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

PI: F. Colin Busby  
W. L. Gore & Associates, Inc.  
5/12/2011  

Project ID # MN004
Overview

Budget
• Total Project Funding: $4.2MM
  – $2.7MM DOE Share
  – $1.5MM Contractor Share
• Cumulative DOE funding spent as of 3/11/11: $1.1 MM
• Funding received in FY10: $500k
• Funding for FY11: $611k

Timeline
• Project start: 9/01/08
• Project end: 9/30/12
• 65% Percent Complete as of 3/11/11

Partners
• University of Delaware (UD)
  – MEA Mechanical Modeling
• University of Tennessee, Knoxville (UTK)
  – 5-Layer Heat / Water Management Modeling & Validation
• UTC Power, Inc. (UTCP)
  – Stack Testing
• W. L. Gore & Associates, Inc. (Gore)
  – Project Lead

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

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2003 Status</th>
<th>2005 Status</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost$</td>
<td>$ / kW</td>
<td>200</td>
<td>70$</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>Durability with cycling</td>
<td>hours</td>
<td>N/A</td>
<td>2,000</td>
<td>5,000</td>
<td>5,000</td>
</tr>
</tbody>
</table>
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.

1. Mfg. process scalable to fuel cell industry MEA volumes of at least 500k systems/year
2. Mfg. process consistent with achieving $15/kW_e DOE 2015 transportation stack 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>
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<td>5,000$h</td>
<td>5,000$h</td>
</tr>
</tbody>
</table>

• RD&D Plan Section 3.4, Task 3, Milestone 38: Evaluate progress toward 2015 targets. (4Q, 2012)
• RD&D Plan Section 3.5, Task 1, Milestone 4: Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2013)
Relevance: Objectives

• Low-cost MEA R&D
  – New 3-Layer (3-L) MEA Process Exploration (Gore) FY ’09, ’10, ‘11
    • 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) FY ’09, ’10, ‘11
    • Use model to optimize membrane reinforcement for 5,000+ hour durability and maximum performance
  – 5-Layer (5-L) Heat & Water Management Modeling (UTK) FY ’10,’11
    • 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) FY’ 11
    • 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) FY ’11
  – Evaluate potential for new process to achieve DOE cost targets prior to process scale-up ( Go / No-Go Decision) FY ’11

• Scale Up (Gore) FY ’11 &‘12

• Stack Validation (UTC) FY ’12
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
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 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
Approach: 5-L Heat & Water Management Modeling (UTK)

- Model Concept:
  Steady state 2D non-isothermal, non-isotropic, performance model. Physics include phase-change induced flow in porous media, condensation/evaporation heat transfer and capillary flow, anode and cathode kinetics with agglomerate based formulation.

- Experimental Work:
  Determine gas diffusion media properties and perform in-situ 5-L MEA testing (pol curves over a range of targeted operating conditions, EIS, net water balance).

- Validation Criteria:
  Model must accurately predict polarization curve and net water transport coefficient for a 5-L structure with a defined range of GDM properties.

- Success Criteria:
  Optimize GDM thermal, geometric, & transport properties to complement thin, reinforced membranes and unique properties of direct-coated electrodes for the MEA that will be made in the new low-cost process.
Technical Accomplishments & Progress: Summary

• Equipment procurement and qualification (Gore) 100% Complete
• Mechanical Modeling of Reinforced 3-L MEA (UD)
  – Layered model development 100% Complete
  – RH & time-dependent mechanical testing 85% Complete
  – Parametric analysis of layered structure 10% Complete
• 5-L Heat & Water Management Modeling (UTK)
  – Gas diffusion media properties testing 25% Complete
  – Performance testing 40% Complete
  – Model development 100% Complete
  – Computational studies 60% Complete
• New 3-L MEA Process Exploration (Gore)
  – Process feasibility screening 100% Complete
  – Determine primary and alternative paths 100% Complete
  – Cathode Layer
    • Power density and robustness BOL testing
    • Electrochemical diagnostics
    • Durability testing 90% Complete
  – Reinforced Membrane Layer 80% Complete
    • Power density and robustness BOL testing
  – Anode Layer 95% Complete
    • Power density and robustness BOL testing
    • Electrochemical diagnostics
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>No backers</td>
<td></td>
</tr>
<tr>
<td>Backers</td>
<td>all backers</td>
<td></td>
<td></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>No backers</td>
<td></td>
</tr>
<tr>
<td>Solvent/disposables</td>
<td>all</td>
<td></td>
<td></td>
</tr>
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<td>time</td>
<td></td>
<td></td>
</tr>
</tbody>
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<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>Eliminate this process</td>
<td></td>
</tr>
<tr>
<td>Membrane</td>
<td>edge trim</td>
<td>Eliminate this process</td>
<td></td>
</tr>
<tr>
<td>Process/MOH</td>
<td>time</td>
<td>Eliminate this process</td>
<td></td>
</tr>
<tr>
<td>DL</td>
<td>time</td>
<td>Eliminate this process</td>
<td></td>
</tr>
</tbody>
</table>

**2009 Result**

- On track to meet expected cost reductions in new process

**2011 New Process Status Update**

- Additional cost savings beyond 2009 model assumptions
Technical Accomplishments: Direct Coated Anode Results In Improved Interface

- High current density performance was significantly increased (particularly in wet conditions) by improving the membrane/anode interface through direct coating (DC).
- Anode made by primary path process. Control cathode and membrane used for all samples.
Dry high current density performance was significantly increased through direct coating.

Cathode made by primary path process. Control anode and membrane were used for all samples.
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

Integrated I-V to quantify oxidized impurities which are associated with conditioning time

Investigated impact of direct-coated electrode structure on molecular diffusion

Quantified improved ionic conductivity of direct coated cathode
Technical Accomplishments:
DC Cathode Electrochemical Diagnostics

EIS (V. Dry, 95°C cell, 55|55°C)

Measurement Parameters
25 cm² Active Area
H₂|N₂, 0.2|0.2 slpm
5mV Amplitude
10kHz → 0.1Hz
0.2V vs. RE

Z' - HFR [mΩ·cm²]
Compared to Gore’s current commercial membrane (~20 µm), Gore’s new state-of-the-art membrane (~10 µm) shows greatly enhanced performance at high current density, especially under hot, dry conditions.

Note: Membrane Testing Not Funded by DOE
Technical Accomplishments:
Durability of Thin GORE-SELECT® Membrane

Gore N₂ RH Cycling Protocol:

<table>
<thead>
<tr>
<th>Tcell (°C)</th>
<th>Pressure (kPa)</th>
<th>Flow (Anode/Cathode, cc/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>270</td>
<td>500 N₂ / 1000 N₂</td>
</tr>
</tbody>
</table>

- Cycle between dry feed gas and humidified feed gas (sparger bottle temp = 94°C)
- Dry feed gas hold time: 50 sec.
- Humidified feed gas hold time: 10 sec.

Note: 12 μm Membrane Testing Not Funded by DOE

GORE, GORE-SELECT and designs are trademarks of W. L. Gore & Associates, Inc.
Measured properties for membrane acquired through experiments

Loaded under “Gore” and “DOE” accelerated test conditions

Preliminary results indicate higher max stresses in DOE cycle test

Water Volume Fraction

\[ \phi_w = \frac{18\lambda}{E \frac{W}{\rho_p} + 18\lambda} \]

Swelling Strain

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

Thermal Strain

\[ \varepsilon^{th} = \alpha(\theta - \theta_0) \]
Technical Accomplishments: Mechanical Modeling (UD)

Preliminary Results for Layered Configurations Using Reinforced PFSA

Layered configurations with varying thicknesses analyzed, keeping total thickness constant at 30 µm

Tensile residual stress in unreinforced PFSA eliminated by addition of reinforced layer(s)

Tensile residual stresses of the order of 0-3 MPa observed in the reinforced layers
Technical Accomplishments: 5-L Heat & Water Management Modeling (UTK)

- Model upgraded with multi-phase physics, phase-change induced flow, multi-component diffusion, and agglomerate based resistance in electrodes.
- Parametric simulations reveal key controlling phenomena in water removal related to temperature and temperature gradient in the GDL/MPL.
- As GDL gets thinner, role of MPL in thermal boundary becomes dominant, and **MPL and CL thermal conductivity are key engineering parameters**.
- Thinner membrane has higher performance enhancement (18→5 µm) compared to DM thickness changes.

Case A: Thick Macro DM (330 µm) 0.432V  
Case B: Thin Macro DM (82.5 µm) 0.474V

Results shown at 1.8 A/cm², all other parameters equal
Proposed Future Work for FY11: Summary

- **FY 11**
  - Continue development of primary path

- **FY 12**
  - **Conditioning**
  - **Cost review**
  - **Scale-up**
  - **Stack Validation**

- Mechanical Modeling (UD)
  - Optimize reinforced membrane

- 5-Layer heat / water management Modeling (UTK)
  - Optimize electrode and GDM properties
Proposed Future Work for FY11: Summary

- **FY 11**
  - Continue development of primary path
  - Mechanical Modeling (UD)
  - Optimize reinforced membrane
  - 5-Layer heat / water management Modeling (UTK)
  - Optimize electrode and GDM properties

- **FY 12**
  - Conditioning
  - Cost review
  - Scale-up
  - Stack Validation

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**Timeline:**

- **Phase 1**
  - Characterize Current Commercial MEA
  - Test Current Commercial MEA
  - Cost Model Current Commercial MEA
  - Mechanical Modeling (UD)
  - Equipment Procurement & Qualification

- **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

- UTC Power, Inc. (industry, sub-contractor)
  - Stack Testing
  - T. Madden

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

- W. L. Gore & Associates, Inc. (industry, lead)
  - Project Lead
  - F. Busby

*New partner added in late 2010
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
    • 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 a **12 µm reinforced membrane** that is used in the new low-cost process and can meet automotive power density and durability targets
    • **Model development at UD and UTK is complete** and both partners are on track to enable efficient optimization of the new 3-L MEA 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.
• Will Johnson
• Glenn Shealy
• Mark Edmundson
• Simon Cleghorn
• Laura Keough

Department of Energy
• Jesse Adams
• Pete Devlin
• Nancy Garland

University of Tennessee, Knoxville
• Matthew M. Mench
• Ahmet Turhan

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

UTC Power, Inc.
• Thomas Madden
Technical Back Up Slides
Technical Accomplishments:

9,000 Hour GORE-SELECT® Membrane Durability in 80°C Duty Cycle

- Both MEAs were stopped at 9,000 hrs and were far from failure
- H₂ crossover at 9,000 hr: \( \leq 0.017 \text{ cc/min.cm}^2 \)
- Very little change in membrane thickness after 9,000 hrs on test
- This test data gathered in 2007 using a membrane that is equivalent to the 18 µm membrane used in the baseline MEA construction

<table>
<thead>
<tr>
<th>( T_{\text{Cell}} ) (°C)</th>
<th>Load (mA/cm²)</th>
<th>Stoic (A and C)</th>
<th>Pressure (kPa)</th>
<th>Inlet RH (%)</th>
<th>Exit RH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20-1000</td>
<td>10-1.7</td>
<td>170</td>
<td>50</td>
<td>60-120</td>
</tr>
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Table 3.4.11 Technical Targets: Membranes for Transportation Applications

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2006 Status</th>
<th>2010</th>
<th>2016</th>
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<tbody>
<tr>
<td>Durability with cycling</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At operating temperature of ( \leq 80°C )</td>
<td>hours</td>
<td>-2,000 °</td>
<td>5,000 f</td>
<td>5,000 f</td>
</tr>
<tr>
<td>At operating temperature of ( &gt;80°C )</td>
<td>hours</td>
<td>N/A g</td>
<td>2,000</td>
<td>5,000</td>
</tr>
<tr>
<td>Oxygen cross-over (^b)</td>
<td>mA/cm²</td>
<td>5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Hydrogen cross-over (^b)</td>
<td>mA/cm²</td>
<td>5</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Note: Membrane Testing Not Funded by DOE

GORE, GORE-SELECT and designs are trademarks of W. L. Gore & Associates, Inc.
Technical Accomplishments:

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

![Graph showing mV decay per cycle (100 cycles) for different currents and processes.](image)

- **Control** electrode (8953-101, 8953-103) for 20 mA/cm², 400 mA/cm², and 1000 mA/cm².
- **Primary Path** electrode (initial process) (8953-104) for 20 mA/cm², 400 mA/cm², and 1000 mA/cm².
- **Primary Path** electrode (improved process) (8953-104, 8953-107) for 20 mA/cm², 400 mA/cm², and 1000 mA/cm².
Technical Accomplishments: Mechanical Modeling (UD)

Constitutive Model: Visco-elastic-plastic Model

Spring Element
\[ \sigma = K \varepsilon \]
Strain dependence

杆菌
\[ K_p \]
(Long-term modulus)

杆菌
\[ K_p + K_v \]
(Instantaneous modulus)

Dashpot Element
\[ \sigma = \eta \dot{\varepsilon} \]
Strain-rate dependence

杆菌
\[ \dot{\varepsilon}_v = A(\sigma_v)^n \]
Viscous power law

Visco-elastic-plastic model is tuned to match measured constitutive responses for MEA materials

Parameters
\[ A, n, f, \theta, \lambda, E(K_p + K_v), \nu, \sigma_{yield}, H \]
**Properties of NAFION® 211 membrane, MEA and Reinforced PFSA measured**

Technical Accomplishments: Mechanical Modeling (UD)

Visco-elasto-plastic behavior of NAFION® 211 membrane determined.

Visco-elasto-plastic properties of NAFION® 211 membrane determined.

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.