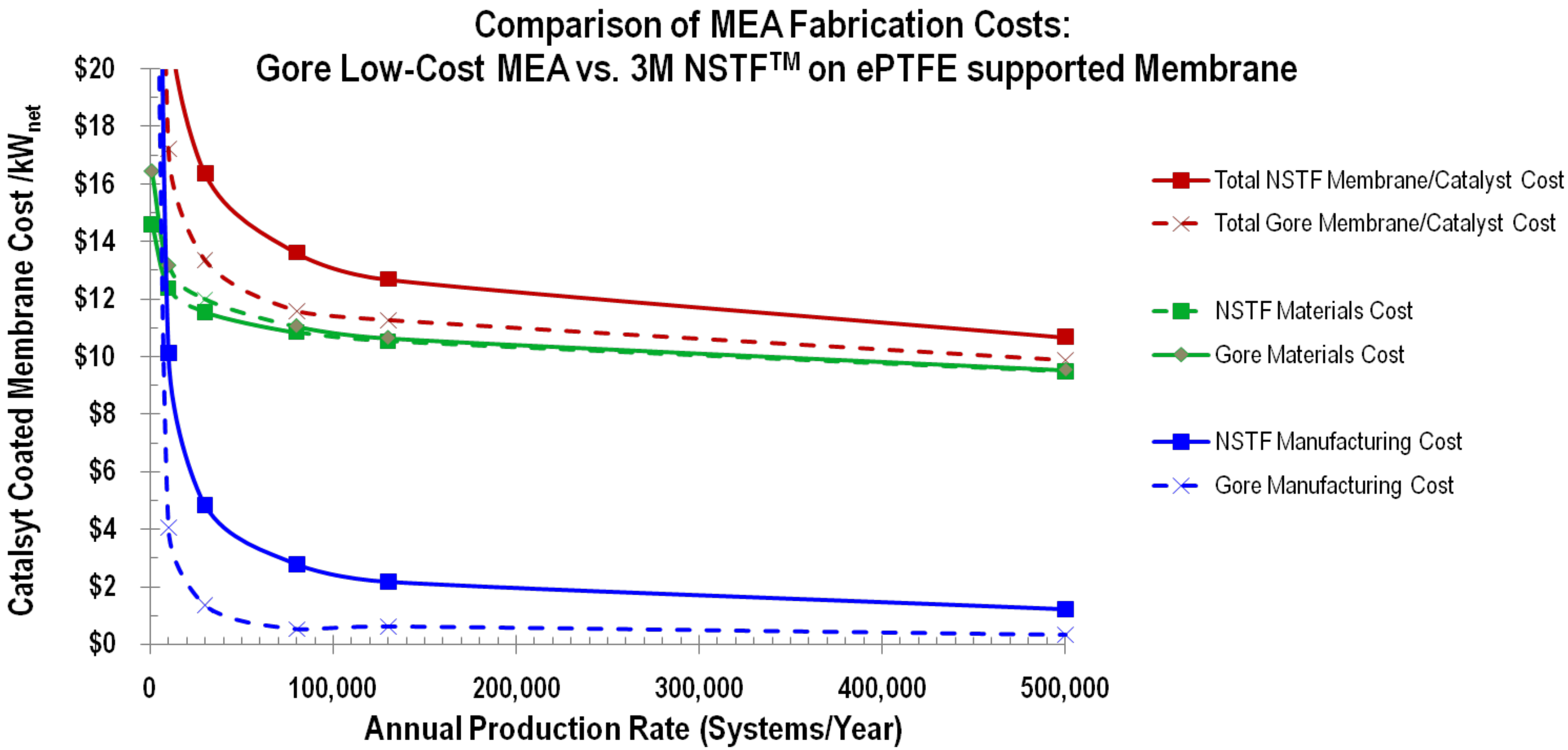
Technical Accomplishments:

Gore and SA Cost Model Collaboration

Gore MEAs and 3M NSTF™/Membrane Catalyst Coated Membrane are expected to have similar costs



- Material costs are about the same (since dominated by Pt cost)
- Gore processing costs are expected to be lower due to non-vacuum processing and faster line speeds
- Total costs are quite similar
- Polarization performance is critical factor in selection

Technical Accomplishments:
New multi-layer low-cost backer(s)

- Gore began evaluation of low-cost backers in June 2011
  - Thickness uniformity
  - Mechanical stability up to max drying and piece-part conversion temperatures
  - Chemical stability
  - Cleanliness
  - Electrode release
  - Supply chain reliability
  - Cost
- By August 2011, two promising low-cost multi-layer backer candidates were identified
- In June 2012, electrode was coated on the most promising backer in a 30 cm wide high-speed-capable roll-to-roll coating/drying process. Release and BOL performance exceeded the targets, and work on roll-to-roll direct-coating of the membrane layer was begun.
- After a successful root-cause analysis and multiple unsuccessful attempts to eliminate direct-coated membrane-layer defects which occurred in roll to roll pilot line coating, the backer was changed to the alternative candidate in November 2012.
- Preliminary cost estimate of the current low-cost multi-layer backer is \$1 to \$5 per square meter
- In February 2013, electrode was coated on the current backer in a 30 cm wide high-speed-capable roll-to-roll coating/drying process. Release and BOL performance exceeded the targets.

Technical Accomplishments: Excellent Performance of Direct Coated Cathode

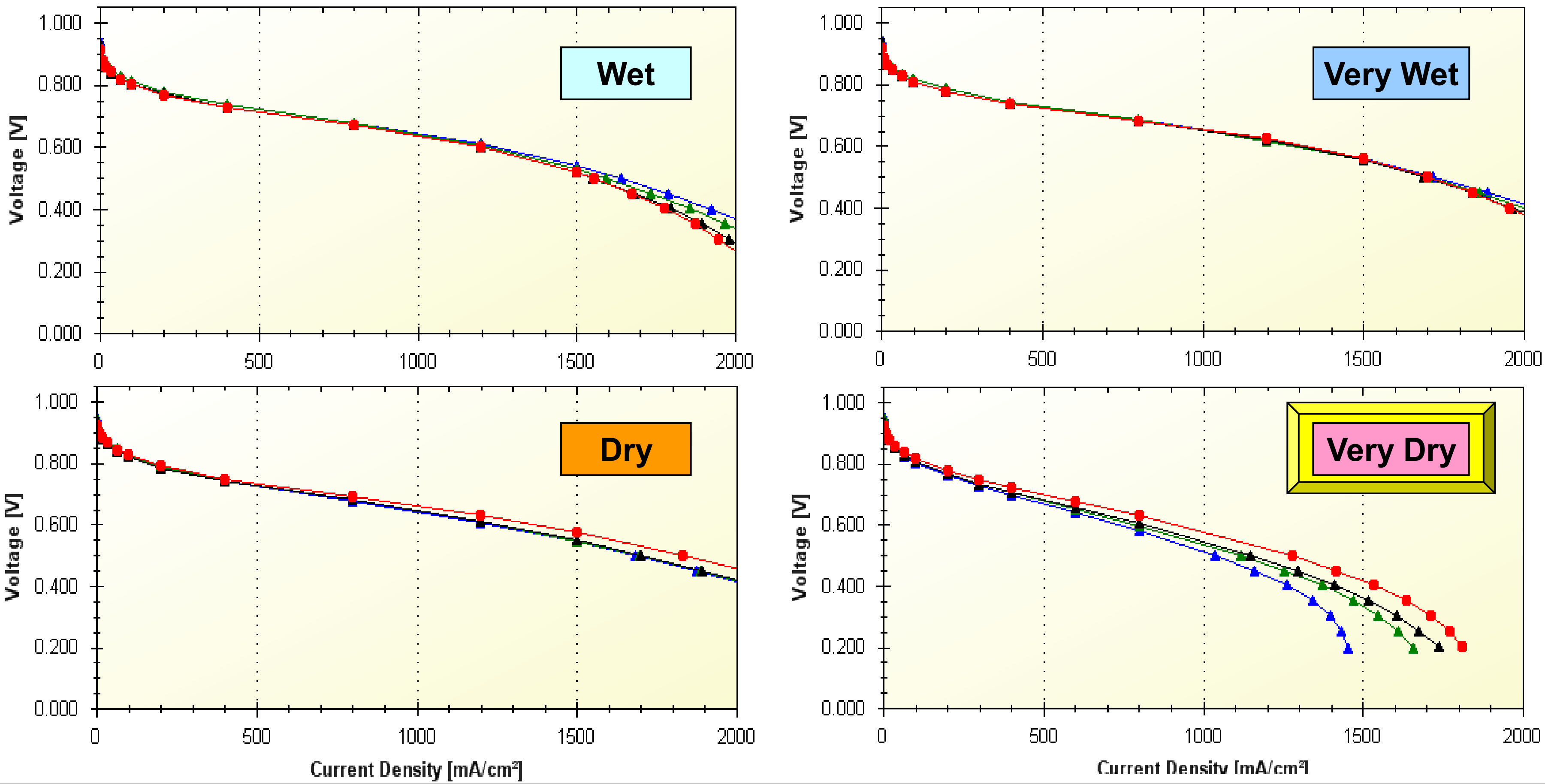
DC Ca.3, low-cost ML backer, 9543-29
DC Ca.3, low-cost ML backer, 9543-30
Control Ca.3, 9543-53
Control Ca.3, 9543-55

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%



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

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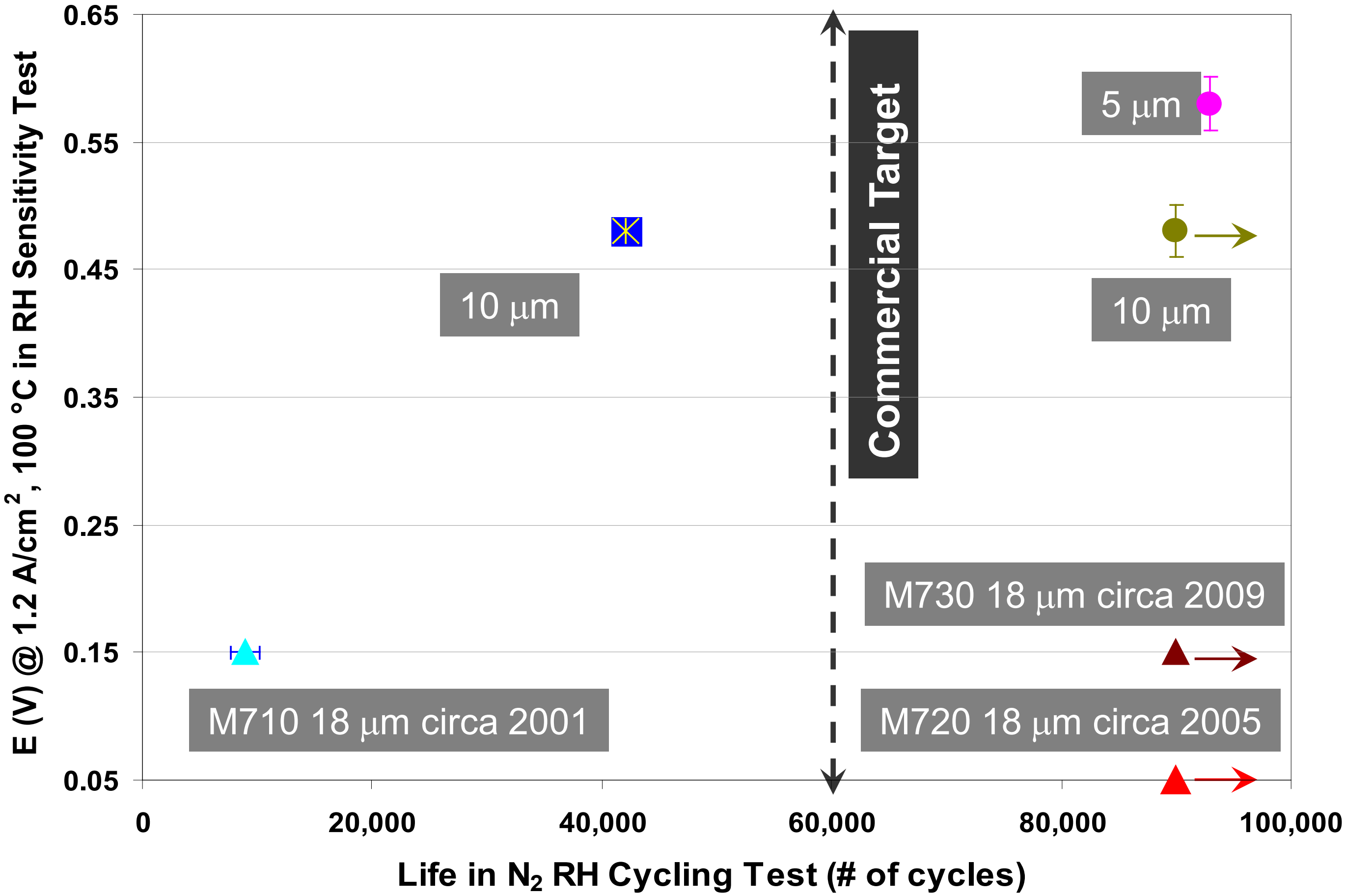
Technical Accomplishments:

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

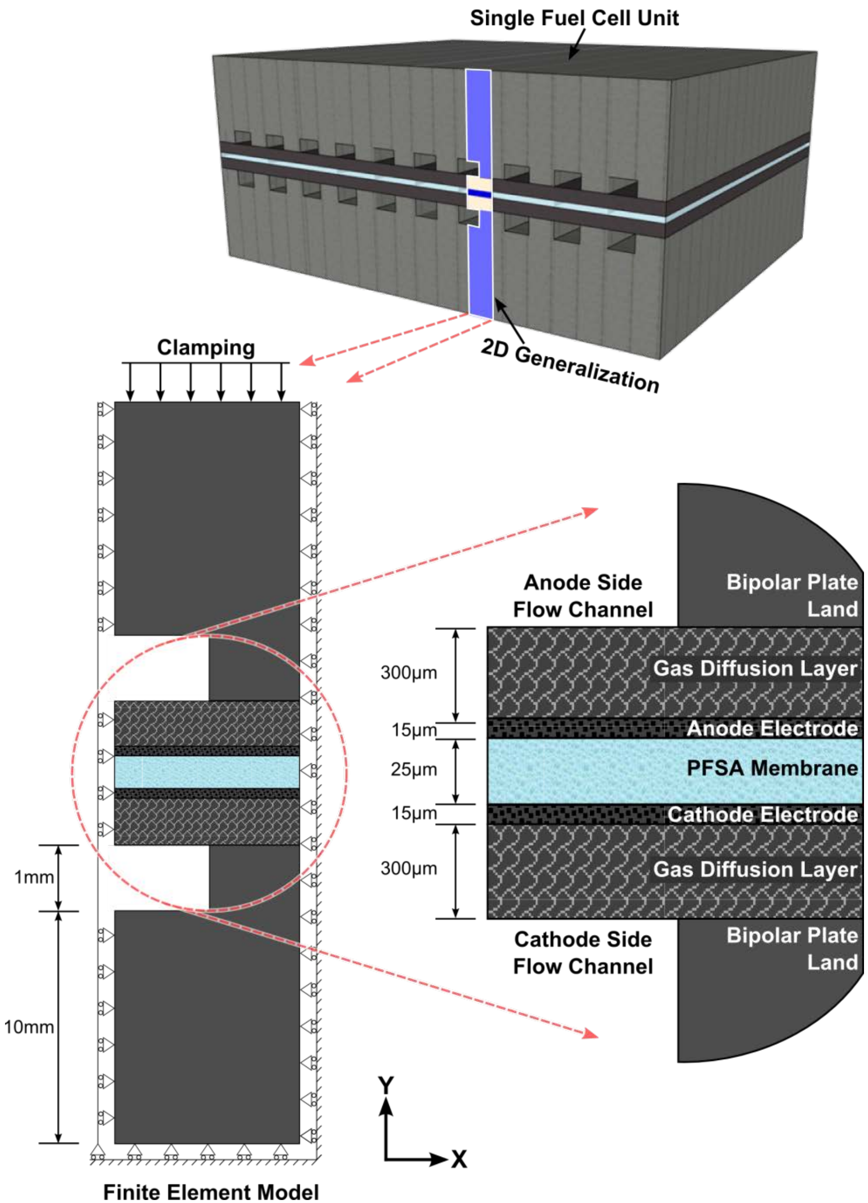


Compared to Gore's current commercial membrane (~20 μm), Gore's thin state-of-the-art membranes (~5 and ~10 μm) show greatly enhanced performance at high current density, especially under hot, dry conditions

Note: Membrane Testing Not Funded by DOE

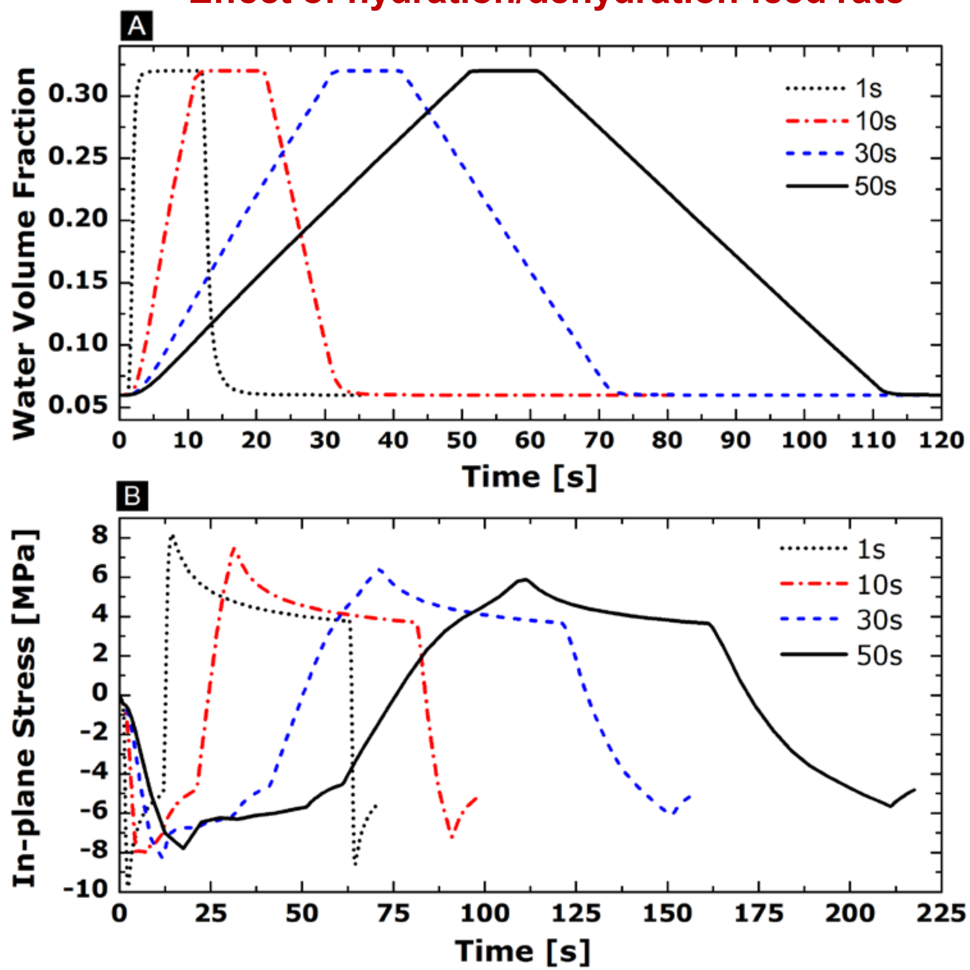
Technical Accomplishments: Mechanical Modeling (UD)

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



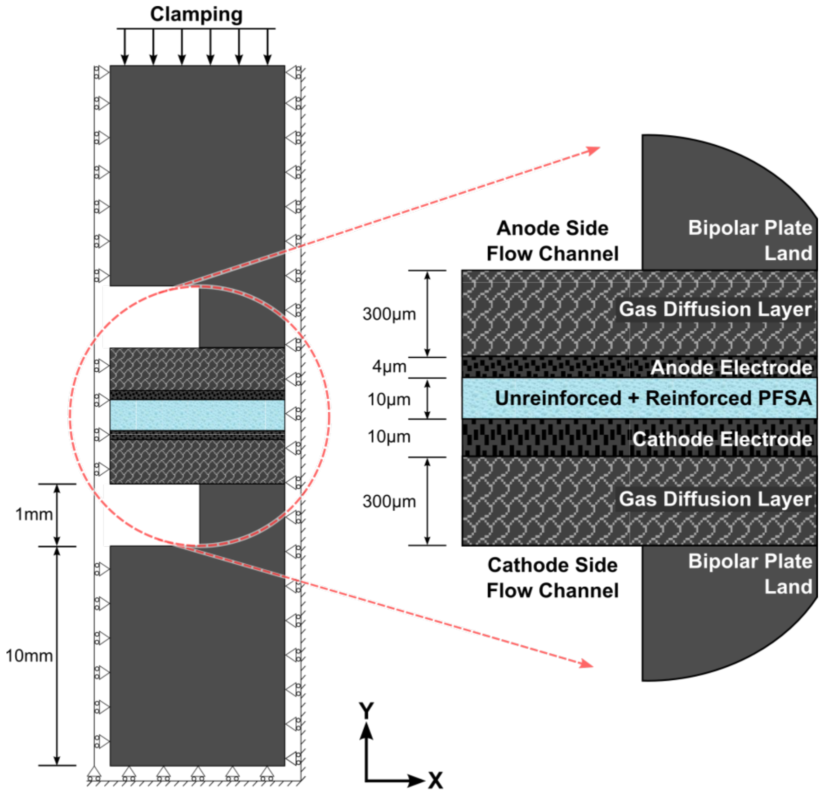
Water Volume Fraction	Swelling Strain	Thermal Strain
$\phi_w = \frac{18\lambda}{EW/\rho_P + 18\lambda}$	$\varepsilon^{sw} = \left(\frac{\theta + 273}{\theta_0 + 273}\right)\ln(1-\phi_w)$	$\varepsilon^{th} = \alpha(\theta - \theta_0)$

Effect of hydration/dehydration feed rate



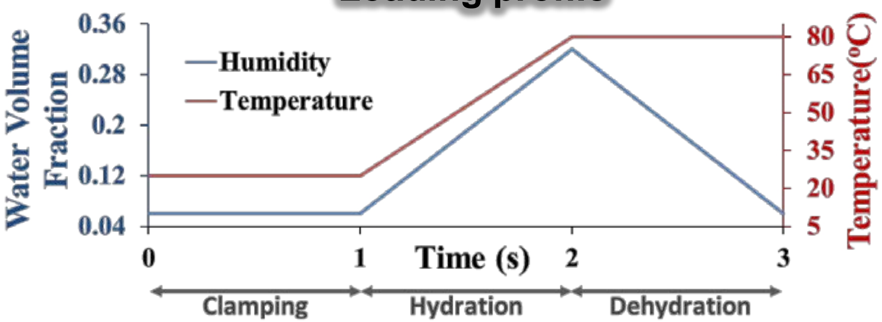
Technical Accomplishments: Mechanical Modeling (UD)

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



Finite Element Model

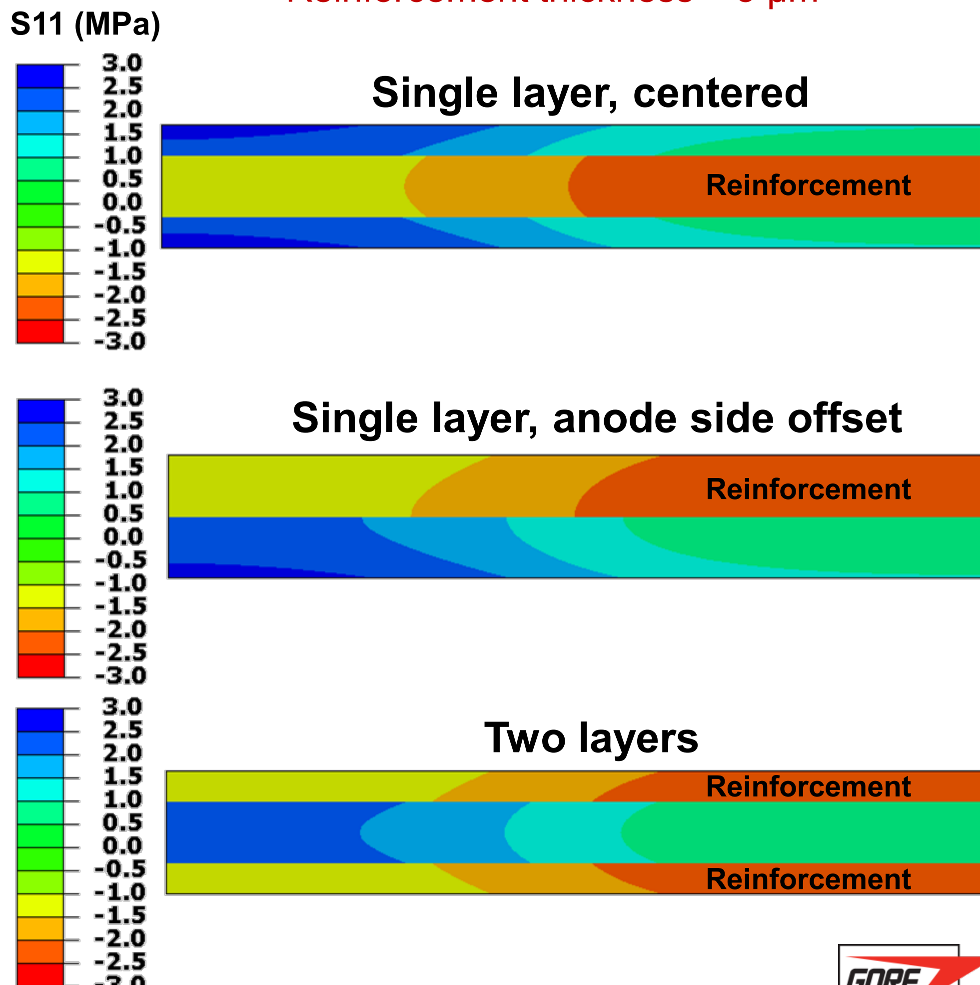
Loading profile



In-plane stress contours after dehydration

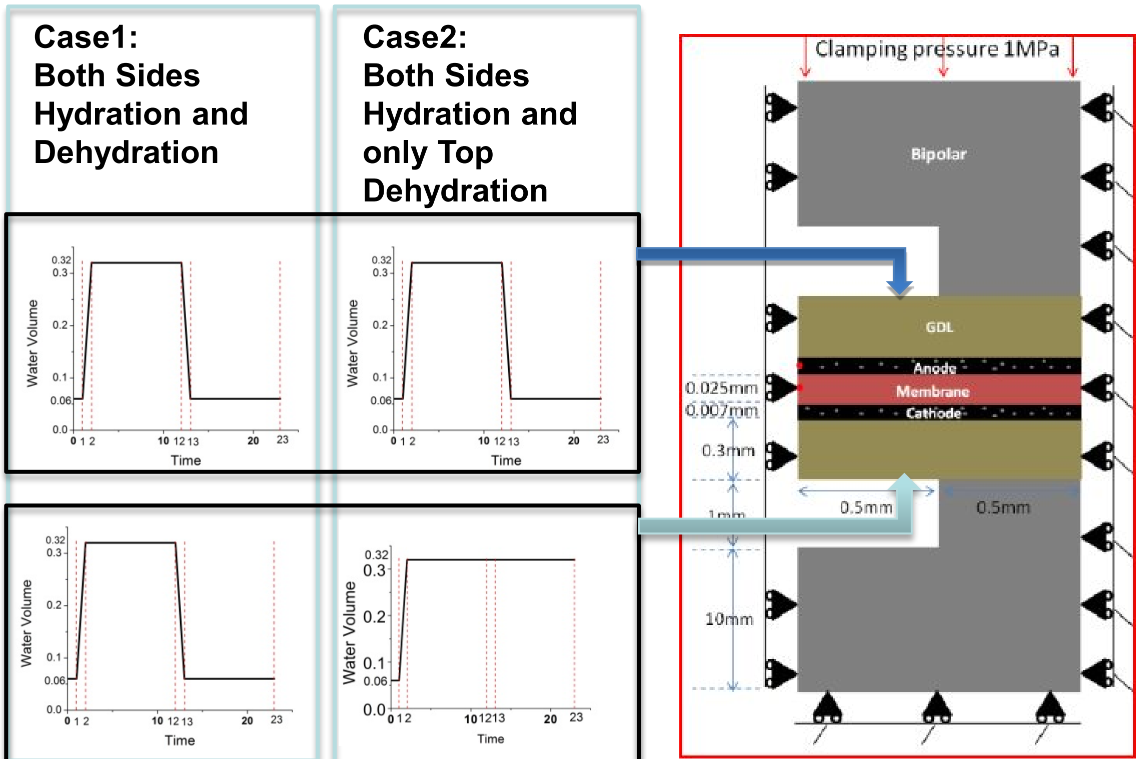
Total membrane thickness = 10 µm

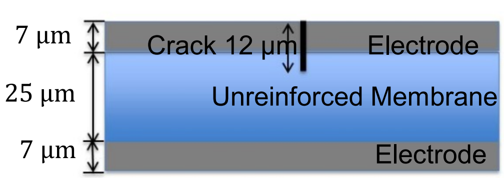
Reinforcement thickness = 5 µm

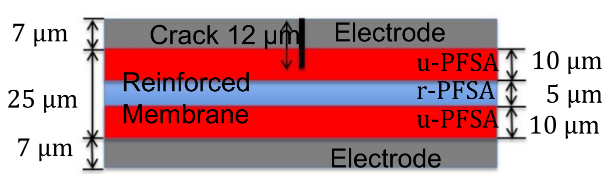


Technical Accomplishments: Mechanical Modeling (UD)

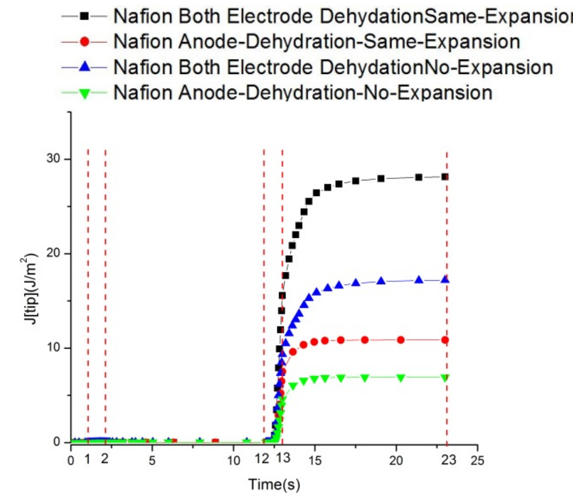
J integral response under one cycle



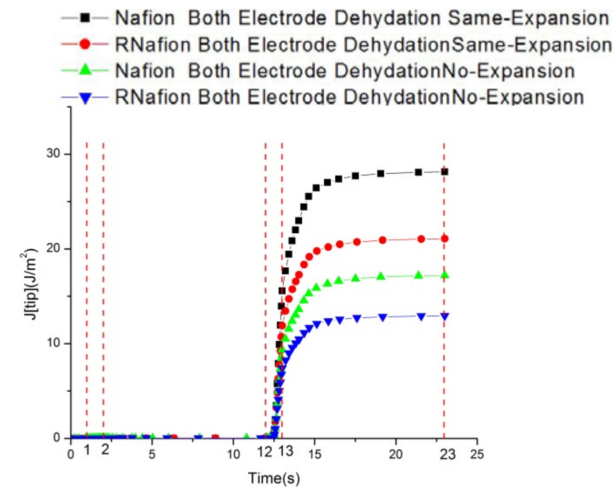




❖ Effect of hydration mode



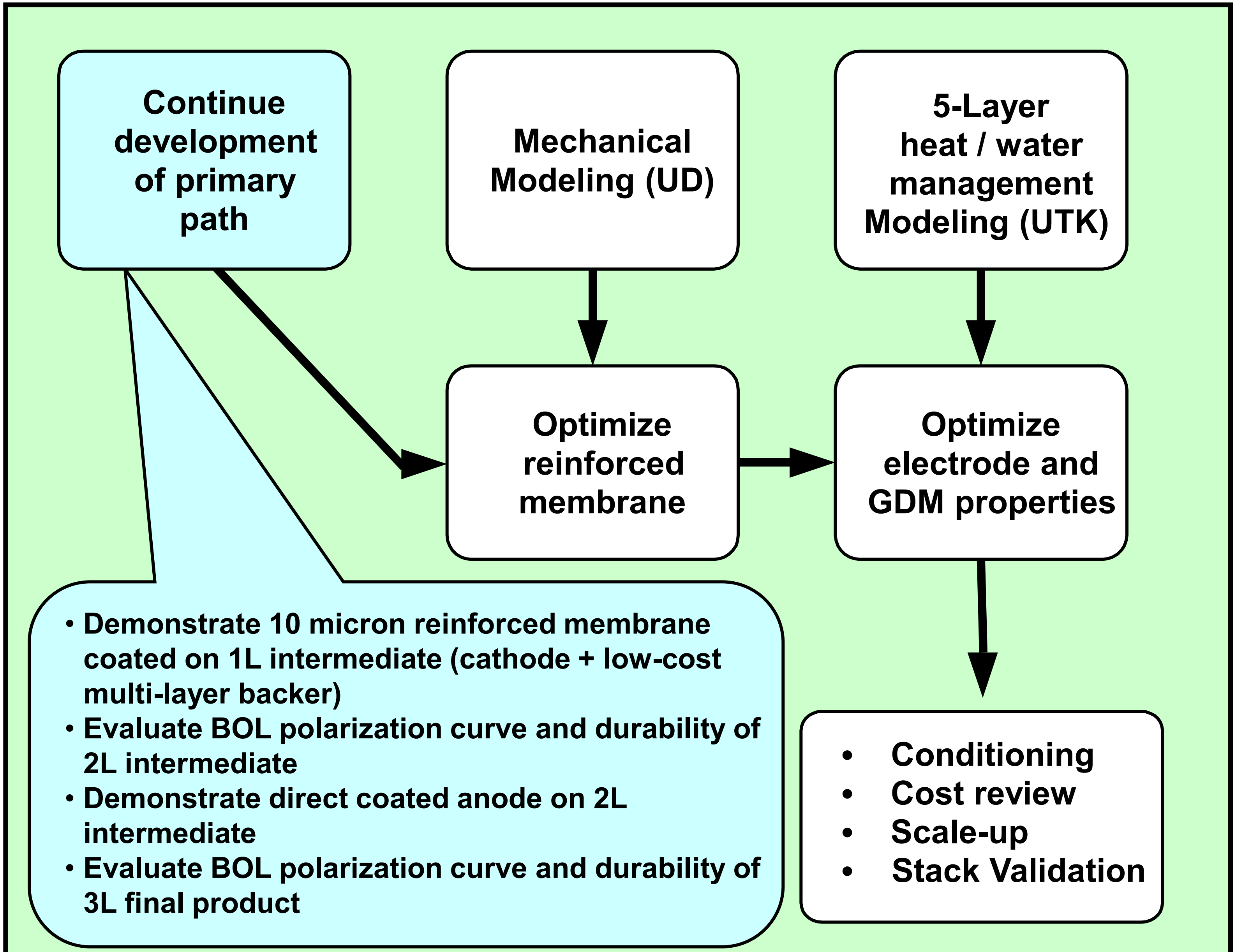
❖ Effect of reinforced membrane



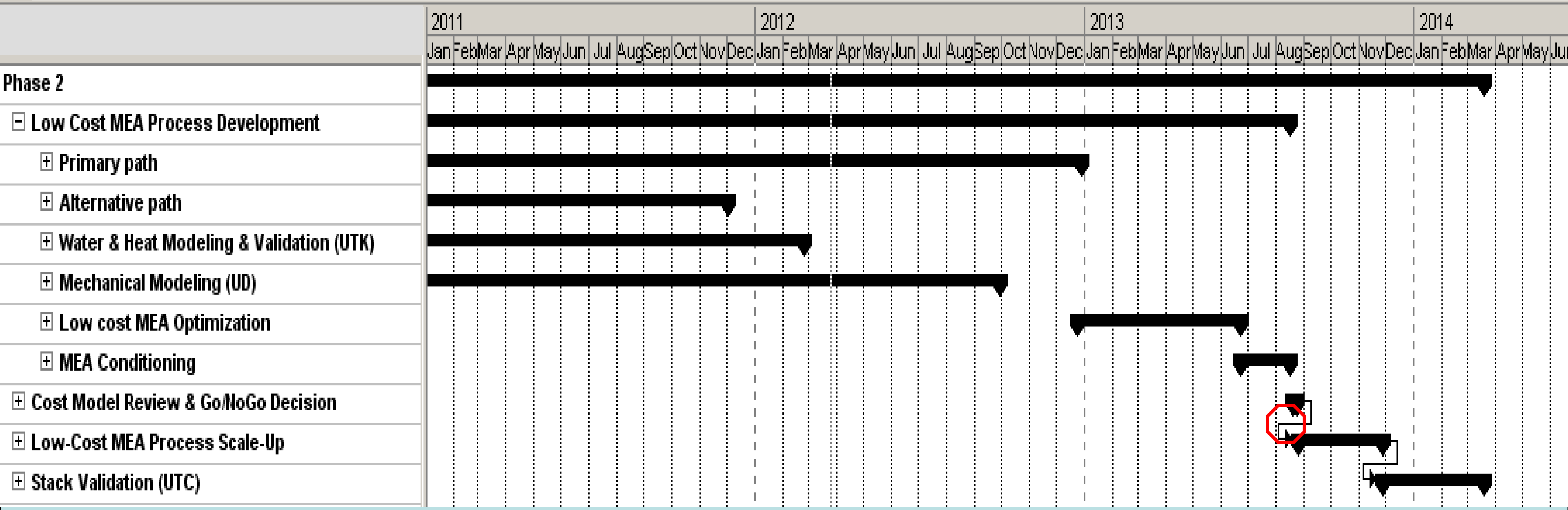
Nafion is a registered trademark of E. I. duPont de Nemours and Company.

* Narinder Singh Khattra, PhD Dissertation, University of Delaware, 2012

Proposed Future Work: Summary



Proposed Future Work for FY13: 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
- UTRC (industry, sub-contractor)
  - Stack Testing
- NREL (federal, collaborator)
  - On-line quality control systems research
  - M. Ulsh
- Strategic Analysis, Inc. (industry, collaborator)
  - Cost Modeling
  - B. James
- 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

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**
  - 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
    - Modeling tasks at UD and UTK are on track to enable efficient optimization of the new 3-L MEA process as soon as direct coated 3-L MEA feasibility has been demonstrated on a roll-to-roll 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

Acknowledgements:

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- Mike Santare
- Narinder Singh
- Zongwen Lu

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- Brian James

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- Jesse Adams
- Pete Devlin
- Nancy Garland

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Technical Back Up Slides

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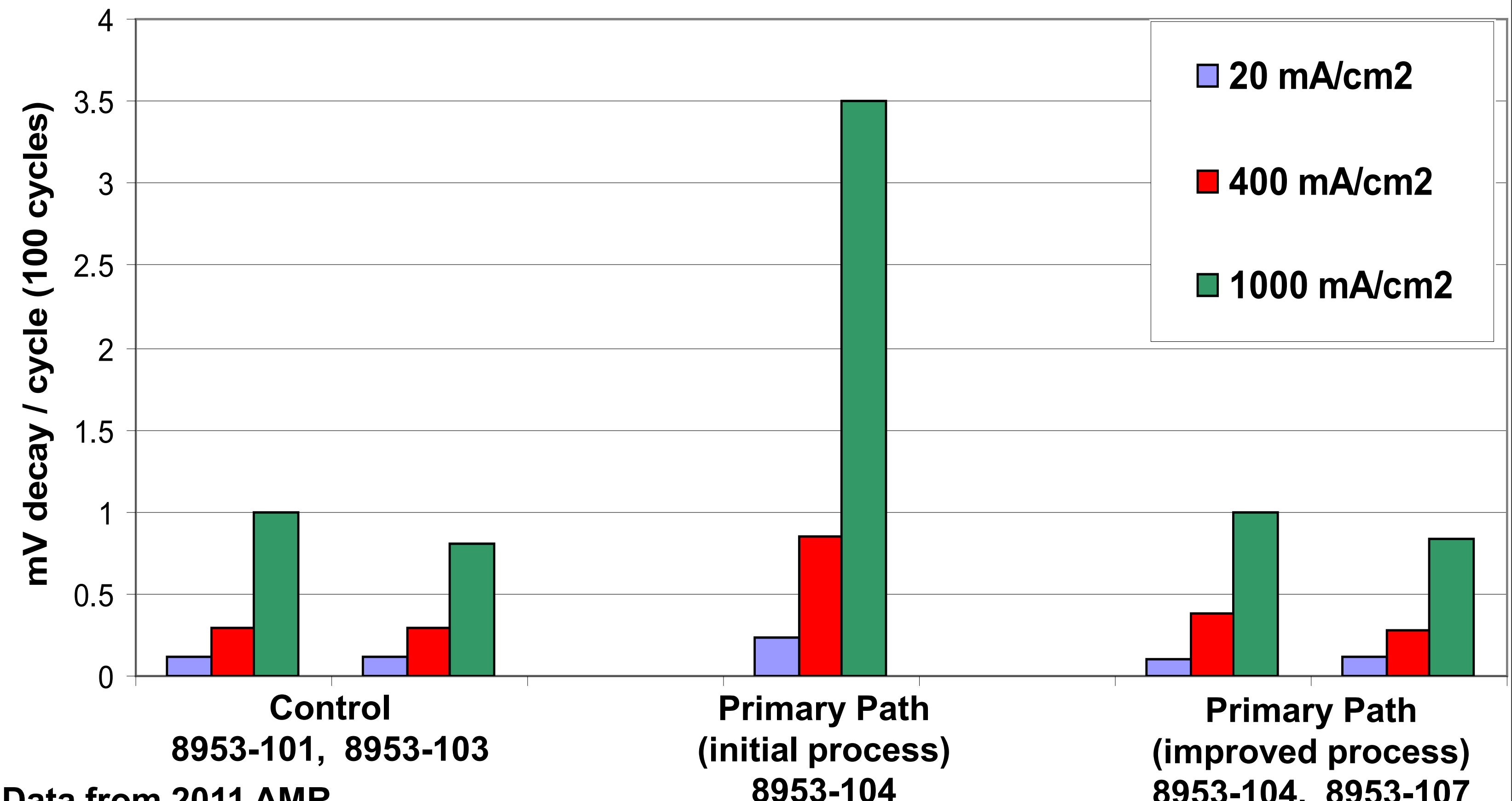
Technical Accomplishments:

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

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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

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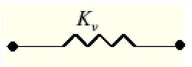
Technical Accomplishments: Mechanical Modeling (UD)

Constitutive Model: Visco-elastic-plastic Model



$\sigma = K\ \varepsilon$

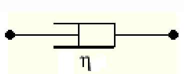
Spring Element
Strain dependence

K_P

(Long-term modulus)

$K_P + K_v$

(Instantaneous modulus)

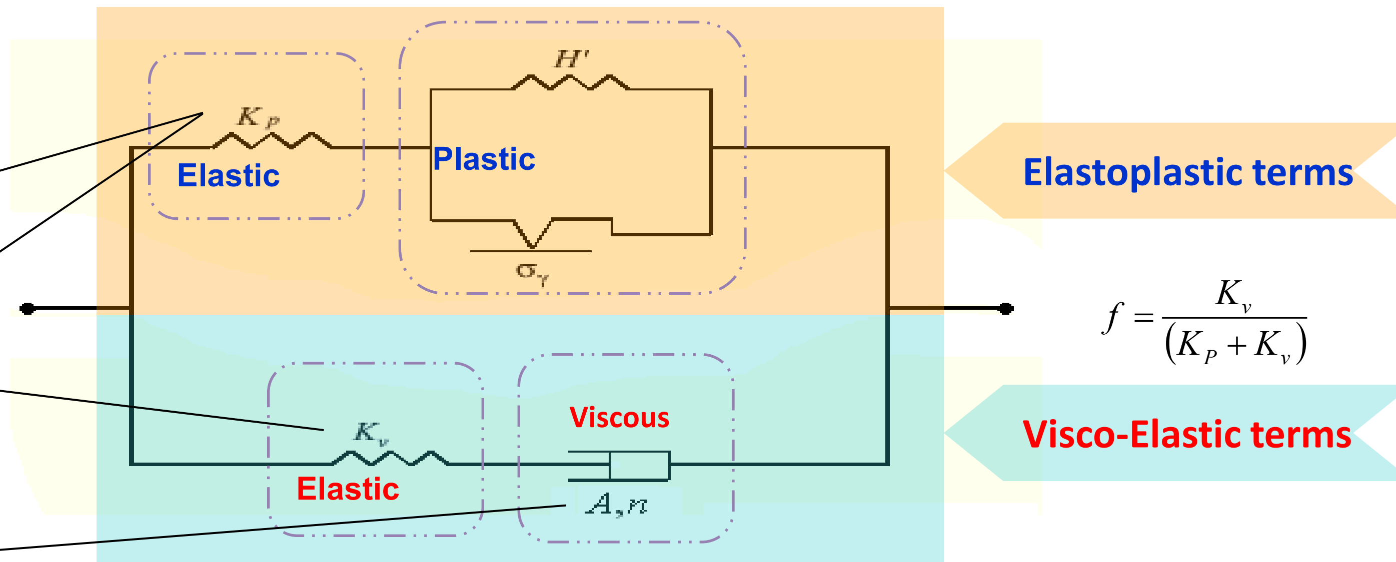


$\sigma = \eta\dot{\varepsilon}$

Dashpot Element
Strain-rate dependence

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

Viscous power law



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

Parameters

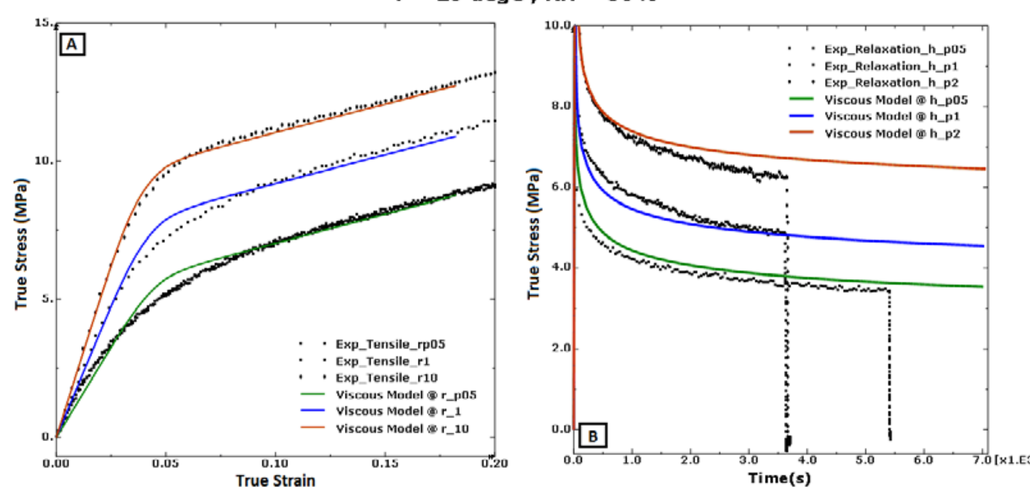
A, n, f, θ, λ

$E(K_P + K_V),$

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

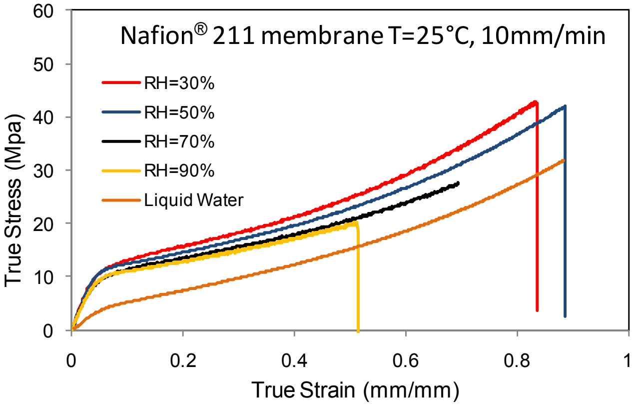
Visco-elastic-plastic model is tuned to match measured constitutive responses for MEA materials

T = 25 degC , RH = 30%



Technical Accomplishments: Mechanical Modeling (UD)

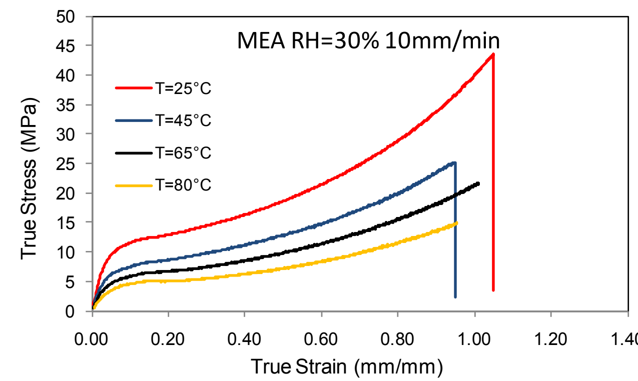
Properties of NAFION® 211 membrane, MEA and Reinforced PFSA measured

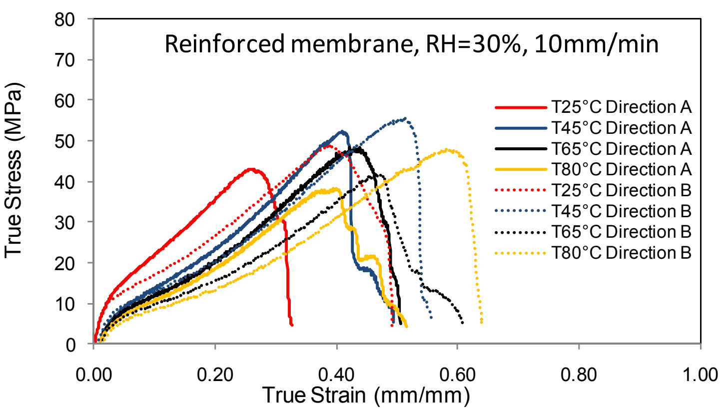


Condition	Rate	K_V [MPa]	K_P [MPa]	A	n	σ_y [MPa]	H [MPa]
T=25, RH=30%	1mm/min	160	31	1.50E-09	6.5	1.55	19.8
	10mm/min	220	31	3.00E-09	6.5		
T=80, RH=30%	10mm/min	80	10.64	1.00E-05	4.5	0.532	7.0
	250mm/min	127	10.64	5.00E-06	4.5		

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