

VII.A MEAs

VII.A.1 Integrated Manufacturing for Advanced Membrane Electrode Assemblies

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Objectives

- Create improved cathode structures and catalysts for proton exchange membrane fuel cells (PEMFCs) at temperatures $<100^{\circ}\text{C}$ that allow a significant reduction of precious metal (PM) without loss in performance [target of 0.3 mg/cm^2 total PM, $0.8\text{ V @ }0.4\text{ A/cm}^2$, $0.85\text{ V @ }0.1\text{ A/cm}^2$ (H_2/air , DOE conditions)].
- Develop a durable membrane for fuel cell operation at higher temperature and low water vapor pressure [$>120^{\circ}\text{C}$, $<25\%$ relative humidity (RH), >5000 hrs].
- Incorporate the advances of the first two objectives with advanced membrane electrode assembly (MEA) fabrication processes that are amenable to mass production.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Durability
- B. Cost
- C. Electrode Performance
- D. Thermal, Air and Water Management

Technical Targets

Progress Toward Meeting DOE Membrane Targets for Transportation Applications (from January 21, 2005 Plan)

Characteristic	Units	2005 Goal	2010 Goal	Cell Status	Stack Status*
Electrocatalyst/Electrode for Transport ($<100^{\circ}\text{C}$)					
PGM** specific power	g/kW rated	2.67	0.5	0.6	1.5
PGM total loading	mg/cm ²	0.7	0.3	0.39	0.63
MEA (high temperature, status at 30% RH)					
Operating Temp.	$^{\circ}\text{C}$	120	120	120	---
PGM specific power	g/kW	2.7	0.33	3.13	---
Performance at 0.8 V (1/4 power)	mA/cm ²	250	400	400	---
	mW/cm ²	200	320	320	---
Degradation***	%	10	10	20	---
Membrane for high temperature (Du Pont)					
Conductivity @ 100°C & 25 kPa water vapor	S/cm	0.10	0.10	0.025	---
Conductivity @ -20°C	S/cm	0.01	0.01	0.023	---
Survivability	$^{\circ}\text{C}$	-30	-40	recovers	---
Durability with cycling at 120°C	hours	N/A	2000	200 hr, total of 20 cycles of RH & current	---

*non-DOE conditions: 70°C , 150 kPa total pressure, H_2/air

**PGM = platinum group metal

***1,000 hr accelerated under %RH and open circuit potential/high current cycling

Approach

- Fabricate highly controlled fine gradient gas diffusion layers (GDLs) through machine coating methods; exploit a new structure-function approach to designing improved catalysts and catalyst alloys; combine the two to create enhanced electrode and gas diffusion layer structures.
- Develop new machine-based or ion beam assisted deposition (IBAD) coating methodologies to create ultra-low loaded PM MEAs.
- Synthesize and evaluate small-molecule organic electrolytes to test functional groups; incorporate promising functional groups into polymeric electrolytes and evaluate.
- Synthesize new monomers and polymers; fabricate membranes and evaluate; develop methods of increasing membrane durability at higher temperature.

Accomplishments

- Published quantitative method to measure hydrophobicity of GDL materials.
- Manufactured fine gradient ELAT[®] completely by machine; achieved interim goal of <0.4 mg/cm² total PM while generating 0.8 V at 0.4 A/cm².
- Improved single-cell MEA power for ultra-low loaded precious metal fabrications (IBAD) from 330 mW/cm² to 450 mW/cm² while maintaining total PM <0.2 mg/cm².
- Demonstrated high-temperature gas diffusion electrode (GDE) interface mated to “Membrane V” from DuPont to operate at DOE power targets at 120°C and 30% RH.
- AE-type polymer electrolytes were made with high molecular weight (124k) and cast into tough membranes.
- Improved thermal stability of BA membrane to -0.0079 %/hr (wt. loss rate at 150°C), to equal that of Nafion[®].

Future Directions

- Scale up high-temperature MEAs to stack level; verify performance and durability.
- Decrease PM content in high-temperature MEAs.
- Scale-up fine gradient approach to stack level and achieve program goal of 0.3 mg/cm² total PM at DOE power goals; evaluate for durability.
- Design interface/MEA for new high-temperature membrane “BA” from DuPont.
- Synthesize and evaluate new AE-type monomers and polymers.
- Decrease wrinkles and swelling of BA membrane; evaluate permeation; improve durability.

Introduction

Continuing challenges for PEMFC technology include precious metal thrift and creating new ion exchange membranes that are capable of stable operation at temperatures exceeding 120°C and preferably 150°C. The greatest barrier to reduction of platinum metal in the MEA is the cathode half reaction, which can be addressed through both improved catalysts and the electrode structure around the catalyst. Operation of fuel cells at low RH (20-30%) would allow simplification or elimination of

complex humidification systems and allow stack temperatures of 100 – 120°C with minimal or no pressurization. Incentives to increase the operating temperature above the current 60 – 80°C to 120 – 150°C include a) smaller radiators, b) more efficient use of by-product heat, c) faster electrode kinetics, and d) increased tolerance to CO in reformed-hydrogen feed streams. Existing membranes fail to retain water at low RH and have creep at elevated temperatures.

During this report period, we have focused on machine-made cathode structures with improved

power and reduced PM loading, three-dimensional cathode structures created with the ion beam, and evaluation of single-cell high-temperature MEAs. Our work continues to show improvements in the new electrolytes/membranes that provide the requisite conductivity at high temperature and low RH, including conductivity at sub-freezing temperatures.

Approach

Our project proposed the “fine gradient” ELAT as a new design for the GDE or GDL that would facilitate both gas and proton transport to the catalyst. By reducing undesired variations in coating quality, we were able to create fine gradients of architectural features such as pore size distribution and hydrophobicity within the gas diffusion layer structure and, with this year’s work, extend the approach to scaling these structures to the stack level ($>225 \text{ cm}^2$ per element). All these structures are fabricated on a sophisticated developmental coating machine so they are readily assessed for suitability towards high-volume manufacturing. As part of the project, we are also developing IBAD methods to create three-dimensional cathode structures and comparing them to the ink-based methods to achieve low PM loadings. Finally, the most promising MEAs are advanced to Nuvera Fuel Cell for short-stack testing/verification.

Work on higher-temperature membranes has focused on electrolytes with the ability to conduct protons at low RH. Development was continued on two new non-Nafion[®] polymer electrolytes in the last year. The first, AE, is a low-EW (equivalent weight), high-acid-strength polymer electrolyte that has the best combination of thermal and chemical stability along with high conductivity. However AE is water soluble and needs to be made with higher molecular weight and strength. The second candidate, BA, is a composite membrane which has $\sim 3\text{X}$ conductivity increase over Nafion[®] and is water insoluble. However, previous versions of BA (AO, BG) had low thermal stability and high swelling, and work was undertaken to improve these properties. In addition, methods of increasing the durability of membranes in fuel cells above 100°C were investigated using Nafion[®]/inorganic composites (candidate or membrane V).

Results

Last year we demonstrated the fine gradient concept for creating optimized cathode structures mated to catalyst alloy, ionomer, and membrane components of the MEA. Those structures were partially fabricated by hand and machine coating operations. For this reporting period, we have successfully scaled the hand processing steps to machine, making for the first time a fine gradient ELAT[®] entirely by machine. Figure 1 summarizes the performance gain now possible through the fine gradient approach. Trace (1) of Figure 1 is our first “all machine made” structure, employing an excess of precious metal (total 1 mg/cm^2) and operating under DOE standard conditions (80°C , 250 kPa total pressure), which yields 0.82 V at 0.4 A/cm^2 . Having exceeded the performance target, we were able to reduce precious metal loading to 0.39 mg/cm^2 total in subsequent builds while remaining within the power requirement of 0.8 V at 0.4 A/cm^2 (not shown) for our interim goal. Traces (2) and (3) compare the performance of the high loaded fine gradient structure to one of the commercial leaders in MEA technology, employing the same operating conditions and precious metal loading of the commercial assembly. The fine gradient approach provides roughly a 20 mV improvement over the commercial assembly up to 1 A/cm^2 . Fine gradient assemblies have been scaled to Nuvera stack assemblies, and at 70°C and 150 kPa total pressure, they have come close to the power target 0.8 V and 0.4 A/cm^2 , albeit with total precious metal loading of 0.6 mg/cm^2 .

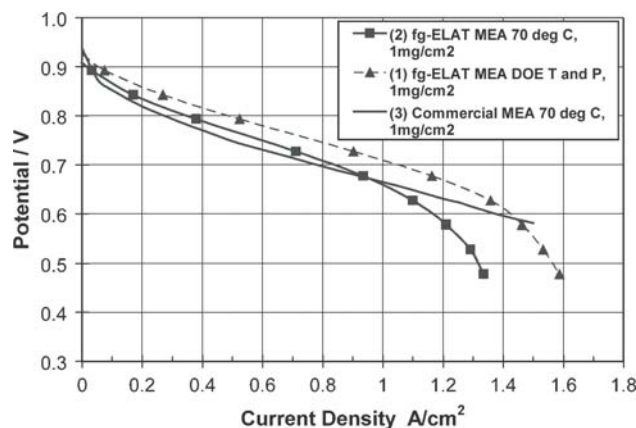


Figure 1. Single-Cell Testing of Three Cathode MEA Configurations at 80°C , 250 kPa air/ H_2 (DOE conditions) or 70°C , 150 kPa air/ H_2

Considerable progress has been made using ion beam assisted deposition to create MEAs with ultra-low PM loadings. While we had been hampered in the past by cathode mass transport limitations, we have now identified a breakthrough approach in creating three-dimensional structures on the cathode gas diffusion layer. These new structures have improved high-current operation from 0.62 A/cm² (at 0.5 V) to 0.85 A/cm² (at 0.5 V) under standard DOE conditions, all the while maintaining under 0.2 mg/cm² total precious metal content. Figure 2 is a summary metric whereby g Pt/kW is plotted versus voltage for three cases: beginning of project (“ELAT benchmark”), current best fine gradient approach, and current best IBAD approach at DOE conditions. Currently, the IBAD approach, while not achieving the highest current output, has achieved the best power output per gram of platinum, exceeding 2005 goals, and is well on the way to 2010 goals.

The DuPont team has begun to submit new “high temperature” membranes to the E-TEK group for design of a high-temperature interface as part of the electrode structure. DuPont’s “membrane V” shows acceptable lifetime at 120°C under accelerated degradation protocols. We have constructed our first version of a high-temperature interface for this membrane. Through the interface design, we have achieved 0.82 V, 0.4 A/cm² at 30% RH and 120°C with this new modified interface, although the total precious metal loading is 1 mg/cm².

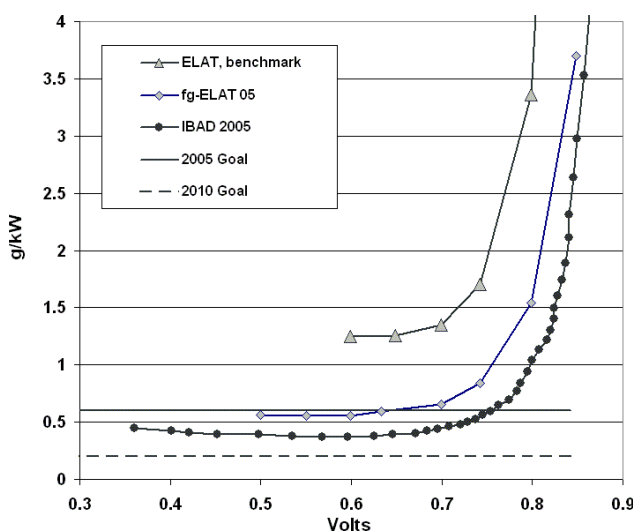


Figure 2. Platinum Specific Power (g Pt/kW) for ELAT Benchmark, Fine Gradient ELAT, and IBAD ELAT, at 80°C, 250 kPa air/H₂

Candidate V, a Nafion[®]/inorganic composite, had shown promising durability. A single-cell test of a relatively thin 30 μm membrane achieved 725 hrs operation without failure at 120°C and with cycling current from 0.3 to 0.9 A/cm² and feed RH down to 25%. Though the conductivity of this membrane is not significantly increased over Nafion[®], the composite approach is potentially also applicable to the newer high-conductivity membranes. During this reporting period, membrane V was scaled up to make seventeen membranes of sufficient size for 250 cm² short stacks and delivered to De Nora.

With the goal of increasing the molecular weight (MW) and also insolubilizing the AE-type polymer electrolyte, a new monomer and associated copolymer BL were synthesized. The polymerization chemistry finally succeeded in achieving a high MW of 124,000, and the molecular design provided an intended crystalline component. These resulted in tough membranes which were insoluble in room-temperature water and gave 360 mS/cm conductivity at high RH. However, the monomer chemistry ended up compromising the thermal stability (with an onset of degradation at 228°C), the low-RH conductivity was very low, and the crystalline component’s melting point T_m of 120°C and degree of crystallinity were not as high as desired. Alternate monomers and polymers have been designed to increase crystallinity, thermal stability, and low-RH conductivity while still retaining the good polymerization chemistry and high MW of BL. Synthesis of these and associated polymers is underway.

For the BA membrane, fluorine nuclear magnetic resonance was used to identify a chemically weak link responsible for low thermal stability of early samples of BA. The amount of weak link was first reduced by 14X, and then later by >200X. This resulted in BA membranes which have a weight loss rate of -0.0079 %/hr (thermal gravimetric analysis at 150°C isothermal after 10 hr in air + 3 kPa water vapor). This is similar to weight loss rate of Nafion[®] N112 (-0.0070 %/hr), which is believed to have sufficient thermal stability for transportation applications at 120°C. Conductivity of BA is 24 to 30 mS/cm @ 120°C and 25% RH (~3X Nafion) and 23 mS/cm for a humidified membrane @ -20°C. Water uptake in boiling water is 65 wt%, and

strength varies from 13 to 24 MPa. While the swelling is higher than desired, BA is our first membrane candidate which combines low-RH conductivity significantly higher than Nafion[®], thermal stability, and water insolubility. MEAs were made using non-optimized GDEs with perfluorinated sulfonic acid-containing electrodes. BA was tested in 25-cm² cells at 120°C and gave similar performance as N112 at high RH, but higher performance than N112 at 25%-RH feeds (see Figure 3).

Conclusions

- The fine gradient approach continues to provide a path to lower PM loading and is being scaled to stack elements and subjected to durability cycles.
- New cathode structures using IBAD have increased overall current density; if scalable to stack size, these structures represent the next-generation approach to achieving 2010 goals ahead of plan.
- Initial interface structures for high-temperature MEAs with membrane V have achieved power goals at low % RH; performance justifies scaling to stack scale for testing.
- High acid strength of AE-type electrolytes constrains molecular design to obtain high thermal stability in combination with membrane-forming properties.
- The effort to increase thermal stability of previously reported AO-type membranes succeeded by preparing new monomer used in the BA membrane.
- Fuel cell performance at low RH can be significantly improved using membranes with higher conductivity than Nafion[®].

FY 2005 Publications/Presentations

1. "Characterization of Transport Properties in Gas Diffusion Layers for PEMFCs", M. Bluemle, V. Gurau, J. A. Mann, T. A. Zawodzinski Jr., E. S. De Castro, Y. M. Tsou: *206th Meeting of Electrochem. Soc.*, Honolulu, HI, October 2-8, 2004
2. "Permeability and Wettability Measurements for Gas Diffusion Layers for PEM Fuel Cells", M. Bluemle, V. Gurau, J. A. Mann, T. A. Zawodzinski Jr., E. S. De Castro, Y. M. Tsou: *2004 Fuel Cell Seminar*, San Antonio, TX, November 1-5, 2004

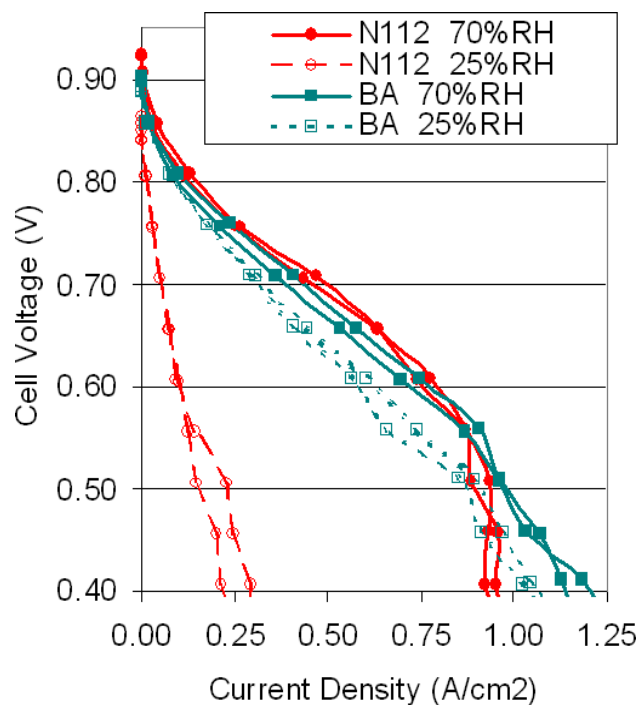


Figure 3. Polarization Curves Using N112 and BA Membranes with H₂/air at 120°C and 250 kPa (Issues with BA membrane include the presence of a large number of wrinkles from the fabrication process, too high a swelling, and low tear strength when swollen.)

3. "High Performance Electrode with Very Low Pt Loading Prepared by Dual Ion Beam Assisted Deposition in PEM Fuel Cells", M. S. Saha, S. Mukerjee, A. F. Gulla and R. J. Allen: Extended Abstracts for the Meeting of the Electrochemical Society held in Quebec, Canada, May 2005
4. "Dual Ion Beam Assisted Deposition as a Method to Obtain Low Loading-High Performance Electrodes for Proton Exchange Membrane Fuel Cells", A. F. Gulla, M. S. Saha, R. J. Allen and S. Mukerjee: *Electrochemical and Solid State Letters*, (Submitted)
5. "Oxygen Reduction and Transport Characteristics at a Platinum and Alternative Proton Conducting Membrane Interface", L. Zhang, C. Ma and S. Mukerjee: *J. Electroanalytical Chemistry* 58, 273 (2004)
6. "An Investigation of Ionic Conductivity of the PEMFC by AC Impedance Spectroscopy", H. Deng, Q. Guo, M. Cayetano, Y.-M. Tsou, E. S. De Castro: *Meeting of Electrochem. Soc.*, Honolulu, HI, October 2-8, 2004

7. “High Performance Oxygen Reduction Catalyst for PEM and DMFC Fuel Cells”, Y.-M. Tsou, L. Cao, E. S. De Castro: *Meeting of Electrochem. Soc.*, San Antonio, TX, May 2004
8. “Approaches for Low Cost Components and MEAs for PEFCs: Current and Future Directions”, E. S. De Castro, Y.-M. Tsou, L. Cao and C. Hou: *Fuel Cell Seminar*, San Antonio, November 2004
9. “Integrated Manufacturing for Advanced MEAs”, E. S. De Castro: *2005 DOE Hydrogen Program Review*, Crystal City, VA, May 23, 2005

Special Recognitions & Awards/Patents Issued

1. Patents pending on “fine gradient ELAT” (2) and new cathode structures created through IBAD (2).
2. Ten patent applications relating to high-temperature membranes in this program are pending.