2011 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.
5/12/2011

Project ID #
MN004

Overview

Budget

- Total Project Funding: $4.2MM
  - $2.7MM DOE Share
  - $1.5MM Contractor Share
- Cumulative DOE funding spent as of 3/11/11: $1.1 MM
- Funding received in FY10: $500k
- Funding for FY11: $611k

Barriers Addressed

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

Timeline

- Project start: 9/01/08
- Project end: 9/30/12
- 65% Percent Complete as of 3/11/11

Partners

- University of Delaware (UD)
  - MEA Mechanical Modeling
- University of Tennessee, Knoxville (UTK)
  - 5-Layer Heat / Water Management 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]

GORE Creative Technologies Worldwide

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
Cost[e]	$ / kW$_e$	200	70 [f]	25	15
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)**

GORE
Creative Technologies Worldwide

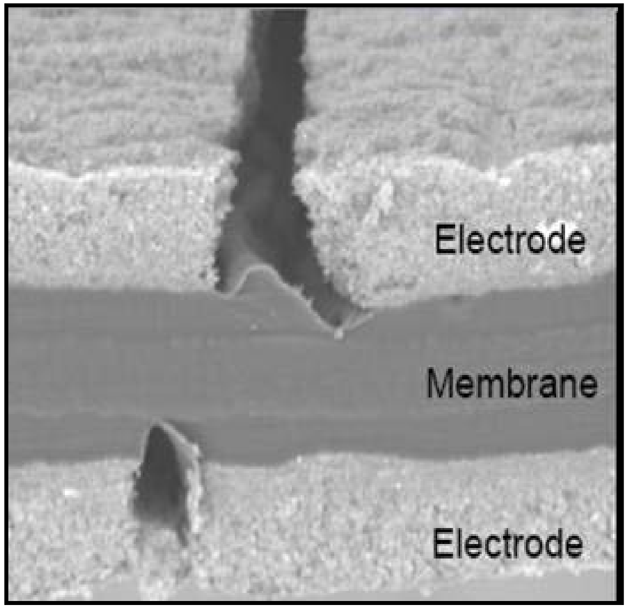
Relevance: Objectives

- Low-cost MEA R&D
  - New 3-Layer (3-L) MEA Process Exploration (Gore) FY '09, '10, '11
    - 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) FY '09, '10, '11
    - Use model to optimize membrane reinforcement for 5,000+ hour durability and maximum performance
  - 5-Layer (5-L) Heat & Water Management Modeling (UTK) FY '10,'11
    - 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) FY' 11
    - 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) FY '11
  - Evaluate potential for new process to achieve **DOE cost targets** prior to process scale-up (Go / No-Go Decision) FY '11
- Scale Up (Gore) FY '11 &'12
- Stack Validation (UTC) FY '12

GORE
Creative Technologies Worldwide

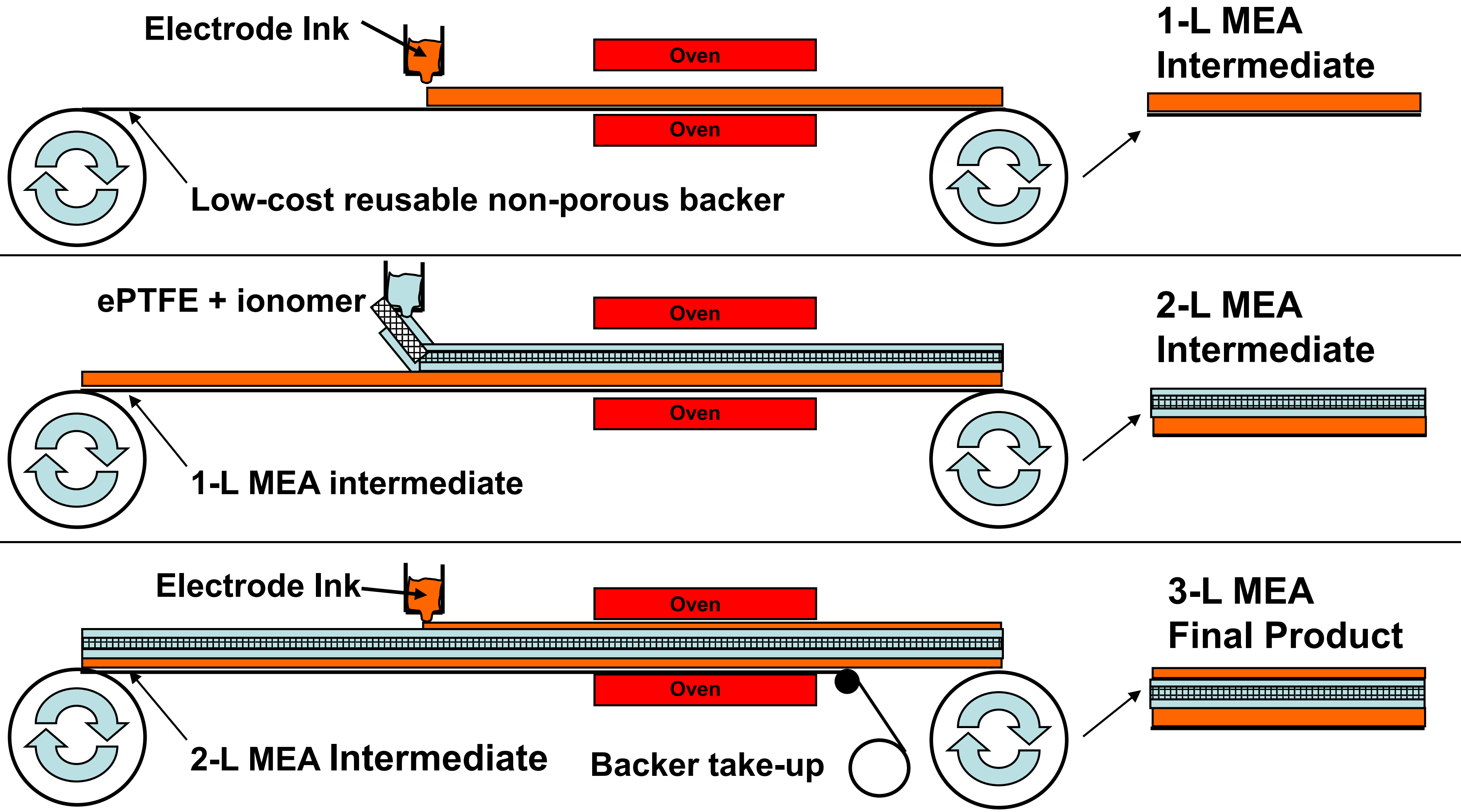
Approach: Summary

- 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



GORE Creative Technologies Worldwide

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

GORE Creative Technologies Worldwide

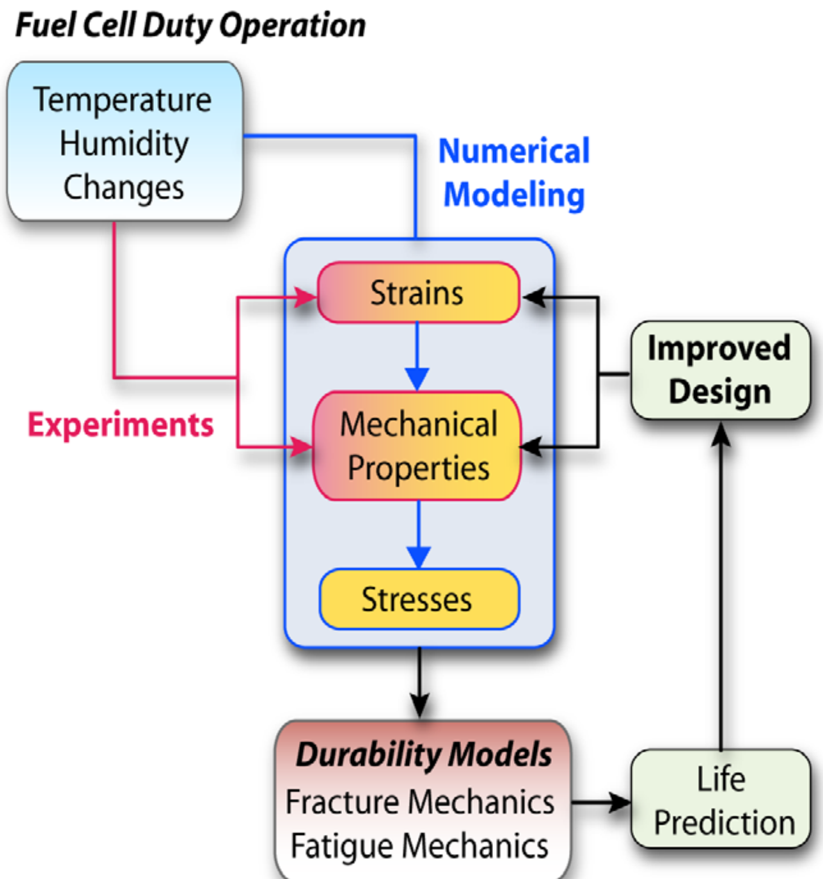
Approach: Mechanical Modeling (UD)

- **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



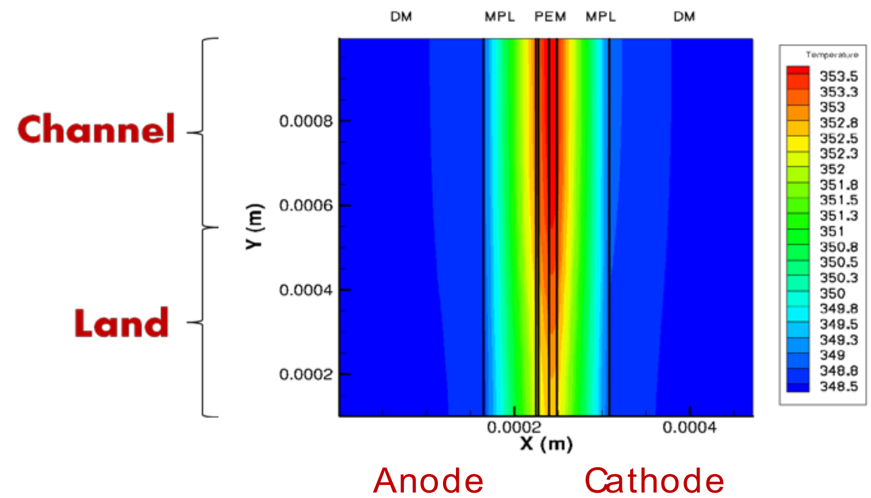
Approach: 5-L Heat & Water Management Modeling (UTK)

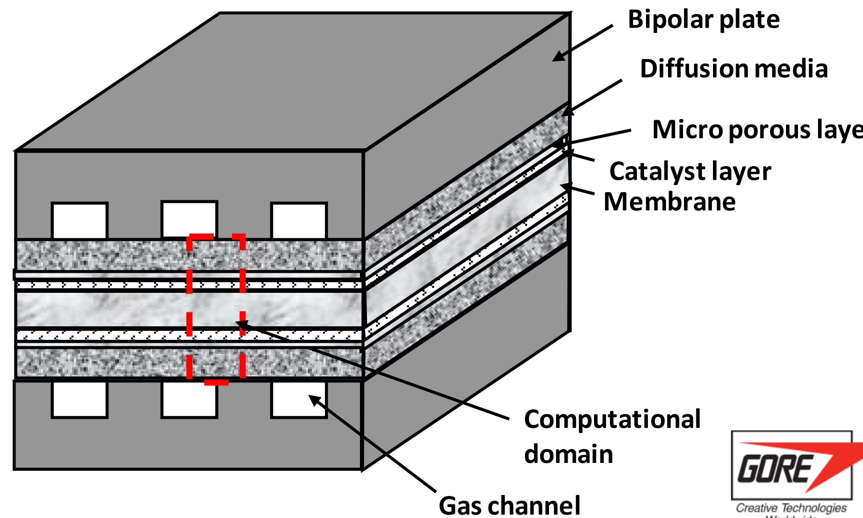
- **Model Concept:**
  Steady state 2D non-isothermal, non-isotropic, performance model. Physics include phase-change induced flow in porous media, condensation/evaporation heat transfer and capillary flow, anode and cathode kinetics with agglomerate based formulation

- **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





GORE
Creative Technologies Worldwide

Technical Accomplishments & Progress: Summary

- Equipment procurement and qualification (Gore) — 100% Complete
- Mechanical Modeling of Reinforced 3-L MEA (UD)
  - Layered model development — 100% Complete
  - RH & time-dependent mechanical testing — 85% Complete
  - Parametric analysis of layered structure — 10% Complete
- 5-L Heat & Water Management Modeling (UTK)
  - Gas diffusion media properties testing — 25% Complete
  - Performance testing — 40% Complete
  - Model development — 100% Complete
  - Computational studies — 60% Complete
- New 3-L MEA Process Exploration (Gore)
  - Process feasibility screening — 100% Complete
  - Determine primary and alternative paths — 100% Complete
  - Cathode Layer — 90% Complete
    - Power density and robustness BOL testing
    - Electrochemical diagnostics
    - Durability testing
  - Reinforced Membrane Layer — 80% Complete
    - Power density and robustness BOL testing
  - Anode Layer — 95% Complete
    - Power density and robustness BOL testing
    - Electrochemical diagnostics

Creative Technologies Worldwide

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

2011 New Process Status Update

2009 Process Waste Map

Membrane Coating

Process Costs	Primary forms of waste	Modeled Process Improvements	2011 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	2011 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		+

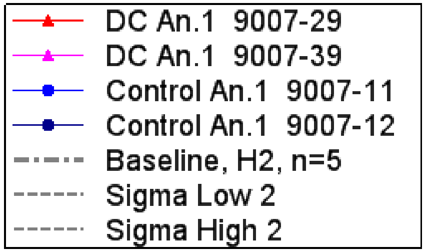
3 Layer Roll-Good Finishing Operations

Process Costs	Primary forms of waste	Modeled Process Improvements	2011 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

Technical Accomplishments: Direct Coated Anode Results In Improved Interface

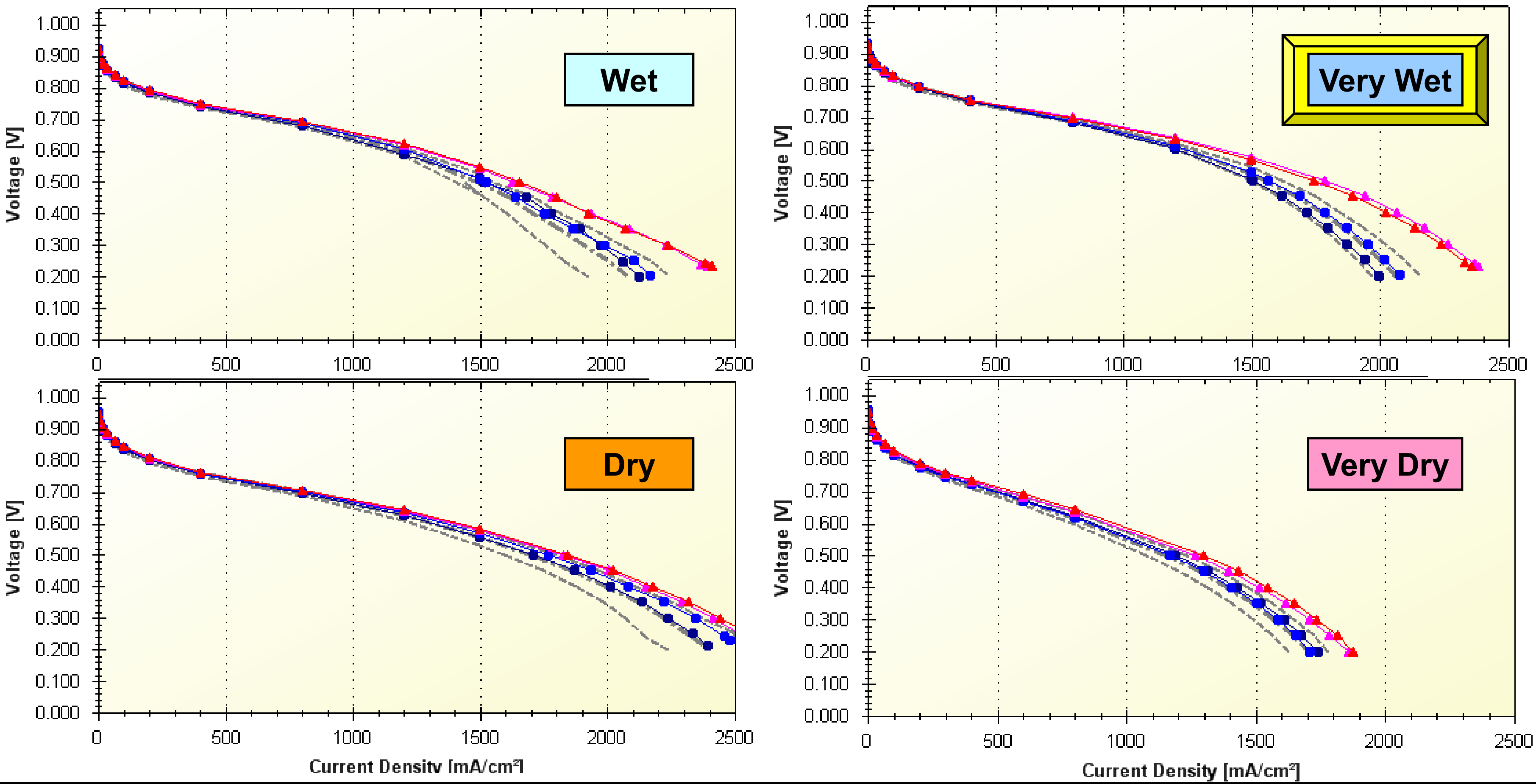


V. Wet: 70°C cell, 80|80°C, S=1.3|2.0, 0 psig, RHavg=170%

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%

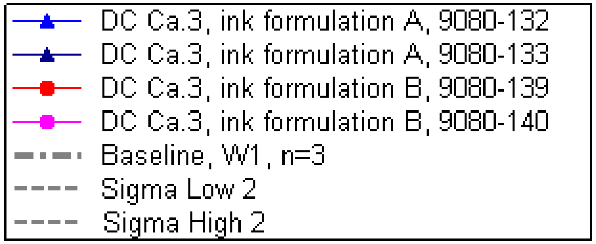
V. Dry 95°C cell, 55|55°C, S=1.3|2.0, 7.25 psig, RHavg=34%



- **High current density performance was significantly increased (particularly in wet conditions) by improving the membrane/anode interface through direct coating (DC)**
- **Anode made by primary path process. Control cathode and membrane used for all samples.**

GORE
Creative Technologies Worldwide

Technical Accomplishments: Improved Performance of Direct Coated Cathode

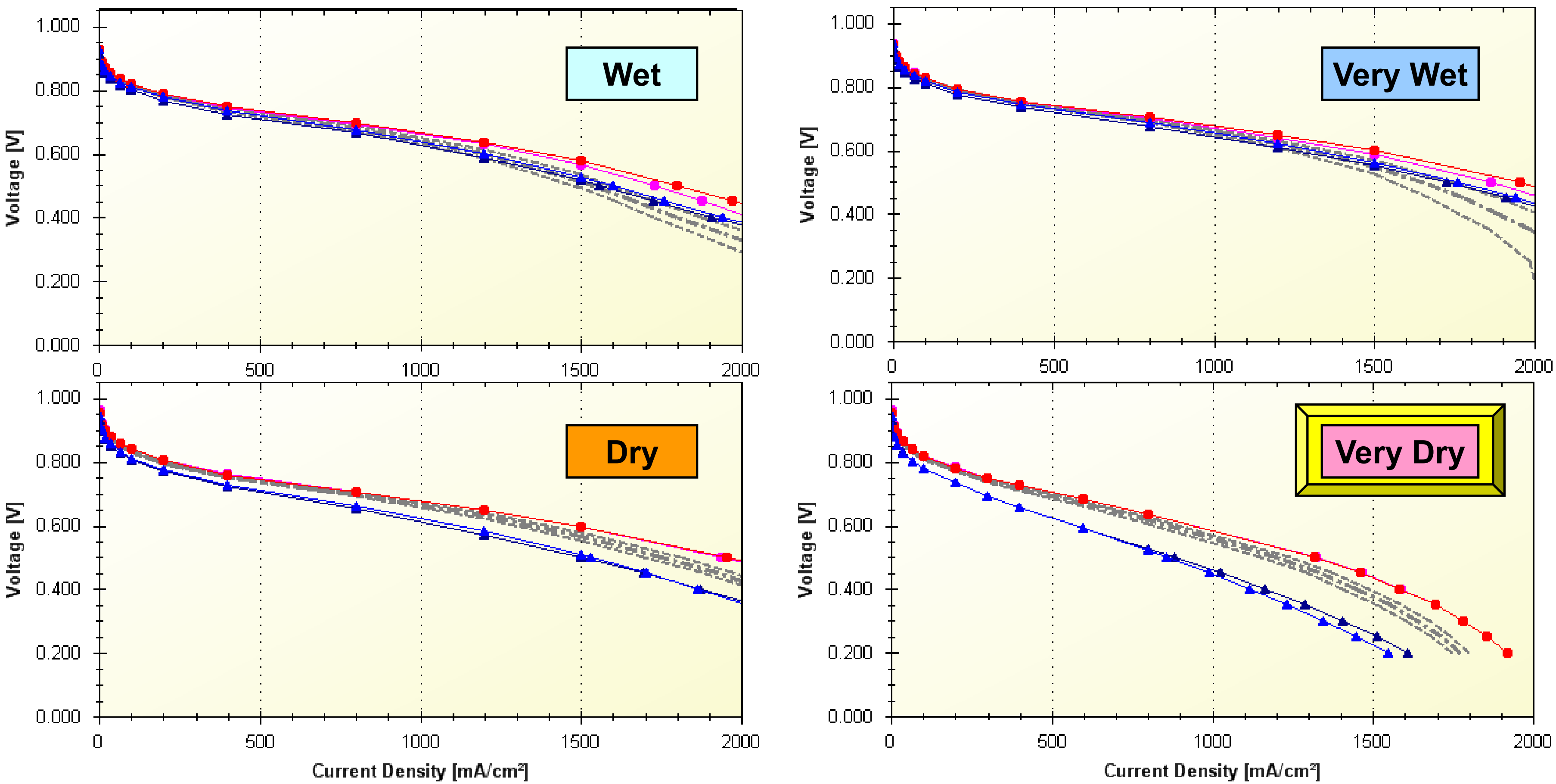


V. Wet: 70°C cell, 80|80°C, S=1.3|2.0, 0 psig, RHavg=170%

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%



- **Dry high current density performance was significantly increased through direct coating**
- **<u>Cathode made by primary path process</u>. Control anode and membrane were used for all samples**

Creative Technologies Worldwide

Technical Accomplishments:

DC Cathode Electrochemical Diagnostics

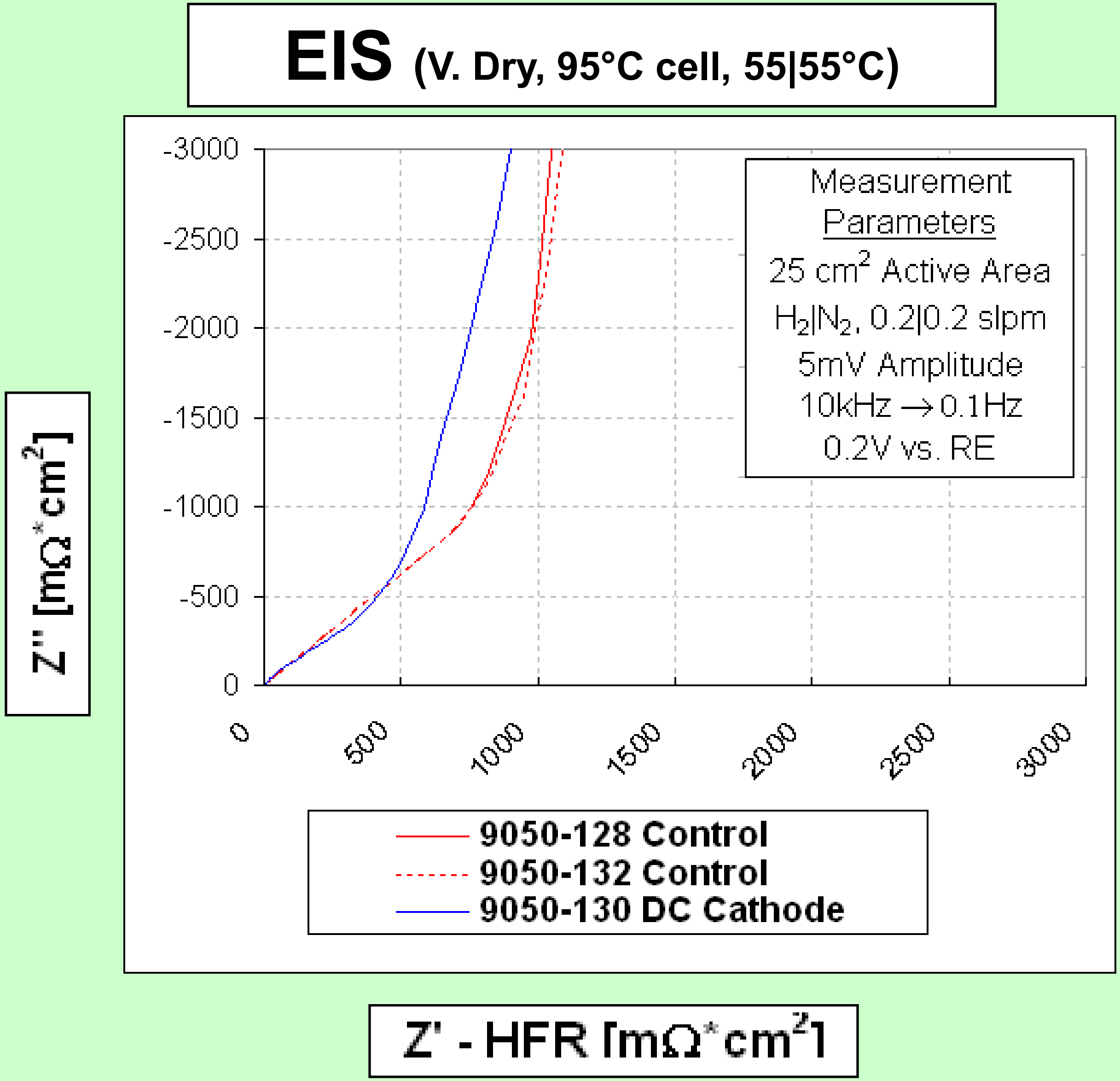
- Standardized protocol that combines BOL robustness testing with key cathode diagnostics at wet and dry conditions
- Test summary
  - **Pre-Conditioning Diagnostics**
    - Cleaning Cyclic Voltammograms (CVs)
    - CV, H_2 Cross-Over, Electrochemical Impedance Spectroscopy (EIS)
  - **Conditioning**
  - **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

Integrated I-V to quantify oxidized impurities which are associated with conditioning time

Investigated impact of direct-coated electrode structure on molecular diffusion

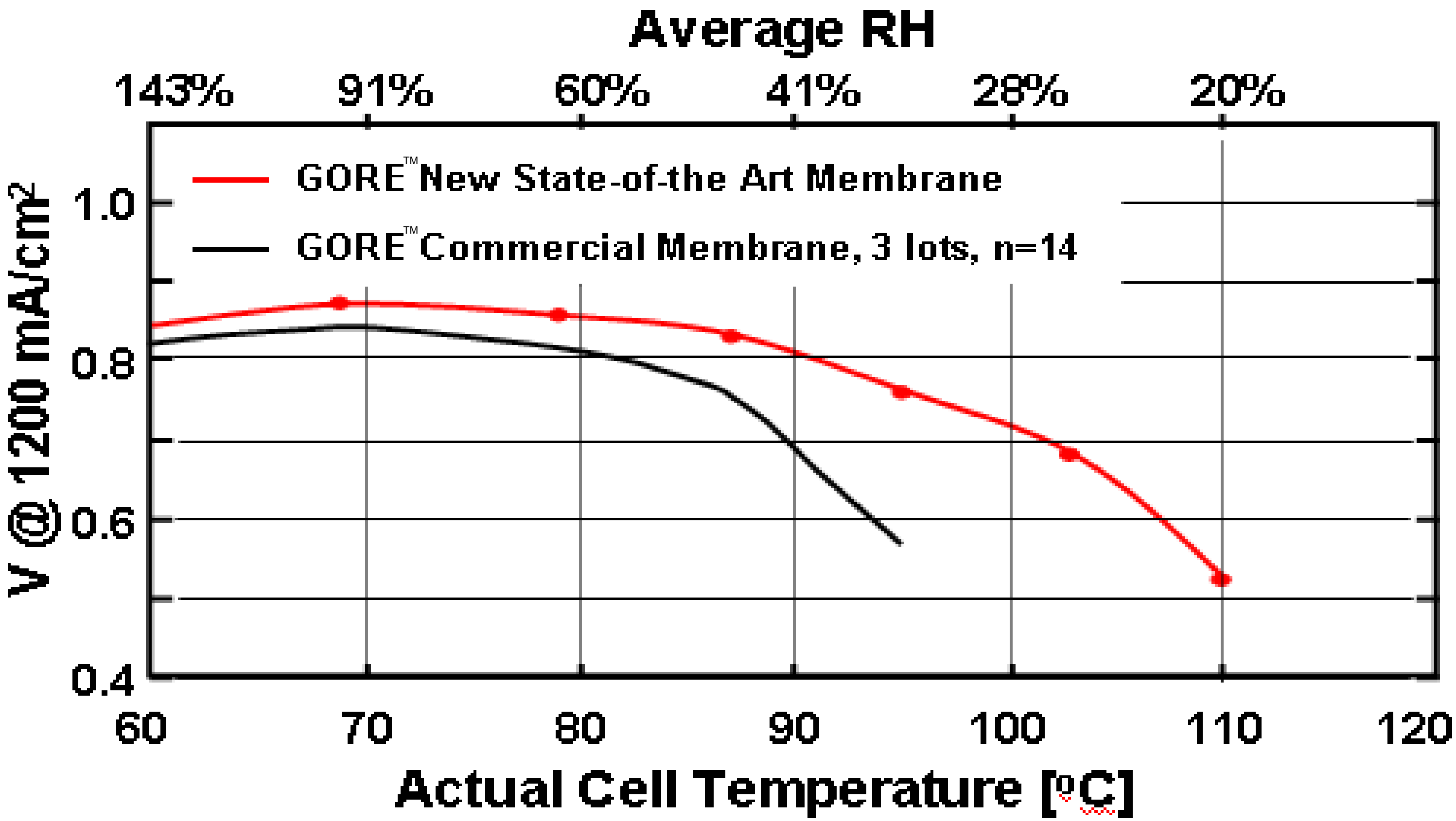
Quantified improved ionic conductivity of direct coated cathode

Technical Accomplishments:
DC Cathode Electrochemical Diagnostics



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 new 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

GORE Creative Technologies Worldwide

Technical Accomplishments:

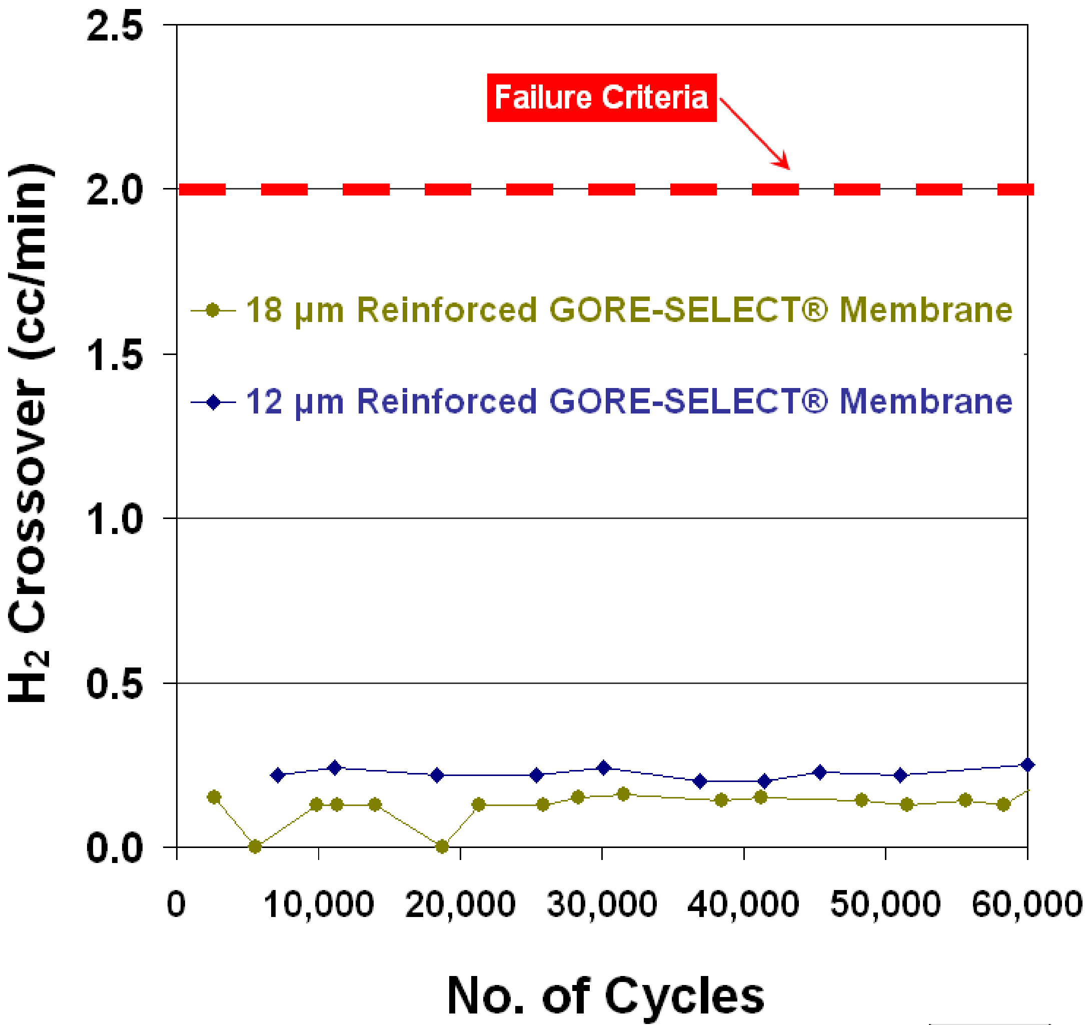
Durability of Thin GORE-SELECT® Membrane

Gore N_2 RH Cycling Protocol:

Tcell (ÁC)	Pressure (kPa)	Flow (Anode/Cathode, cc/min)
80	270	500 N_2 / 1000 N_2

- Cycle between dry feed gas and humidified feed gas (sparger bottle temp = 94˚C)
- Dry feed gas hold time: 50 sec.
- Humidified feed gas hold time: 10 sec.
- For further information, reference: W. Liu, M. Crum ECS Transactions 3, 531-540 (2007)

Note: 12 µm Membrane Testing Not Funded by DOE



GORE Creative Technologies Worldwide

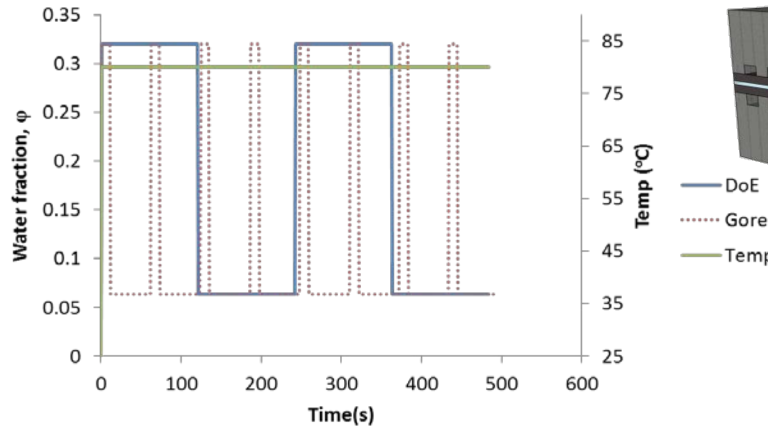
Technical Accomplishments: Mechanical Modeling (UD)

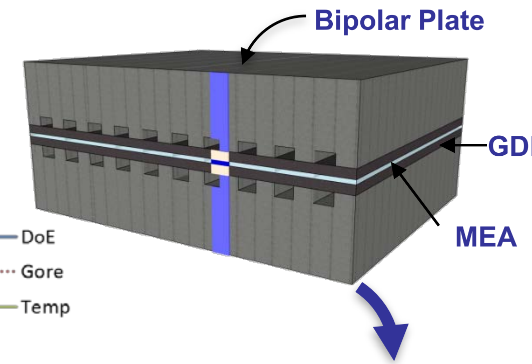
2D Plane Strain Finite Element Model for a Single Cell

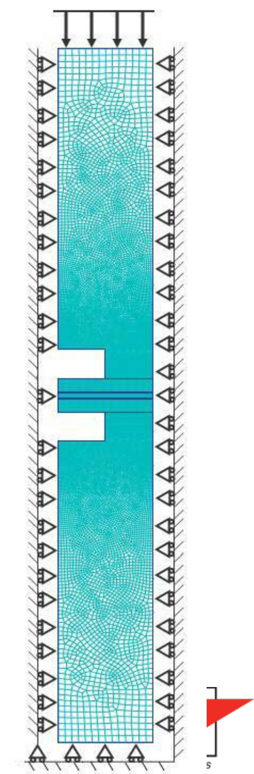
Measured properties for membrane acquired through experiments

Loaded under “Gore” and “DOE” accelerated test conditions

Preliminary results indicate higher max stresses in DOE cycle test







Water Volume Fraction

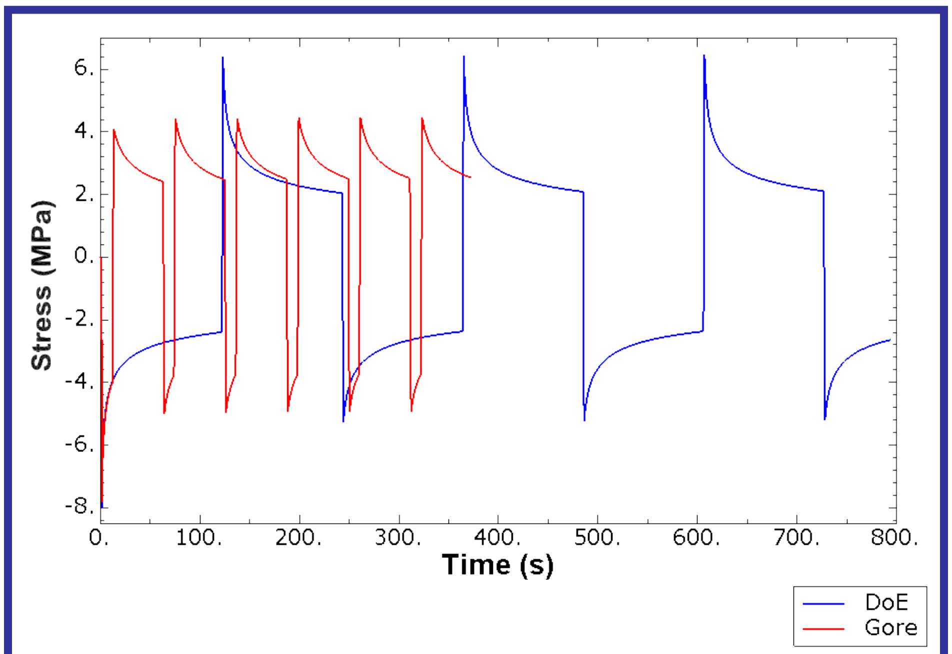
$$\phi_w = \frac{18\lambda}{EW/\rho_P + 18\lambda}$$

Swelling Strain

$$\varepsilon^{sw} = \left(\frac{\theta + 273}{\theta_0 + 273}\right)\ln(1 - \phi_w)$$

Thermal Strain

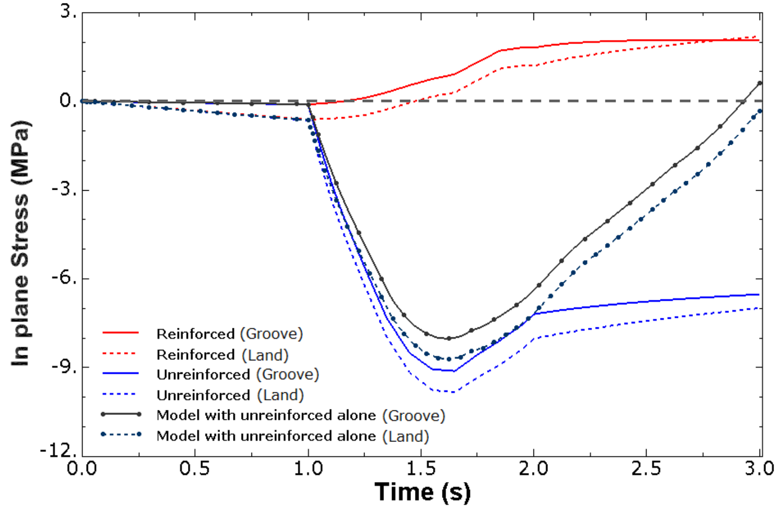
$$\varepsilon^{th} = \alpha(\theta - \theta_0)$$



Technical Accomplishments: Mechanical Modeling (UD)

<u>Preliminary Results</u> for Layered Configurations Using Reinforced PFSA

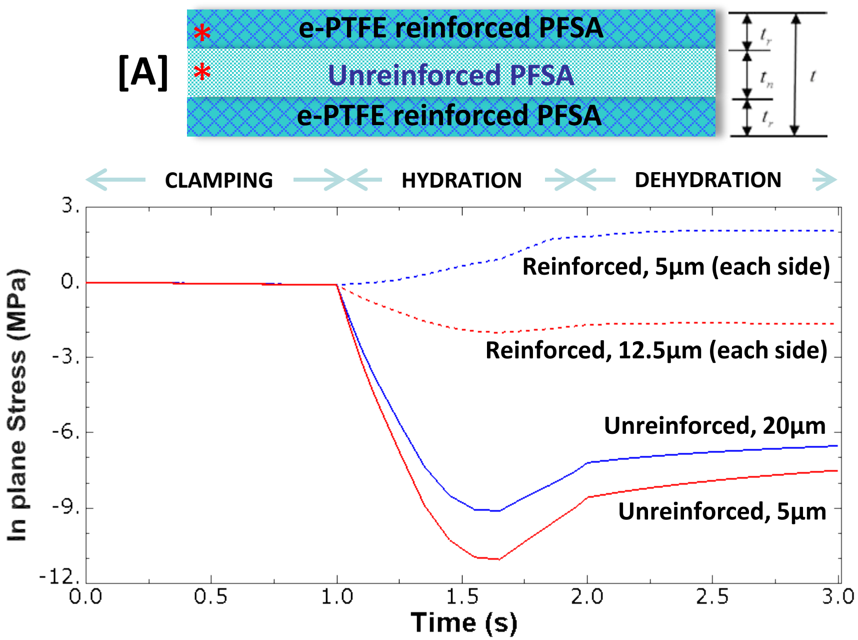
Layered configurations with varying thicknesses analyzed, keeping total thickness constant at 30 µm



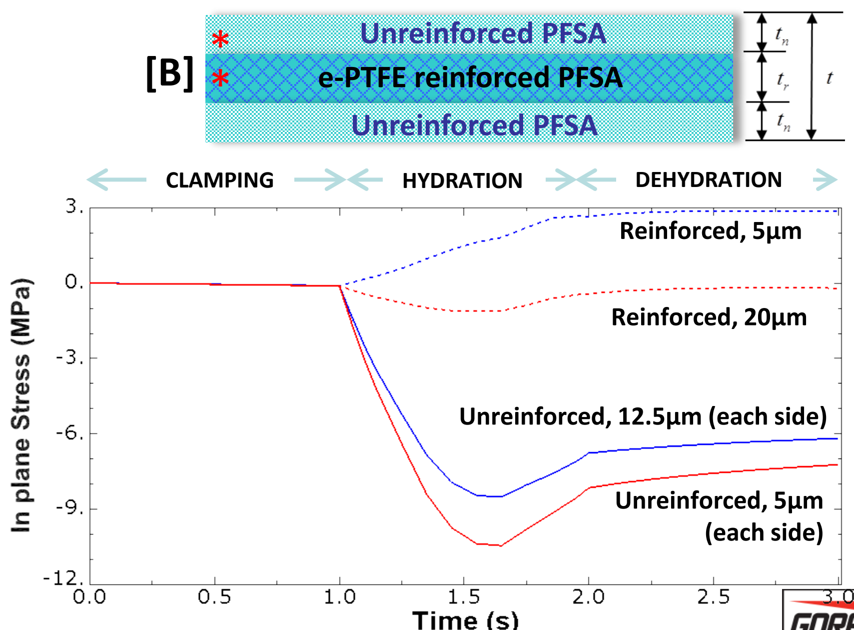
Tensile residual stress in unreinforced PFSA eliminated by addition of reinforced layer(s)

Tensile residual stresses of the order of 0-3 MPa observed in the reinforced layers

[A]



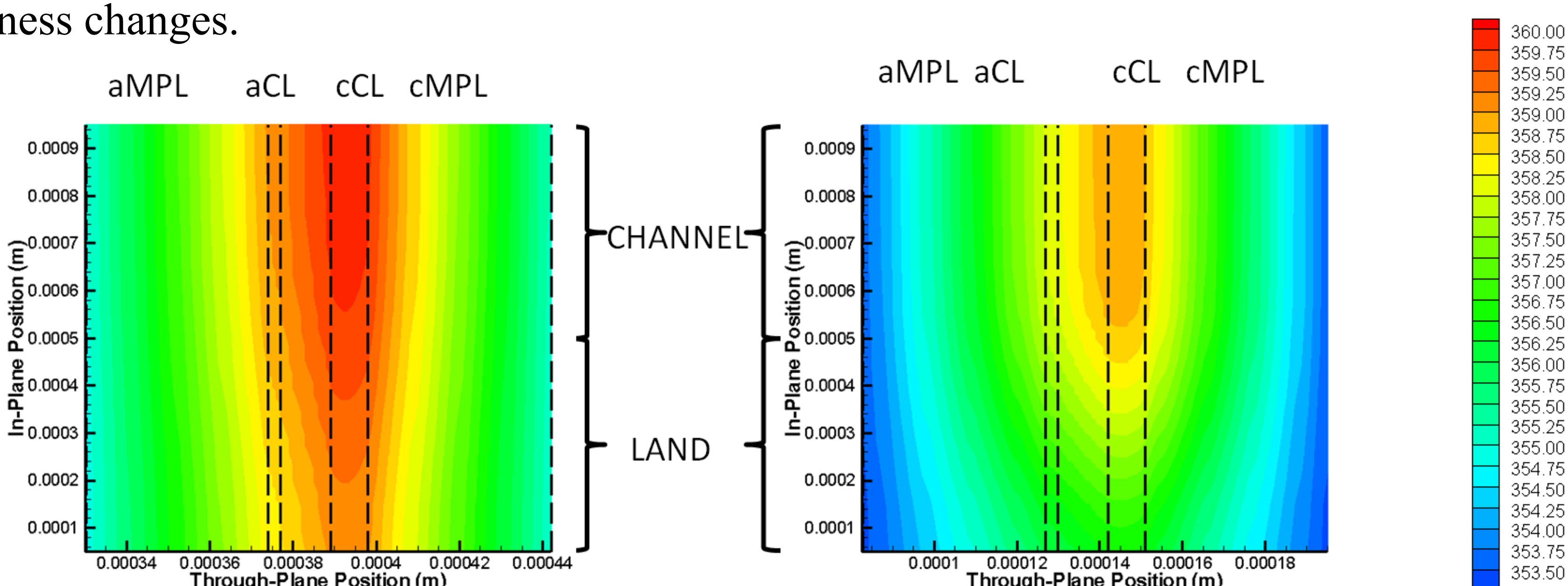
[B]



GORE Creative Technologies Worldwide

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

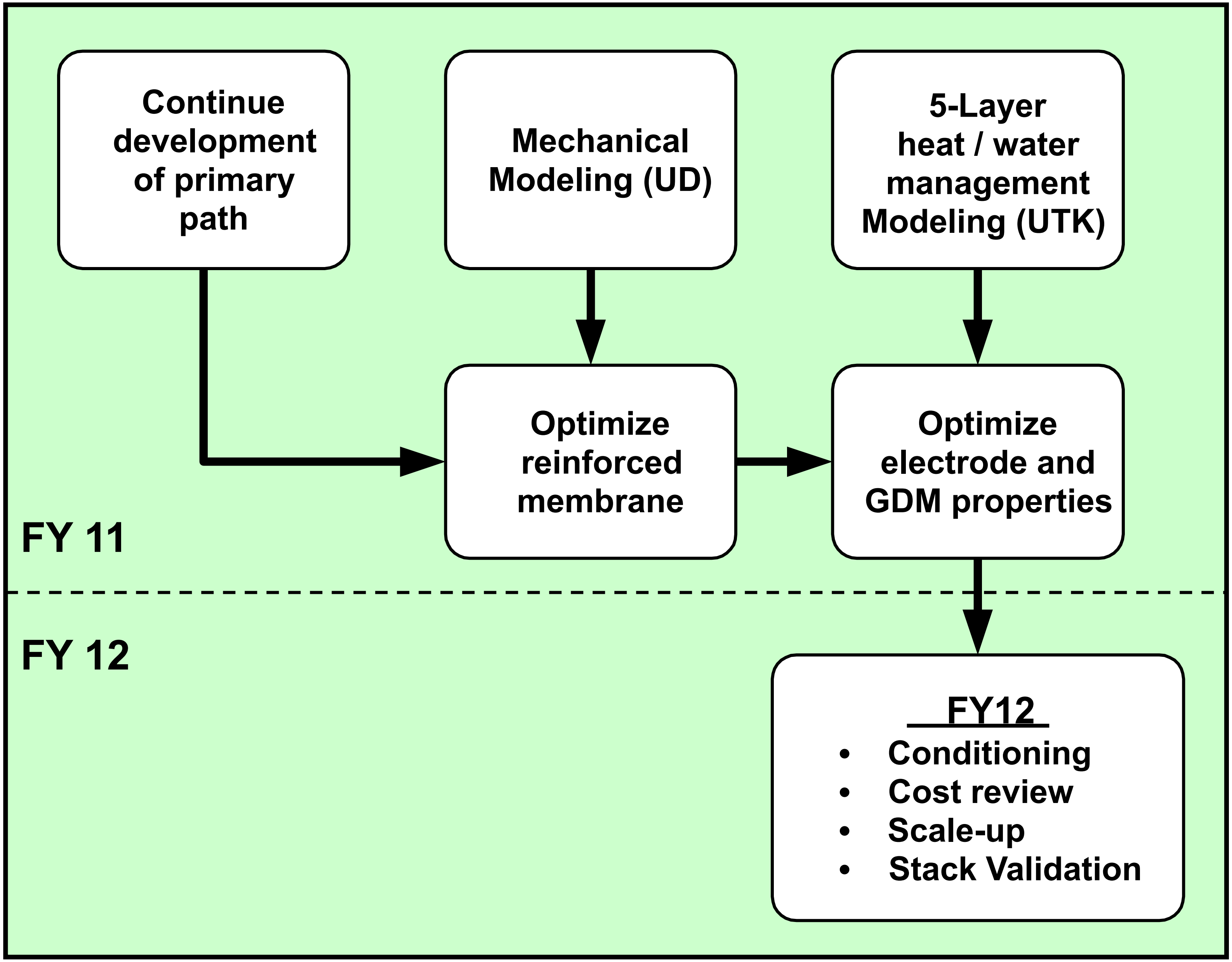
- Model upgraded with multi-phase physics, phase-change induced flow, multi-component diffusion, and agglomerate based resistance in electrodes.
- Parametric simulations reveal key controlling phenomena in water removal related to temperature and temperature gradient in the GDL/MPL.
- As GDL gets thinner, role of MPL in thermal boundary becomes dominant, and ***MPL and CL thermal conductivity are key engineering parameters***.
- Thinner membrane has higher performance enhancement (18→ 5 μm) compared to DM thickness changes.



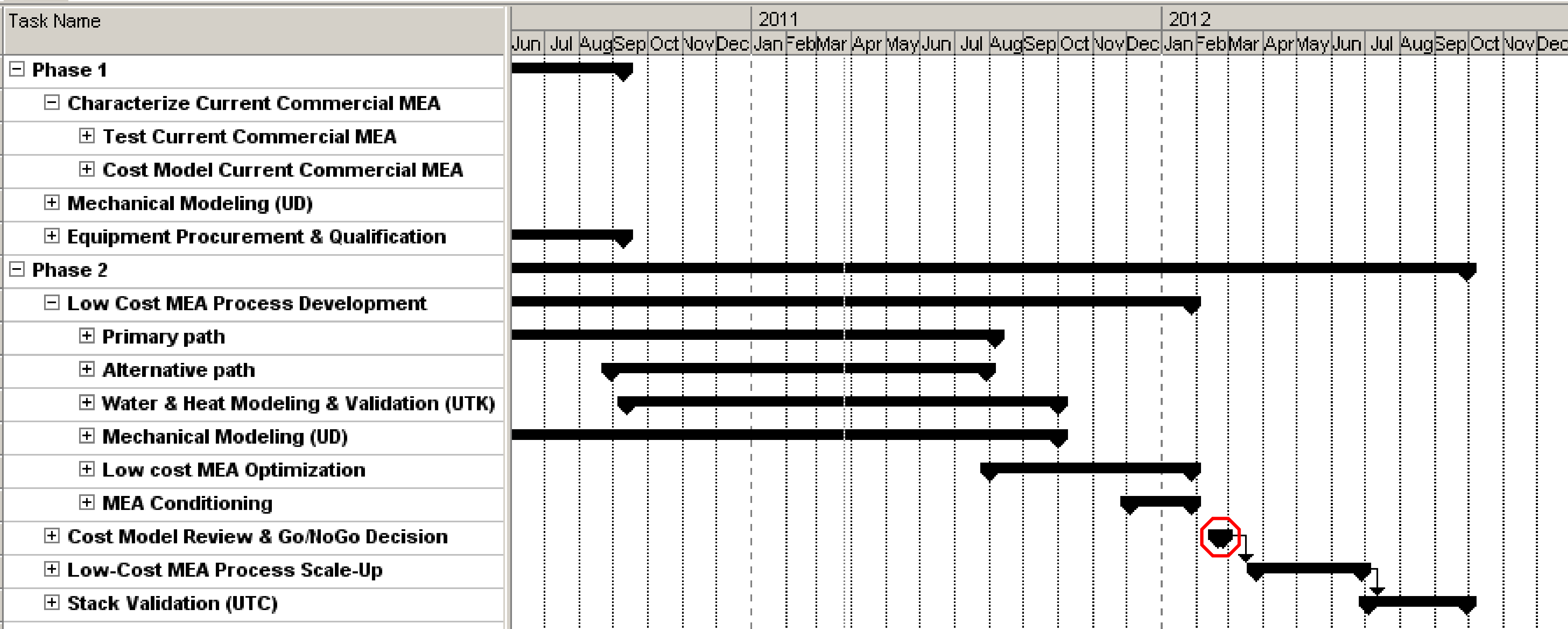
Case A: Thick Macro DM (330 μm) 0.432V   Case B: Thin Macro DM (82.5 μm) 0.474V

Results shown at 1.8 A/cm^2,all other parameters equal

Proposed Future Work for FY11: Summary



Proposed Future Work for FY11: 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. Madden
- NREL (federal, collaborator)
  - On-line quality control systems research
  - M. Ulsh
- W. L. Gore & Associates, Inc. (industry, lead)
  - Project Lead
  - F. Busby

*New partner added in late 2010

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

GORE Creative Technologies Worldwide

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
    - Primary and alternative paths have been determined
    - 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 12 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

GORE
Creative Technologies Worldwide

Acknowledgements:

W. L. Gore & Associates, Inc.

- Will Johnson
- Glenn Shealy
- Mark Edmundson
- Simon Cleghorn
- Laura Keough

University of Delaware

- Anette Karlsson
- Mike Santare
- Narinder Singh
- Zongwen Lu

Department of Energy

- Jesse Adams
- Pete Devlin
- Nancy Garland

UTC Power, Inc.

- Thomas Madden

University of Tennessee, Knoxville

- Matthew M. Mench
- Ahmet Turhan

GORE Creative Technologies Worldwide

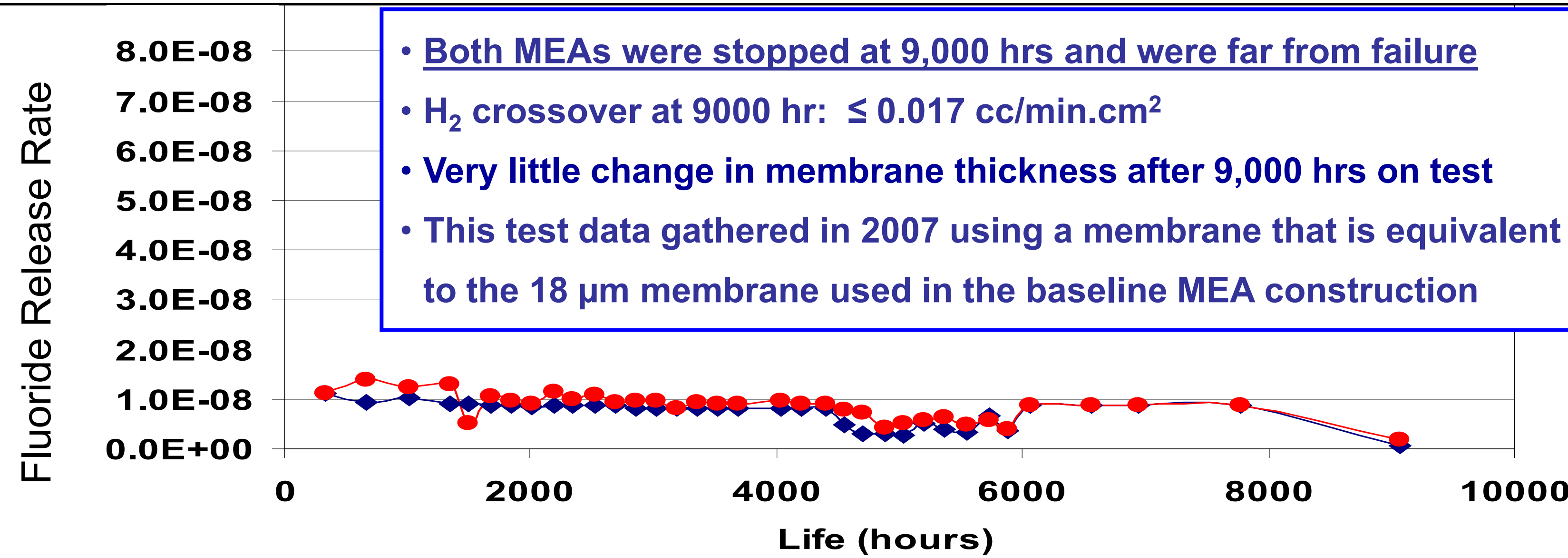
Technical Back Up Slides

Creative Technologies Worldwide

Technical Accomplishments:

9,000 Hour GORE-SELECT® Membrane Durability in 80°C Duty Cycle

- Both MEAs were stopped at 9,000 hrs and were far from failure
- H_2 crossover at 9000 hr: ≤ 0.017 cc/min.cm^2
- Very little change in membrane thickness after 9,000 hrs on test
- This test data gathered in 2007 using a membrane that is equivalent to the 18 µm membrane used in the baseline MEA construction



T_{Cell} (°C)	Load (mA/ cm²)	Stoic (A and C)	Pressure (kPa)	Inlet RH (%)	Exit RH (%)
80	20-1000	10-1.7	170	50	60-120

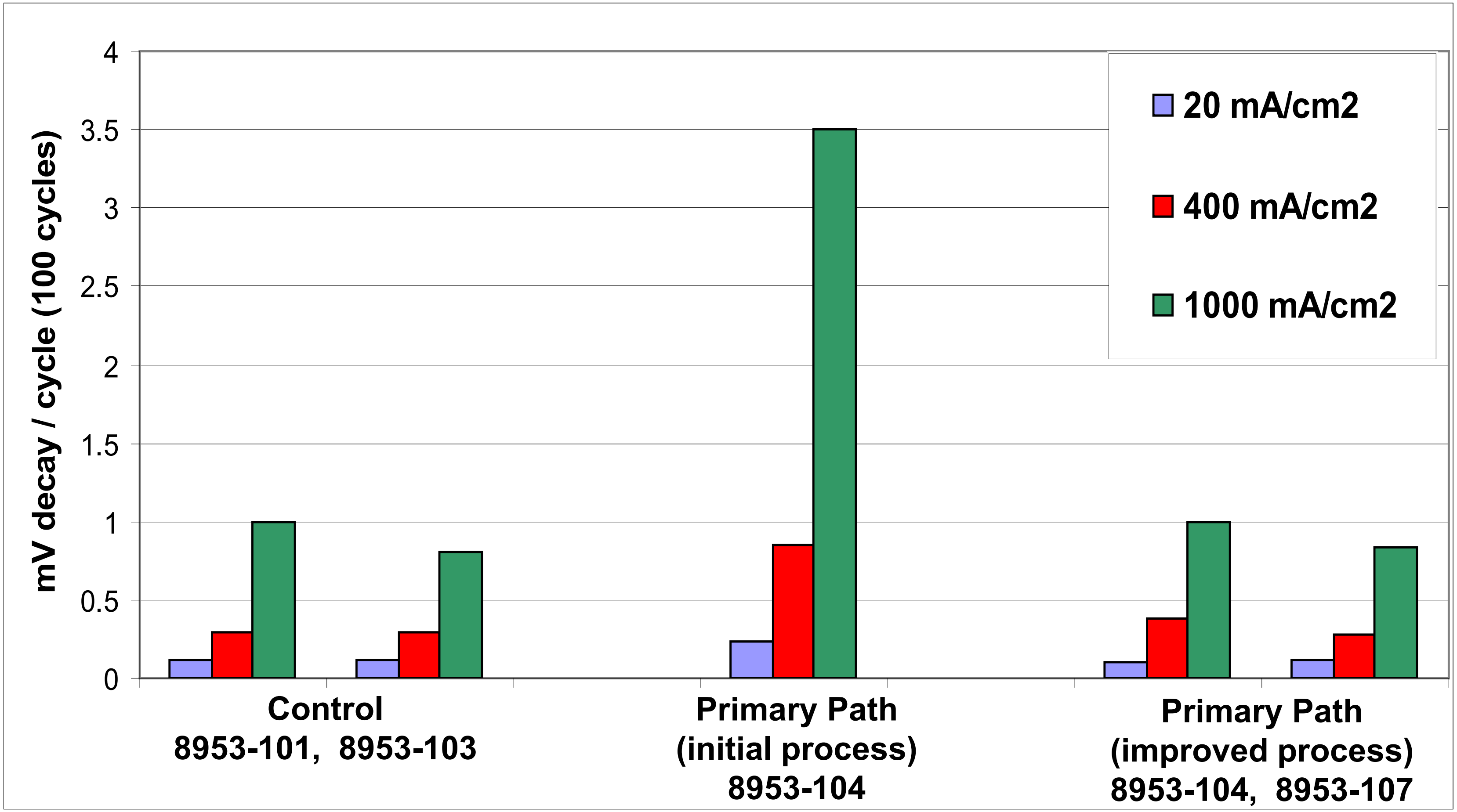
Table 3.4.11 Technical Targets: Membranes for Transportation Applications

Characteristic	Units	2005 Status [a]	2010	2015
Durability with cycling				
At operating temperature of ≤80°C	hours	~2,000 [e]	5,000 [f]	5,000 [f]
At operating temperature of >80°C	hours	N/A [g]	2,000	5,000 [f]
Oxygen cross-over [b]	mA / cm^2	5	2	2
Hydrogen cross-over [b]	mA / cm^2	5	2	2

Note: Membrane Testing Not Funded by DOE

Technical Accomplishments:

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



GORE
Creative Technologies Worldwide

Technical Accomplishments: Mechanical Modeling (UD)

Constitutive Model: Visco-elastic-plastic Model

$\sigma = K\ \varepsilon$

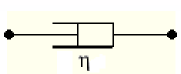
Spring Element
Strain dependence

K_P

(Long-term modulus)

$K_P + K_v$

(Instantaneous modulus)

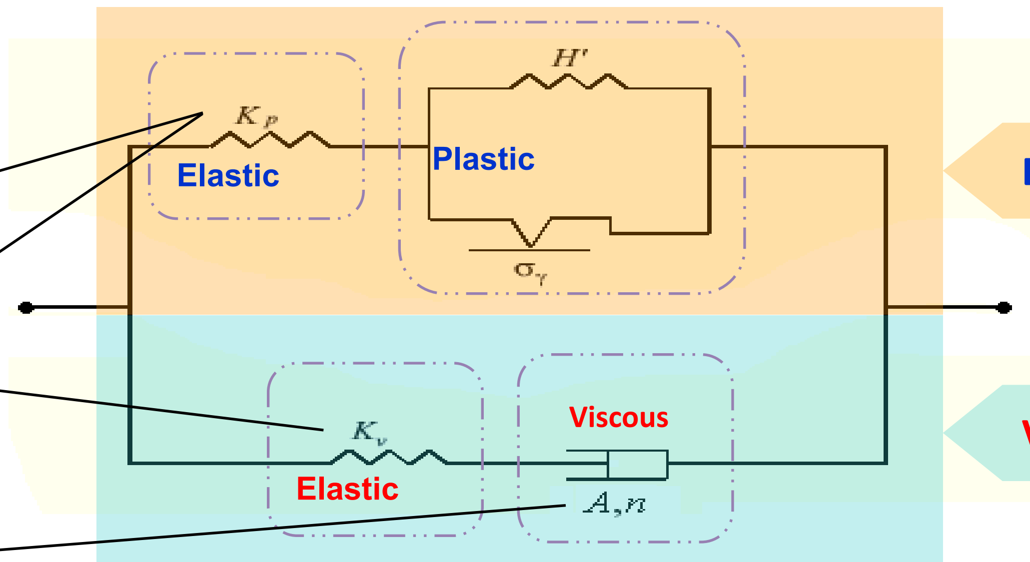


$\sigma = \eta\dot{\varepsilon}$

Dashpot Element
Strain-rate dependence

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

Viscous power law



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

Parameters

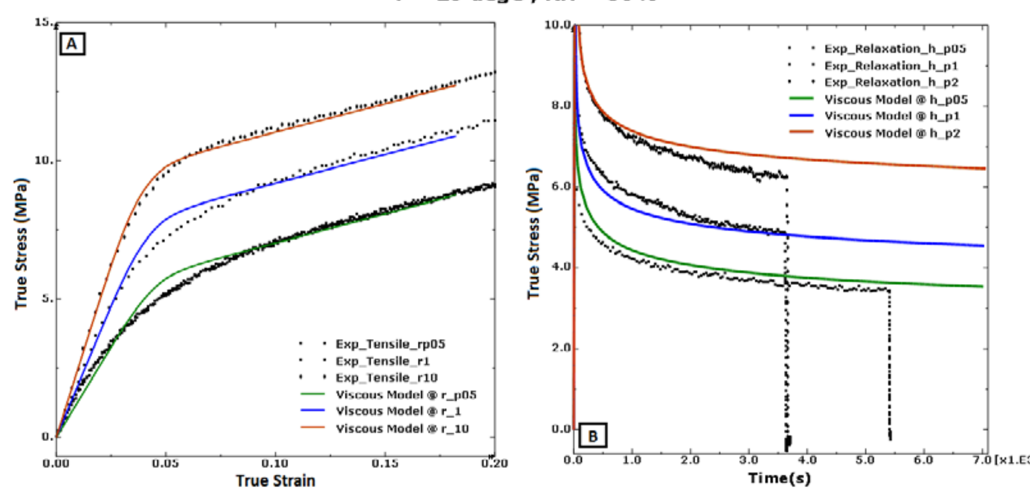
A, n, f, θ, λ

$E(K_P + K_V),$

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

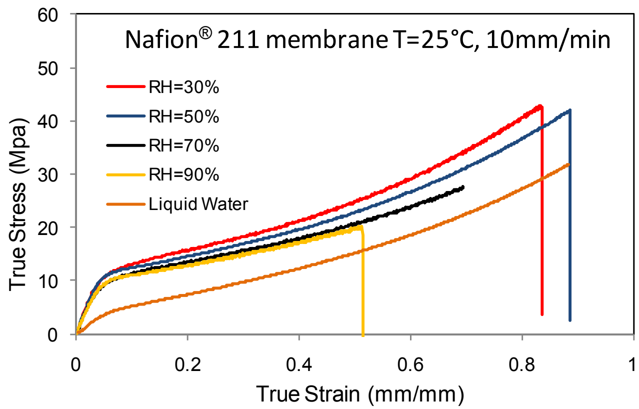
Visco-elastic-plastic model is tuned to match measured constitutive responses for MEA materials

T = 25 degC , RH = 30%



Technical Accomplishments: Mechanical Modeling (UD)

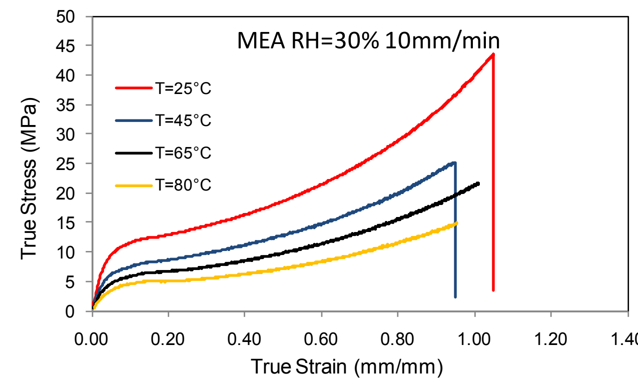
Properties of NAFION® 211 membrane, MEA and Reinforced PFSA measured

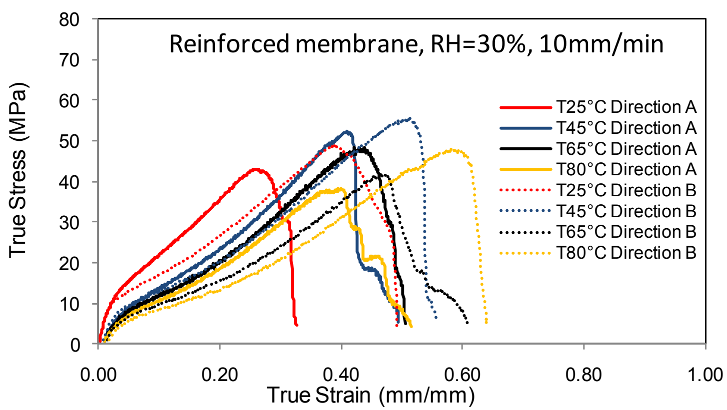


Condition	Rate	K_V [MPa]	K_P [MPa]	A	n	σ_y [MPa]	H [MPa]
T=25, RH=30%	1mm/min	160	31	1.50E-09	6.5	1.55	19.8
	10mm/min	220	31	3.00E-09	6.5		
T=80, RH=30%	10mm/min	80	10.64	1.00E-05	4.5	0.532	7.0
	250mm/min	127	10.64	5.00E-06	4.5		

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)

NAFION is a registered trademark of E. I. DuPont de Nemours & Company

GORE Creative Technologies Worldwide