VI.5 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

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Objectives

The overall objective of this project is to develop unique, high-volume manufacturing processes 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 by at least 50% compared to the product made in today's process, and break-in strategies employed must be consistent with cost targets.

For contractual reasons, this project has been split into two phases. The scope of this report is limited to Phase 1.

Phase 1 Objectives

- Characterize current commercial MEA performance:
  - Utilize advanced test protocols to understand gaps between current MEA performance and DOE targets.
  - Obtain data to enable future comparison with MEAs made by new processes.
- Develop a high-volume cost model for the current commercial MEA and estimate potential savings:
  - Understand gaps between current process costs and 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:
  - Develop a deeper understanding of failure mechanisms of the current MEA.
  - Use model to optimize properties of the MEA that will be made in the new low-cost process.
- Develop an MEA conditioning model:
  - Develop a deeper understanding of conditioning mechanisms of the current MEA and conditioning protocol.
  - Use model to optimize:
    - Properties of the 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.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing section of the Hydrogen, Fuel Cells and Infrastructure 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/ Fuel Cells Milestones

This project will contribute to achievement of the following DOE milestones from the Manufacturing and Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure 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)

Accomplishments

- Characterization (power density, conditioning, mechanical durability, chemical durability) of current commercial MEA performance is complete. Gore's 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.
- Cost modeling of the current commercial MEA process is complete. The model results indicate that a 17% reduction in the cost of the high-volume base case 3-layer MEA is attainable, given the potential process improvements that will be explored in Phase 2.
- A quasi-static elastic/plastic layered structure MEA mechanical model has been modified to include visco-elastic/plastic behavior and data collection to calculate model input parameters has begun. The model will be used to predict MEA lifetimes for a variety of temperature and relative humidity cycling scenarios.

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 MEAs of fuel cell stacks.

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. 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 expanded polytetrafluoroethylene membrane reinforcement and advanced perfluorosulfonic acid ionomers which enable durable high-performance MEAs.
- Advanced fuel cell testing and diagnostics.

Results

Characterization (power density, conditioning, mechanical durability, chemical durability) of the current commercial MEA performance is complete.

- MEA power density was characterized in fuel cell performance tests that were designed to be relevant to a variety of fuel cell applications (see Figure 1). Polarization curves were generated using the following operating conditions:

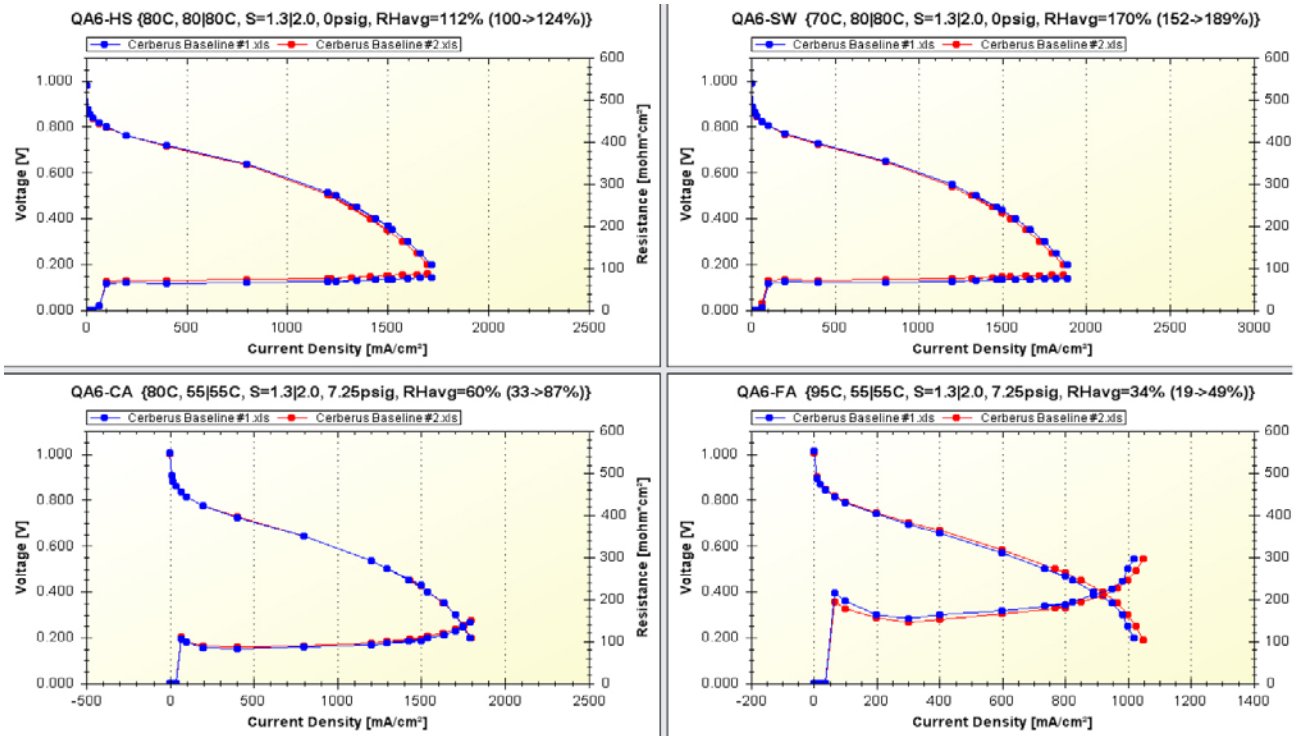

FIGURE 1. Power Density Characterization of the MEA Made in the Current Commercial Process

Condition	Description	Tcell (°C)	Inlet RH (Anode/ Cathode)	Stoich (Anode/ Cathode)	Pressure (psig)
1	Stationary	80	100/100%	1.3 H2/2.0 Air	0
2	Wet	70	152/152%	1.3 H2/2.0 Air	0
3	Current Auto	80	33/33%	1.3 H2/2.0 Air	7
4	Future Auto	95	19/19%	1.3 H2/2.0 Air	7

RH – relative humidity

- Break-in was characterized using the following protocol. Gore's current commercial MEAs achieved break-in within 2 hours of cycling.

Tcell (°C)	Pressure (psig)	Inlet RH (Anode/ Cathode)	Stoich (Anode/Cathode)
80	25	100/100%	1.2 H2/2.0 Air

Step cycle between 0.6V, open-circuit voltage (OCV), 0.3 V, OCV, 0.6 V, OCV, etc. for 2 hours.

- Replicate MEAs from Gore exceeded 2,000 hours of single-cell accelerated mechanical durability testing using the cycle given below, which has been equated to achieving 9,000 hours of membrane durability in an 80°C automotive duty cycle. This result exceeds the DOE 2015 membrane durability target of 5,000 hours.

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).

- Chemical durability was characterized using the protocol given below. After 300 hours of testing, replicate Gore MEAs maintained low degradation as evidenced by fluoride release rates under 5.45E-08 g F/hr cm^2.

Tcell (°C)	I (mA cm^2)	Inlet RH (Anode/ Cathode)	Pressure (kPa)	Flow (Anode/Cathode, cc/min)
95	0	50/50%	270	100/200 cc/min

For further protocol information, see: W. Liu, M. Crum, ECS Transactions **3**, 541-550 (2007).

Cost modeling of the current commercial MEA process has been completed.

- Model results indicate that a 17% reduction in the cost of the high-volume base case 3-layer MEA is attainable given the potential process improvements that will be explored in Phase 2. See Figure 2

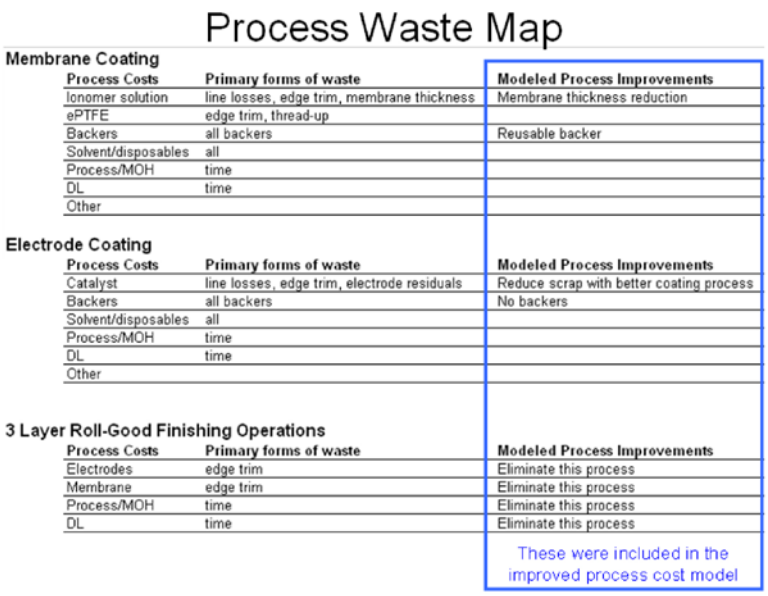

FIGURE 2. 3-Layer MEA Manufacturing Process Waste Map

for process waste map and key improved process assumptions.

Possible paths for establishing time-dependent mechanical properties were investigated.

- Methods to characterize ionomer membrane visco-elastic and visco-plastic properties were investigated using a TMA (thermal mechanical analyzer) modified for humidity control. As a pilot investigation, small samples (1/8" diameter discs) of NAFION®[1] 112 membrane were mounted onto the custom-built stage equilibrated within the test chamber at selected temperature humidity combinations (25˚C and 30% RH; 50% and 90% RH). A 0.01 Newton preload was applied to hold the specimen flat on the loading stage while allowing 30 minutes for the sample and chamber to equilibrate. The sample was then loaded compressively with a 1 Newton load (corresponding to 0.125 MPa pressure) and held for 15 minutes before releasing the load. During this loading, three distinct phases of deformation were observed. During the application of the compressive load, the specimen thickness decreased rapidly, corresponding to an elastic stress-strain response. As the load was held, the specimen continued to compress, indicting a creep response. When the load was released, the specimen slowly began to regain thickness in a recovery response. For these pilot investigations, the load cycle was held constant. Full equilibrium and recovery were not realized at any stage in the test. Consequently, in future studies, an optimum load-time cycle will be established and used to collect the relevant time-dependent data.

Existing numerical model was extended to include time-dependent (visco-elastic/plastic) properties.

- The applicability of ABAQUS finite element modeling was investigated for simulating the time-dependent response of ionomer membrane by constructing a small axisymmetric model. Data were from a previous study in which the University of Delaware conducted a preliminary investigation of time-dependent properties of NAFION® 112 membrane in a water environment. In the model, a load sequence corresponding to the sequence used in the experimental investigation (load-hold at constant displacement) was applied. The time-dependent deformation was calculated for this load sequence and compared to the experimental results (see Figure 3). The results show that a simple Maxwell model with nonlinear strain is adequate to capture the experimental response. This material model will be implemented in numerical simulations of stresses in fuel cell operation.

Various changes in the conditioning model were made to simulate the conditioning mechanism.

- Expression for oxygen reduction reaction kinetics was modified to capture the effect of available active area and to allow incorporation of the effects of certain contaminants.
- A two-step approach has been adopted for the model validation with the baseline of Gore's MEA conditioning experimental data:

[1] NAFION is a registered trademark of E. I. DuPont de Nemours company.

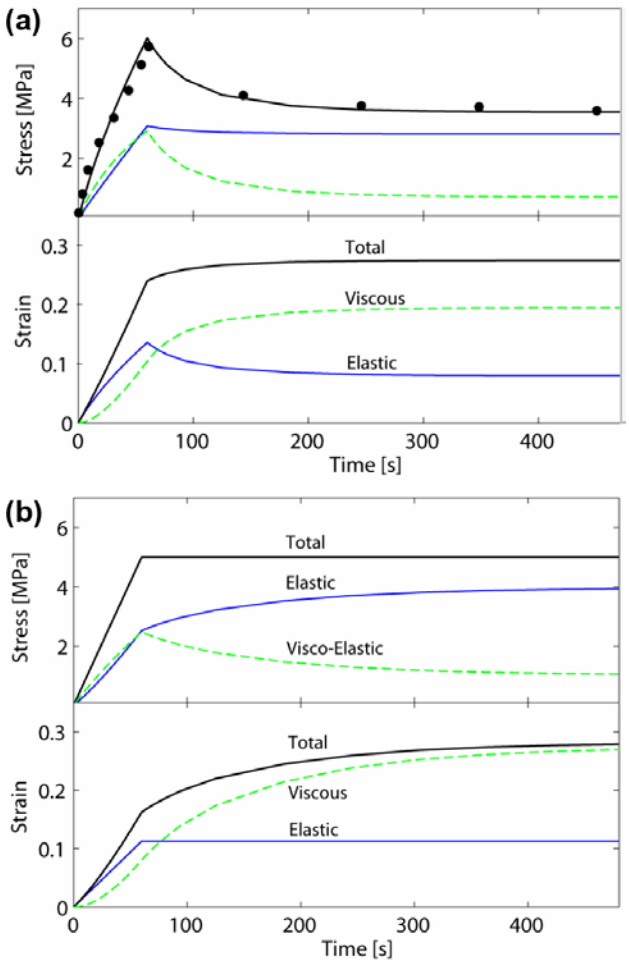

FIGURE 3. (a) Experiment conducted via loading and hold at constant strain. Markers indicate experimental values; solid black line indicates the deformation using a Maxwell model for viscoelastic response. (b) Using the extracted material parameters for the Maxwell model, the graphs show the predicted response for a case of loading followed by holding at constant force.

  - Polarization curve of a conditioned cell will be used to fit the model results. This step will ensure that the model is using correct property values for the baseline MEA and is in quantitative agreement with the experimental results.
  - Intermediate polarization curves collected throughout the conditioning protocol will be used to fit the model. At the end of the second step, the model will be fully validated with baseline MEA conditioning data.
- Preliminary results of validation analysis are shown in Figure 4. Using sensitivity analysis and resistance information from experiments, ionomer ionic conductivity and available catalyst area (A_s) were tuned to match the model results with the experimental data. Figure 4 clearly shows excellent

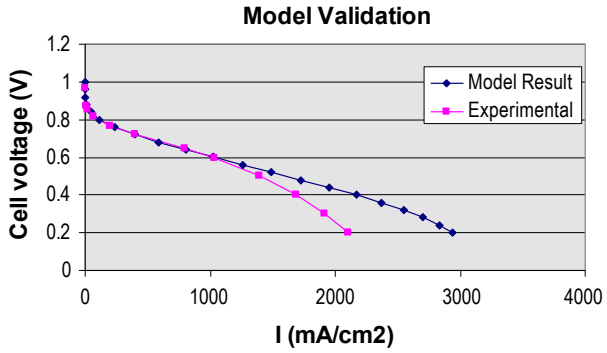

FIGURE 4. Preliminary results for model validation. Experimental data corresponds to the polarization curve for historic stationary (HS) operating condition (T_{cell} = 80°C, anode/cathode T_i = 80°C, anode/cathode stoichiometry = 1.3/2.5) for a fully conditioned cell.

agreement between the model and experimental data in the activation and ohmic regions. However, there is a disagreement in the mass transport limitation (I >1 A/cm^2). An investigation to identify the causes of disagreement between model results and experimental data at higher current density is underway. Potential causes could be inappropriate capillary pressure relationship and/or diffusion media/catalyst layer water transport properties.

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 fuel cell modeling experience of UTC Power, enables a robust approach to development of a new low-cost MEA manufacturing process.

- A quasi-static elastic/plastic layered structure MEA mechanical model has been modified to include visco-elastic/plastic behavior and data collection to calculate model input parameters has begun. When data collection is complete, the model will be validated with MEA durability testing and then used to predict degradation for different MEA constructions in a variety of temperature and relative humidity cycling scenarios.
- Further modifications of a MEA performance model, which includes conditioning phenomena, will be made in order to better represent break-in and peak performance. The model will be validated with experiments and exercised to explore the effects of MEA processing and in situ conditioning protocols on conditioning time.
- MEA cost model results indicate that a 17% reduction in the cost of the high-volume base case 3-Layer MEA is attainable given the potential process improvements that will be explored in

Phase 2. Laboratory-scale equipment which has the potential to achieve the MEA process cost reductions determined by the cost model will be specified, procured, and qualified in preparation for prototype process development in Phase 2.

FY 2009 Publications/Presentations

1. 2009 Hydrogen Program Annual Merit Review: mf_04_busby.