# VI.2 Manufacturing of Low-Cost, Durable Membrane Electrode Assemblies Engineered for Rapid Conditioning


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Subcontractors:

- UTC Power, South Windsor, CT
- University of Delaware, Newark, DE (UD)
- University of Tennessee, Knoxville, TN (UTK)

Project Start Date: October 1, 2008
Project End Date: June 30, 2014


## Fiscal Year (FY) 2012 Objectives

The overall objective of this project is to develop a unique, high-volume manufacturing process that will produce low-cost, durable, high-power density 5-layer membrane electrode assemblies (MEAs) that minimize stack conditioning:

- Manufacturing process scalable to fuel cell industry MEA volumes of at least 500k systems/year.
- Manufacturing process consistent with achieving $9/kW$_e$ DOE 2017 transportation MEA cost target.
- 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.
- 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.
- 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.
- The stack break-in time should be reduced to 4 hours or less.

### Phase 2 Objectives

- Low-Cost MEA Research and Development (R&D)
  - New 3-Layer (3-L) MEA Process Exploration
    - Investigate equipment configuration for low-cost MEA production
    - Investigate raw material formulations
    - Map out process windows for each layer of the MEA
  - Mechanical Modeling of Reinforced 3-L MEA
    - Use model to optimize membrane reinforcement for 5,000+ hour durability and maximum performance
    - Develop a deeper understanding of MEA failure mechanisms
  - 5-Layer (5-L) Heat and Water Management Modeling
    - Optimization of gas diffusion media (GDM) thermal, thickness, and transport properties to enhance the performance of thin, reinforced membranes and unique properties of direct-coated electrodes using a validated model
  - Optimization
    - 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
  - Evaluate potential for new process to achieve DOE cost targets prior to process scale-up (Go/No-Go decision)
- Scale-Up and Process Qualification
- Stack Validation

## Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Lack of High-Volume Membrane Electrode Assembly Processes

### Contribution to Achievement of DOE Manufacturing R&D Milestones

This project will contribute to achievement of the following DOE milestones from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- 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)

## FY 2012 Accomplishments

- Direct Coating Process Development
  - 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:
    - Each layer in the primary path process has been sheet coated on control substrate materials.
    - Gore identified a replacement for a discontinued backer which satisfied the criteria for:
      - Thickness uniformity
      - Mechanical stability up to max drying and piece-part conversion temperatures
      - Chemical stability
      - Cleanliness
      - Electrode release
      - Supply chain reliability
      - Cost
    - Cathode electrode coating on the new backer has been demonstrated on a roll-to-roll coating line and is equivalent to or better than the current commercial electrode in Gore's beginning-of-life test, start/stop accelerated stress test (AST), and voltage cycling AST.
- Gore has demonstrated mechanical durability of a 10-micron expanded polytetrafluoroethylene (ePTFE)-reinforced membrane. In previous testing, GORE™ MEAs exceeded 2,000 hours of accelerated mechanical durability testing, which has been equated to achieving 9,000 hours of membrane durability in an 80°C automotive duty cycle. This exceeds the DOE 2015 membrane durability target of 5,000 hours. Gore's 10-micron ePTFE reinforced membrane technology has been successfully incorporated into the lab-scale new 3-L MEA process.
- A quasi-static elastic/plastic layered structure MEA mechanical model has been modified to include visco-elastic/plastic behavior. Mechanical property experiments which are required to calculate model input parameters are complete and modeling of different membrane reinforcement geometries is underway. The final model will be used to predict reinforced MEA mechanical lifetime for a variety of temperature and relative humidity cycling scenarios. The model will also be used to explore different reinforcement strategies and optimize mechanical durability of the MEA structure targeted by the new low-cost process.
- 5-Layer Heat & Water Management Model development at UTK is complete.

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## Introduction

Over the past 20 years, great technical progress has been made in the area of improving power density and durability of fuel cell stacks, so much so that most of the requisite technical targets are now within reach. Yet, three major technical challenges remain. First and foremost is meeting the cost targets. The second challenge is producing components that are amenable for use in a high-speed, automotive assembly line. One impediment to this latter goal is that stack components must currently go through a long and tedious conditioning procedure before they produce optimal power. This so-called "break-in" can take many hours, and can involve quite complex voltage, temperature and/or pressure steps. These break-in procedures must be simplified and the time required reduced, if fuel cells are to become a viable power source. The third challenge is to achieve the durability targets in real-world operation. This project addresses all three challenges: cost, break-in time, and durability for the key component of fuel cell stacks: MEAs.

## Approach

The overall objective of this project is to develop unique, high-volume manufacturing processes for low-cost, durable, high-power density 3-Layer MEAs that require little or no stack conditioning. In order to reduce MEA and stack costs, a new process will be engineered to reduce the cost of intermediate backer materials, reduce the number and cost of coating passes, improve safety and reduce process cost by minimizing solvent use, and reduce required conditioning time and costs. MEA mechanical durability will be studied and optimized using a combination of ex situ mechanical property testing, non-linear mechanical model optimization, and in situ accelerated mechanical durability testing. Fuel cell heat and water management will be modeled to optimize electrode and GDM thermal, geometric, and transport properties and interactions. Unique enabling technologies that will be employed in new process development include:

- Direct coating which will be used to form at least one membrane–electrode interface.
- Gore's advanced ePTFE membrane reinforcement and advanced perfluorinated sulfonic acid ionomers which enable durable high-performance MEAs.
- Advanced fuel cell testing and diagnostics.

## Results

### Low-Cost MEA Process Development

Primary path

- Process step 1: Coat bottom electrode on low-cost, non-porous backer
- Process step 2: Direct coat reinforced membrane on top of the bottom electrode
- Process step 3: Direct coat top-side electrode on top of the reinforced membrane

The alternate path is to directly coat the anode electrode onto a backer-supported reinforced half-membrane to make an anode-side 1.5-layer intermediate rolled-good. The cathode electrode is then directly coated onto a backer-supported reinforced half-membrane in a similar process. In the final step, the backers are removed from the anode-side and cathode-side 1.5-layers intermediates and the webs are laminated together to form the 3-layer product.

Electrodes made using lab-scale versions of the current primary path process equipment have demonstrated performance equivalent to or better than the current commercial electrodes across a broad range of operating conditions. Figures 1 and 2 show performance of direct coated electrodes paired with opposing control electrodes in a range of operating conditions which can be used to assess the viability of an MEA for different applications (automotive, stationary, portable, etc.), or for dynamic operation within a single application.

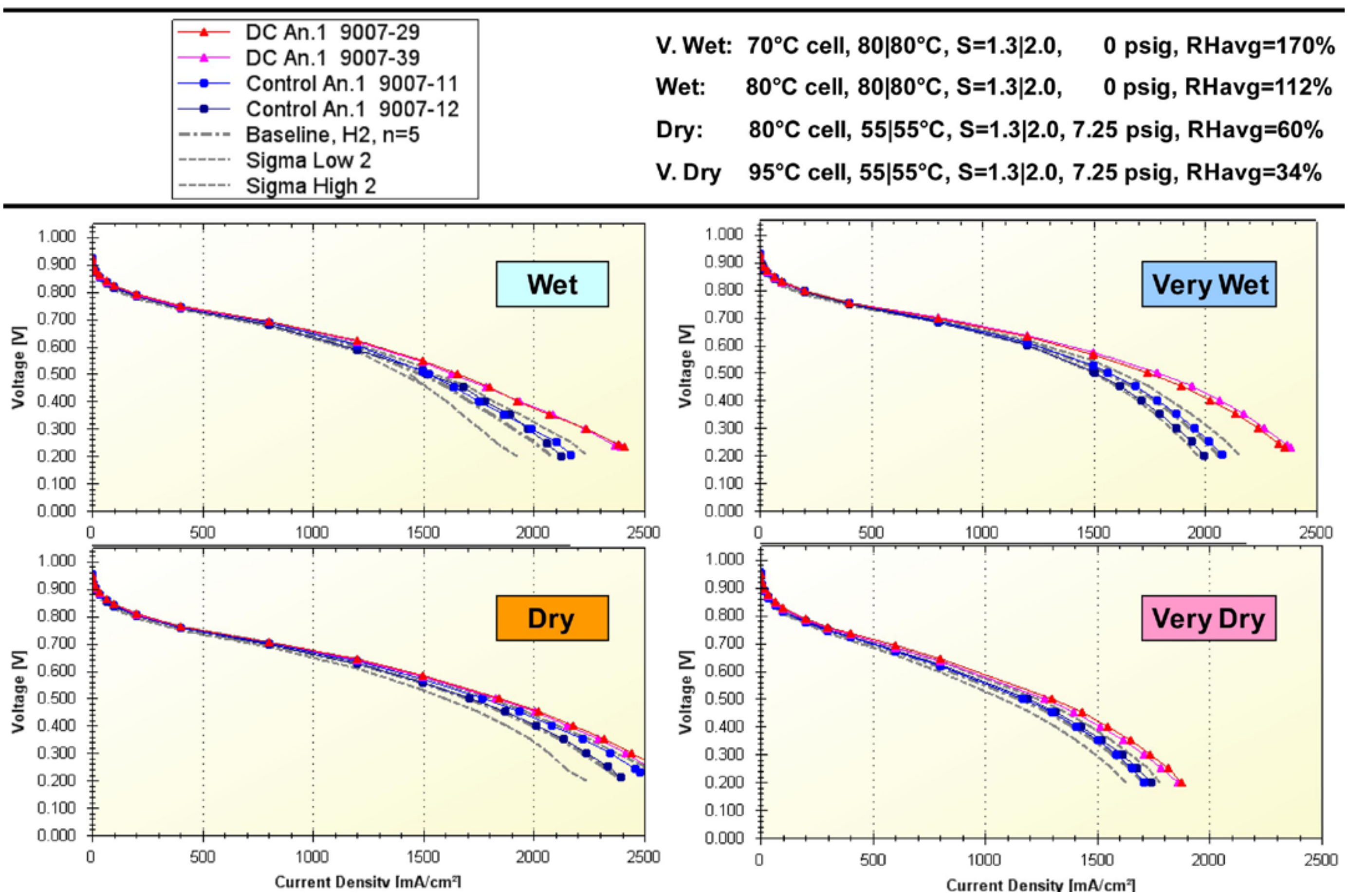


**FIGURE 1.** Direct-Coated Anode Performance (DC = direct coated)

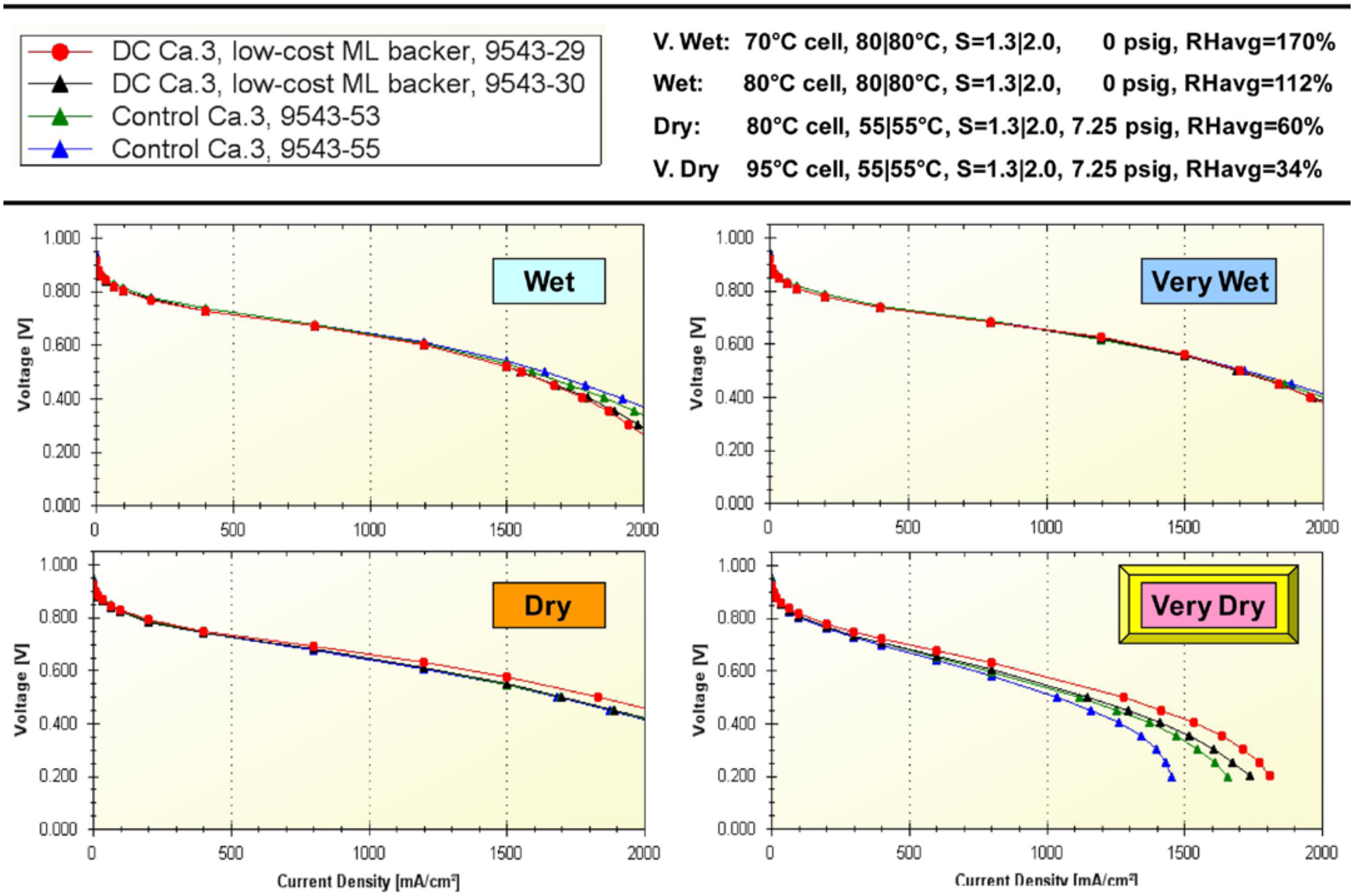


**FIGURE 2.** Direct-Coated Cathode Performance

Coating research during the past year focused on backer development and demonstration of cathode-on-backer coating on a roll-to-roll pilot line. Future experiments will combine direct-coated anodes and direct-coated cathodes and test the durability of direct-coated MEA.

## Mechanically Durable 10-µm Reinforced Membrane

Gore has successfully incorporated a mechanically durable 10-µm reinforced membrane into the current primary path process. The 10-µm membrane construction has demonstrated high performance due to reduced resistance and increased water back-diffusion (see Figure 3). In previous testing, GORE™ MEAs exceeded 2,000 hours of accelerated mechanical durability testing, which has been equated to achieving 9,000 hours of membrane durability in an 80°C automotive-duty cycle. This exceeds the DOE 2015 membrane durability target of 5,000 hours. The accelerated mechanical durability testing protocol is summarized in Table 1.:

For further protocol information, see: W. Liu, M. Crum, ECS Transactions **3**, 531-540 (2007).

**TABLE 1.** Accelerated Mechanical Durability Testing Protocol

| Tcell (°C) | Pressure (kPa) | Flow (Anode/Cathode, cc/min) |
|---|---|---|
| 80 | 270 | 500 N2/1,000 N2 |

Cycle between dry feed gas and humidified feed gas
(sparger bottle temp = 94˚C)
Dry feed gas hold time: 15 seconds
Humidified feed gas hold time: 5 seconds

## Mechanical Modeling of Reinforced 3-L MEA (UD)

A quasi-static elastic/plastic layered structure MEA mechanical model has been modified to include visco-elastic/plastic behavior. Mechanical property experiments which are required to calculate model input parameters are complete and modeling of different membrane reinforcement geometries is underway.

Nafion® 211 membrane is used for the model membrane and the temperature, relative humidity (RH), and time dependent properties are calculated from the ongoing experimental results. The viscous properties are modeled

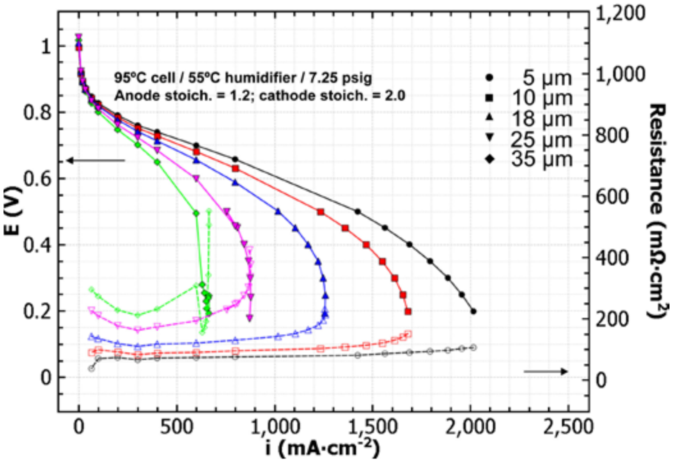


**FIGURE 3.** Performance of Thin, Mechanically Durable Reinforced Membranes

using a 2-layer viscoplastic constitutive model. This material model consists of an elastoplastic "arm" that is in parallel with an elastoviscous "arm." The elastoplastic arm consists of an elastic spring (stiffness $K_p$) and a plastic component (yield stress, $\sigma_y$ and hardening $H'$). Yielding according to the Mises criterion is used here. The elastoviscous arm has two elements, one spring (stiffness $K_v$) and one dashpot (using a time hardening law $\dot{\varepsilon}_v = A\sigma_v^{\,n}$). Thus, the instantaneous elastic stiffness of the material is the sum of the elastic elements, $K_p + K_v$. In summary, the parameters that are required for this model are $K_p$, $\sigma_y$, $H'$, $K_v$, $A$ and $n$. These properties are determined from the experimental results. Tensile testing was conducted for a range of displacement rates to investigate the influence of this parameter on the mechanical response. The rates were selected so that the full visco-elastic-plastic constitutive equations can be determined. The relationships obtained from the MEA testing are "composite properties," combining the properties of the membrane with the electrodes. The constitutive equations for the electrodes will be obtained via reverse analysis. The experimental results have shown that the mechanical response of Nafion® 211 membrane and the MEA is dependent on temperature and humidity as well as displacement rate. Figure 4 shows the dynamic response of modeled membrane stress as a function of RH in the flow channels. Peak stress after dehydration decreases by about 25% with a reduction of humidity transition time from 1 s to 50 s, indicating that an abrupt change in hydration is a more severe case than a gradual change in hydration. Results also indicate that lower

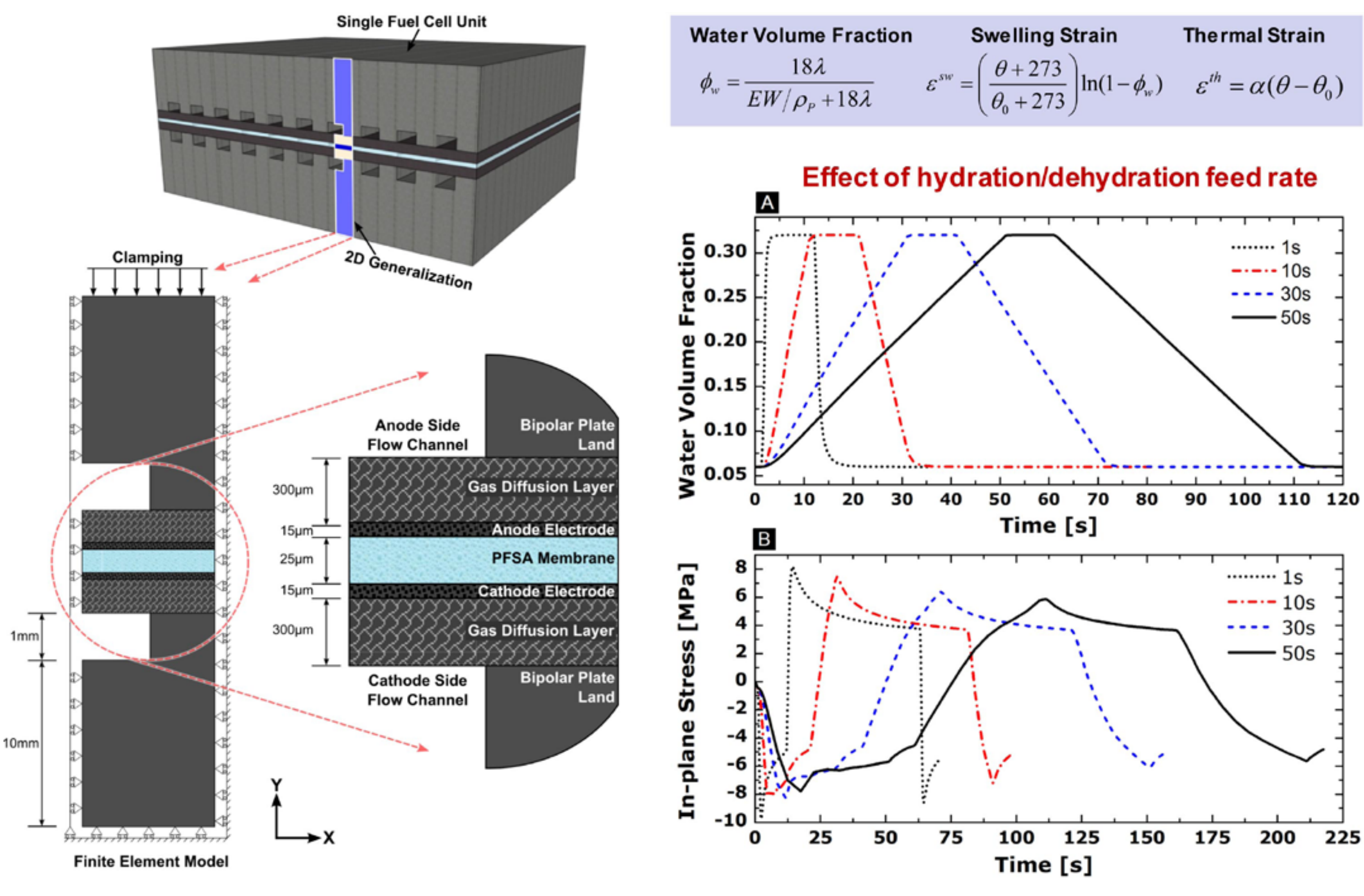


**FIGURE 4.** Two-Dimensional Plane Strain Finite Element Model for a Single Cell under RH Cycling

temperature, lower humidity or faster displacement rate result in a larger stress for a given strain.

### 5-L Heat & Water Management Modeling (UTK)

Membrane electrode assemblies and diffusion media materials were selected and experimental testing was initiated. Computationally, an initial first round of two-dimensional single-phase computational model simulation was completed to simulate the impact of diffusion media and membrane thickness and thermal properties. This analysis has enabled some understanding of the consequences of the various micro/macro diffusion media designs. The thermal properties of the diffusion media and microporous layer were shown to be critical to facilitate proper water management and are critical engineering parameters.

## Conclusions and Future Directions

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

- Electrodes made using lab-scale versions of the current primary path process equipment have demonstrated performance equivalent to or better than the current commercial electrodes across a broad range of operating conditions. Cathode coating on the new low-cost backer has been demonstrated on a roll-to-roll process. Future work will focus on combining direct coated anodes and cathodes as well as accelerated stress testing to ensure that durability of the new, direct-coated MEAs is equivalent to or better than the current commercial control MEA.
- Fuel cell heat and water management modeling will be used to efficiently optimize electrode and GDM thermal, geometric, and transport properties and interactions. Direct-coated electrodes will be paired with the most appropriate GDM materials identified in this study. In this way, GDM will enable maximum performance and durability of the low-cost 3-layer MEA.
- A quasi-static elastic/plastic layered structure MEA mechanical model has been modified to include visco-elastic/plastic behavior. Mechanical property experiments which are required to calculate model input parameters are complete and modeling of different membrane reinforcement geometries is underway. The model will be validated with MEA accelerated durability testing. The final model will then be used to predict reinforced MEA lifetime for a variety of temperature and relative humidity cycling scenarios. The model will also be used to optimize mechanical durability of the MEA structure targeted by the new low-cost process.



## FY 2012 Publications/Presentations

**1.** 2012 Hydrogen Program Annual Merit Review: mn004_busby_2012_o.pdf