2014 DOE Hydrogen and Fuel Cells Program

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

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W. L. Gore & Associates, Inc.

6/18/2014

Project ID # MN004

Overview

Budget

- Total Project Value: $4.2MM
  - $2.7MM DOE Share (65%)
  - $1.5MM Contractor Share (35%)
- Total DOE Funding Spent: $1.87MM*

*As of 3/31/2014

Timeline

- Project start: 9/01/08
- Project end: 12/30/14
- 90% complete as of 4/15/14

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
  - Stack Testing
- W. L. Gore & Associates, Inc. (Gore)
  - Project Lead

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)**

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
  - Evaluate potential for new process to achieve **DOE cost targets** prior to process scale-up (Go / No-Go Decision)
- Scale Up
  - Equipment setup (Gore)
  - 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
- Stack Validation (UTK)

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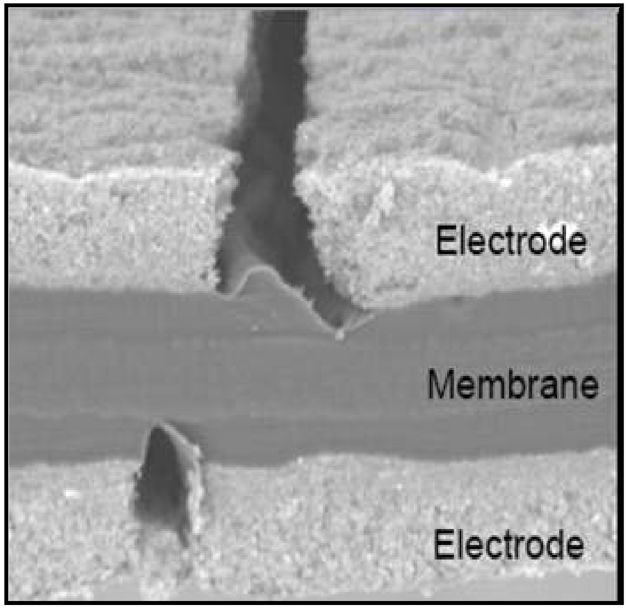
Approach: Summary

- 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: Go / No-Go Criteria

<u>"Go" decision was made in September 2013</u>

- ✓ >25% cost reduction in high-volume manufacturing of 3-layer MEAs
- ✓ Process will be scalable to FC industry MEA volumes in 2015 (estimate 100,000 m^2 / year)
- ✓ Process will be consistent w/ achieving $9/kW DOE 2017 automotive MEA cost target
- ✓ The product will also meet/exceed current MEA durability & power densities.

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Approach: End of Project Milestone

- A fuel cell stack will be built and tested using Gore's new 3-layer MEA manufacturing process. These MEAs will not only be scalable to potential fuel cell industry MEA volumes in 2015 (estimate 100,000 m^2 / year), but they will also meet or exceed Gore's current power density (950 mA/cm^2 @ 0.6 V) and durability (Fluoride Release Rate< 1*10-7 g/cm^2*hr, Voltage Cycling Decay < 50%) under the following conditions: H_2/Air, 1.3/2.0 stoich, 80°C dew points and cell temperature, 0 psig)

- Cost modeling of the process used to manufacture the MEA will indicate >25% cost reduction in high-volume manufacturing of 3-layer MEAs and the process will be consistent with achieving DOE's $9/kW DOE 2017 automotive MEA cost target.

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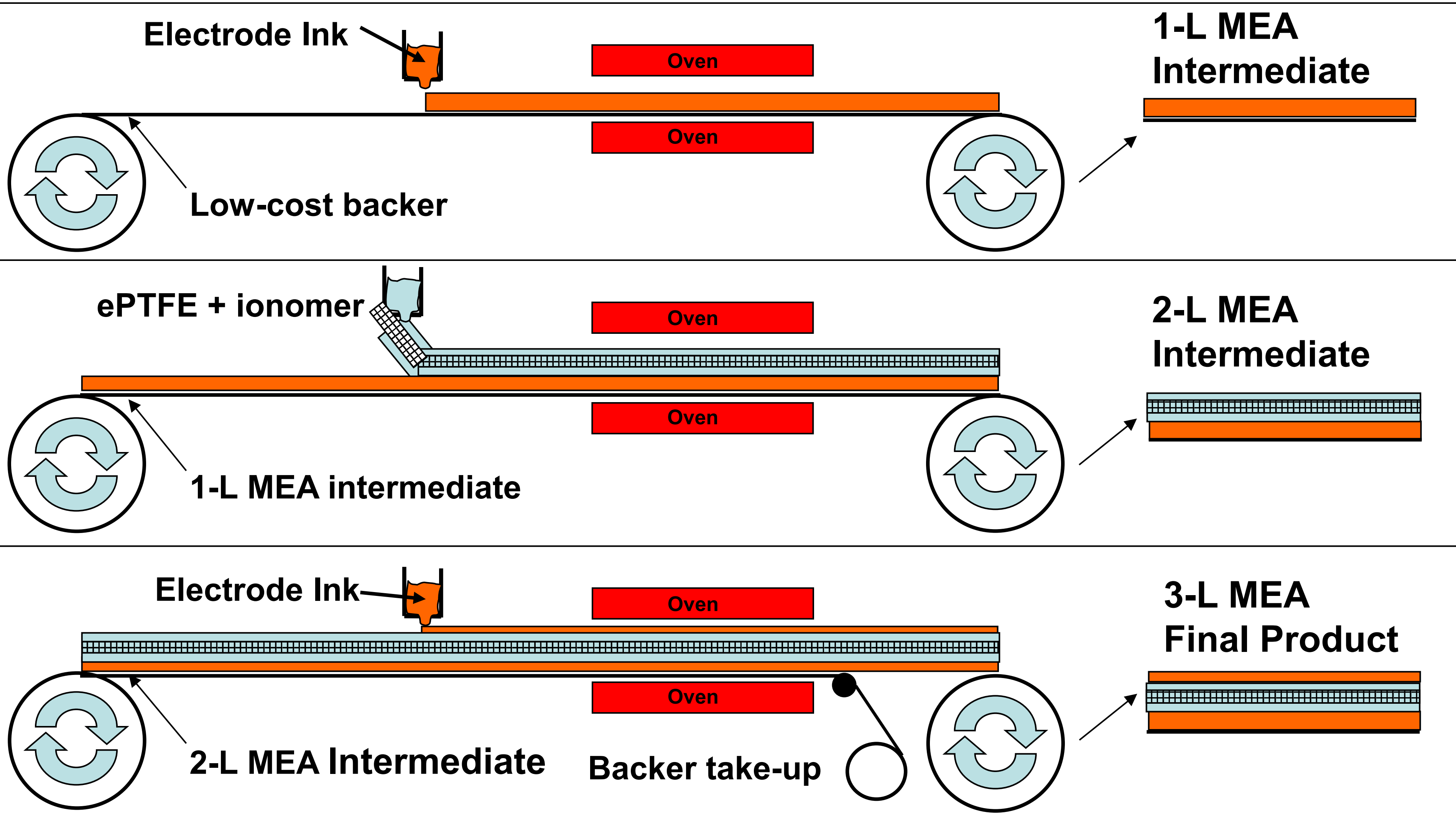
Approach: Low-Cost MEA Mfg Process



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Technical Accomplishments & Progress: Summary

- Mechanical Modeling of Reinforced 3-L MEA (UD)
  - –Parametric analysis of layered structure — 100% Complete
  - –Fatigue analysis of layered structure — 100% Complete
- New 3-L MEA Process Exploration (Gore)
  - –Low-cost backer — 100% Complete
  - –Cathode Layer — 100% Complete
    - Power density beginning of life (BOL) testing
    - Electrochemical diagnostics
    - Durability testing
  - –Reinforced Membrane Layer — 100% Complete
    - Power density and robustness BOL testing
  - –Anode Layer — 100% Complete
    - Power density and robustness BOL testing
    - Electrochemical diagnostics
  - –Phase 2 Cost analysis (Gore and SA collaboration) — 100% Complete
- Scale-up and optimization
  - –Demonstrate entire 3-L process on a roll to roll coating line — 95% Complete
  - –Optimize membrane, electrodes, and GDM based on scale-up results and model predictions — 50% Complete

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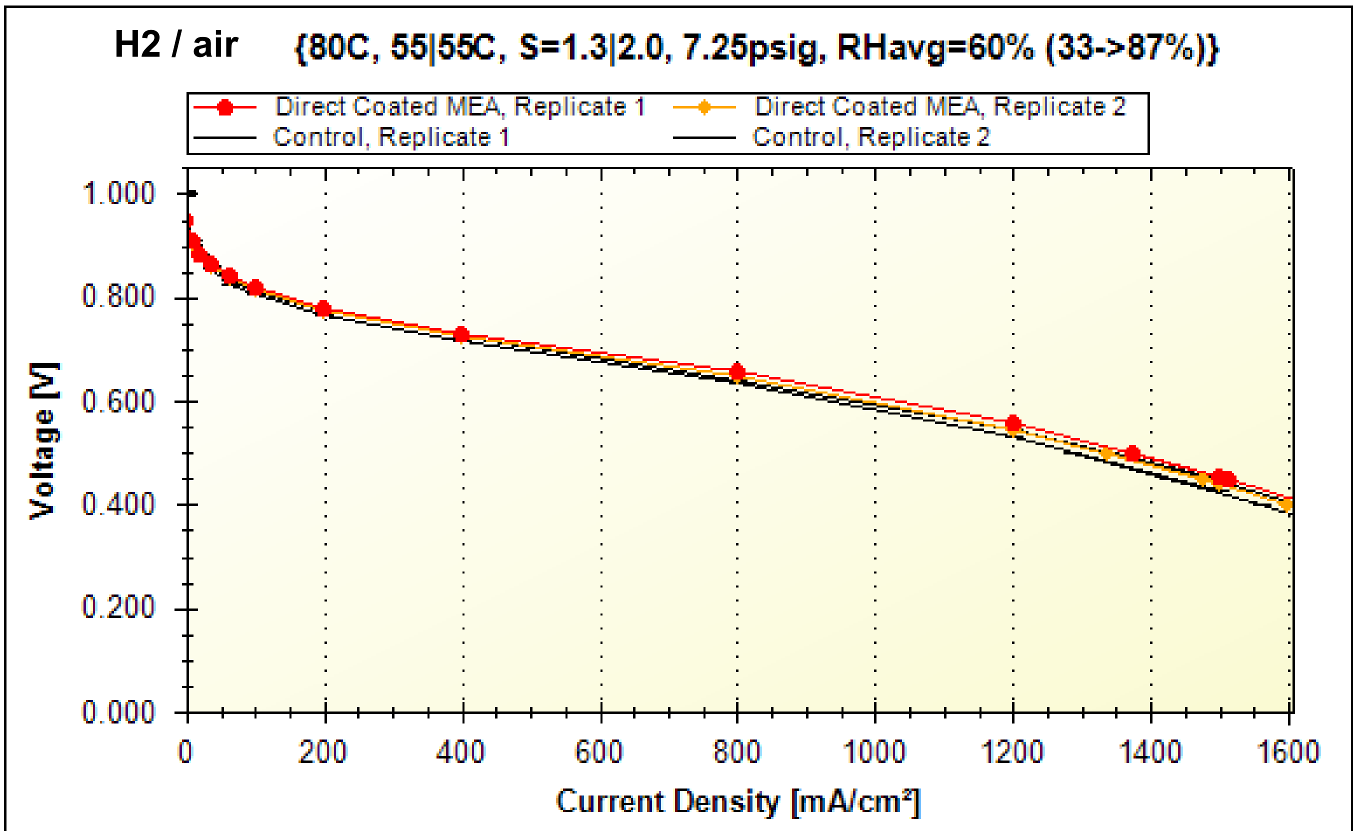
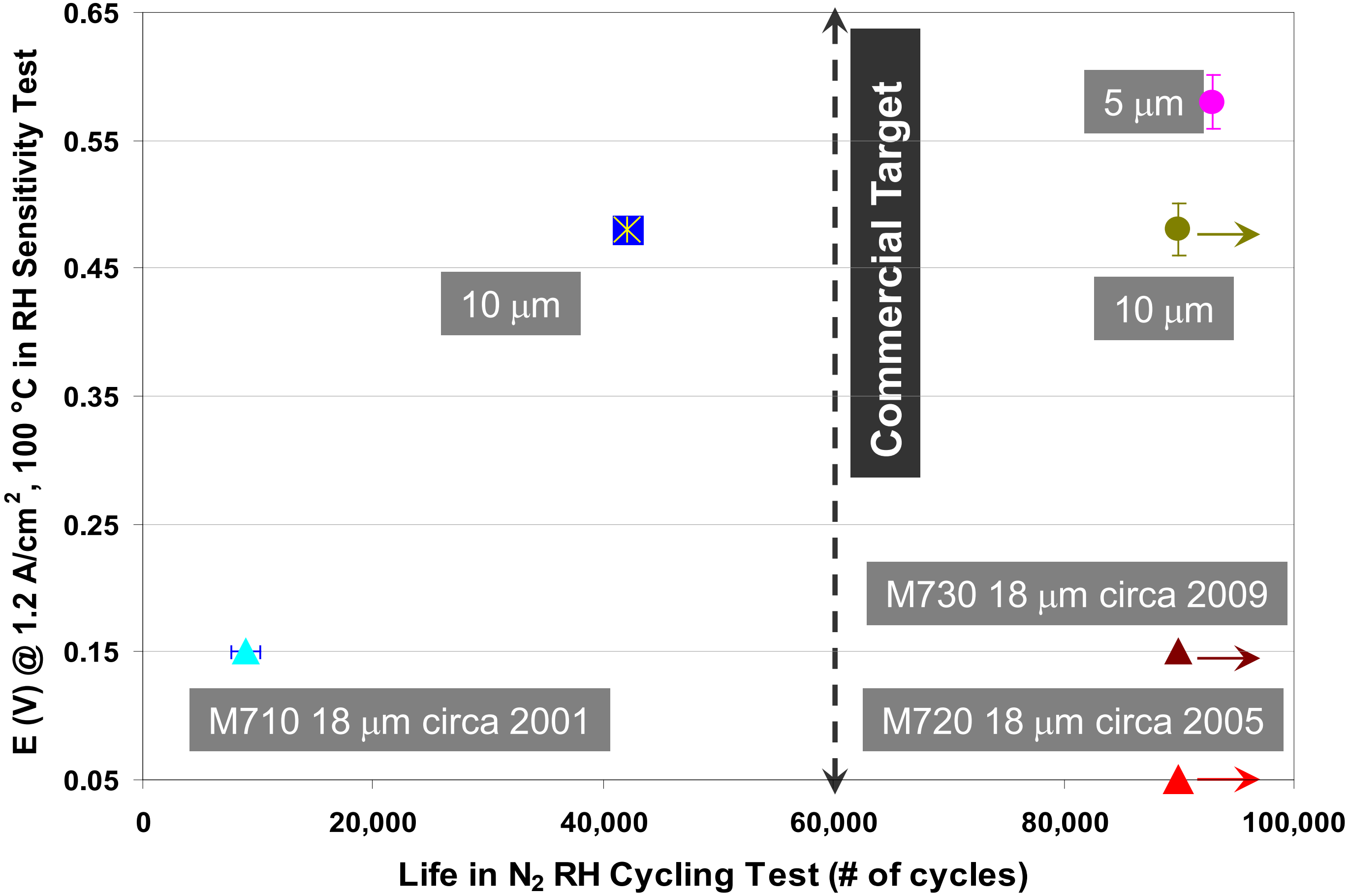
Technical Accomplishments: Backer & pilot line progress

- Minor equipment modifications were needed to direct coat the membrane layer on top of the cathode layer using the modified backer
- Gore has since coated over 100 meters of intermediate MEA material on a roll to roll process
- Optimization of direct coated 3L MEA is in progress



Technical Accomplishments:

Gore's state-of-the-art thin, durable reinforced membranes have been DEMONSTRATED in the roll-to-roll 3L process



Compared to Gore's current commercial membranes (15-20 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:
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

2014 New Process Status Update

2009 Process Waste Map

Membrane Coating

Process Costs	Primary forms of waste	Modeled Process Improvements	2014 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	2014 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	2014 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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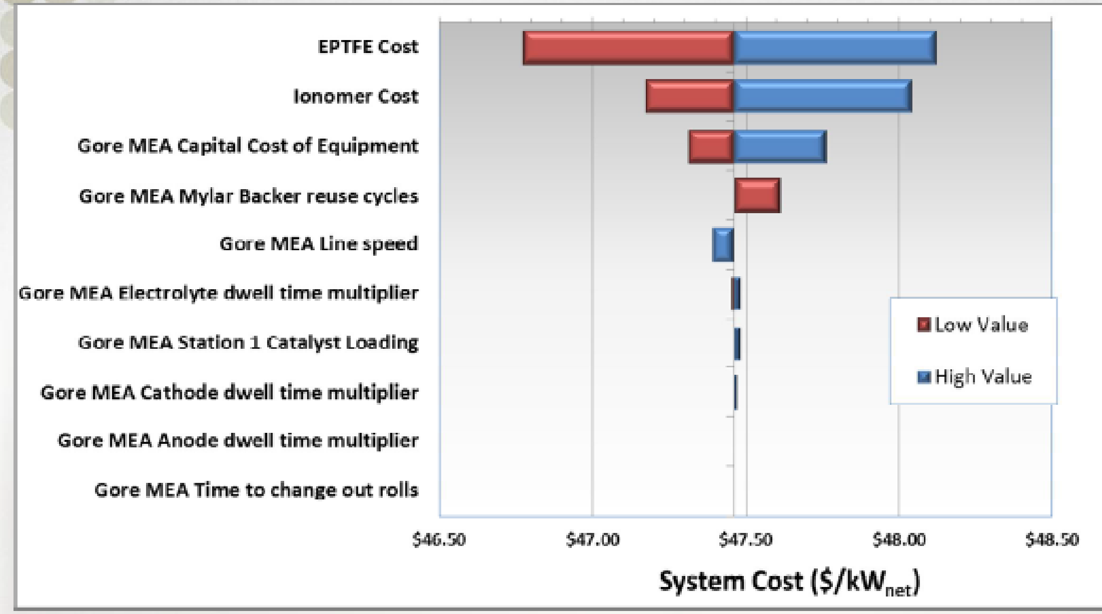
Technical Accomplishments:
Gore and SA Cost Model Collaboration

MEA Sensitivity



System Cost ($/kWnet), 500,000 sys/year				
Parameter	Units	Low Value	Base Value	High Value
EPTFE Cost	$/m²	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.

Technical Accomplishments: Response to Reviewers' Comments

- The project team should conduct a cost model analysis of manufacturing MEAs through electrode coating on diffusion media approach
  - This was recently added to the cost modeling scope of work

- Researchers should seek to make the results of the project more broadly applicable to other MEA manufacturers.
  - MEA performance data, durability data, and manufacturing cost models are shared publicly
  - Academic work at UD has been published extensively

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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
  - Stack Testing
  - M. Mench
- 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

Remaining Challenges and Barriers

- **Challenge:** Optimize membrane and electrode properties within the constraints of the scaled-up 3L process so that the MEAs with direct coated electrodes can match the performance and durability of Gore's baseline commercial MEA

- **Barrier:** Evaluation of higher-activity supported catalyst, such as the core-shell catalysts that are being developed under separate DOE funded projects, is out of the scope of this project. Better catalysts are needed to reach the DOE precious metal cost target. The scope of this project is the cost of the MEA manufacturing process, not the raw materials.

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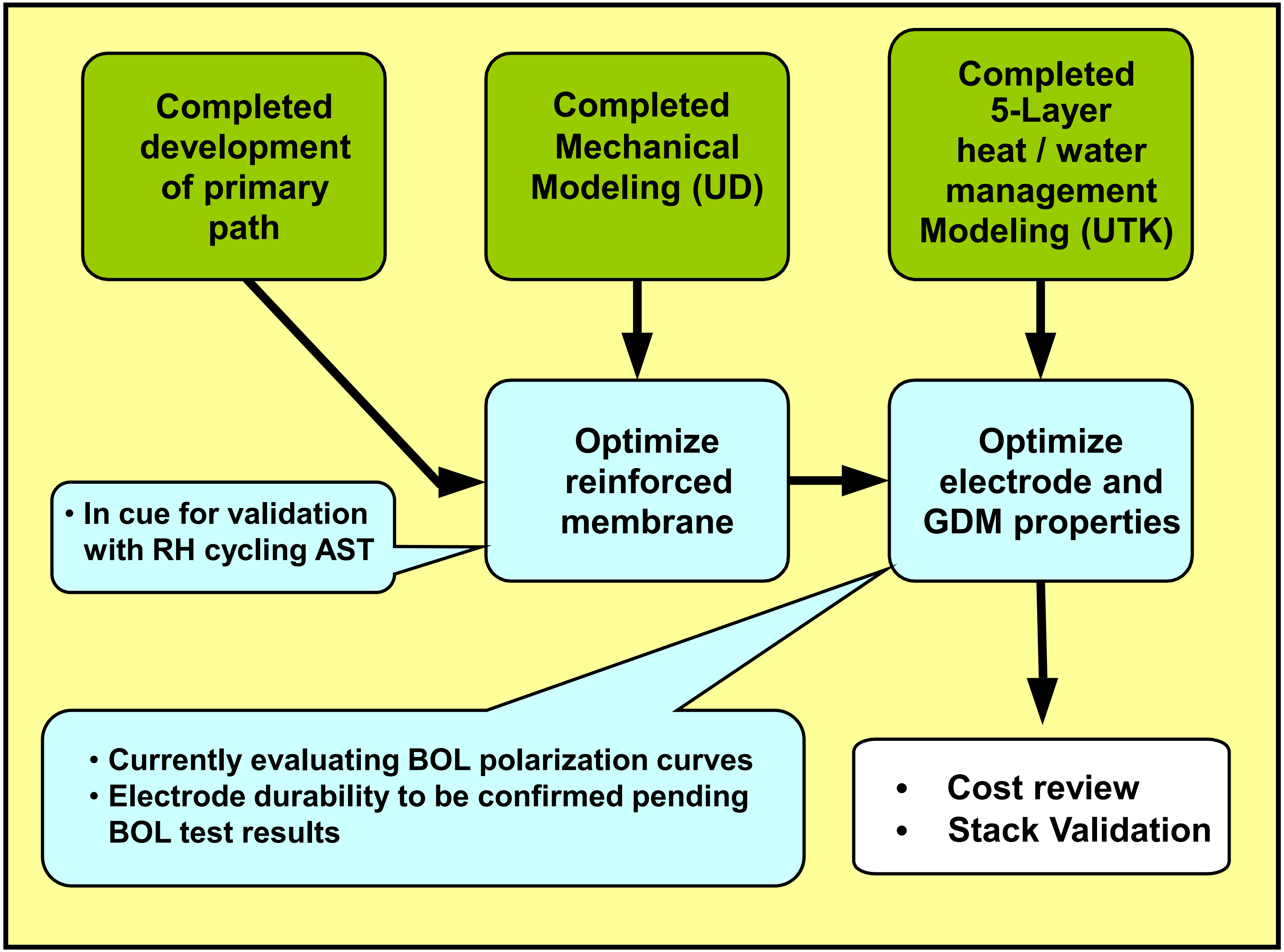
Proposed Future Work: Summary



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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**
    - Direct Coating to form membrane–electrode interfaces
    - 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**
  - **Pilot-scale** demonstration of the new 3-L MEA process is nearing completion
    - 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 an **8 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 complete
- 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

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- Brian James

Department of Energy

- Jesse Adams
- Nancy Garland

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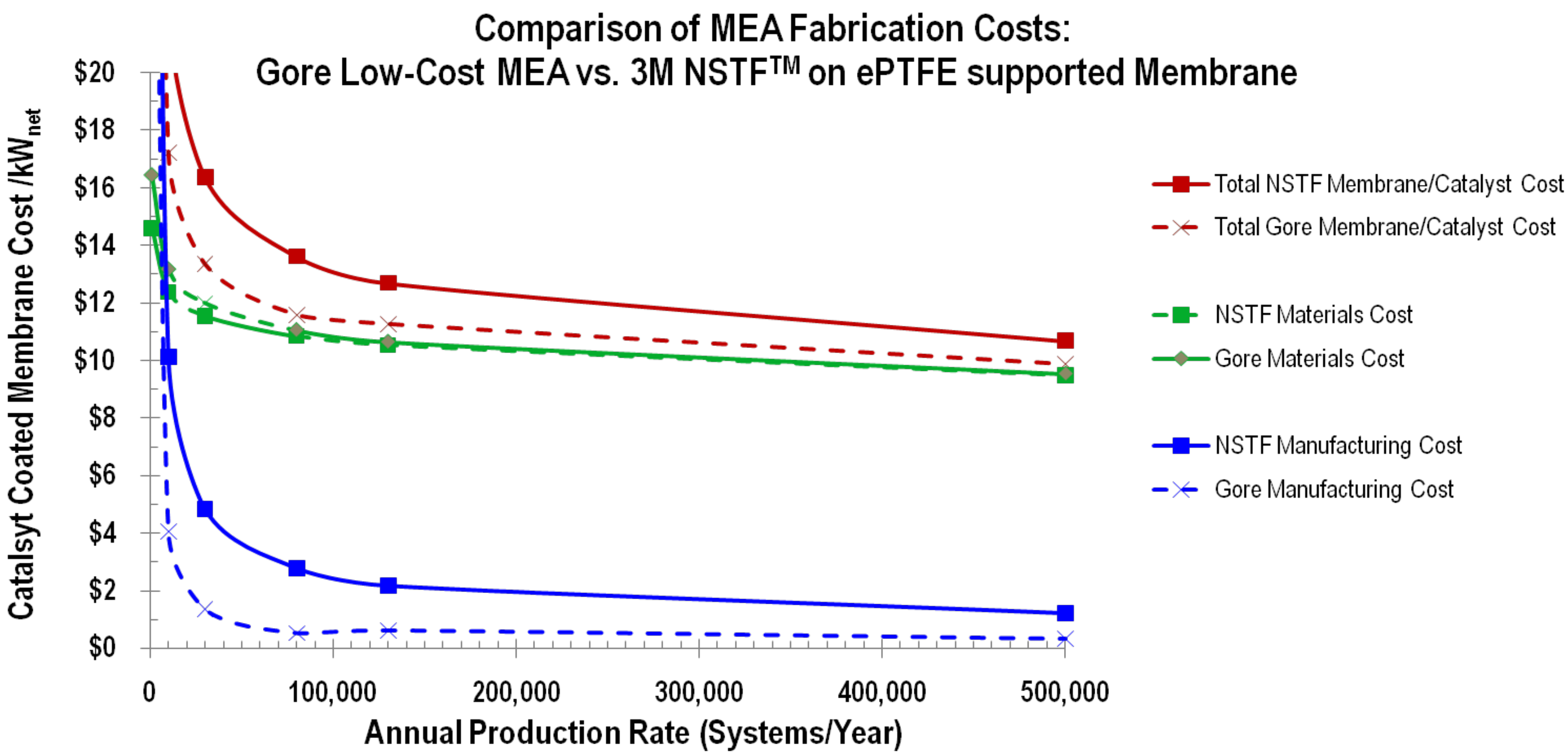
Technical Back Up Slides

Technical Accomplishments:

Gore and SA Cost Model Collaboration

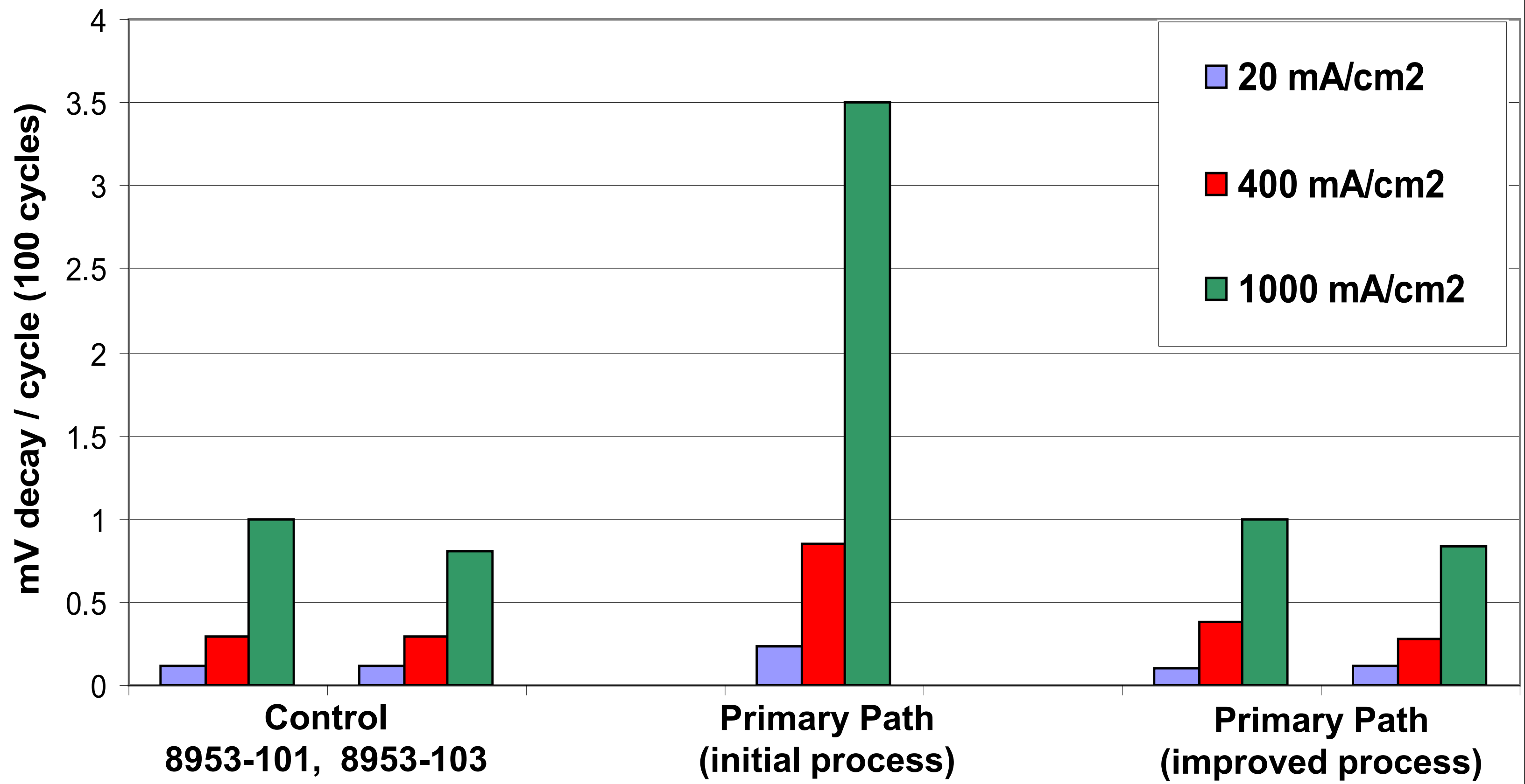
Gore MEAs and 3M NSTF™/Membrane Catalyst Coated Membrane are expected to have similar costs



- 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:

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

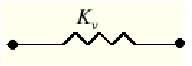
Collected data to quantify oxidized impurities which are associated with conditioning time

Investigated impact of direct-coated electrode structure on molecular diffusion

Quantified ionic conductivity of direct coated cathode

Technical Accomplishments: Mechanical Modeling (UD)

Constitutive Model: Visco-elastic-plastic Model



$\sigma = K\ \varepsilon$

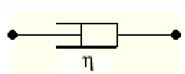
Spring Element
Strain dependence

K_P

(Long-term modulus)

$K_P + K_v$

(Instantaneous modulus)



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

Dashpot Element
Strain-rate dependence

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

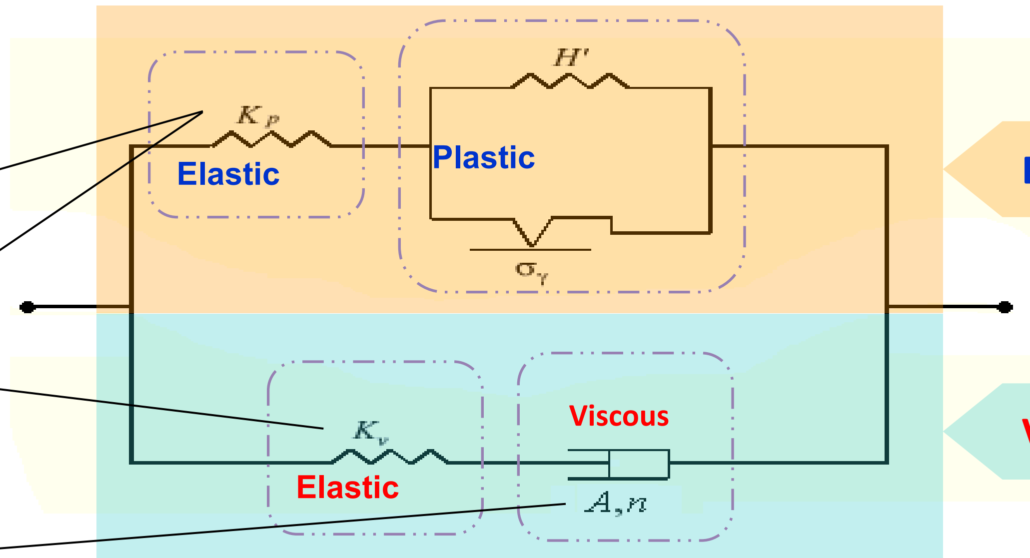
Viscous power law

Parameters

A, n, f, θ, λ

$E(K_P + K_V),$

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

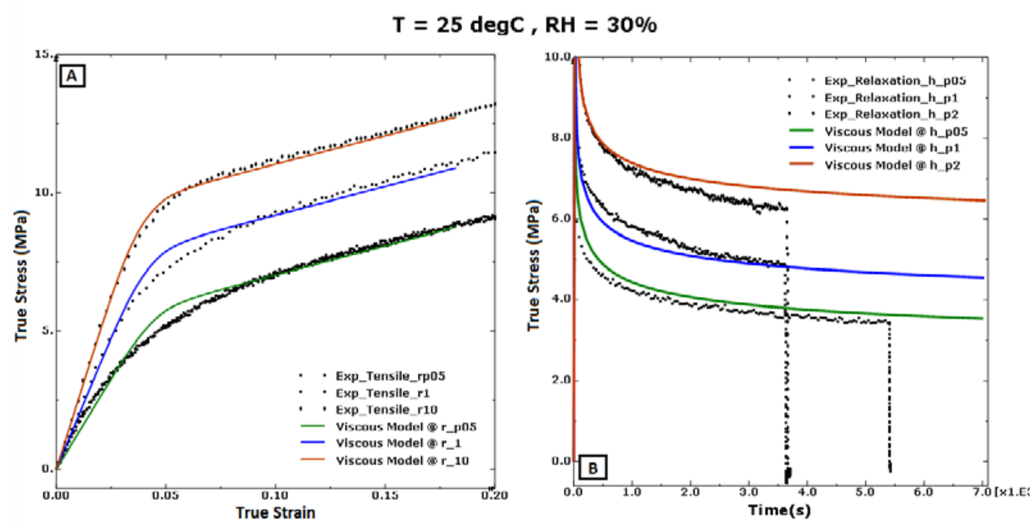


Elastoplastic terms

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

Visco-Elastic terms

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



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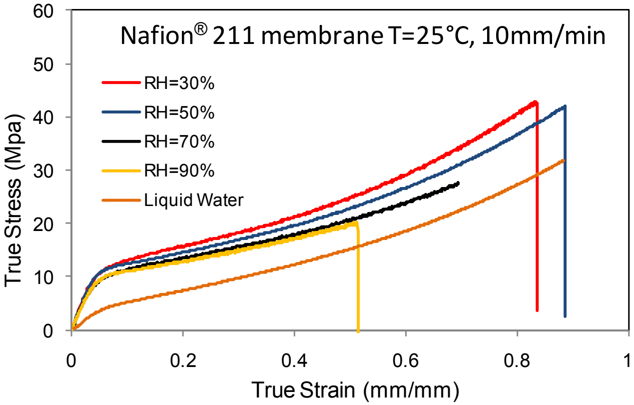
Technical Accomplishments: Mechanical Modeling (UD)

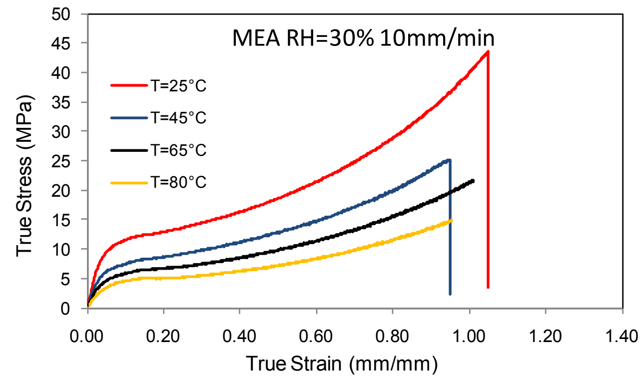
Properties of NAFION® 211 membrane, MEA and Reinforced PFSA measured

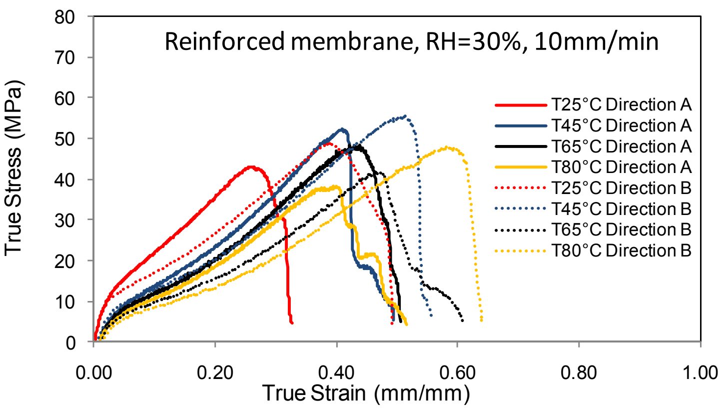


Condition	Rate	K_V [MPa]	K_P [MPa]	A	n	σ_y [MPa]	H [MPa]
T=25, RH=30%	1mm/min	160	31	1.50E-09	6.5	1.55	19.8
	10mm/min	220	31	3.00E-09	6.5		
T=80, RH=30%	10mm/min	80	10.64	1.00E-05	4.5	0.532	7.0
	250mm/min	127	10.64	5.00E-06	4.5		

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

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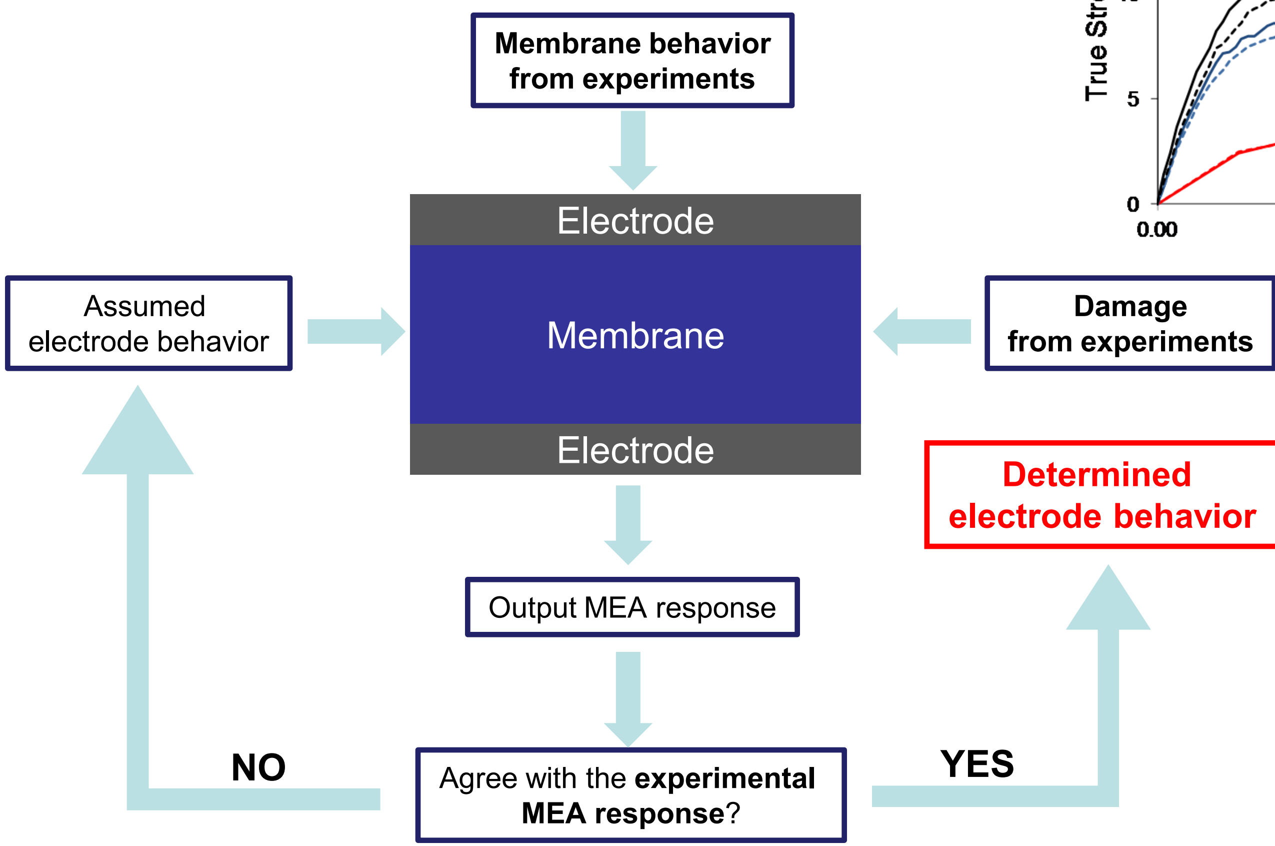
Technical Accomplishments: Mechanical Modeling (UD)

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