2010 DOE Hydrogen Program

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

PI: F. Colin Busby
W. L. Gore & Associates, Inc.
6/11/2010

Project ID #
MN004

Overview

Budget

- Total Project Funding: $4.4MM
  - $2.8MM DOE Share
  - $1.6MM Contractor Share
- Received in FY09: $654k
  - $890k spent as of 4/8/10
- Funding for FY10: $700k

Barriers Addressed

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

Timeline

- Project start: October 1, 2008
- Project end: March 31, 2012
- 35% Percent Complete as of 4/8/10

Partners

- University of Delaware (UD)
  - MEA Mechanical Modeling
- Penn State University (PSU)
  - Fuel Cell Heat / Water Management Modeling & Validation
- UTC Power, Inc. (UTCP)
  - Stack Testing
- W. L. Gore & Associates, Inc. (Gore)
  - Project Lead

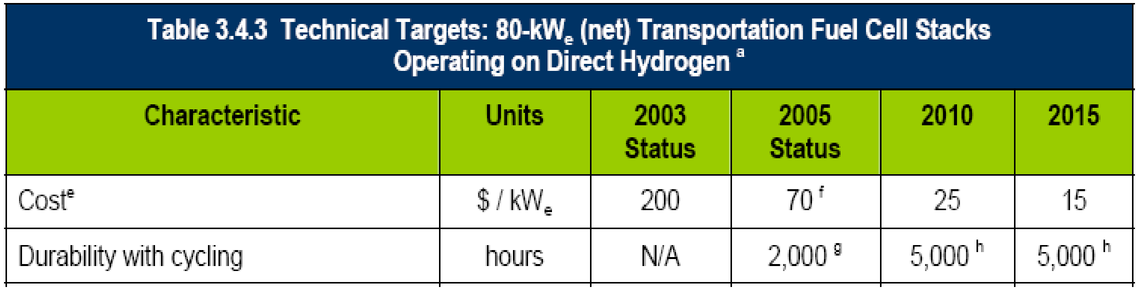


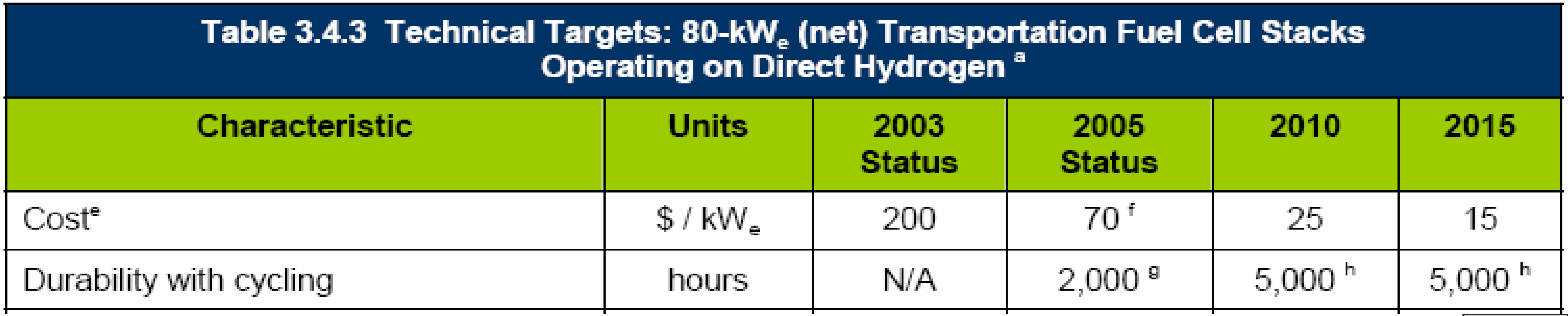
Table 3.4.3 Technical Targets: 80-kW$_e$ (net) Transportation Fuel Cell Stacks Operating on Direct Hydrogen [a]

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]

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] 3L MEAs[5] that require little or no 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 3 layer MEA roll-good (Anode Electrode + Membrane + Cathode Electrode)
6. The stack break-in time should be reduced by at least 50 % compared to the product made in today's process, and break-in strategies employed must be consistent with cost targets



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Relevance: Objectives

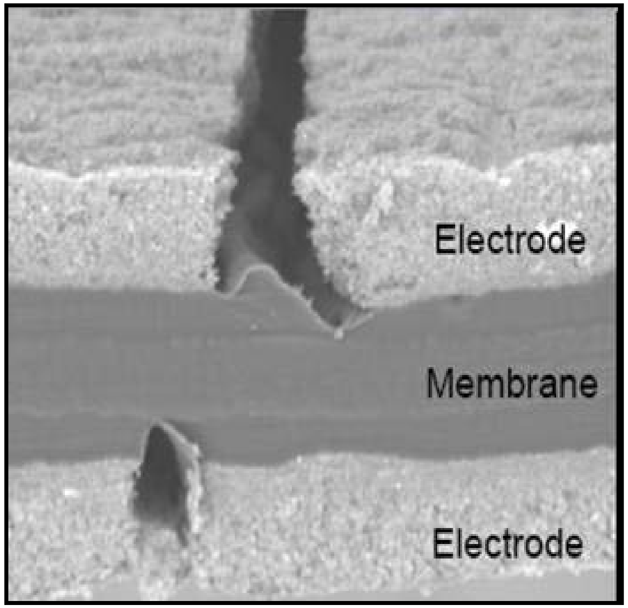
- Develop a relevant high-volume cost model for membrane electrode assembly (MEA) production and estimate potential savings for an MEA made in an improved process (Gore)
  - Estimate potential savings to justify kick-off of new process development FY '09
  - Evaluate potential for new process to achieve **DOE cost targets** prior to process scale-up (Go / No-Go Decision) FY '11
- R&D equipment procurement and qualification (Gore)
  - Low-cost membrane coating FY '09
  - Low-cost cathode electrode coating FY '09
  - Low-cost anode electrode coating FY '09

Relevance: Objectives

- Low-cost MEA R&D
  - New Process Exploration (Gore) FY ’09 & ‘10
    - Investigate equipment configuration for MEA production
    - Investigate raw material formulations
    - Map out process windows for each layer of the MEA
  - Fuel Cell Heat & Water Management Modeling & Validation (PSU) FY ’10
    - Low cost processes result in a different range of electrode properties
    - Electrode and GDL thermal, geometric, & transport properties and interactions need to be optimized efficiently to meet project goals
  - Multi-layer Mechanical Modeling (UD) FY ’09 & ’10
    - Develop a deeper understanding of MEA failure mechanisms
    - Use model to optimize mechanical durability of the MEA structure targeted by the new low-cost process
  - MEA optimization FY’ 11
    - Utilize modeling results & designed experiments
- Conditioning FY ‘11
- Scale Up FY ‘11
- Stack Validation FY ’11

Approach: Summary

- Reduce MEA & Stack Costs
  - Reduce the cost 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 properties and performance of the 3L 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



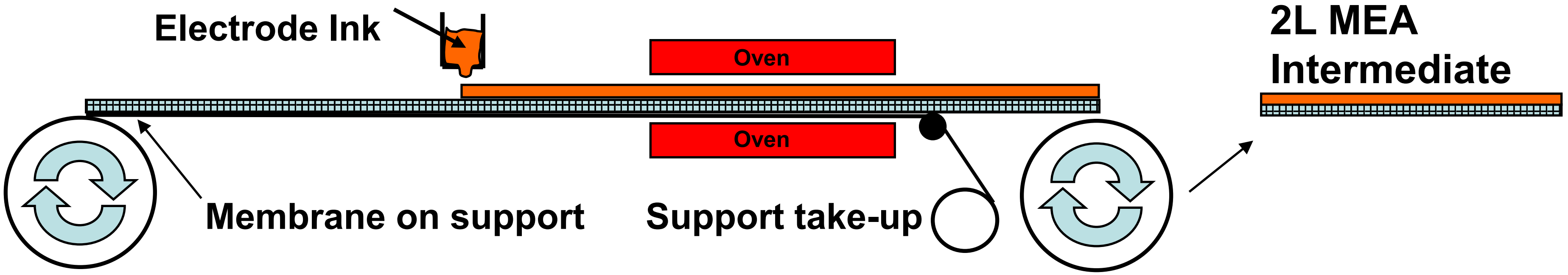
Approach:

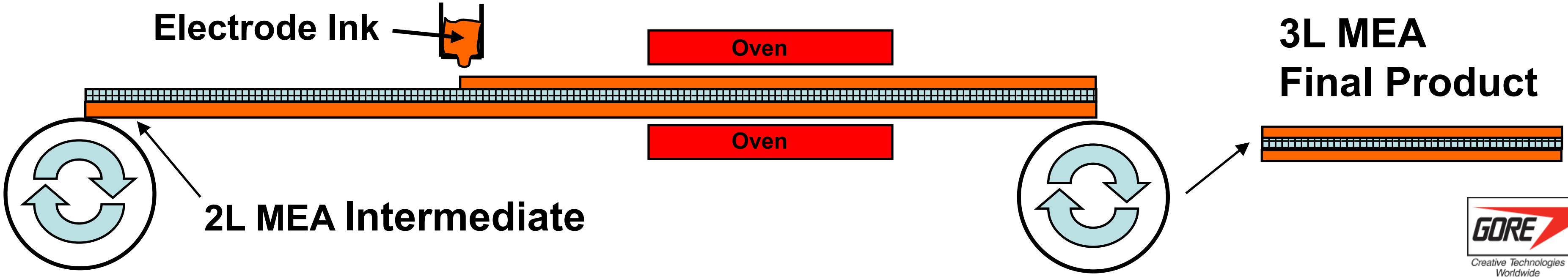
- Low-cost MEA R&D
  - R&D Equipment Procurement and Qualification
  - Primary path
    - Direct coated cathode on a backer-supported reinforced membrane
    - Direct coated anode on 2-layer intermediate
  - Alternate path
    - Direct coat anode on supported ½ membrane
    - Direct coat cathode on supported ½ membrane
    - Bond the membrane-membrane interface of the 1.5 layer webs to make a 3-layer web

Approach:
Low-Cost MEA Mfg Process: Primary Path

High-Volume, Low-Cost, Full Width MEA Production

- ➢ Reduce the cost 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





Approach: Mechanical Modeling

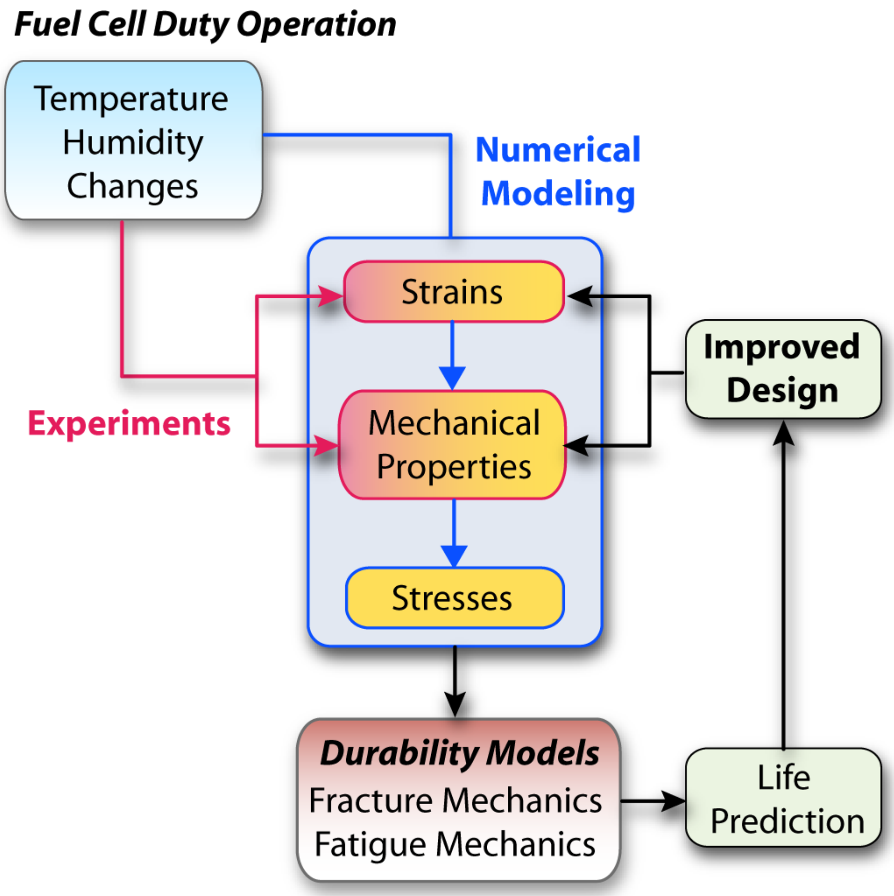
- Model Concept:

  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

- Devise & perform experiments to determine mechanical properties of MEA materials as functions of:
  - Temperature
  - Humidity
  - Time

- Use numerical modeling to predict mechanical response of MEA during cell operation and accelerated testing

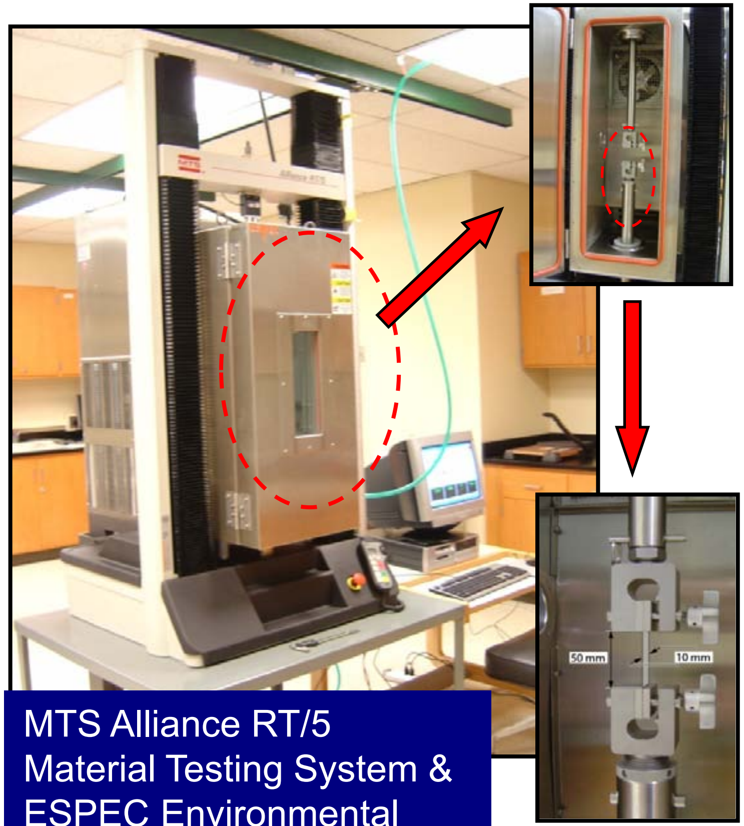
- Use model to explore new MEA designs and optimize prototypes that will be made in the new low-cost process



Approach: Mechanical Modeling

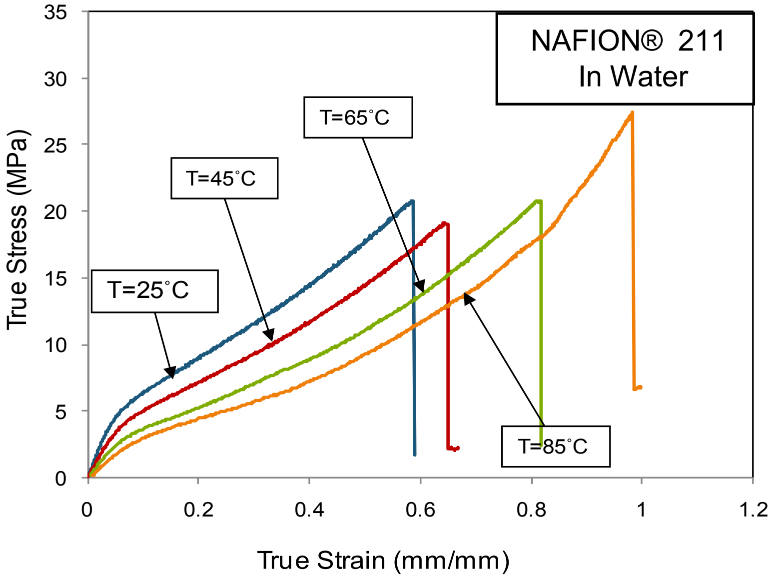
MTS Tensile Tester RT/5

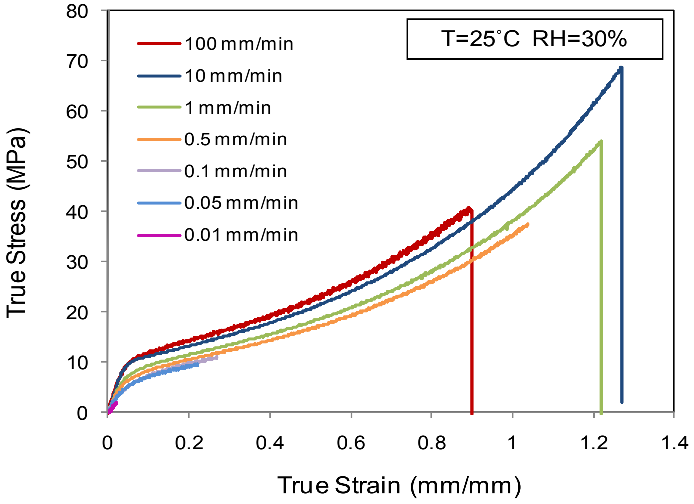
Humidity controlled environment



MTS Alliance RT/5 Material Testing System & ESPEC Environmental Chamber

Temperature and Relative Humidity Capability:
T: 25˚C - 85 ˚C; RH: 30-90%





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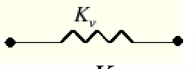
Approach: Mechanical Modeling

Constitutive Model: Visco-elastic-plastic Model



$\sigma = K\ \varepsilon$

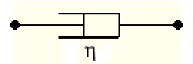
Spring Element
Strain dependence

K_P

(Long-term modulus)

$K_P + K_v$

(Instantaneous modulus)



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

Dashpot Element
Strain-rate dependence

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

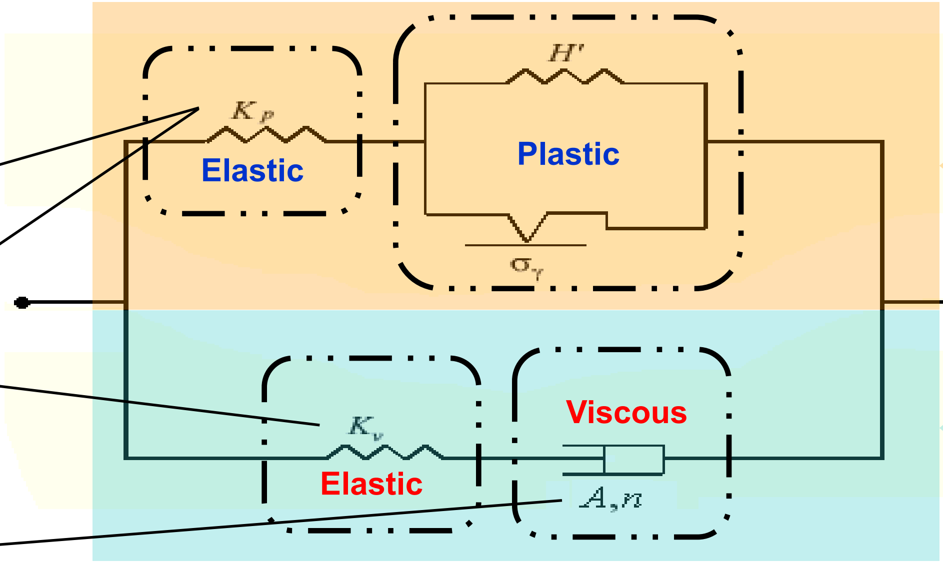
Viscous power law

Parameters

A, n, f, θ, λ

$E(K_P + K_V),$

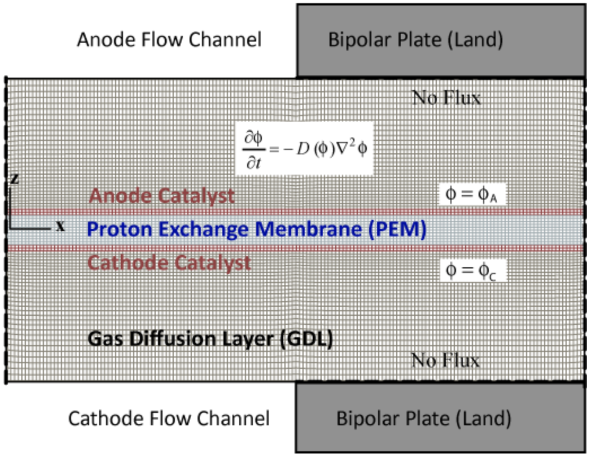
$\upsilon, \sigma_{yield}, H$



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

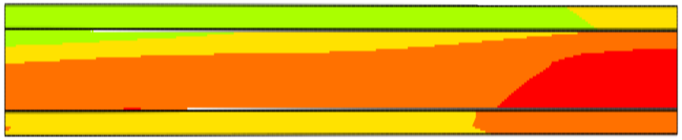
Elastoplastic terms

Visco-Elastic terms



Potential Model Output Data:

- **Water Transport and MEA Stresses**
  - **3L Residual In-plane Stress After De-Hydration**



Technical Accomplishments & Progress: Summary

- **Test Current Commercial MEA (Gore)**

– Power density baseline testing	FY08 Completed
– Conditioning baseline testing	FY08 Completed
– Mechanical durability baseline testing	FY08 Completed
– Chemical durability baseline testing	FY08 Completed

- **Cost Model Current Commercial MEA (Gore)**

– Model generic decal lamination process	FY08 Completed
– Perform raw material sensitivity analysis	100% Complete

- **Mechanical Modeling (UD)**

– Layered model development	90% Complete
– RH & time-dependent mechanical testing	35% Complete

Technical Accomplishments & Progress: Summary

- **Equipment Procurement and Qualification (Gore)**

– Membrane coating	100% Complete
– Cathode coating	100% Complete
– Anode coating	60% Complete

- **MEA Alternative Concepts Generation and New Process Design (Gore)**

– Process feasibility screening	75% Complete
– Determine primary and alternative paths	100% Complete
– Direct coated cathode	25% Complete
• Power density baseline testing	
• Electrochemical diagnostics	
– Direct coated anode	35% Complete
• Power density baseline testing	

Technical Accomplishments:

3L MEA Manufacturing Process Cost Model

Cost model results indicate that a new 3L MEA process has potential to reduce MEA cost by 25%

Process Waste Map

Membrane Coating

Process Costs	Primary forms of waste	Modeled Process Improvements
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	

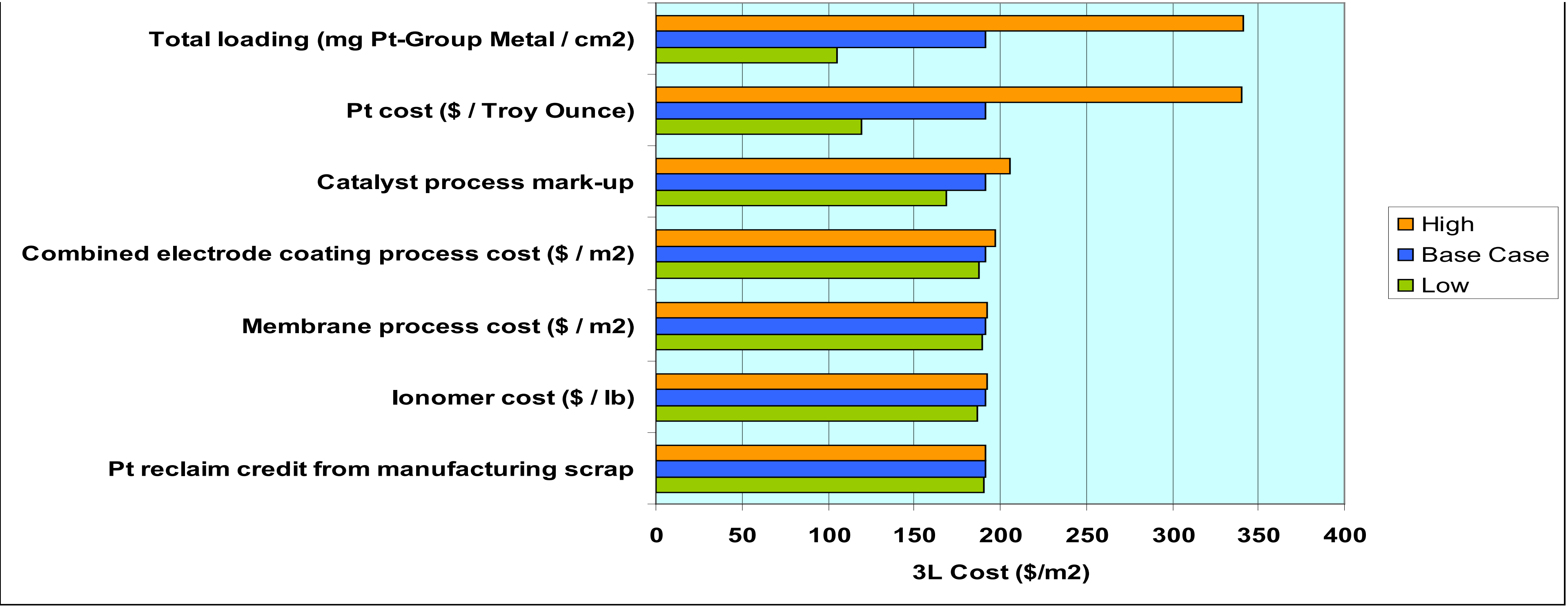
Electrode Coating

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

Technical Accomplishments: Single-Variable Sensitivity Analysis Base Case (0.4 mg Pt/cm^2 total loading), Improved Process



Key Input Assumptions and Justification

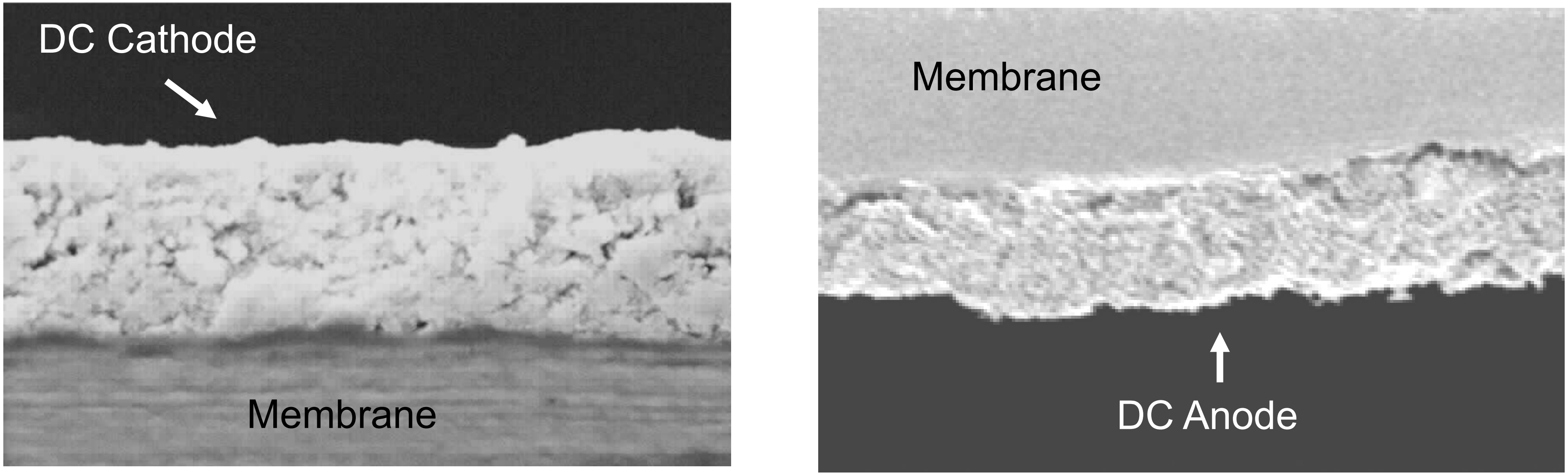
Category	Description	Base Case	Sensitivity Range	Sensitivity notes
Catalyst	Pt cost ($ / Troy Ounce)	1100	640 - 2060	Min: mean real price[3] Max: 2008 monthly avg maximum[4]
	Catalyst process mark-up	20%	5 - 30%	Based on Gore interactions with catalyst suppliers
	Total loading (mg Pt-Group Metal / cm2)	0.40	0.2 - 0.75	Min: DOE 2015 target[5], table 3.4.12 Max: 2005 TIAX Report[2] Table 14
	Pt reclaim credit from manufacturing scrap	95%	90 - 98%	Based on Gore interactions with catalyst suppliers
Ionomer	Ionomer cost ($ / lb)	88	22 - 110	2005 TIAX Report[2] Table 20 ($20 - $100/lb in 2005 dollars)
Coating	Membrane process cost ($ / m2)	2.18	1.00 - 4.00	Gore assumption, MOH & DL only, adapted from TIAX methodology
	Combined electrode coating process cost ($ / m2)	6.00	3.00 - 12.00	Gore assumption, MOH & DL only, adapted from TIAX methodology

References

1 2008 TIAX Tech Team Review "Direct Hydrogen PEMFC Manufacturing Cost Estimation for Automotive Applications" DE-AD36-06GO26044
2 2005 TIAX Report "Cost Analysis of PEM Fuel Cell Systems for Transportation" NREL/SR-560-39104
3 2004 TIAX "Platinum Availability and Economics for PEMFC Commercialization" DE-FC04-01AL67601
4 http://www.platinum.matthey.com/prices/price_charts.html
5 http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

Technical Accomplishments:

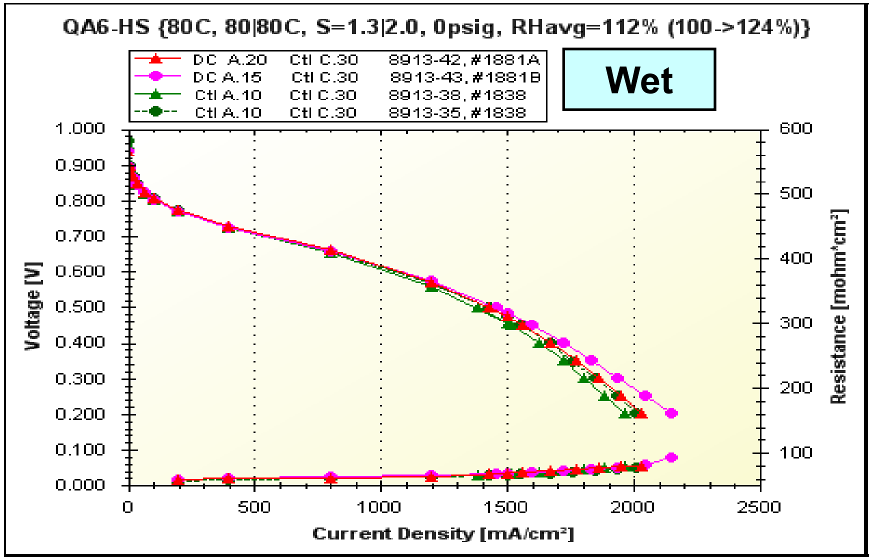
Direct Coated (DC) Electrodes

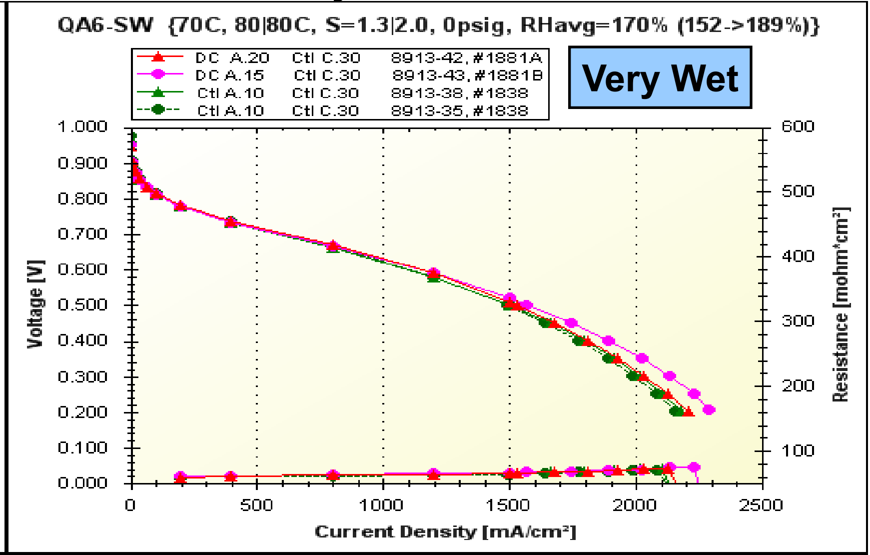


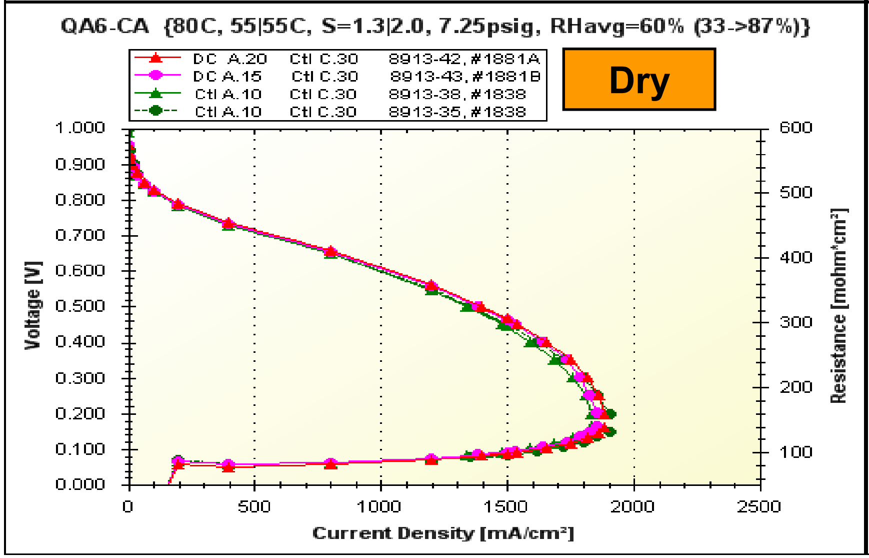
Scanning electron microscopy images of direct-coated electrodes on GORE-SELECT® Membrane

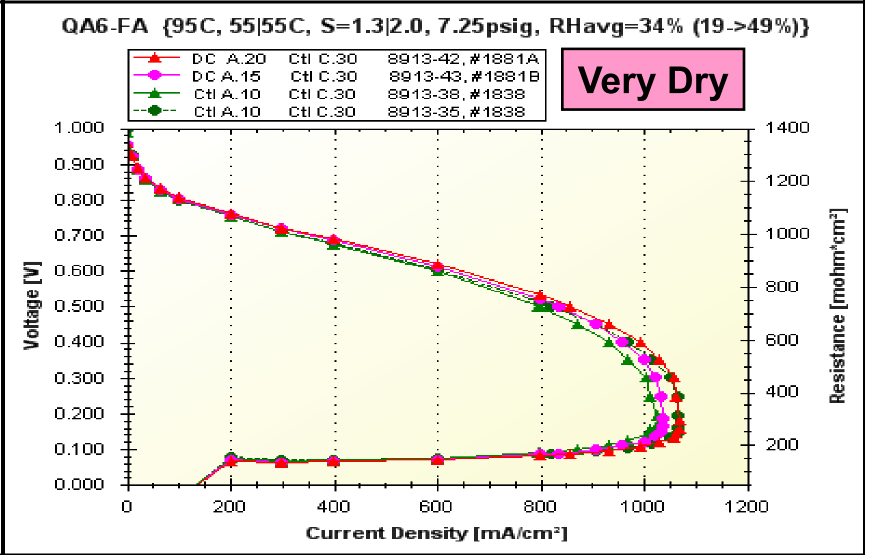
Technical Accomplishments:

DC Anode: Power Density





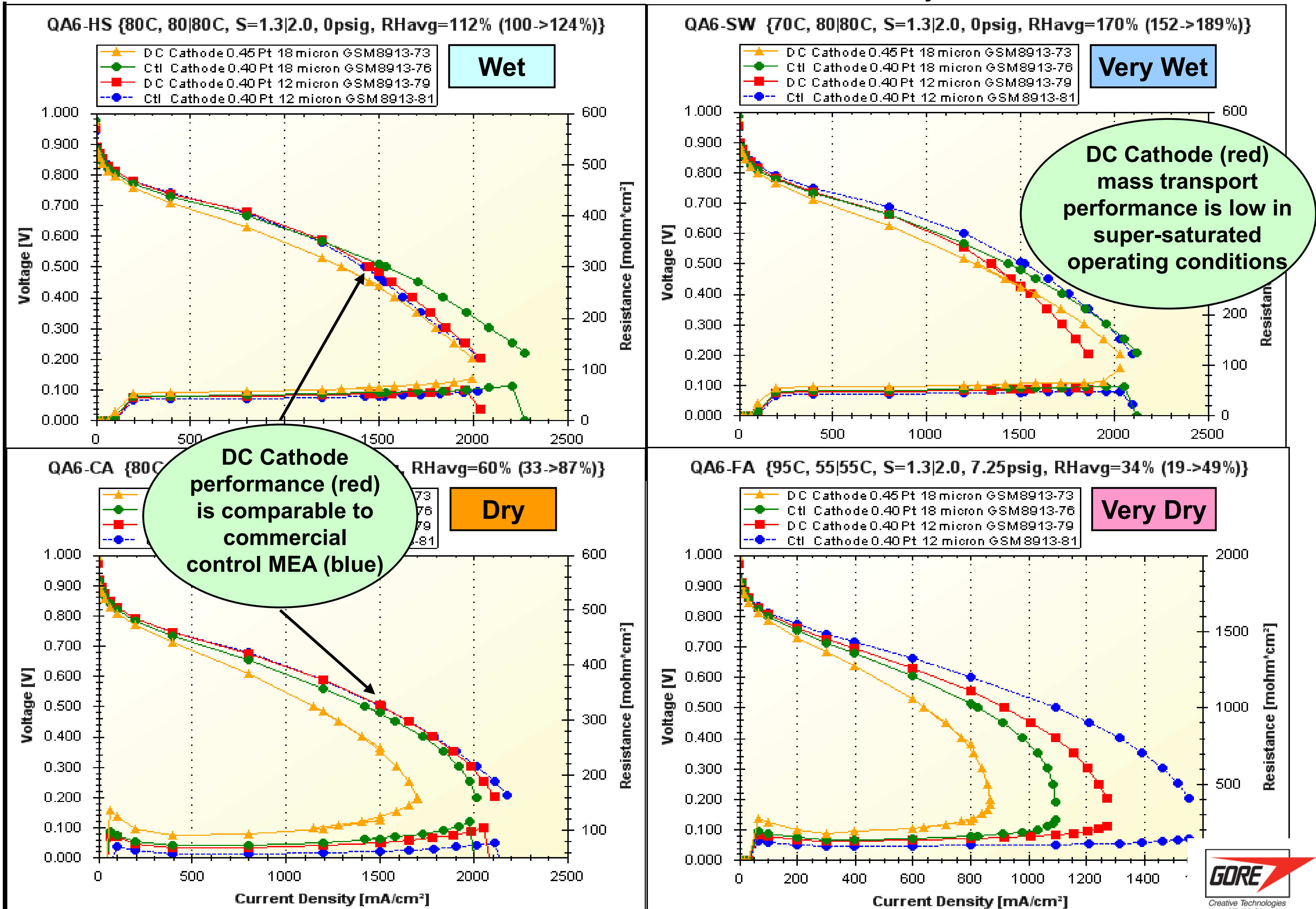




Performance of an MEA made with DC anode is comparable to a commercial control MEA. Due to process challenges that have since been overcome, DC anode Pt loadings were higher than the current commercial control anode for this data set.

Technical Accomplishments:

Direct Coated Cathode: Power Density

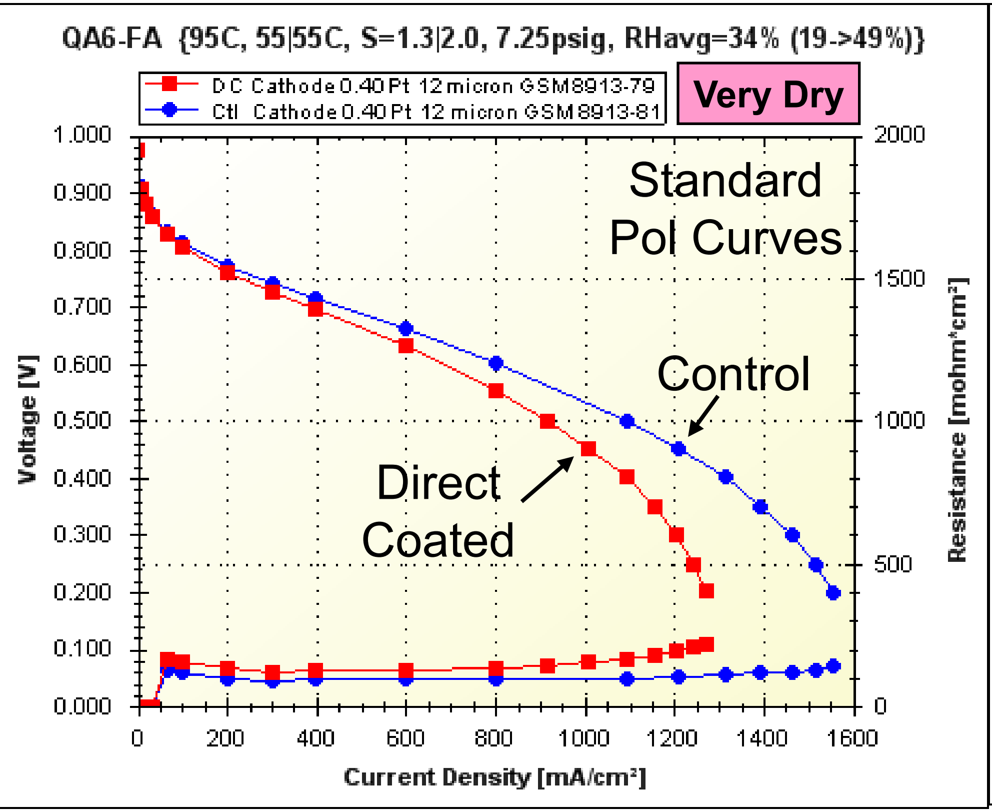


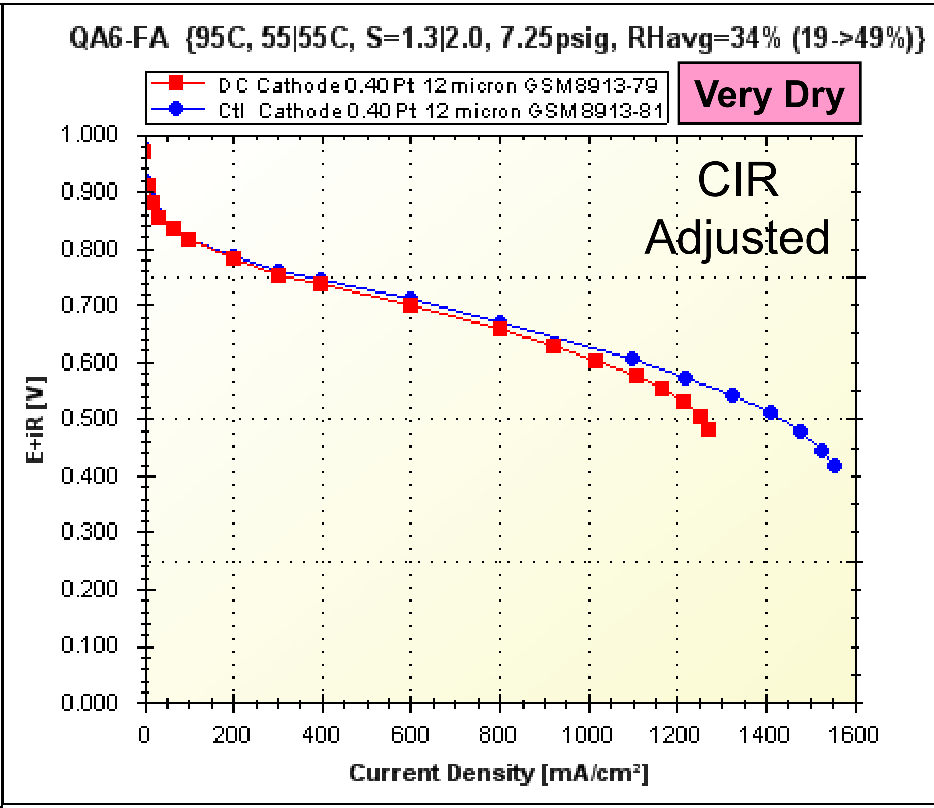
DC Cathode (red) mass transport performance is low in super-saturated operating conditions

DC Cathode performance (red) is comparable to commercial control MEA (blue)

Technical Accomplishments:

Direct Coated Cathode: Power Density

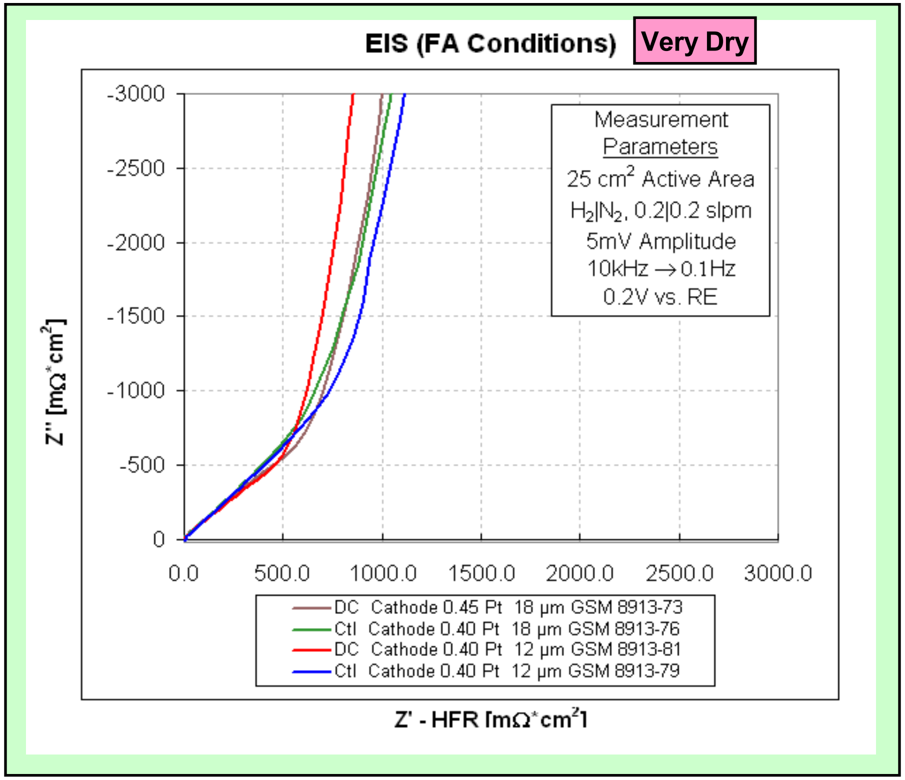


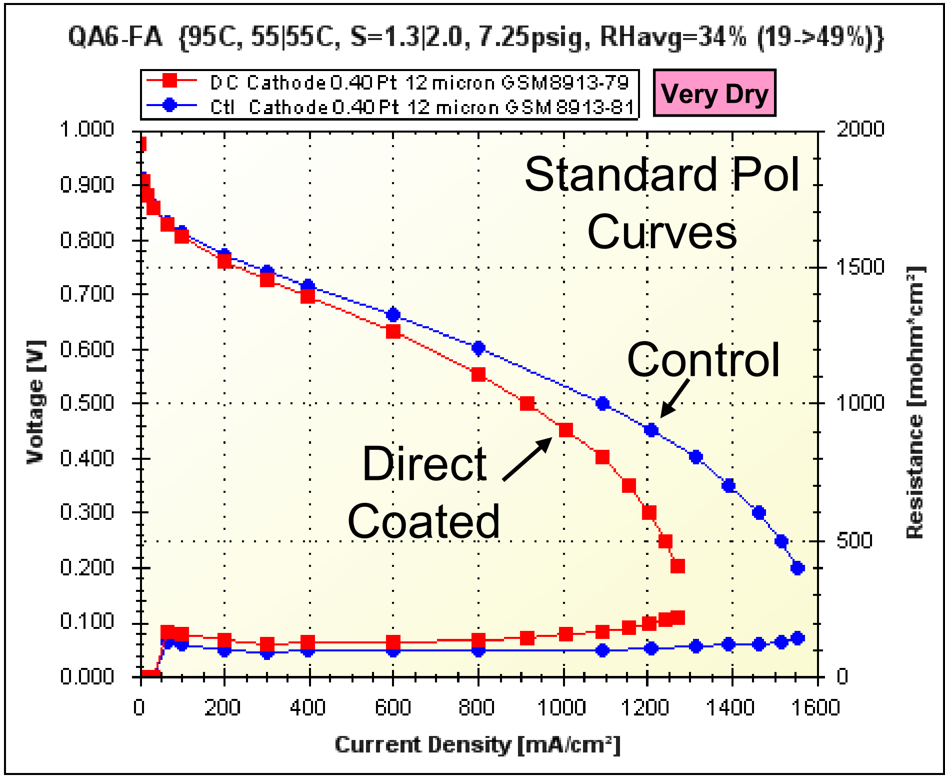


- **Current interrupt resistance accounts for most of the difference between the direct coated cathode MEA and the commercial control MEA in the ohmic region of the pol curve (~200 to ~1,000 mA/cm^2)**

Technical Accomplishments:

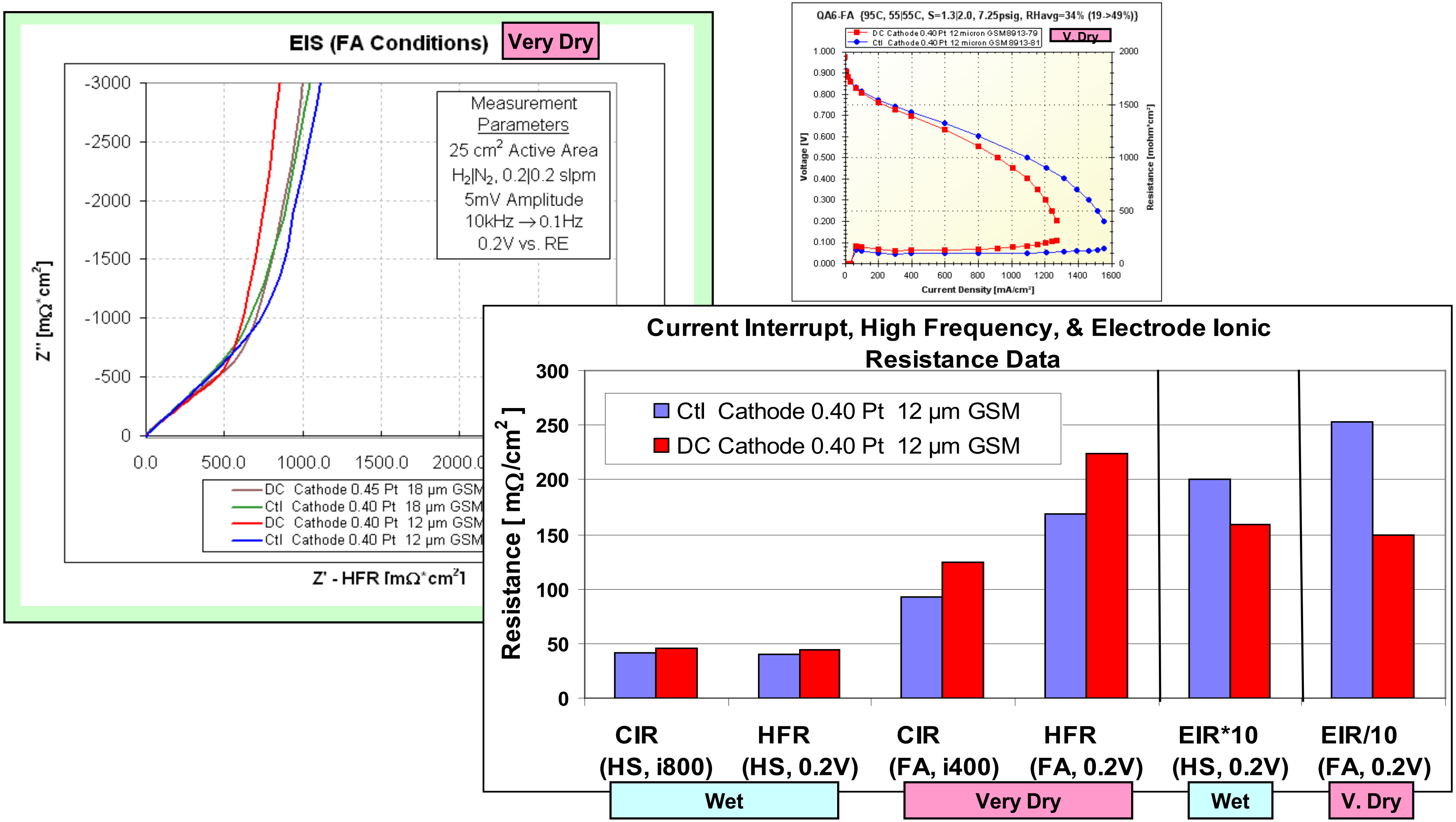
DC Cathode Electrochemical Diagnostics





- **Current interrupt resistance and high frequency resistance correlate well with performance data in FA conditions, where ohmic losses are very significant**
- **Electrode ionic resistance is inversely correlated to performance**
- **Direct coating changes water management – modeling has potential to accelerate development**

Technical Accomplishments:
DC Cathode Electrochemical Diagnostics



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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

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

Determined flooding sensitivity is the biggest gap to close for DC cathode

Investigated impact of direct-coated electrode structure on molecular diffusion

Technical Accomplishments:

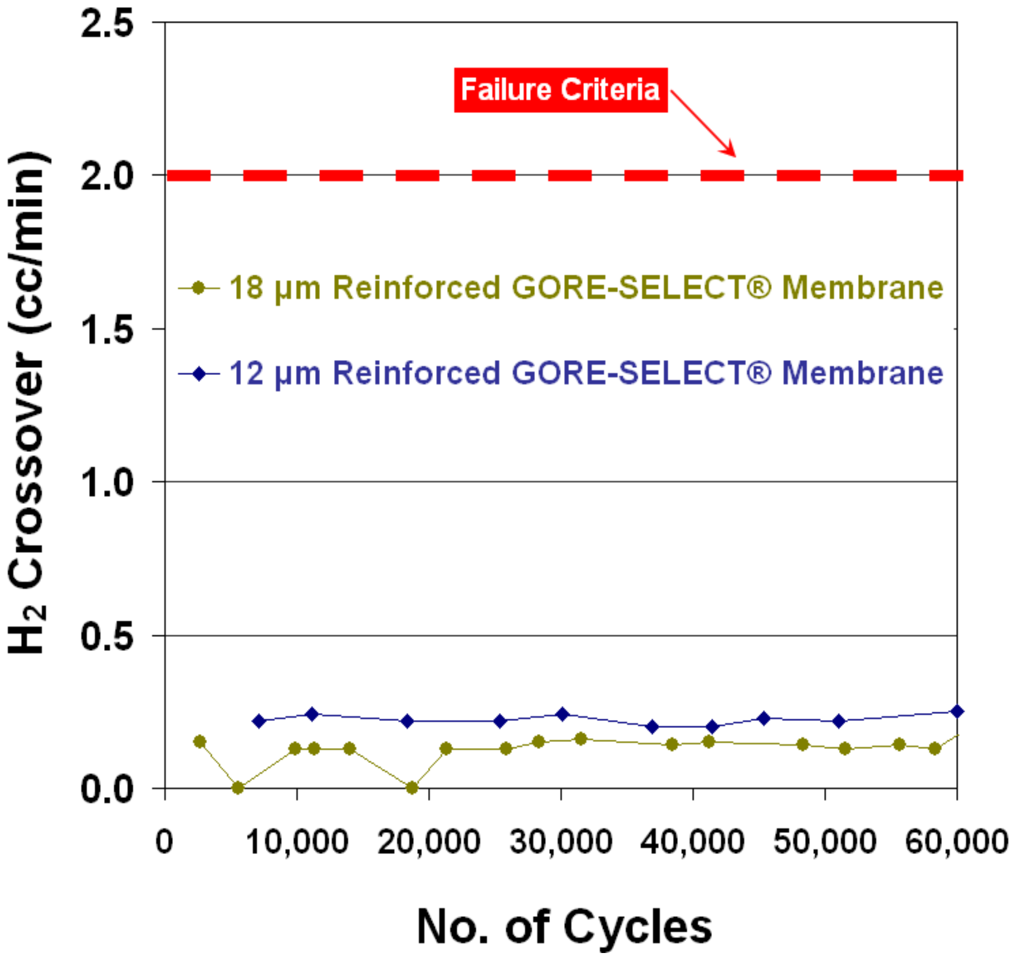
Durable 12 µm GORE-SELECT® Membrane

Gore N_2 RH Cycling Protocol:

Tcell (C)	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



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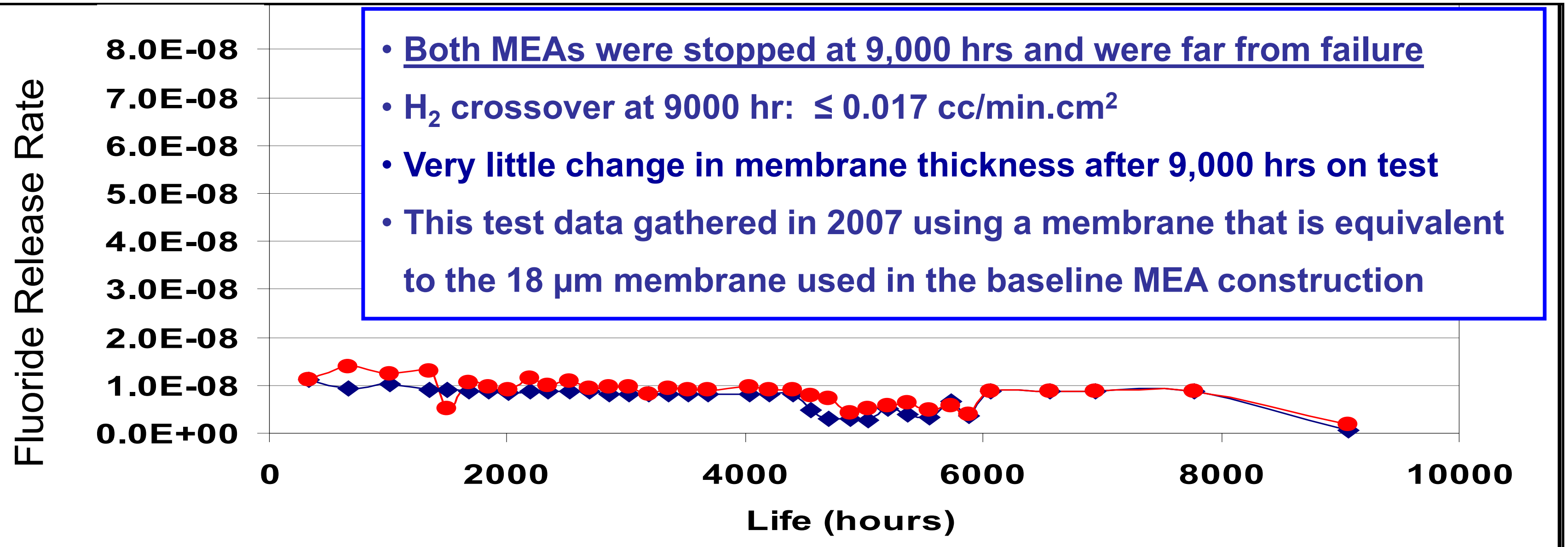
Technical Accomplishments:

9,000 Hour GORE-SELECT® Membrane Durability in 808C 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

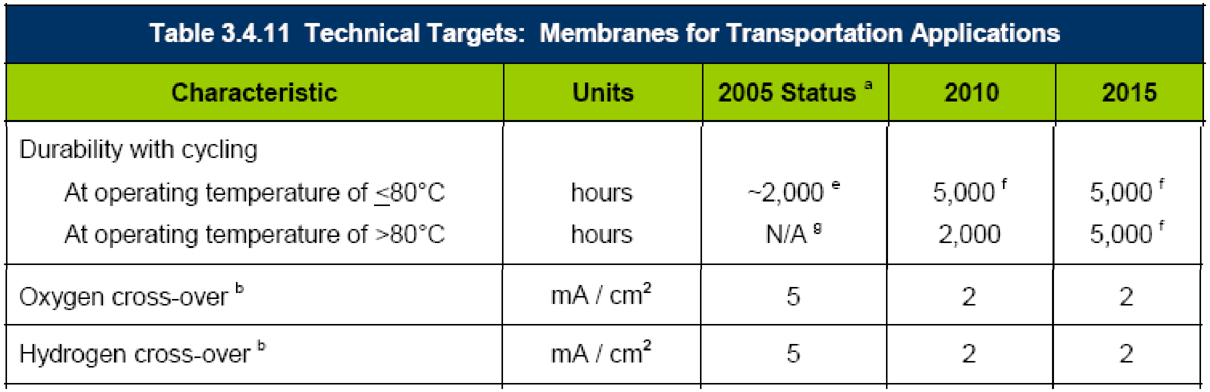


Table 3.4.11 Technical Targets: Membranes for Transportation Applications

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

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Technical Accomplishments: Mechanical Modeling

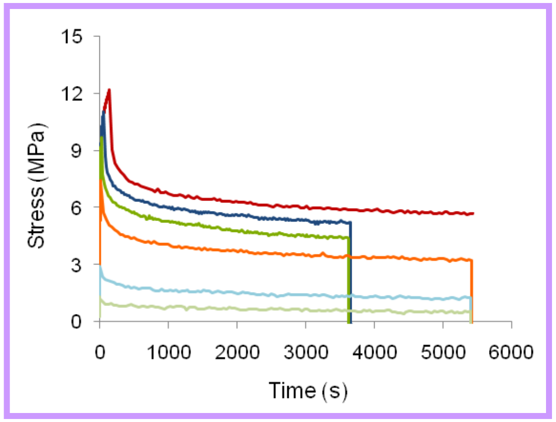
Determining Parameters for the Numerical Model

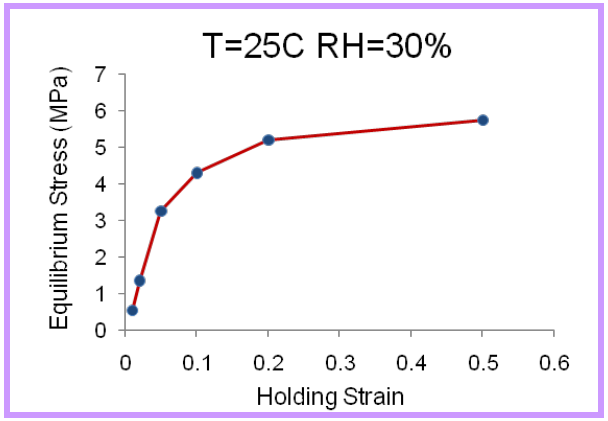
Relaxation Experiments At various hold strains

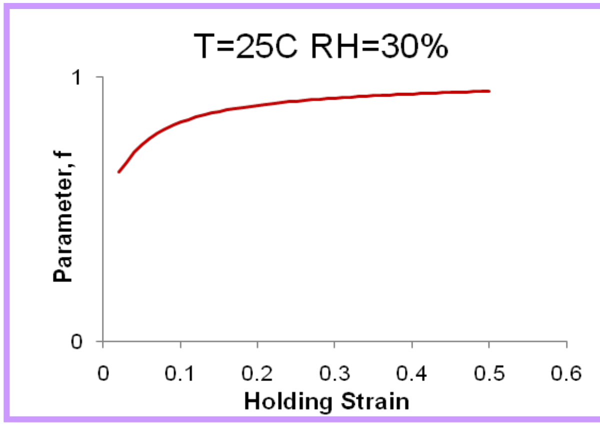
Long-term modulus variation K_P

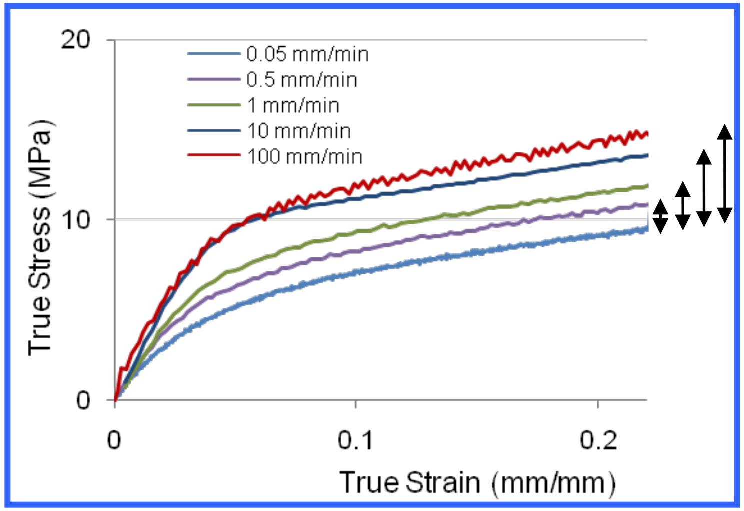
Log-fit $\sigma_{eq} = A\ln(\varepsilon_h) + B$

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









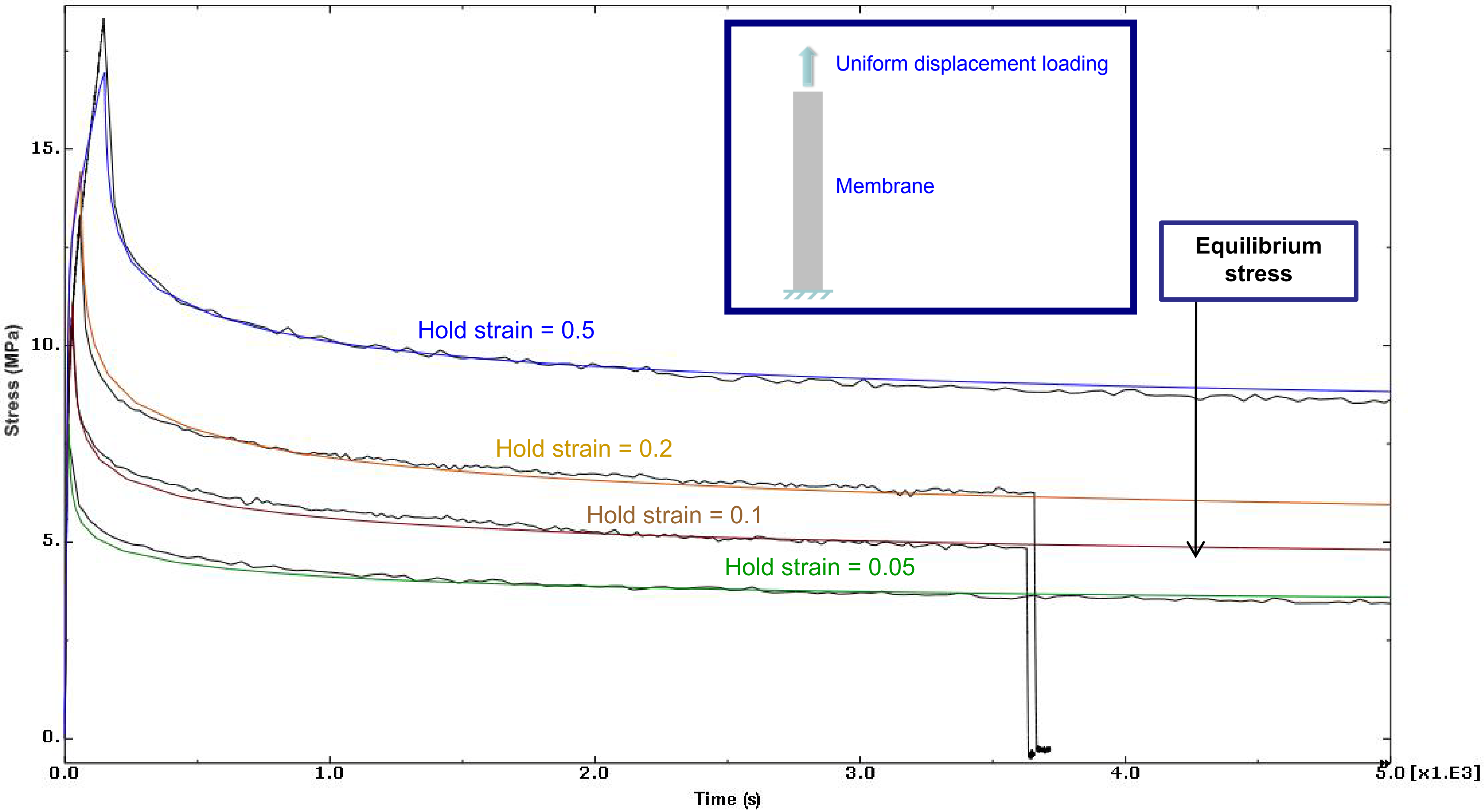
Overstress from Tensile tests

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

$$A \,\&\, n$$

Technical Accomplishments: Mechanical Modeling

Visco-Elastic Relaxation
Simulation Results Compared with the Experimental Data

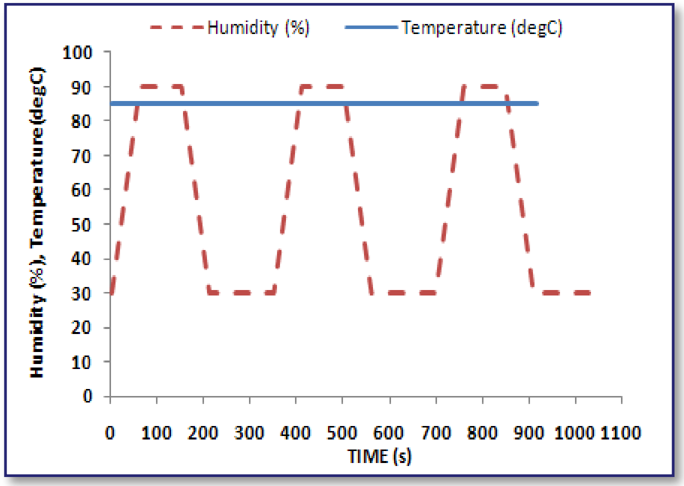


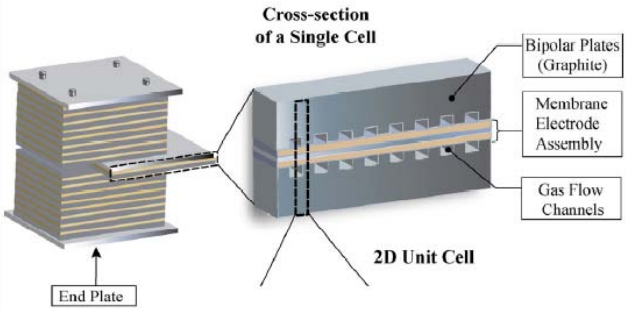
Technical Accomplishments: Mechanical Modeling

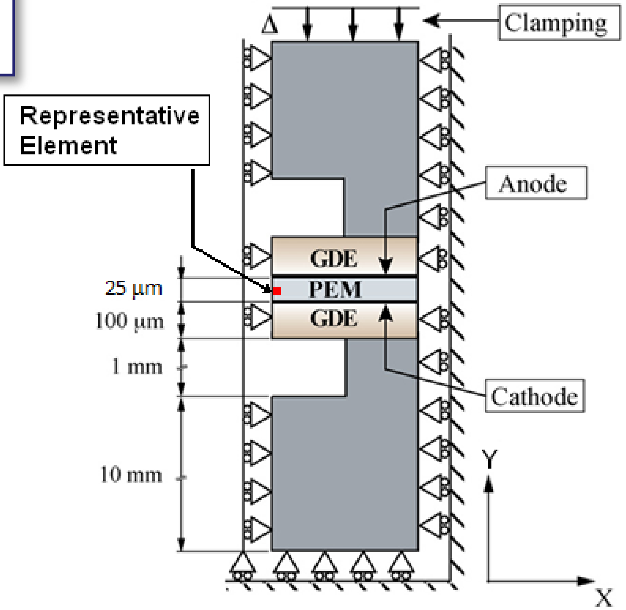
2D Plane Strain Finite Element Model for a Single Cell

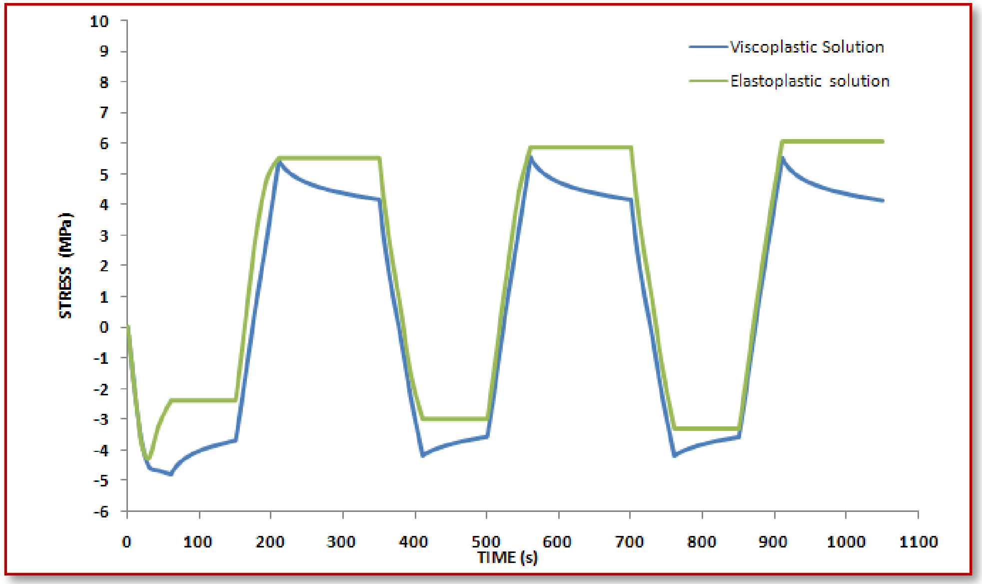
- Membrane's material properties at various temperature and humidity values acquired through experiments

- Loading consists of pre-stressing and hygrothermal variations









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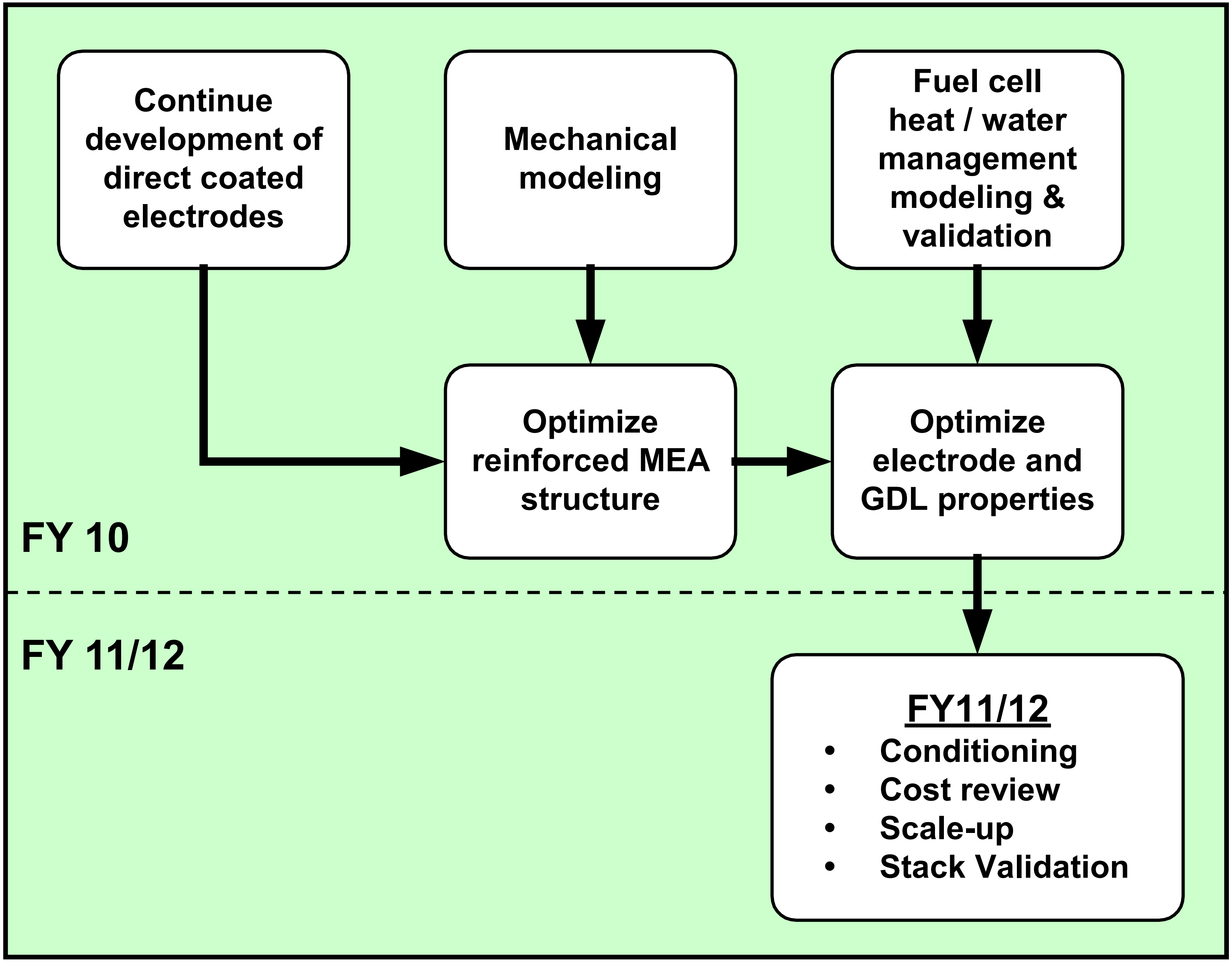
Proposed Future Work for FY10: Summary



FY 10

Continue development of direct coated electrodes

Mechanical modeling

Fuel cell heat / water management modeling & validation

Optimize reinforced MEA structure

Optimize electrode and GDL properties

FY 11/12

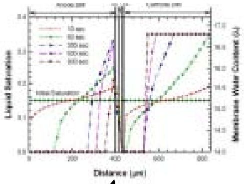
<u>FY11/12</u>

- Conditioning
- Cost review
- Scale-up
- Stack Validation

Proposed Future Work for FY10:

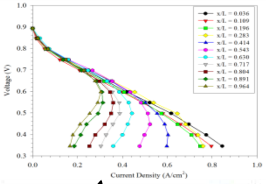
Water Management Modeling

- Determine critical GDL characteristics, understand cost-performance relationships, and select alternative GDL options for fuel cell testing
- Measure unknown critical properties of GDLs: Liquid Water distribution (neutron imaging) and polarization measurement including quantification of mass, ionic, and kinetic losses as well as overall water transport coefficient
- Comprehensive modeling of effects of various GDL, electrode, and membrane parameters on performance, RH distribution, temperature gradient and water accumulation
- Characterize interactions between alternative GDL's and break-in and performance testing

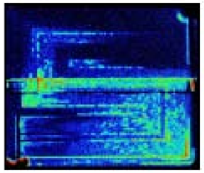


Computational Modeling

SEM



Segmented Cell

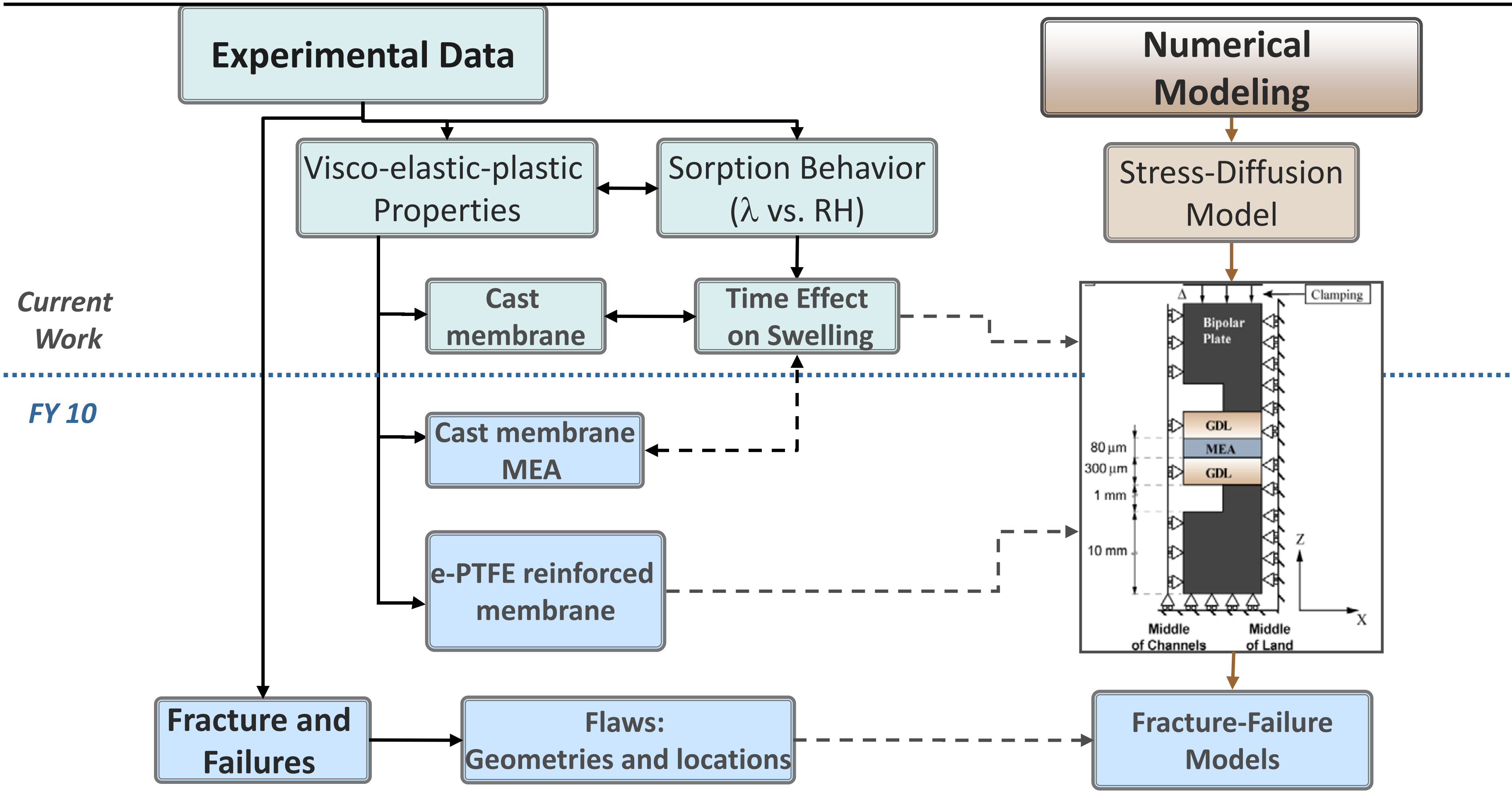


Neutron imaging

Proposed Future Work

Mechanical Modeling

- Static and time dependent (viscoelastic/viscoplastic) testing of baseline materials
- Numerical simulation of stress evolution around MEA imperfection



Experimental Data

Visco-elastic-plastic Properties

Sorption Behavior (λ vs. RH)

Current Work

Cast membrane

Time Effect on Swelling

FY 10

Cast membrane MEA

e-PTFE reinforced membrane

Fracture and Failures

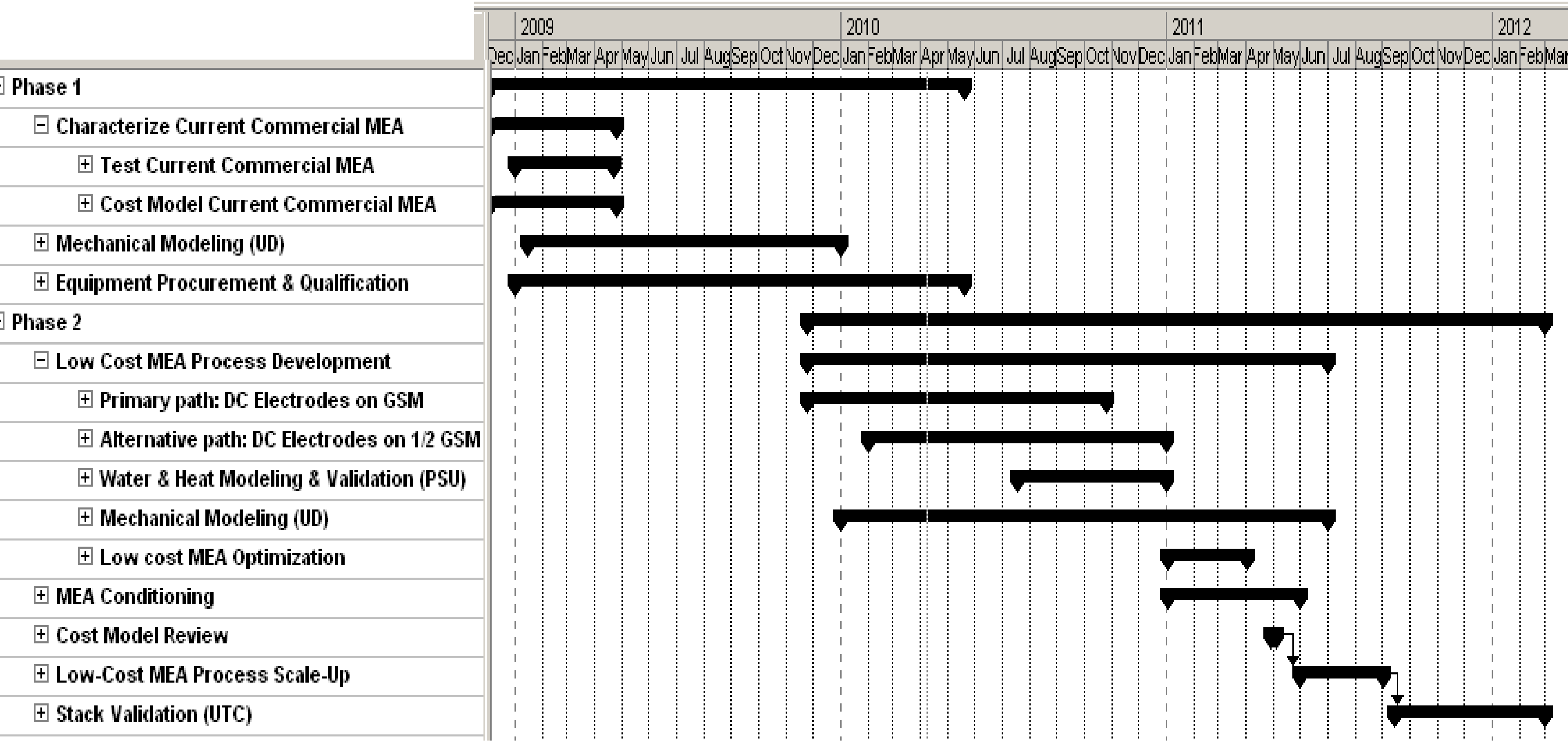
Flaws: Geometries and locations

Numerical Modeling

Stress-Diffusion Model

Fracture-Failure Models

Proposed Future Work for FY10:



- Phase 1
  - Characterize Current Commercial MEA
    - Test Current Commercial MEA
    - Cost Model Current Commercial MEA
  - Mechanical Modeling (UD)
  - Equipment Procurement & Qualification
- Phase 2
  - Low Cost MEA Process Development
    - Primary path: DC Electrodes on GSM
    - Alternative path: DC Electrodes on 1/2 GSM
    - Water & Heat Modeling & Validation (PSU)
    - Mechanical Modeling (UD)
    - Low cost MEA Optimization
  - MEA Conditioning
  - Cost Model Review
  - Low-Cost MEA Process Scale-Up
  - Stack Validation (UTC)

- Coating equipment which had long lead times was purchased in Phase 1
- Only 20% of the project budget was spent as of 4/8/10
- When direct coating equipment was installed and qualified in March, more resources were added to the project
- Spending and technical progress are both in agreement with the project forecast

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Collaborations

- **University of Delaware**
  - **MEA Mechanical Modeling**
  - **A. Karlsson & M. Santare**
- **Penn State University***
  - **Fuel Cell Heat and Water Management Modeling and Validation**
  - **M. Mench**
- **UTC Power, Inc.**
  - **Stack Testing**
  - **T. Madden**
- **W. L. Gore & Associates, Inc.**
  - **Project Lead**
  - **F. Busby**

***New partner added for FY10**

Summary (1)

- **The overall objective of this project is to develop unique, high-volume manufacturing processes for low-cost, durable, high-power density 3L MEAs that require little or no 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 properties and performance of the 3L construction
  - **Unique Enabling Technologies**
    - Direct Coating: Use 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

Summary (2)

- **Key Accomplishments**
  - Cost model results indicate that a new 3L MEA process has potential to reduce 3L MEA cost by 25%
  - Development of direct coated anode and cathode electrodes is underway
    - Primary and alternative paths have been determined
    - Current density of direct coated electrodes on reinforced 12 µm membrane is equivalent to current commercial MEA
    - Gore has demonstrated 9,000 hour membrane durability (DOE 2015 target is 5,000 hours)
  - Development of a layered structure MEA mechanical model using non-linear (viscoelastic & viscoplastic) polymer and electrode properties which will predict MEA durability for a variety of temperature & relative humidity cycling scenarios is underway

- The combination of Gore's advanced materials, expertise in MEA manufacturing, & fuel cell testing with the mechanical modeling experience of University of Delaware and the heat and water management experience of Penn State University enables a robust approach to development of a new low-cost MEA manufacturing process

Acknowledgements:

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- Mike Santare
- Melissa Lugo
- Narinder Singh

Penn State University
- Matthew M. Mench

UTC Power, Inc.
- Thomas Madden