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

Budget
• Total Project Funding: $4.2MM
  – $2.7MM DOE Share
  – $1.5MM Contractor Share
• Funding received in FY12: $400k
• Funding for FY13: $502k

Timeline
• Project start: 9/01/08
• Project end: 6/30/14
• 80% complete as of 4/11/13

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

Partners
• University of Delaware (UD)
  – MEA Mechanical Modeling
• University of Tennessee, Knoxville (UTK)
  – Heat & Water Management Modeling
• UTC Power
  – Stack Testing
• W. L. Gore & Associates, Inc. (Gore)
  – Project Lead
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\(^4\) 5-Layer MEAs\(^5\) that minimize 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 $9/kW DOE 2017 automotive MEA 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 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
6. The stack break-in time should be reduced to 4 hours or less

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2011 Status (^a)</th>
<th>2017 Targets</th>
<th>2020 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost(^f)</td>
<td>$/kW</td>
<td>13 (without frame and gasket)</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18 (including frame and gasket)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Durability with cycling</td>
<td>hours</td>
<td>9,000(^*)</td>
<td>5,000(^f)</td>
<td>5,000(^f)</td>
</tr>
</tbody>
</table>

**Table 3.4.14 Technical Targets: Membrane Electrode Assemblies**

- **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)
Relevance: Objectives

• Low-cost MEA R&D
  – New 3-Layer (3-L) MEA Process Exploration (Gore)
    • Investigate equipment configuration for MEA production
    • Investigate raw material formulations
    • Map process windows for each layer of the MEA
  – Mechanical Modeling of Reinforced 3-L MEA (UD)
    • Use model to optimize membrane reinforcement for 5,000+ hour durability and maximum performance
  – 5-Layer (5-L) Heat & Water Management Modeling (UTK)
    • Optimization of GDM thermal, thickness, & transport properties to enhance the performance of thin, reinforced membranes and unique properties of direct-coated electrodes using a validated model
  – Optimization (Gore)
    • 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 (Gore)
  – Evaluate potential for new process to achieve **DOE cost targets** prior to process scale-up (Go / No-Go Decision)

• Scale Up (Gore)
• Stack Validation (UTC)
Approach: Summary

• Reduce MEA & Stack Costs
  – Reduce cost by elimination 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

• Optimize Durability
  – Balance tradeoffs between mechanical durability and power density of the 3-L construction

• Enabling Technologies:
  – Direct coating: Use coating to form at least one membrane–electrode interface
  – Gore’s advanced ePTFE membrane reinforcement & advanced PFSA ionomers enable durable, high-performance MEAs
  – Utilize modeling of mechanical stress and heat / water management to accelerate low-cost MEA optimization
  – Advanced fuel cell testing & diagnostics
**Approach: Low-Cost MEA Mfg Process, Primary Path**

1-1 MEA Intermediate

- Electrode Ink
- Oven

1-L MEA Intermediate

- Low-cost backer
- Oven

2-L MEA Intermediate

- ePTFE + ionomer
- Oven

3-L MEA Final Product

- Electrode Ink
- Oven

2-L MEA Intermediate

- Backer take-up

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**Alternate path:**

1. Direct coat anode on backer-supported ½ membrane to make 1.5-L MEA intermediate
2. Direct coat cathode on backer-supported ½ membrane to make 1.5-L MEA intermediate
3. Bond membrane-membrane interface of the 1.5-L webs to make a 3-L MEA
Approach: Mechanical Modeling (UD)

• Model Concept:
  Develop a layered structure MEA mechanical model using non-linear (viscoelastic & viscoplastic) membrane and electrode properties to predict MEA stresses and fatigue failure for input temperature & relative humidity cycling scenarios

• Experimental Work:
  Devise & perform experiments to determine mechanical properties of MEA and reinforced membrane materials as functions of:
  – Temperature
  – Humidity
  – Time

• Validation Criteria:
  Model predictions must correlate to in-situ nitrogen RH cycling accelerated mechanical stress test

• Success Criteria:
  Use model to optimize membrane reinforcement (5,000+ hour durability and maximum performance) for the MEA that will be made in the new low-cost process
Technical Accomplishments & Progress: Summary

• Mechanical Modeling of Reinforced 3-L MEA (UD)
  – Layered model development 100% Complete
  – RH & time-dependent mechanical testing 100% Complete
  – Parametric analysis of layered structure 80% Complete
  – Fatigue analysis of layered structure 30% Complete

• New 3-L MEA Process Exploration (Gore)
  – Low-cost backer 100% Complete
  – Cathode Layer 95% Complete
    • Power density and robustness beginning of life (BOL) testing
    • Electrochemical diagnostics
    • Durability testing
  – Reinforced Membrane Layer 85% Complete
    • Power density and robustness BOL testing
  – Anode Layer 95% Complete
    • Power density and robustness BOL testing
    • Electrochemical diagnostics
  – Cost analysis (Gore and SA collaboration) 100% Complete
Technical Accomplishments:
3-L MEA Manufacturing Process Cost Model

2009 cost model results indicate that the modeled process improvements have the potential to reduce MEA cost by 25%.

### 2009 Process Waste Map

<table>
<thead>
<tr>
<th>Membrane Coating</th>
<th>Process Costs</th>
<th>Primary forms of waste</th>
<th>Modeled Process Improvements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionomer solution</td>
<td>line losses, edge trim, membrane thickness</td>
<td>Membrane thickness reduction</td>
<td></td>
</tr>
<tr>
<td>ePTFE</td>
<td>edge trim</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Backers</td>
<td>all backers</td>
<td></td>
<td>No backers</td>
</tr>
<tr>
<td>Solvent/disposables</td>
<td>all</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process/MOH</td>
<td>time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DL</td>
<td>time</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrode Coating</th>
<th>Process Costs</th>
<th>Primary forms of waste</th>
<th>Modeled Process Improvements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>line losses, edge trim, electrode residuals</td>
<td>Reduce scrap with better coating process</td>
<td></td>
</tr>
<tr>
<td>Backers</td>
<td>all backers</td>
<td></td>
<td>No backers</td>
</tr>
<tr>
<td>Solvent/disposables</td>
<td>all</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process/MOH</td>
<td>time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DL</td>
<td>time</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3 Layer Roll-Good Finishing Operations</th>
<th>Process Costs</th>
<th>Primary forms of waste</th>
<th>Modeled Process Improvements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode</td>
<td>edge trim</td>
<td></td>
<td>Eliminate this process</td>
</tr>
<tr>
<td>Membrane</td>
<td>edge trim</td>
<td></td>
<td>Eliminate this process</td>
</tr>
<tr>
<td>Process/MOH</td>
<td>time</td>
<td></td>
<td>Eliminate this process</td>
</tr>
<tr>
<td>DL</td>
<td>time</td>
<td></td>
<td>Eliminate this process</td>
</tr>
</tbody>
</table>

- = On track to meet expected cost reductions in new process
+ = Additional cost savings beyond 2009 model assumptions
Technical Accomplishments:
Gore and SA Cost Model Collaboration

MEA Sensitivity

- Top three cost uncertainties:
  - ePTFE cost
  - Maximum coating speed
  - Ionomer cost
- None the less, MEA uncertainty is still only~ +/-2% for each variable.

- Caveat: MEA performance assumed to equal that of modeled 3M NSTF MEA

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Low Value</th>
<th>Base Value</th>
<th>High Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPTFE Cost</td>
<td>$/m²</td>
<td>1.82</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Ionomer Cost</td>
<td>Multiplier</td>
<td>0.5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Gore MEA Capital Cost of Equipment</td>
<td>Multiplier</td>
<td>0.5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Gore MEA Mylar Backer reuse cycles</td>
<td>cycles</td>
<td>1</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Gore MEA Line speed</td>
<td>m/min</td>
<td>3</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>Gore MEA Electrolyte dwell time multiplier</td>
<td></td>
<td>0.5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Gore MEA Station 1 Catalyst Loading</td>
<td>mg/cm²</td>
<td>-</td>
<td>0.05</td>
<td>0.146</td>
</tr>
<tr>
<td>Gore MEA Cathode dwell time multiplier</td>
<td></td>
<td>0.5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Gore MEA Anode dwell time multiplier</td>
<td></td>
<td>0.5</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Gore MEA Time to change out rolls</td>
<td>min</td>
<td>1</td>
<td>10</td>
<td>-</td>
</tr>
</tbody>
</table>

2013 Auto System Cost: $47.46
Technical Accomplishments:
Gore and SA Cost Model Collaboration

Gore MEAs and 3M NSTF™/Membrane Catalyst Coated Membrane are expected to have similar costs

Comparison of MEA Fabrication Costs:
Gore Low-Cost MEA vs. 3M NSTF™ on ePTFE supported Membrane

- Material costs are about the same (since dominated by Pt cost)
- Gore processing costs are expected to be lower due to non-vacuum processing and faster line speeds
- Total costs are quite similar
- Polarization performance is critical factor in selection
Technical Accomplishments: New multi-layer low-cost backer(s)

- Gore began evaluation of low-cost backers in June 2011
  - Thickness uniformity
  - Mechanical stability up to max drying and piece-part conversion temperatures
  - Chemical stability
  - Cleanliness
  - Electrode release
  - Supply chain reliability
  - Cost
- By August 2011, two promising low-cost multi-layer backer candidates were identified
- In June 2012, electrode was coated on the most promising backer in a 30 cm wide high-speed-capable roll-to-roll coating/drying process. Release and BOL performance exceeded the targets, and work on roll-to-roll direct-coating of the membrane layer was begun.
- After a successful root-cause analysis and multiple unsuccessful attempts to eliminate direct-coated membrane-layer defects which occurred in roll to roll pilot line coating, the backer was changed to the alternative candidate in November 2012.
- Preliminary cost estimate of the current low-cost multi-layer backer is $1 to $5 per square meter
- In February 2013, electrode was coated on the current backer in a 30 cm wide high-speed-capable roll-to-roll coating/drying process. Release and BOL performance exceeded the targets.
Technical Accomplishments: Excellent Performance of Direct Coated Cathode

- Ink formulation was modified to optimize performance using new low-cost multi-layer backer
- **Cathode made by primary path process.** Control anode & membrane used for all MEAs.

### Wet
- 70°C cell, 80|80°C, S=1.3|2.0, 0 psig, RHavg=170%
- 80°C cell, 80|80°C, S=1.3|2.0, 0 psig, RHavg=112%

### Dry
- 80°C cell, 55|55°C, S=1.3|2.0, 7.25 psig, RHavg=60%
- 95°C cell, 55|55°C, S=1.3|2.0, 7.25 psig, RHavg=34%
Compared to Gore’s current commercial membrane (~20 µm), Gore’s thin state-of-the-art membranes (~5 and ~10 µm) show greatly enhanced performance at high current density, especially under hot, dry conditions.

Technical Accomplishments:

Gore’s state-of-the-art thin, durable reinforced membranes have been incorporated into the primary path process.

Note: Membrane Testing Not Funded by DOE
Technical Accomplishments: Mechanical Modeling (UD)

2D Plane Strain Finite Element Model for a Single Cell under RH cycling

Water Volume Fraction
\[ \phi_w = \frac{18\lambda}{EW/\rho_p + 18\lambda} \]

Swelling Strain
\[ \varepsilon^{sv} = \left( \frac{\theta + 273}{\theta_0 + 273} \right) \ln(1 - \phi_w) \]

Thermal Strain
\[ \varepsilon^{th} = \alpha(\theta - \theta_0) \]

Effect of hydration/dehydration feed rate

![Graph showing water volume fraction over time for different feed rates](chart-a)

![Graph showing in-plane stress over time for different feed rates](chart-b)
Technical Accomplishments: Mechanical Modeling (UD)

2D Plane Strain Finite Element Model for a Single Cell under RH cycling

**Mechanical Modeling (UD)**

- Single layer, centered
  - S11 (MPa)
- Single layer, anode side offset
- Two layers

**In-plane stress contours after dehydration**

Total membrane thickness = 10 µm
Reinforcement thickness = 5 µm

**Loading profile**

- Humidity
- Temperature

- Water Volume Fraction
- Temperature (°C)

- Time (s)
  - Clamping
  - Hydration
  - Dehydration
Technical Accomplishments: Mechanical Modeling (UD)

J integral response under one cycle

- **Case 1:** Both Sides Hydration and Dehydration
- **Case 2:** Both Sides Hydration and only Top Dehydration

**Effect of hydration mode**

- Nafion Both Electrode Dehydation Same-Expansion
- Nafion Anode Dehydation Same-Expansion
- Nafion Both Electrode Dehydation No-Expansion
- Nafion Anode Dehydation No-Expansion

**Effect of reinforced membrane**

- Nafion Both Electrode Dehydation Same-Expansion
- RNafion Both Electrode Dehydation Same-Expansion
- Nafion Both Electrode Dehydation No-Expansion
- RNafion Both Electrode Dehydation No-Expansion

**Technical Accomplishments:**

- Mechanical Modeling (UD)

**Note:**

Nafion is a registered trademark of E.I. duPont de Nemours and Company.

*Narinder Singh Khattra, PhD Dissertation, University of Delaware, 2012*
Proposed Future Work: Summary

- Continue development of primary path
- Mechanical Modeling (UD)
- Optimize reinforced membrane
- 5-Layer heat / water management Modeling (UTK)
- Optimize electrode and GDM properties

- Demonstrate 10 micron reinforced membrane coated on 1L intermediate (cathode + low-cost multi-layer backer)
- Evaluate BOL polarization curve and durability of 2L intermediate
- Demonstrate direct coated anode on 2L intermediate
- Evaluate BOL polarization curve and durability of 3L final product

- Conditioning
- Cost review
- Scale-up
- Stack Validation
Proposed Future Work for FY13: Summary

Phase 2
- Low Cost MEA Process Development
  - Primary path
  - Alternative path
- Water & Heat Modeling & Validation (UTK)
- Mechanical Modeling (UD)
- Low cost MEA Optimization
- MEA Conditioning
- Cost Model Review & Go/NoGo Decision
- Low-Cost MEA Process Scale-Up
- Stack Validation (UTC)
Collaborations

• University of Delaware (academic, sub-contractor)
  – MEA Mechanical Modeling
  – A. Karlsson & M. Santare

• University of Tennessee, Knoxville (academic, sub-contractor)
  – 5-Layer Heat and Water Management Modeling and Validation
  – M. Mench

• UTRC (industry, sub-contractor)
  – Stack Testing

• NREL (federal, collaborator)
  – On-line quality control systems research
  – M. Ulsh

• Strategic Analysis, Inc. (industry, collaborator)
  – Cost Modeling
  – B. James

• W. L. Gore & Associates, Inc. (industry, lead)
  – Project Lead
  – F. Busby
Summary (1)

The overall objective of this project is to develop unique, high-volume manufacturing processes that will produce low-cost, durable, high-power density 5-Layer MEAs that minimize 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

- **Optimize Durability**
  - Balance tradeoffs between mechanical durability and power density of the 3-L construction

- **Unique Enabling Technologies**
  - Develop Direct Coating: To form at least one membrane–electrode interface
  - Gore’s Advanced ePTFE membrane reinforcement & advanced PFSA ionomers enable durable, high-power density MEAs
  - Utilize modeling of mechanical stress and heat / water management to accelerate low-cost MEA optimization
  - Advanced fuel cell testing & diagnostics
Key Accomplishments

- 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
  - New low-cost multi-layer backer has been proven on a roll-to-roll process and implemented in the primary path
  - 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 a **10 µm reinforced membrane** that is used in the new low-cost process and can meet automotive power density and durability targets
  - Modeling tasks at UD and UTK are on track to enable efficient optimization of the new 3-L MEA process as soon as direct coated 3-L MEA feasibility has been demonstrated on a roll-to-roll process
- The combination of Gore’s advanced materials, expertise in MEA manufacturing, & fuel cell testing in partnership with the mechanical modeling experience of UD and the heat and water management experience of UTK enables a robust approach to developing a new low-cost MEA manufacturing process
Acknowledgements:

W. L. Gore & Associates, Inc.
- Don Freese
- Will Johnson
- Mark Edmundson
- Glenn Shealy
- Simon Cleghorn
- Laura Keough

University of Tennessee, Knoxville
- Matthew M. Mench
- Ahmet Turhan
- Feng-Yuan Zhang

University of Delaware
- Anette Karlsson
- Mike Santare
- Narinder Singh
- Zongwen Lu

Strategic Analysis, Inc.
- Brian James

Department of Energy
- Jesse Adams
- Pete Devlin
- Nancy Garland
Technical Back Up Slides
Technical Accomplishments:

Cathode electrode made by the improved primary path process has demonstrated start/stop durability equivalent to the current commercial control electrode.

Data from 2011 AMR
Technical Accomplishments:
DC Cathode Electrochemical Diagnostics

- Standardized protocol that combines BOL robustness testing with key cathode diagnostics at wet and dry conditions
- Test summary
  - Pre-Conditioning Diagnostics
    - Cleaning Cyclic Voltammograms (CVs)
    - CV, H₂ Cross-Over, Electrochemical Impedance Spectroscopy (EIS)
  - Conditioning
  - Saturated and Super-Saturated Performance
    - Polarization Curves, Current Interrupt Resistance, and Stoich Sensitivity
  - Saturated Diagnostics
    - He/O₂, O₂ Tafel
    - CV, H₂ Cross-Over, EIS
  - Sub-Saturated and Hot Sub-Saturated Performance
    - Polarization Curves, Current Interrupt Resistance, and Stoich Sensitivity
  - Sub-Saturated Diagnostics
    - He/O₂, O₂ Tafel
    - CV, H₂ Cross-Over, EIS

Collected data to quantify oxidized impurities which are associated with conditioning time
Investigated impact of direct-coated electrode structure on molecular diffusion
Quantified ionic conductivity of direct coated cathode
Technical Accomplishments: Mechanical Modeling (UD)

Constitutive Model: Visco-elastic-plastic Model

Spring Element
Strain dependence

\[ \sigma = K \varepsilon \]

Dashpot Element
Strain-rate dependence

\[ \dot{\varepsilon}_v = A(\sigma_y)^n \]

Viscous power law

Elastoplastic terms

\[ f = \frac{K_v}{K_p + K_v} \]

Visco-Elastic terms

Parameters
A, \( n \), f, \( \theta \), \( \lambda \)

\( E(K_p + K_v) \), \( \nu \), \( \sigma_{yield} \), H

Visco-elastic-plastic model is tuned to match measured constitutive responses for MEA materials
Technical Accomplishments: Mechanical Modeling (UD)

Properties of NAFION® 211 membrane, MEA and Reinforced PFSA measured

Visco-elasto-plastic behavior of MEA determined. Follows trends similar to membrane, but lower stress, indicating electrodes are less stiff than membrane.


True stresses are instantaneous force (measured) divided by instantaneous cross sectional area (calculated).

NAFION is a registered trademark of E. I. DuPont de Nemours & Company.
Technical Accomplishments: Mechanical Modeling (UD)

Determination of PEMFC Electrode Mechanical Properties

General methodology

- Within linear elastic region:
  Rule of mixtures
- Beyond linear elastic region:
  Reverse analysis using finite element model (ABAQUS 6.9)

![Experimental results of the membrane and MEA](image)

1. Assumed electrode behavior
2. Membrane behavior from experiments
3. Electrode
4. Membrane
5. Damage from experiments
6. Determined electrode behavior
7. Output MEA response
8. Agree with the experimental MEA response?
9. YES
10. NO