

VI.4 Manufacturing of Low-Cost, Durable Membrane Electrode Assemblies Engineered for Rapid Conditioning

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- University of Delaware, Newark, DE
- University of Tennessee, Knoxville, TN

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Project End Date: June 30, 2013

Fiscal Year (FY) 2011 Objectives

The overall objective of this project is to develop a unique, high-volume manufacturing processes that will produce low-cost, durable, high-power density 5-layer (5-L) 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 \$15/kW_e DOE 2015 transportation stack 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 (3-L) MEA roll-good (anode electrode + membrane + cathode electrode) with separate rolls of gas diffusion media (GDM).

- 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-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-L Heat and Water Management Modeling
 - Optimization of 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 University of Delaware (UD) and University of Tennessee, Knoxville (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 section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Lack of High-Volume Membrane Electrode Assembly (MEA) Processes
- (D) Manual Stack Assembly

Contribution to Achievement of DOE Manufacturing Milestones

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

3.5 Manufacturing R&D/ Fuel Cells/ Task 1: Membrane and MEA

4. Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2013)

3.4 Fuel Cells/ Task 3: Membrane Electrode Assemblies Meeting All Targets

38. Evaluate progress toward 2015 targets. (4Q, 2012)

FY 2011 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:
 - 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 mechanical durability of a 12 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 12 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 95% complete. 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 and the experimental test progress is on track to enable efficient optimization of GDM for the new 3-L MEA.



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-L 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 perfluorosulfonic acid ionomers which enable durable high-performance MEAs.
 - Advanced fuel cell testing and diagnostics.

Results

Low-Cost MEA Process Development

The primary path has changed during the past year and process development for the current primary path is progressing rapidly.

- Previous Primary Path
 - Process step 1: Direct coat cathode electrode on a carrier-film-supported reinforced membrane.
 - Process step 2: Remove carrier film and direct coat anode electrode on 2-layer intermediate.
- Current 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-L 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. This is a substantial improvement over the previous primary path which produced electrodes that were equivalent, at best, to the current commercial electrodes. 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.

Coating research during the past year focused on developing the new primary path process and understanding the interactions between cathode ink formulation and low-cost backer for the current primary path, in which the cathode is the first layer to be coated in the 3-L MEA. Future experiments will combine direct-coated anodes and direct-coated cathodes and test the durability of direct-coated electrodes.

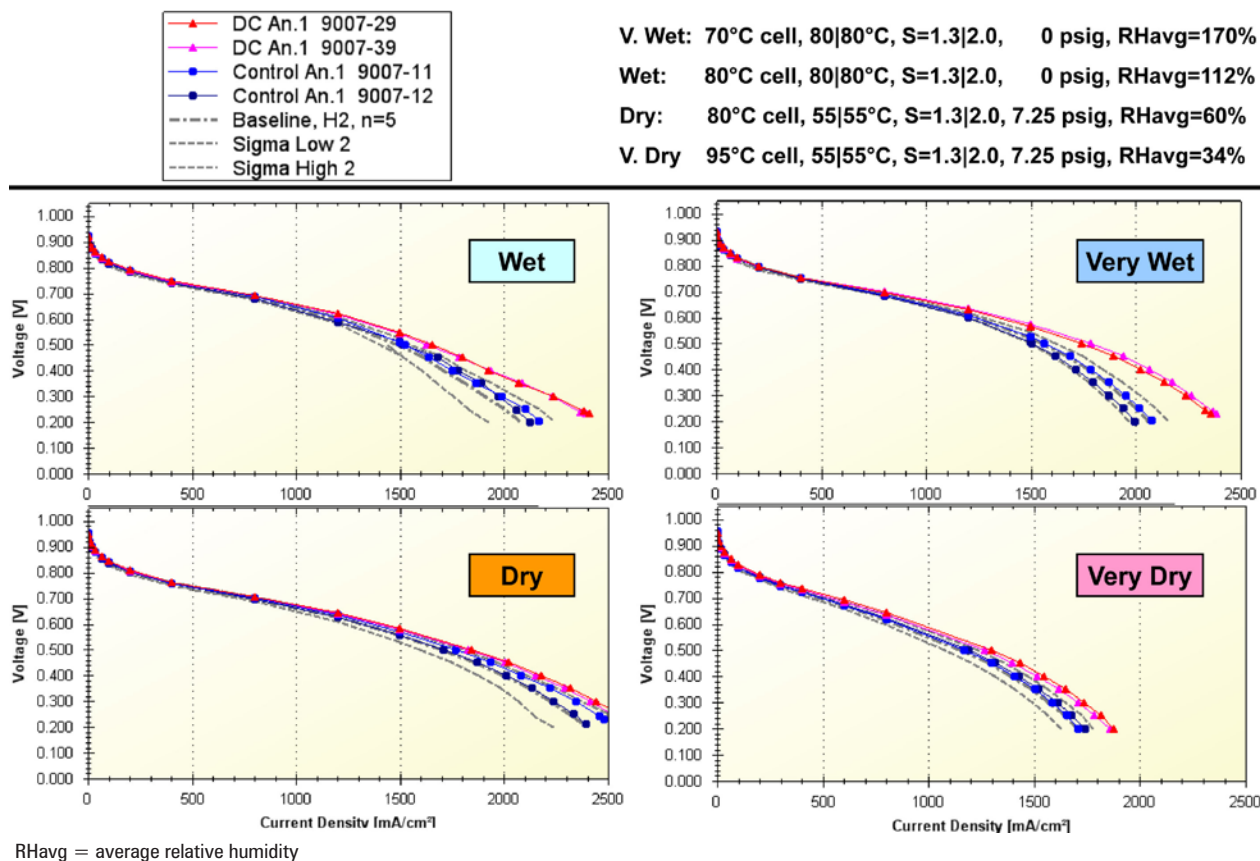


FIGURE 1. Direct Coated Anode Performance (PL = Platinum loading in mg/cm²)

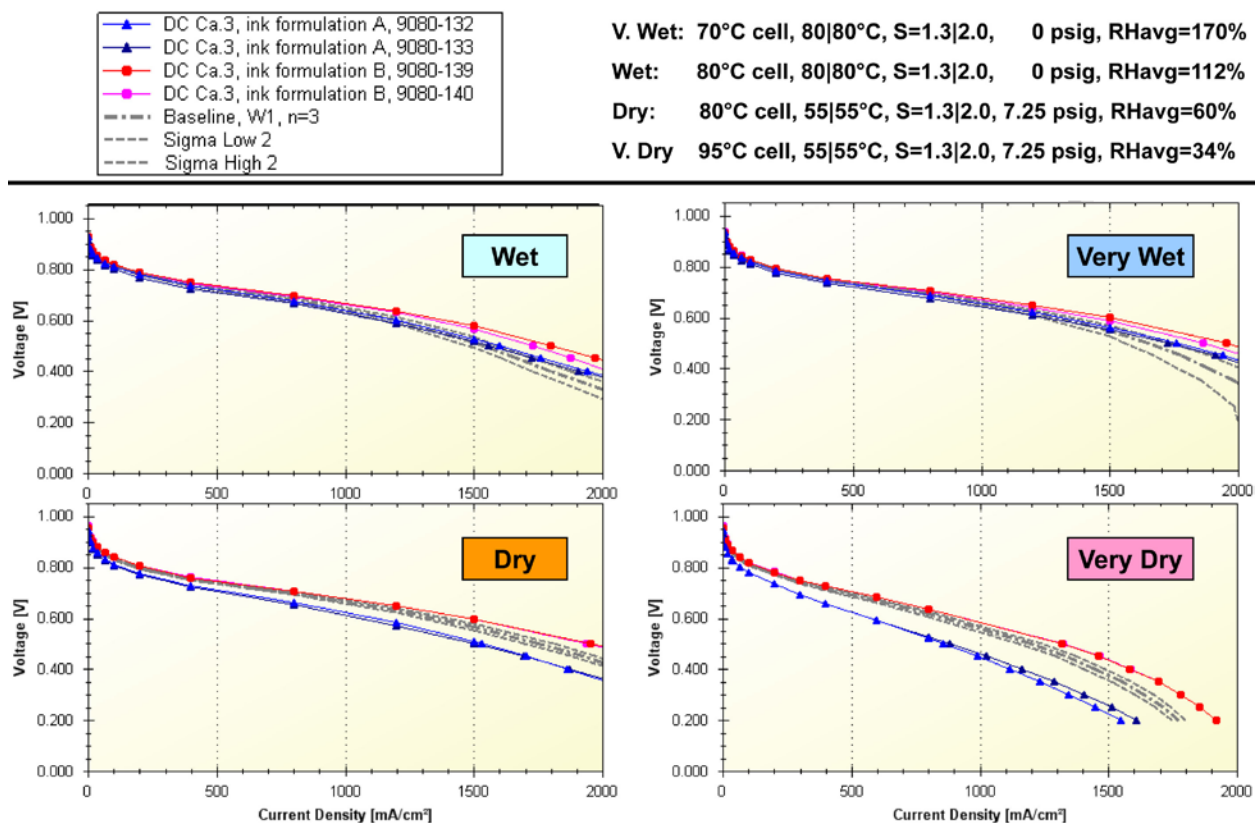


FIGURE 2. Direct Coated Cathode Performance (PL = Platinum loading in mg/cm²)

Mechanically Durable 12 μm Reinforced Membrane

Gore has successfully incorporated a mechanically durable 12 μm reinforced membrane into the current primary path process. The 12 μm membrane construction has also demonstrated high performance due to reduced resistance and increased waster 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 below:

Tcell (°C)	Pressure (kPa)	Flow (Anode/Cathode, cc/min)
80	270	500 N ₂ /1,000 N ₂

- 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
- For further protocol information, see: W. Liu, M. Crum [1]

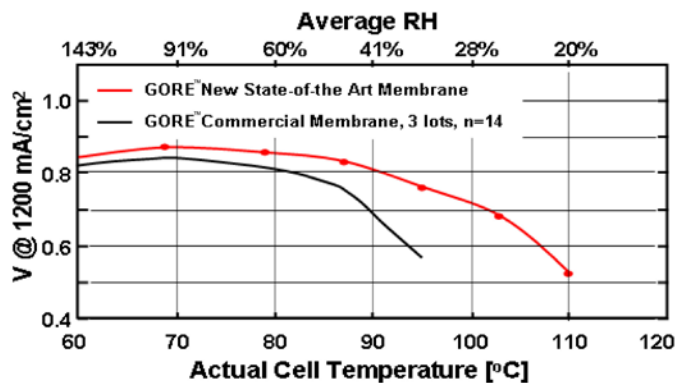


FIGURE 3. Performance of Thin, Mechanically Durable Reinforced Membrane

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 95% complete.

Nafion® 211 membrane is used for the model membrane and the temperature, relative humidity, and time dependant

properties are calculated from the ongoing experimental results. The viscous properties are modeled 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, σ_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 $\dot{\epsilon}_v = A\sigma_v^n$). 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 , σ_y , H' , K_v , A and n . These properties are determined from the experimental results. Figure 4 shows the modeled membrane stress as a function of membrane water fraction for two cycling scenarios using preliminary experimental data.

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

5-L Heat and 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 micro-porous layer were shown to be critical to facilitate proper water management and are critical engineering parameters. Later, computational simulations were upgraded to include multi-phase flow.

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. 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-L 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

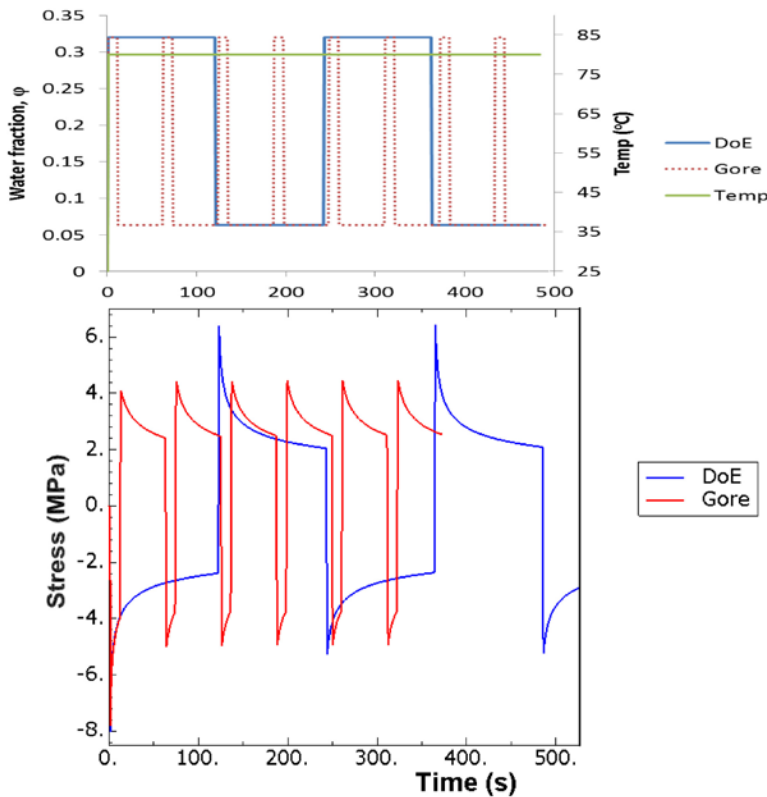


FIGURE 4. Modeled Membrane Stress as a Function of Membrane Water Fraction for Two Cycling Scenarios

required to calculate model input parameters are 95% complete. When data collection is complete, 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 explore different reinforcement strategies and optimize mechanical durability of the MEA structure targeted by the new low-cost process.

FY 2011 Publications/Presentations

1. 2011 Hydrogen Program Annual Merit Review: mn004_busby_2011_o.pdf.

References

1. W. Liu and M. Crum. ECS Transactions 3, 531-540 (2007).

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