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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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 3-layer membrane electrode assemblies (MEAs) that require little or no 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 a 3-layer MEA roll-good (anode electrode + membrane + cathode electrode).
- The stack break-in time should be reduced to 4 hours or less.

Phase 2 Objectives

- New Process Exploration:
  - Investigate equipment configuration for low-cost MEA production.
  - Investigate raw material formulations.
  - Map out process windows for each layer of the MEA.
- Fuel Cell Heat and Water Management Modeling and Validation:
  - Efficiently optimize electrode and gas diffusion media (GDM) thermal, geometric, and transport properties and interactions.
- Multi-Layer Mechanical Modeling:
  - 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:
  - Utilize modeling results and designed experiments.
- Low-Cost MEA Conditioning Research
- 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 and Fuel Cells sections of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

3.5 Manufacturing R&D

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

3.4 Fuel Cells: Membrane Electrode Assemblies Meeting All Targets

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

Accomplishments

- Direct Coating Process Development:
  - Primary and alternative paths for direct-coated 3-layer MEA process development have been determined.
  - Direct coated anodes and cathodes have demonstrated performance which is equivalent to Gore's current commercial MEAs in 'current automotive' operating conditions when paired with control electrodes.
- 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.
- 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 35% complete. The final model will be used to predict reinforced MEA lifetime for a variety of temperature and relative humidity (RH) 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.

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

Results

Low-Cost MEA Process Development

Primary and alternative paths for direct-coated 3-layer process development have been determined. Experiments targeted at both paths have made substantial progress, and direct-coated electrodes have demonstrated performance equivalent with the current commercial electrodes in specific operating conditions (Table 1). 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.

Future experiments will combine direct-coated anodes and direct-coated cathodes. These direct-coated MEAs will be produced according to the primary and/or alternative paths for process development.

The primary path is to directly coat the cathode electrode on a backer-supported reinforced membrane to form a 2-layer intermediate rolled-good. The next

TABLE 1. Operating Conditions

Condition	Description	Tcell (°C)	Inlet RH (Anode/ Cathode)	Stoichiometry (Anode/ Cathode)	Pressure (psig)
1	Stationary	80	100/100%	1.3 H_2/2.0 Air	0
2	Wet	70	152/152%	1.3 H_2/2.0 Air	0
3	Current Automotive	80	33/33%	1.3 H_2/2.0 Air	7
4	Future Automotive	95	19/19%	1.3 H_2/2.0 Air	7

process step is to remove the backer from the anode side of the membrane and directly coat the anode electrode onto the 2-layer intermediate to make a 3-layer product. The 3-layer rolled good can then be converted to a framed MEA with gas diffusion media on a pick-and-place process line.

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.

Mechanically Durable 12 μm Reinforced Membrane

Gore has demonstrated mechanical durability of a 12 µm reinforced membrane (see Figure 3). 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

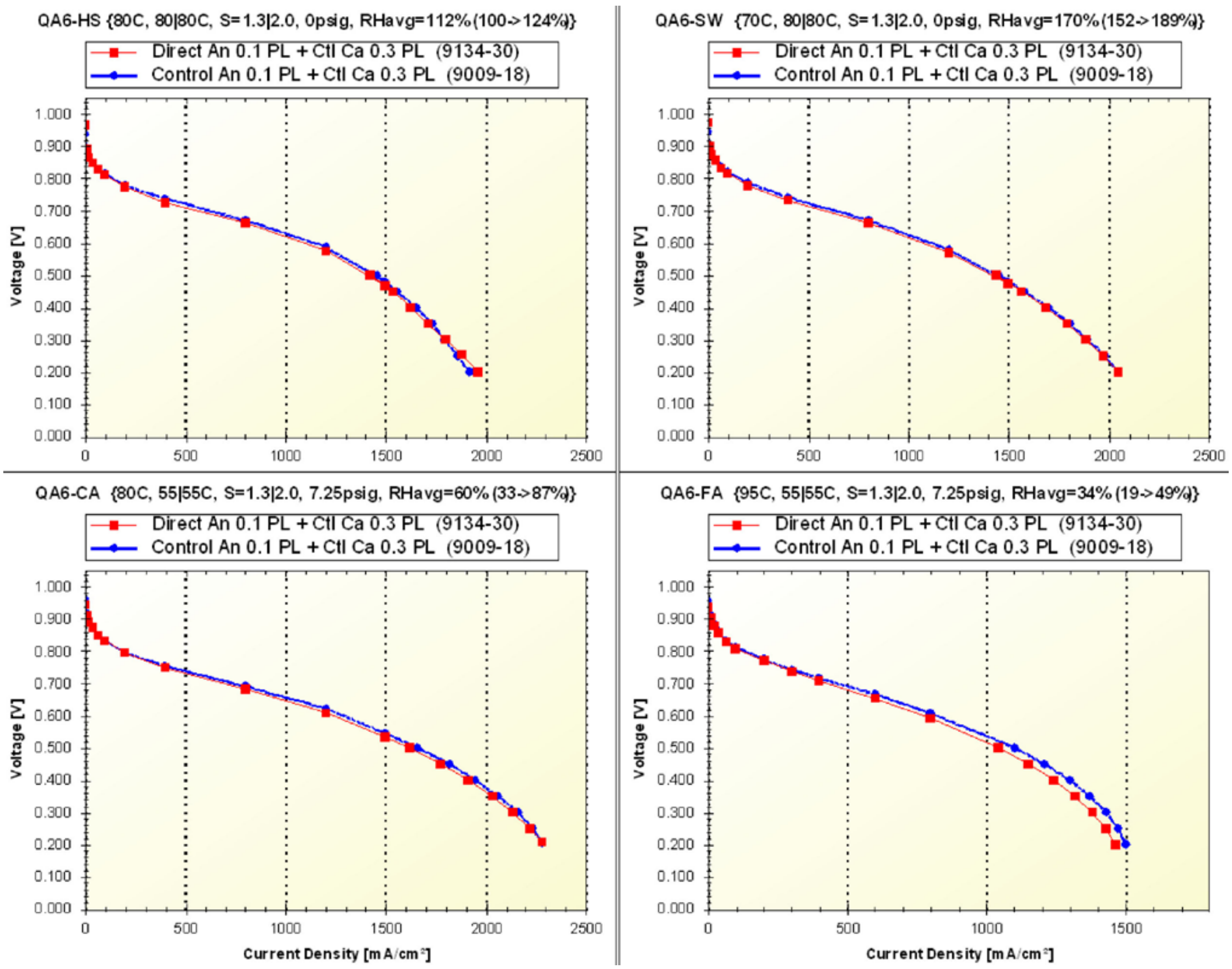

FIGURE 1. Direct-Coated Anode Performance (PL = platinum loading in mg/cm^2)

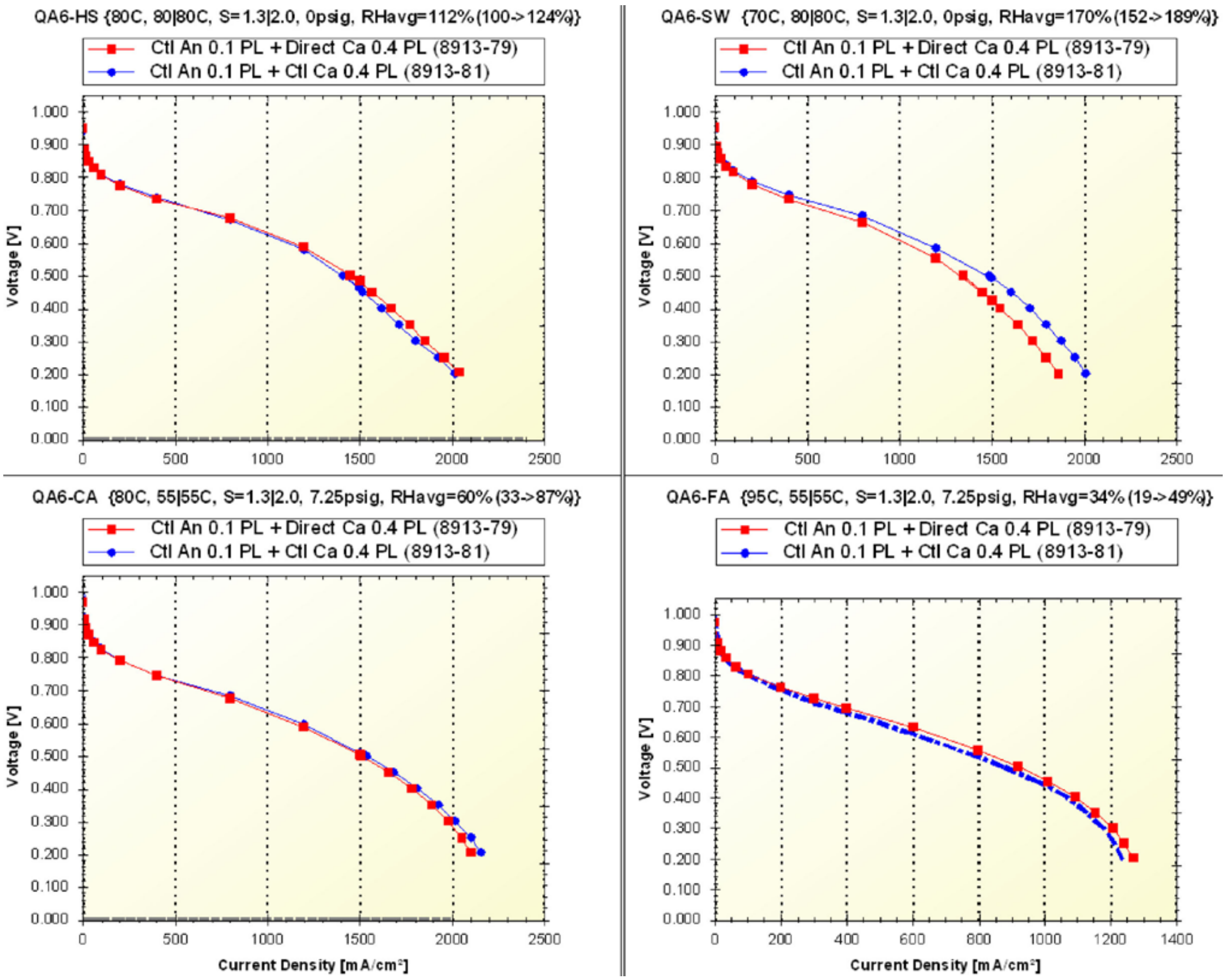

FIGURE 2. Direct-Coated Cathode Performance (PL = platinum loading in mg/cm^2)

accelerated mechanical durability testing protocol is summarized in Table 2.

TABLE 2. Mechanical Durability Testing Protocol

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, ECS Transactions **3**, 531-540 (2007).

Multi-Layer Mechanical Modeling

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 35% complete.

Nafion® PFSA NR-211 membrane is used for the model membrane and the temperature, RH, 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 $\varepsilon_v = A\,\sigma_v^n$). Thus, the instantaneous elastic stiffness of the material 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.

Tensile testing was conducted for a range of displacement rates to investigate the influence of this parameter on the mechanical response. The rates (0.01 mm/min to 250 mm/min) are 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. Figure 4 shows the comparison between the MEA and previously conducted experiments on Nafion® 211 membrane at T=45°C and RH=50%. The mechanical response of the MEA and Nafion® 211 membrane is different at medium or high displacement rates. However, at low displacement rates the mechanical response of the MEA and Nafion® 211 membrane is very similar.

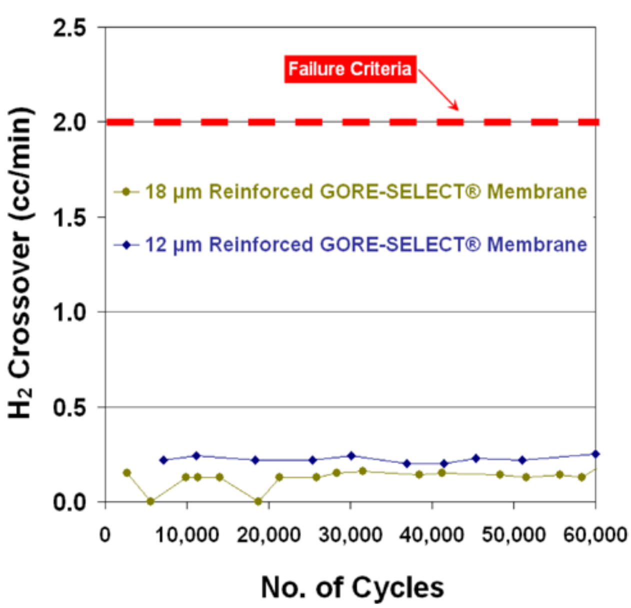

FIGURE 3. Accelerated Mechanical Durability Test Data for 12 μm GORE-SELECT Membrane

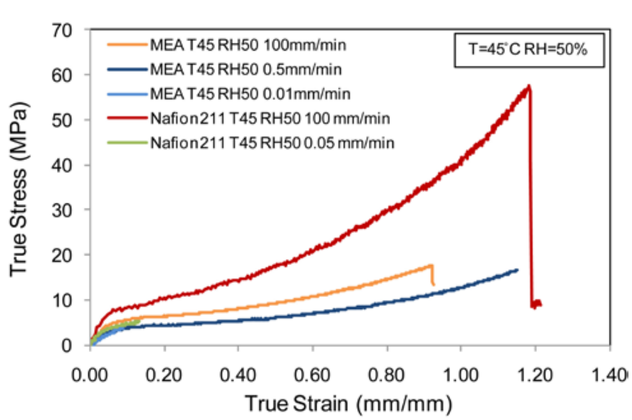

FIGURE 4. Tensile Test Results for MEA and NAFION® 211 membrane at T=45°C and RH=50%

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 the University of Delaware and the heat and water management experience of the University of Tennessee enables a robust approach to development of a new low-cost MEA manufacturing process.

- Low-cost direct-coated electrodes have demonstrated performance equivalent with the current commercial electrodes in specific operating conditions. Future low-cost MEA process development experiments will be focused on improving direct-coated cathode performance in very wet and very dry conditions. Gore will also combine direct-coated anodes with direct-coated cathodes on a durable 12 µm reinforced membrane. This construction will be produced according to the primary and/or alternative paths for direct coating process development.
- 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 35% 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 RH 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 2010 Publications/Presentations

1. 2010 Hydrogen Program Annual Merit Review: mn004_busby_2010_o.pdf.