2009 DOE Hydrogen Program

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

F. Colin Busby
W. L. Gore & Associates, Inc.
5/20/2009

Project ID #
mf_04_busby

Phase 1 Overview

Budget

- Total Project Funding: **$1.28MM**
  - $834k DOE Share
  - $450k Gore, UTCP, & UD Share
- Received in FY08: $654k
  - $77k spent as of 3/20/09
- Funding for FY09: $177k

Barriers Addressed

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

Timeline

- Project start: October 1, 2008
- Project end: December 30, 2009
- 15% Percent Complete as of 3/20/09

Partners

- University of Delaware (UD)
  - MEA Mechanical Modeling
  - A. Karlsson & M. Santare
- UTC Power, Inc. (UTCP)
  - MEA Conditioning Modeling
  - T. Madden & M. Khandelwal
- W. L. Gore & Associates, Inc. (Gore)
  - Project Lead
  - F. Busby

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

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]

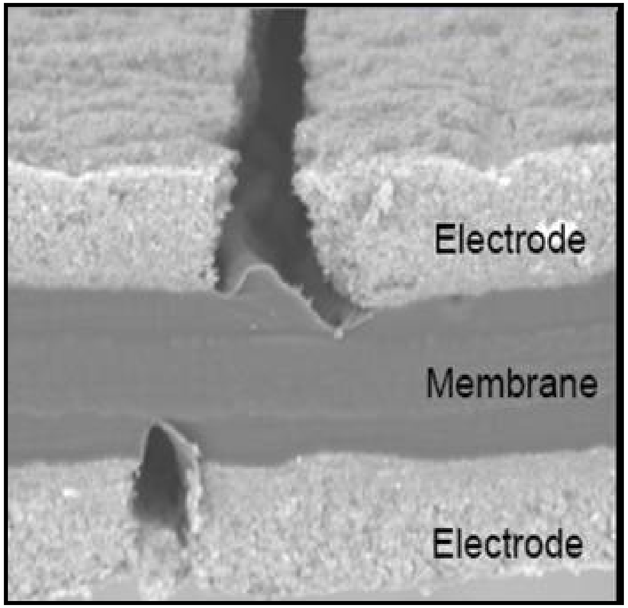
GORE
Creative Technologies Worldwide

Relevance: Phase 1 Objectives

- Characterize current commercial MEA performance (**Gore**)
  – Understand gaps between current MEA performance & DOE targets
  – Obtain data to enable future comparison with MEA's made by new processes
- Develop a cost model for the current commercial MEA and estimate potential savings (**Gore**)
  – Understand gaps between current process costs & DOE targets
  – Obtain baseline data to enable future comparison with new processes
  – Estimate potential savings to justify kick-off of new process development (Go / No-go decision)
- Develop a non-linear multi-layer mechanical model (**UD**)
  – Develop a deeper understanding of failure mechanisms of current MEA
  – Use model to optimize properties of MEA that will be made in the new low-cost process
- Develop an MEA conditioning model (**UTCP**)
  – Develop a deeper understanding of conditioning mechanisms of current MEA & conditioning protocol
  – Use model to optimize:
    - Properties of MEA that will be made in the new low-cost process which affect conditioning
    - Conditioning protocol (in-situ stack protocol and/or ex-situ MEA protocol) for the MEA that will be made in the new low-cost process

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
- Improve Durability
  - Optimize mechanical properties 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
  - Modeling will be used to understand mechanical durability & conditioning mechanisms as well as new MEA optimization
  - Advanced fuel cell testing & diagnostics



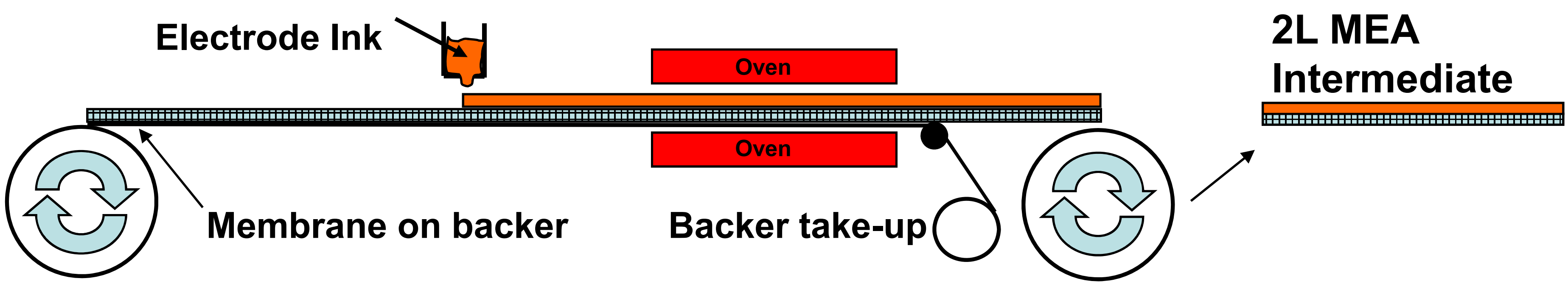
GORE
Creative Technologies Worldwide

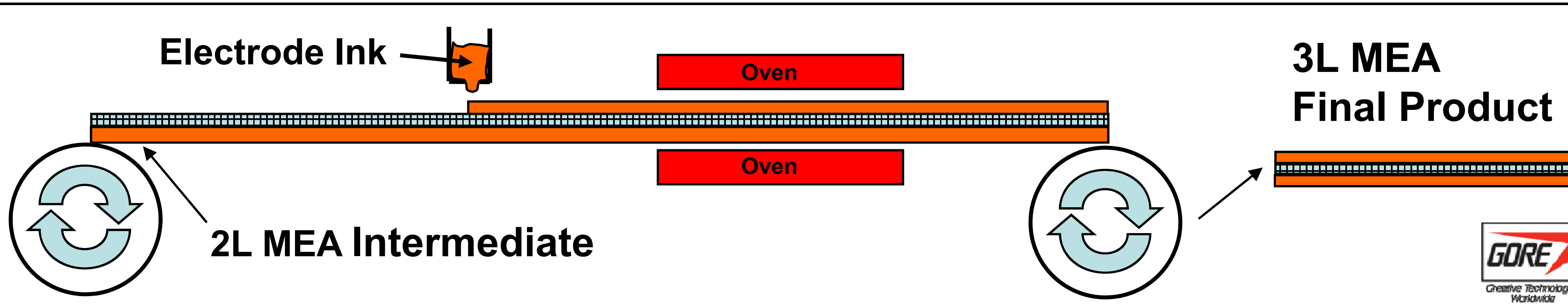
Approach:
Potential Low-Cost MEA Mfg Process

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

- Develop a cost model for the current commercial MEA & estimate potential savings
  - Utilize results of *TIAX Cost Analysis of PEM Fuel Cell* (Report: NREL/SR-560-39104)





Approach: Mechanical Modeling

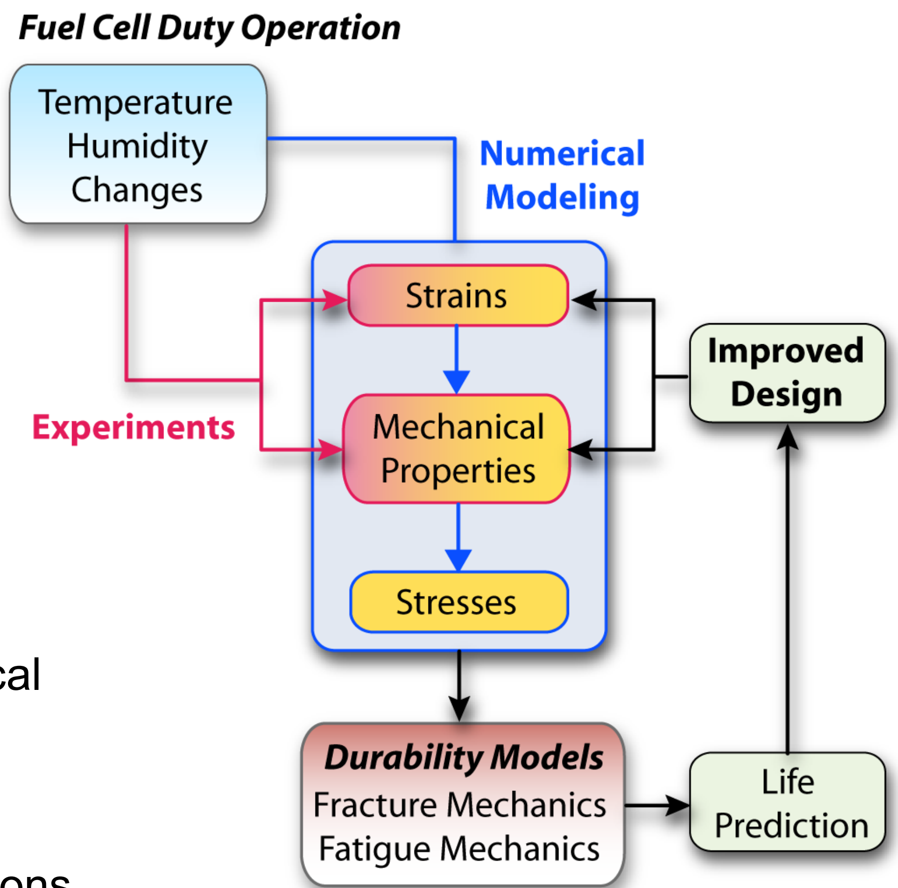
- Model Concept:

  Develop a layered structure MEA mechanical model using non-linear (viscoelastic & viscoplastic) polymer and electrode properties which will predict MEA lifetime for a variety of temperature & relative humidity cycling scenarios

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

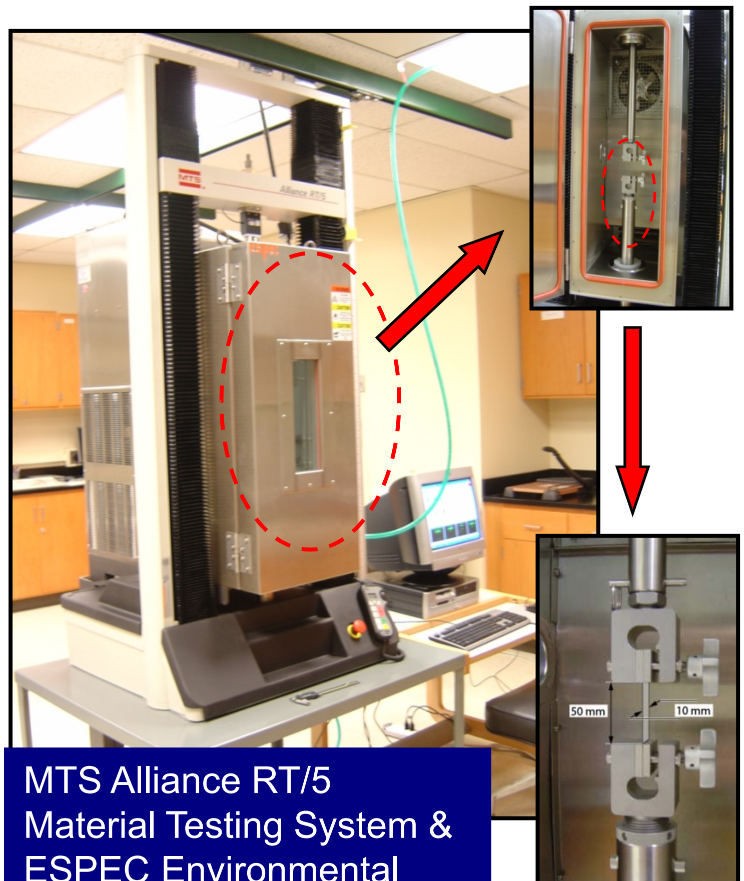
- Use numerical modeling to predict mechanical response of MEA during cell operation by incorporating the properties obtained from experiments

- Utilize model to explore new MEA constructions and optimize prototypes of the MEA that will be made in the new low-cost process



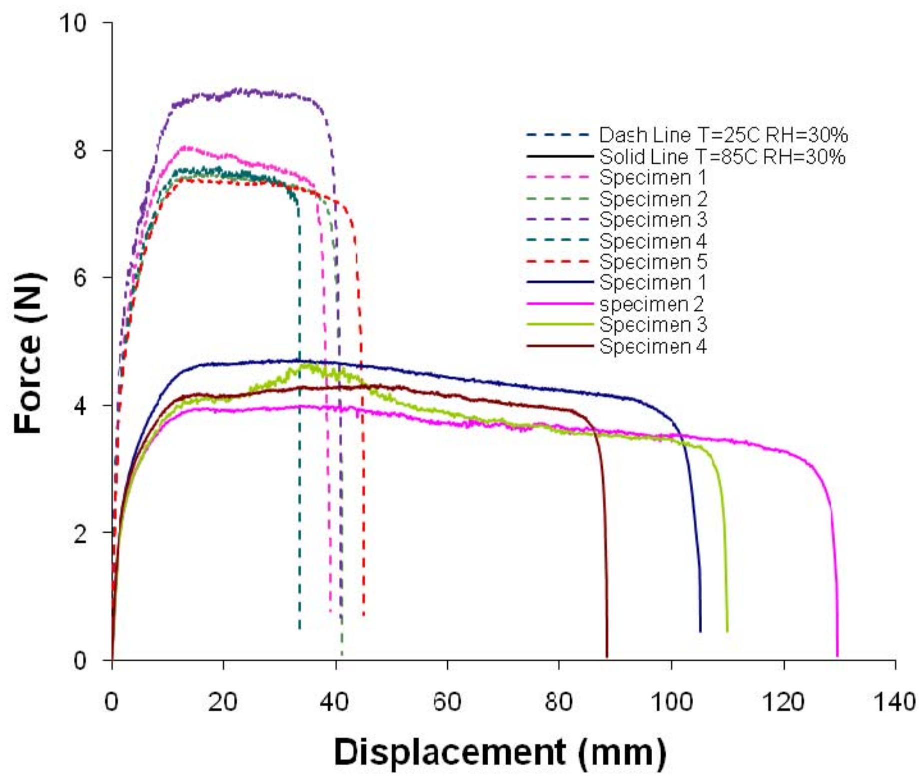
Approach: Mechanical Modeling

MEA Tensile Test Method for MTS Tensile Tester with ESPEC Environmental Chamber.



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

- E and σ_y obtained for MEA
- Current Temperature Capability: 20C - 90C; RH 30-90%
- Developing Low Temperature Capability (down to -40C) with limited RH control



Approach: Mechanical Modeling MEA

Strain-Interrupt Test for Electrode Cracking

Failure Evolution

↓

Using SEM (untested and tested samples)

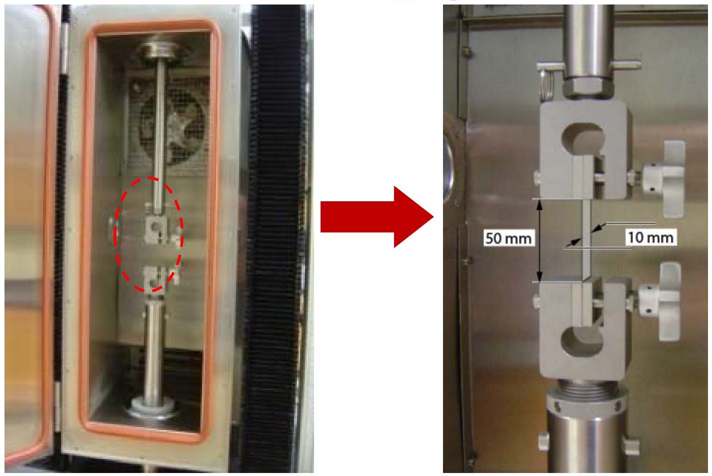
↓

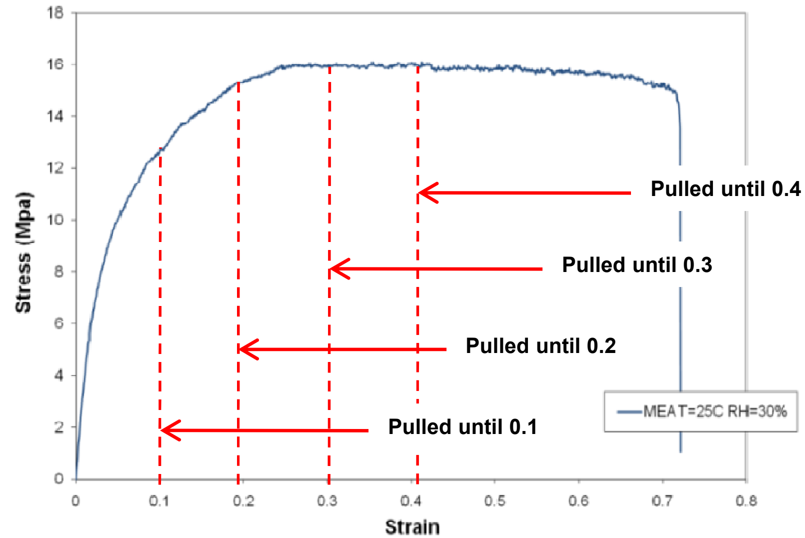
Formation of Cracks

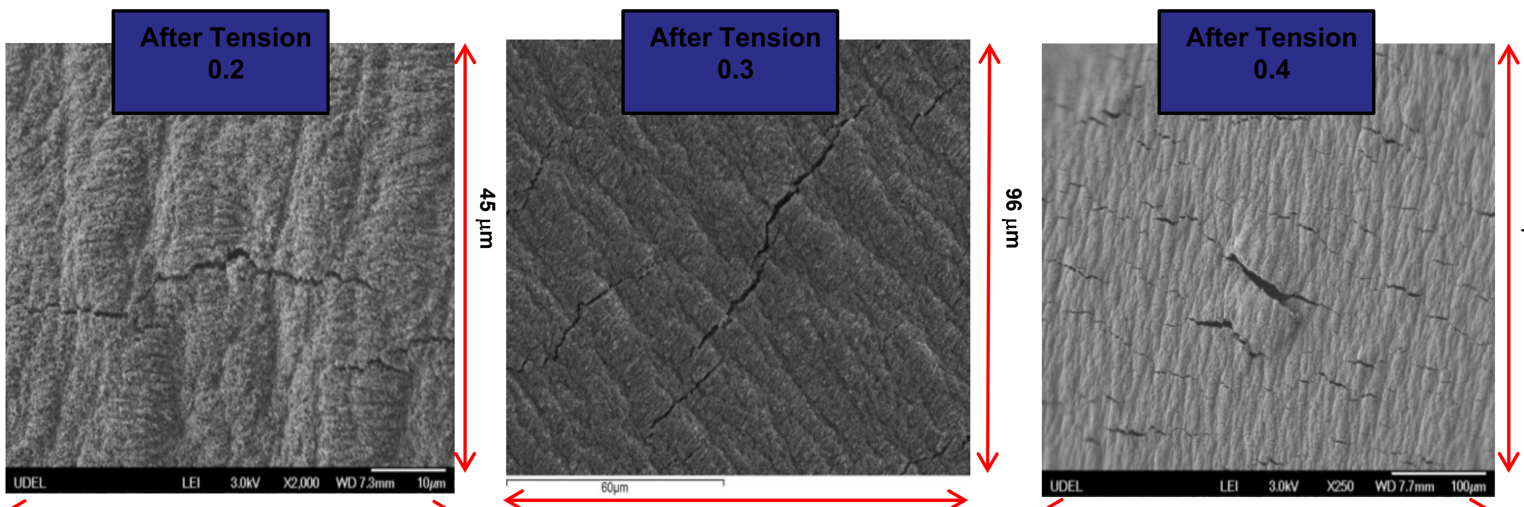
↓

Numerical Model Inputs

MTS Testing System







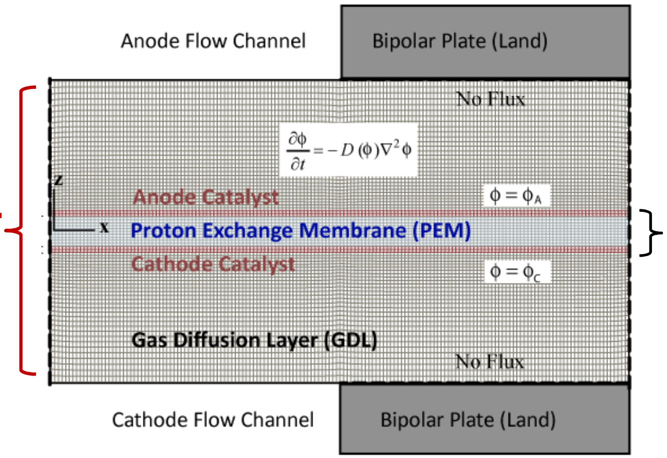
SEM Images

GORE Creative Technologies Worldwide

Approach: Mechanical Modeling

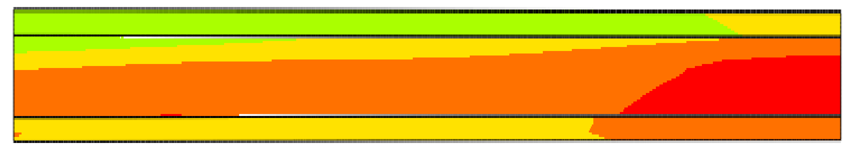
Numerical Simulation Methods

MEA + GDL Layered Structure



Example of Model Output Data:

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



Previously Determined Properties for Membrane Material

Young's Modulus (E) **Yield Stress (σy)**

↓

Tensile Load response from MEA experiments

↓

Unknown Properties for Electrode Material

Young's Modulus (E) **Failure load**

Finite Element Model

Mechanical Properties:

Electrode: Elastic Properties
Membrane: Elasto-Plastic Properties

Geometry:

Lmea: Varies according to the # of cracks included in the model.
Crack Length = Wide electrode

Initial and Boundary Conditions:

- Constant Displacement
- No Cracks
- Cracks
- Cracks and Delaminations

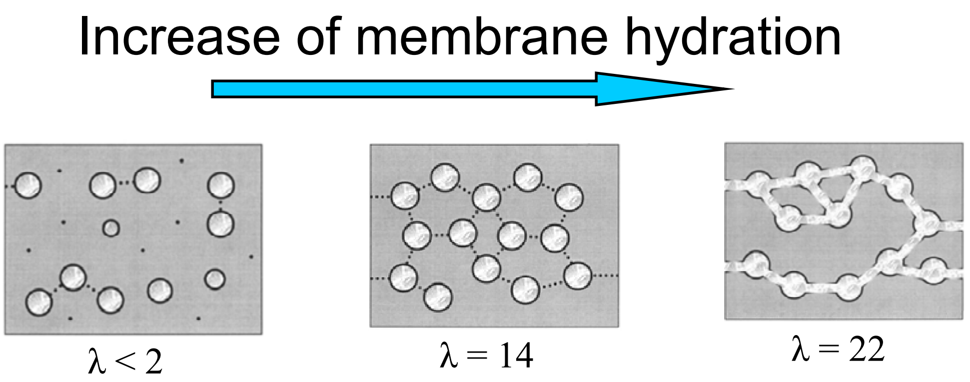
GORE Creative Technologies Worldwide

Approach: Conditioning Model Development

Develop a ***fundamental cell conditioning*** model to estimate the cell/stack break-in time. The model will be ***validated with single cell*** testing at Gore, and used to identify the key controlling parameters affecting the conditioning/break-in time and propose new ***protocols to reduce break-in time for PEFC stack.***

Key Phenomena

- Interfacial Resistance
- Electrode Structure
- Contamination



Evolution of membrane structure as function of water content, Weber and Newman, *JES* 2003

Approach: Conditioning Model Development

An in-house PEFC performance model was used as an *initial model frame work* for conditioning model development.

UTCP Model

- 1D, steady state model
- Mass, energy and charge conservation
- Liquid water transport

Add **new conditioning physics**

Gore MEA Testing

- Conditioning experiments
- Diagnostic experiments

Validate Conditioning Model and Parametric Study

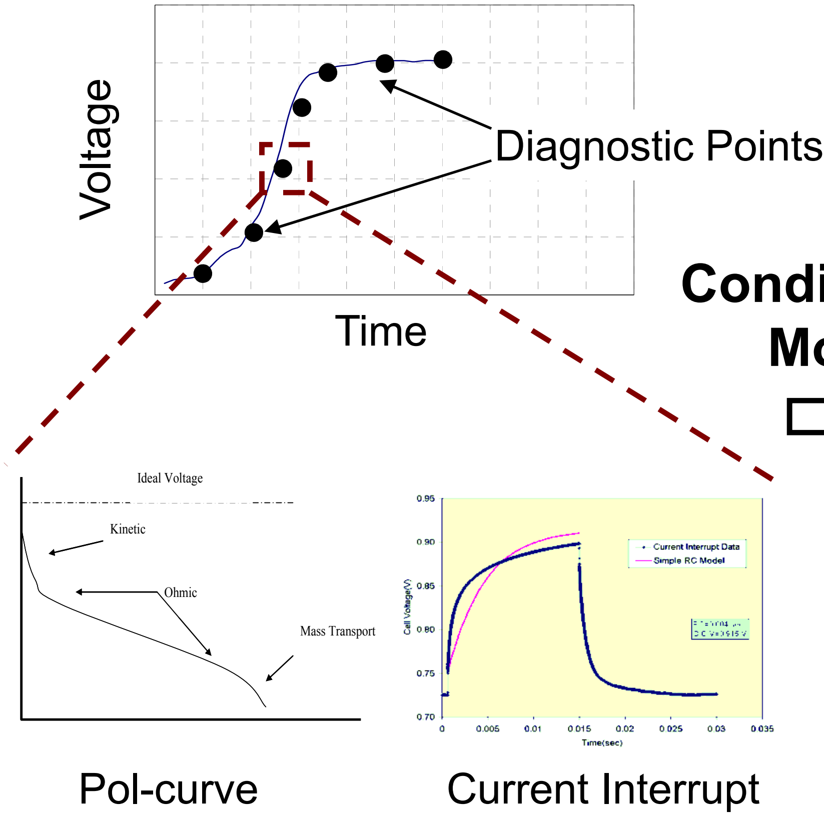
Use Model to Optimize:

- Properties of MEA that will be made in the new low-cost process which affect conditioning
- Conditioning protocol (in-situ stack protocol and/or ex-situ MEA protocol) for the MEA that will be made in the new low-cost process

Approach: Conditioning Model Development

Model Parameter Estimation

Conditioning Experiments



Cell Diagnostics

Conditioning Model

Parameter Estimates

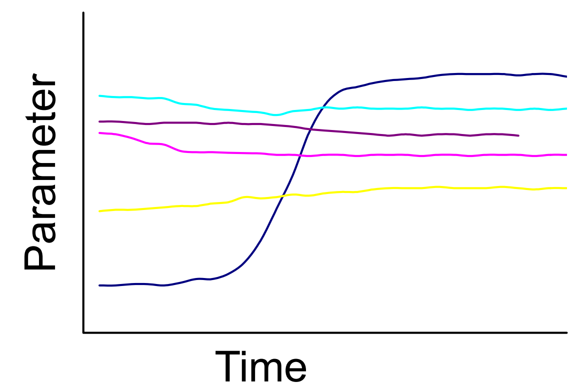
$\sigma = f(t, n_{cycle}, i)$ — Ionomer conductivity

$R = f(t, n_{cycle}, \varepsilon)$ — Interfacial resistance

$\alpha = f(t, n_{cycle}, \varepsilon)$ — Electrode active area

$\varepsilon = f(t, n_{cycle})$ — CL porosity

$\beta = f(t, n_{cycle})$ — MPL porosity



GORE Creative Technologies Worldwide

Technical Accomplishments & Progress: Phase 1 Summary

1.1 Test Current Commercial MEA (Gore)

1.1.1 Power density baseline testing	Complete
1.1.2 Conditioning baseline testing	Complete
1.1.3 Mechanical durability baseline testing	Complete
1.1.4 Chemical durability baseline testing	Complete

1.2 Cost Model Current Commercial MEA (Gore)

1.2.1 Model generic decal lamination process	90% Complete
1.2.2 Perform raw material sensitivity analysis	50% Complete

2.1 Mechanical Modeling (UD)

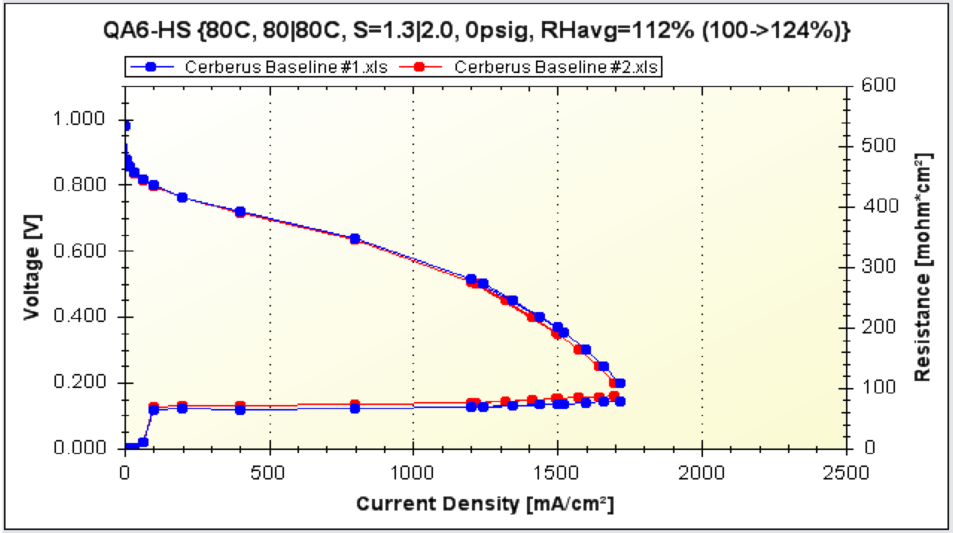
2.1.1 Layered model development	20% Complete
2.1.2 RH & time-dependent mechanical testing	5% Complete

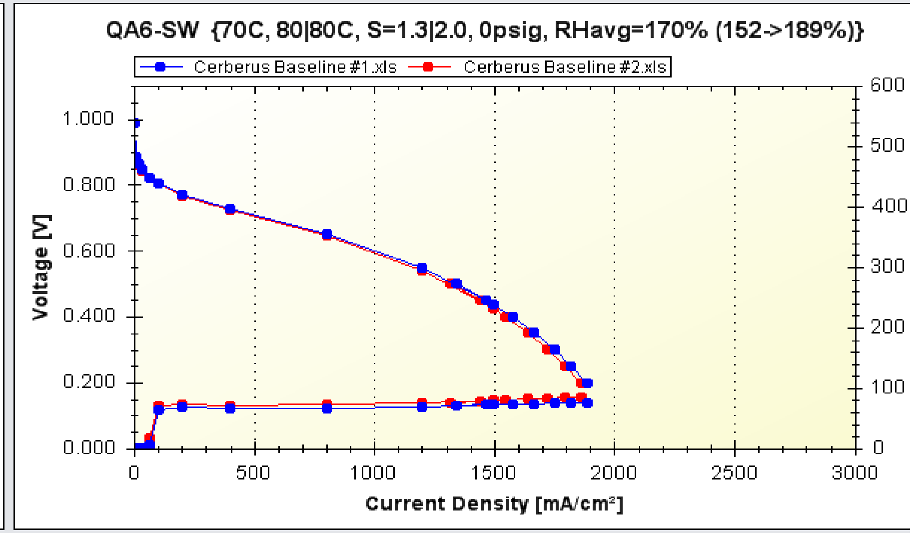
2.2 Conditioning Model Development (UTCP)

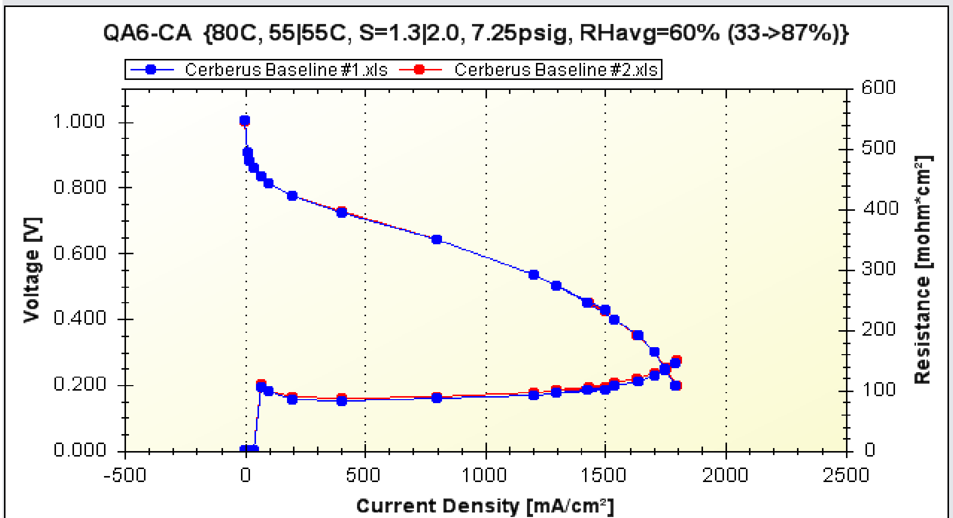
2.2.1 Assess existing models for applicability to conditioning mechanisms	Complete
2.2.2 Adapt & refine model for conditioning and validate with experimental data	10% Complete

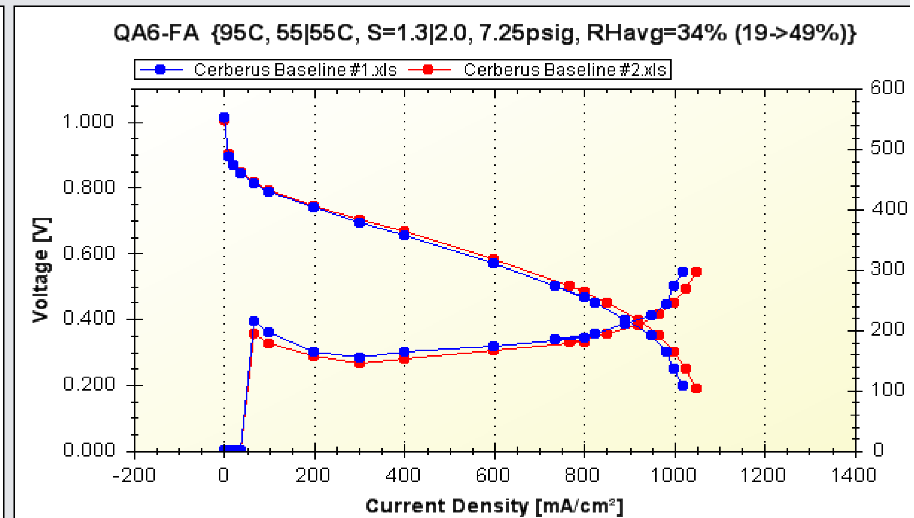
Technical Accomplishments:

Power Density Baseline Testing









'HS' Baseline MEA is consistent with the DOE 2005 status of 1,000 mW/cm2 performance at rated power (~1,000 mA/cm^2 @ 0.6V)

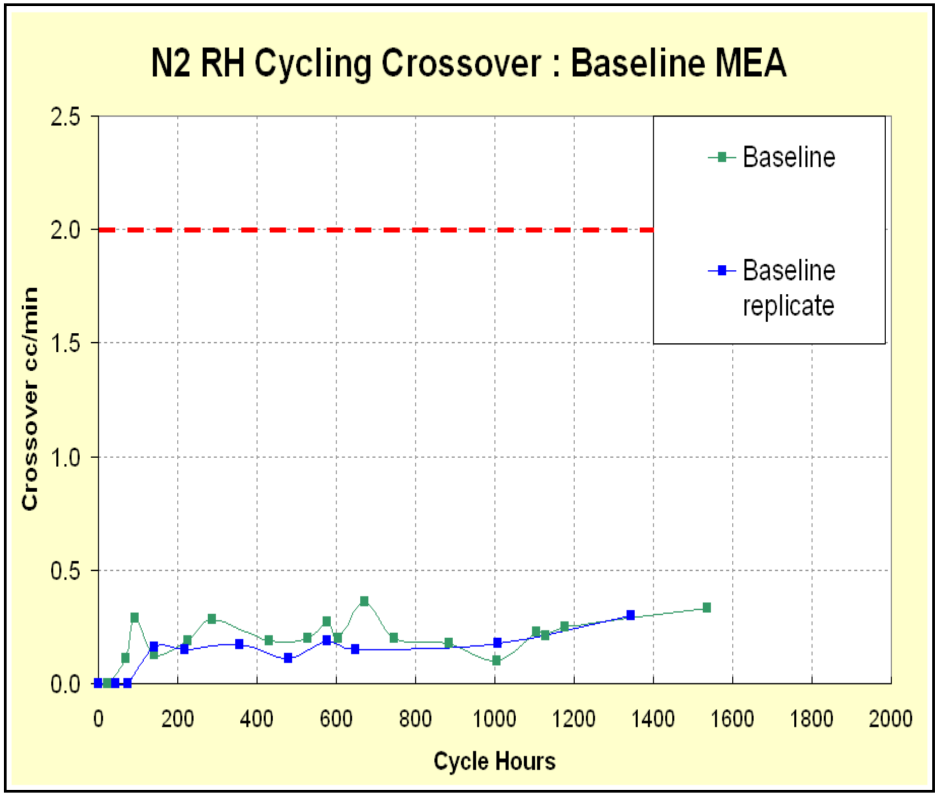
Creative Technologies Worldwide

Technical Accomplishments:
Accelerated Mechanical Durability Baseline

Gore N_2 RH Cycling Protocol:

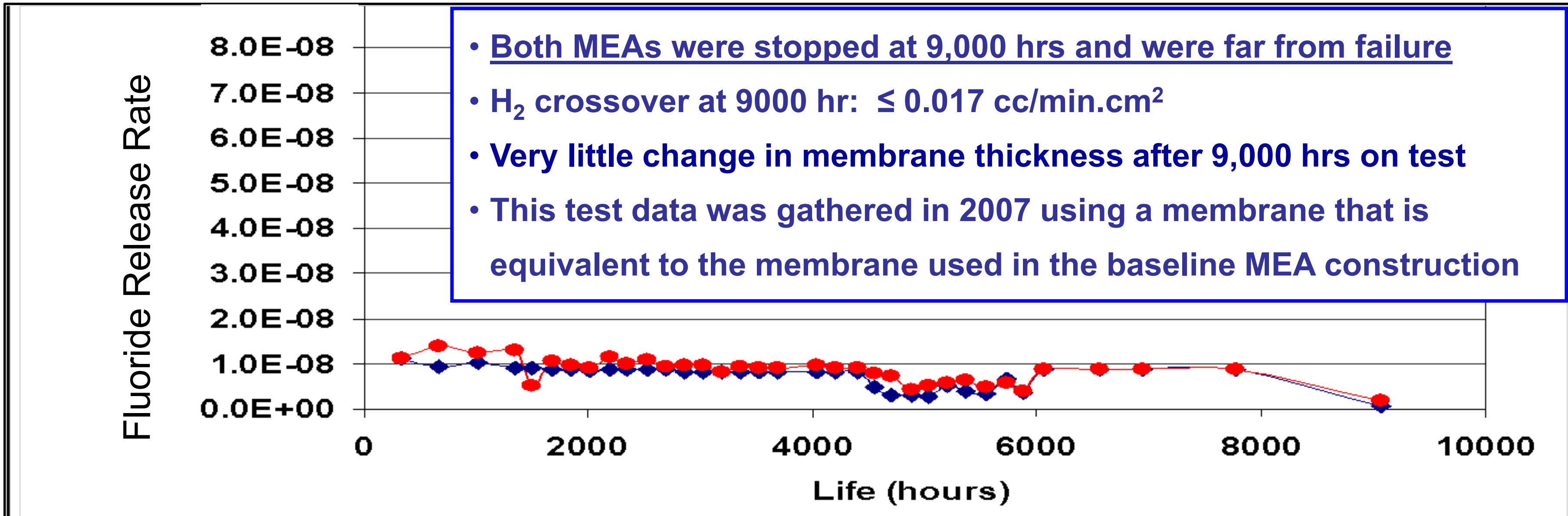
Tcell (C)	Pressure (kPa)	Flow (Anode/Cathode, cc/min)
80	270	500 N_2 / 1000 N_2

- 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)



Technical Accomplishments:

9,000 Hour 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 was gathered in 2007 using a membrane that is equivalent to the 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

Technical Accomplishments:

3L MEA Manufacturing Process Cost Model

Preliminary 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

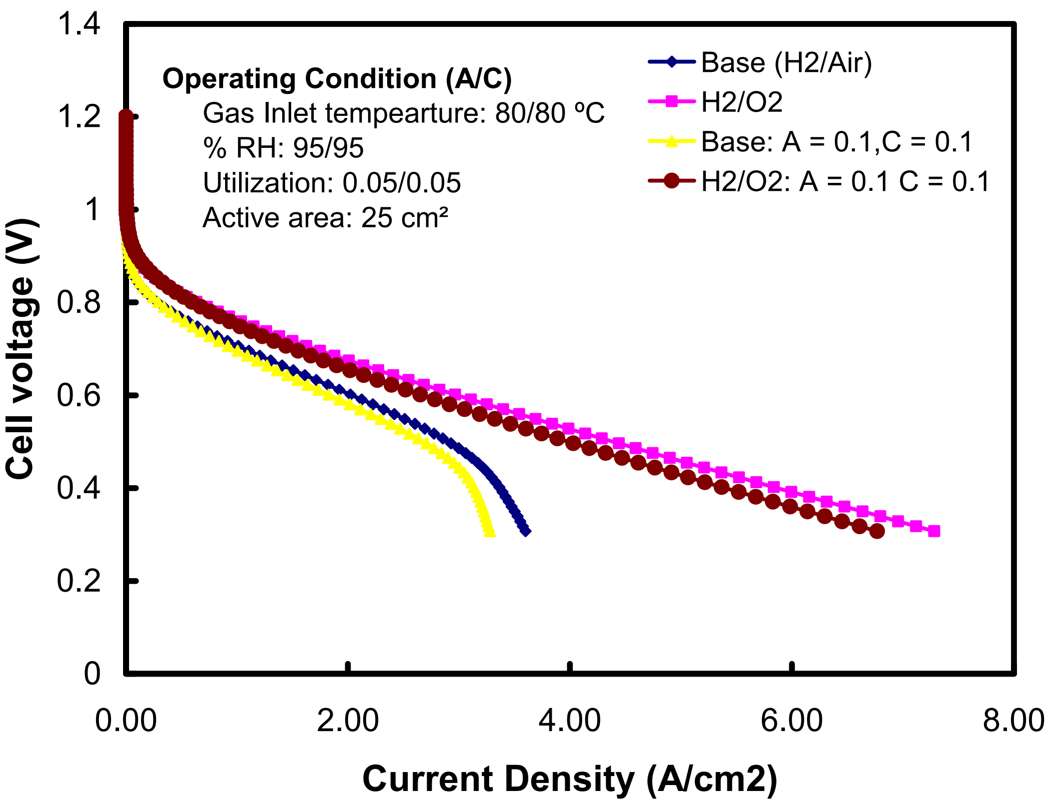
Process Costs	Primary forms of waste	Modeled Process Improvements
Catalyst	line losses, edge trim, electrode residuals	Reduce scrap with better coating process
Backers	all backers	No backers
Solvent/disposables	all	
Process/MOH	time	
DL	time	

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

GORE Creative Technologies Worldwide

Technical Accomplishments:
Conditioning Model Development



Effect of change of CL ionomer content (*Base = 0.21*) on PEFC performance with air and oxygen operation (oxygen gain)

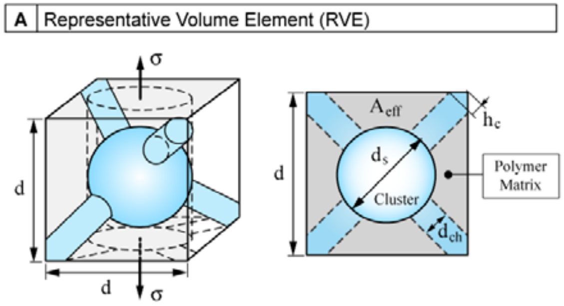
Model captures various polarization losses, flooding phenomenon etc for a *solid-plate configuration*.

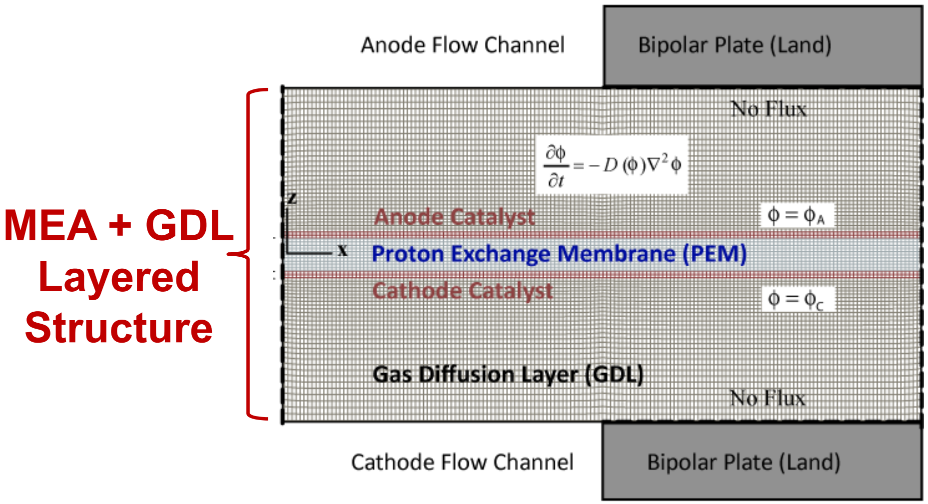
Key physics for conditioning are being incorporated in the model

- Contaminant poisoning & contaminant oxidization
- Interfacial resistance
- Ionomer hydration and swelling

Technical Accomplishments: Mechanical Modeling

- Method for determining quasi-static elastic/plastic properties of membranes
- Empirical constitutive models (quasi-static properties)
- Models to calculate sorption and stresses in membranes during temperature and relative humidity cycling
- Micromechanics models of membrane behavior





GORE
Creative Technologies Worldwide

Proposed Future Work for FY09:
Mechanical Modeling

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

Analytical Modeling

Elastic Properties

Sorption Behavior (λ vs. RH)

Numerical Modeling

Stress-Diffusion Model

Current Work

Future Work

Experimental Data

Time-Dependent Properties

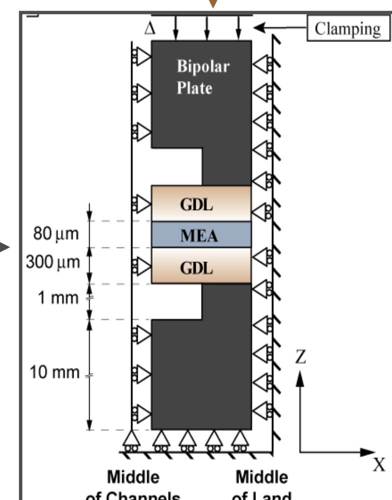
Time Effect on Swelling

Visco-Elasticity

Visco-Plasticity

Fracture

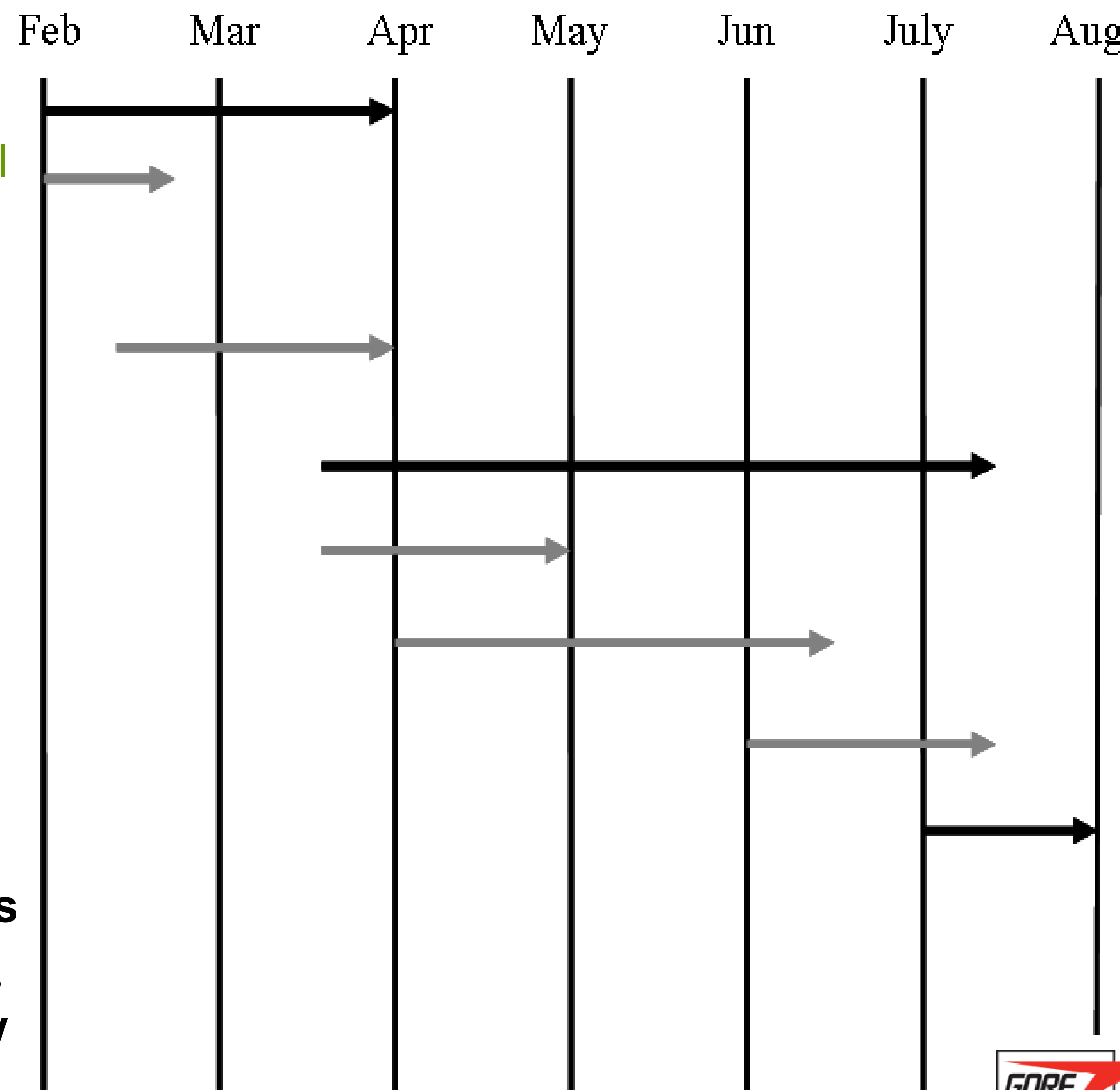
Flaw Geometries



Fracture-Failure Models

Proposed Future Work for FY09:
Conditioning Model Development

- ✓ Assess existing model
  - ✓ Identify suitable initial model frame work for conditioning model development
  - ✓ Understanding existing physics and code structure
- Conditioning analysis
  - Obtain/analyze base line MEA data from Gore
  - Add additional conditioning physics in the model
  - **Calibrate/validate model**
- Parametric study
  - **Identify critical parameters**
  - **Modify critical parameters to devise/recommend new conditioning protocols**



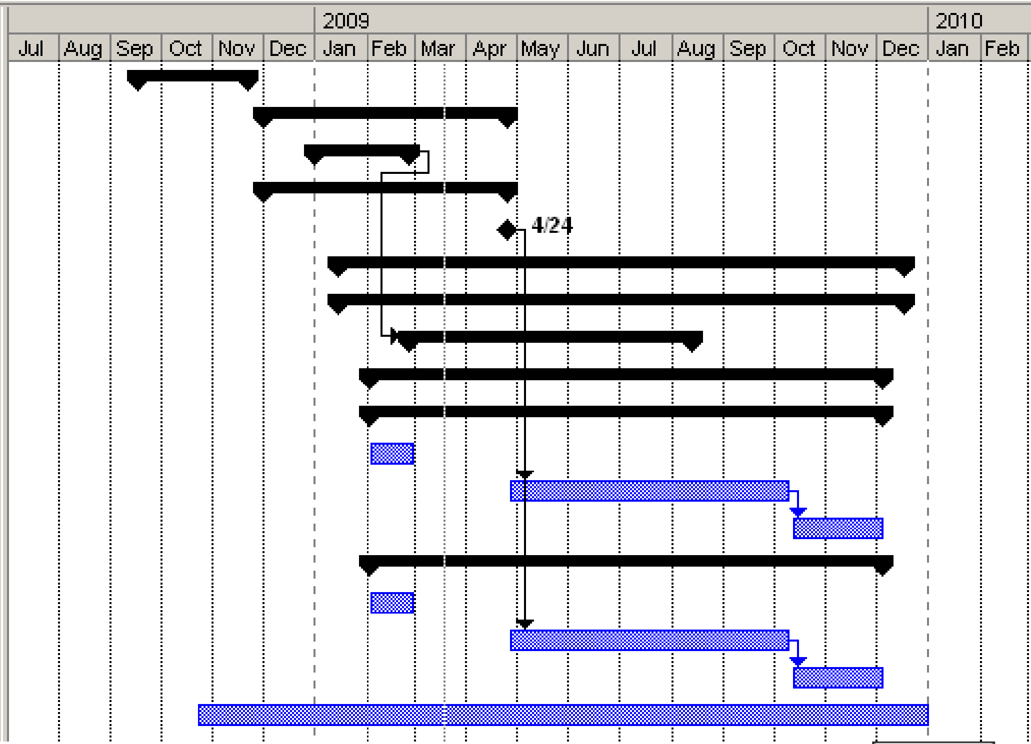
GORE
Creative Technologies Worldwide

Proposed Future Work for FY09:

MEA Process Equipment Scale-Up & Qualification

- Laboratory-scale equipment which has the potential to achieve the MEA process cost reductions determined by the cost model will be specified, procured, & qualified

Task Name	Est Duration
Preparation	
1.0 Characterization of current commercial MEA	2 mo
1.1 Test current commercial MEA	2 mo
1.2 Cost model current commercial MEA	5 mo
GO / NO GO decision on completion of task 1.2.3	-
2.0 Model Development	12 mo
2.1 Mechanical modeling/experimentation (UD)	12 mo
2.2 Conditioning model development (UTC)	6 mo
3.0 Equipment: Scale-Up and Qualification	11 mo
3.1 MEA Process Prototyping Equipment	11 mo
3.1.1 Research equipment	1 mo
3.1.2 Specify, test & purchase & wait	6 mo
3.1.3 Install and qualify new equipment	2 mo
3.2 Continuous Process Lab-Scale Equipment	11 mo
3.2.1 Research equipment	1 mo
3.2.2 Specify, test & purchase & wait	6 mo
3.2.3 Install and qualify new equipment	2 mo
4.0 Project management and Reporting	



Collaborations

- UTC Power - MEA Conditioning Modeling
  - T. Madden & M. Khandelwal
- University of Delaware - MEA Mechanical Modeling
  - A. Karlsson & M. Santare
- W. L. Gore & Associates, Inc. - Project Lead
  - F. Busby

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
  - **Improve Durability**
    - Optimize mechanical properties of the 3L construction
  - **Unique Enabling Technologies**
    - Direct Coating: Use form *at least* one membrane–electrode interface
    - Gore's Advanced ePTFE membrane reinforcement & advanced PFSA ionomers enable durable high-performance MEAs
    - Modeling will be used to understand mechanical durability & conditioning mechanisms as well as new MEA optimization
    - Advanced fuel cell testing & diagnostics

Summary (2)

- **Key Accomplishments**
  - Preliminary cost model results indicate that a new 3L MEA process has potential to reduce 3L MEA cost by 25%
  - Baseline testing of current commercial MEA is complete
    - 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 lifetime for a variety of temperature & relative humidity cycling scenarios is underway
  - Development of a fundamental cell conditioning model which will estimate the cell/stack break-in time 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 fuel cell modeling experience of UTCP enables a robust approach to development of a new low-cost MEA manufacturing process