

V.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°C that allow a significant reduction of precious metal (PM) without loss in performance. The target for this project is

0.3 mg/cm² total PM loading with performance of 0.8 V at 0.4 A/cm² and 0.85 V at 0.1 A/cm² (H₂/air, DOE conditions).

- Develop a durable membrane for fuel cell operation at higher temperature and low water vapor pressure (>120°C, <25% relative humidity (RH), >5,000 hrs).
- Incorporate the advances of (1) and/or (2) 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 (3.4.4.2) 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 and Electrocatalyst Targets for Transportation Applications

Characteristic	Units	2005 goal	2010 goal	Cell status	Stack Status ¹
MEA Electrode for Transport ² (<100°C)					
Platinum group metal (PGM) specific power	g/kW rated	2.7	0.3	0.6	0.7
PGM total loading	mg/cm ²	0.3	0.1	0.39	0.35
Electrocatalyst for Transport ³					
PGM total loading	mg/cm ²	0.3	0.1	0.16	(4)
Kinetic Activity	A/mg Pt at 900 mV	0.3	0.44	0.748	—
Kinetic Activity	uA/cm ² at 900 mV	600	720	2,946	—
MEA (high temperature, status at 30% RH)					
Operating Temp.	°C	≤120	≤120	120	—
PGM specific power	g/kW	2.7	0.3	3.13	—
Performance at 0.8 V (1/4 power)	mA/cm ²	250	400	400	—
	mW/cm ²	200	320	320	—

Notes: (1) Tested at 250 kPa A, H₂ dead-end, Cathode stoichiometry 2-2.5, 70°C; (2) MEA based on fine gradient ELAT[®] methodology; (3) MEA based on dual IBAD methodology; (4) Demonstrated dual IBAD anodes at 500 cm² stack element, 0.08 mg/cm² w/o loss of power; (5) 1,000 hr accelerated under % RH and open circuit potential/high current cycling

Progress Toward Meeting DOE Membrane and Electrocatalyst Targets for Transportation Applications (Continued)

Characteristic	Units	2005 goal	2010 goal	Cell status	Stack Status ¹
Degradation ⁵	%	10	10	20	—
Membrane for high temperature (DuPont)					
Conductivity @ 100°C & 25 kPa water vapor	S/cm	0.10		0.025	—
Conductivity -20°C	S/cm	0.01		0.023	—
Survivability	°C	-40		recovers	—
Durability with cycling 120°C	hours	N/A		200 hr, total of 20 cycles of RH & current	—

Notes: (1) Tested at 250 kPa A, H₂ dead-end, Cathode stoichiometry 2-2.5, 70°C; (2) MEA based on fine gradient ELAT[®] methodology; (3) MEA based on dual IBAD methodology; (4) Demonstrated dual IBAD anodes at 500 cm² stack element, 0.08 mg/cm² w/o loss of power; (5) 1,000 hr accelerated under % RH and open circuit potential/high current cycling

Accomplishments

- Achieved stack durability decay rate <1 uV/hr (1,000 hrs, constant current) with under 0.39 mg Pt/cm² total using coating technology suitable for mass manufacturing.
- The fine gradient approach has led to successes in lowering PM without a loss in power, greater ability for water elimination in the gas diffusion layer (GDL), and with the proper design, greater water retention in the electrode for operation in dry conditions.
- Roll-to-roll ion beam deposition demonstrated that the technology is ready for use in commercial anode structures. There is a further cost savings in the elimination of ionomer. Preliminary data for ion beam assisted deposition (IBAD) cathodes indicates greater stability compared to supported catalyst. Our strategy for introducing designed structures (“patterns”) shows a path to improve mass transport, although we need additional work on GDL design matched to IBAD structures to match current fine gradient cathode performance. Advanced spectroscopic analysis of IBAD MEAs suggests electrodes made from these structures are more stable than traditional supported catalyst electrodes, and less membrane degradation occurs when using materials made from dual IBAD.
- DuPont has developed several new classes of polyelectrolytes that exceed the benchmark Nafion[®] in conductivity at low RH and high temperature; these materials represent a significant advance and justify DuPont’s further pursuit of membranes with these materials beyond the term of this project.

Introduction

Continuing challenges for PEMFC technology are precious metal thrift and creation of 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 due to 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 relative humidity (20-30% RH) 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 90 –120°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 conductivity at low RH, have creep at elevated temperatures, and slowly decompose in the fuel cell with release of fluoride.

During this report period, we have focused on scaling machine-made cathode structures with improved power and reduced PM loading for stack testing, evaluating durability and the failure mechanisms that limit durability, and evaluating 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 gas diffusion electrode (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 cm² 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. We have conducted detailed spectroscopic analysis of failed MEA components that contain low levels of precious metal in order to elucidate degradation pathways. Finally, the most promising MEAs were advanced to Nuvera Fuel Cell for short stack testing/verification and additional 1,000 hour testing with extensive *post-mortem* analysis.

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 introduced last year. The first, AE, is a low-equivalent weight (EW) 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 ~3X 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 (membrane V).

Results

This year, we focused on scaling platinum and platinum alloy catalysts, extending the fine gradient ELAT[®] approach to assemblies that can run longer with stable voltages, and modifying the fine gradient electrode structure to improve performance when operating at lower RH. We also investigated the stability of ultra-low PM membrane electrode assemblies fabricated using dual IBAD. We demonstrated continuous operation of the ion deposition for a roll 30 linear meters long and a platinum deposition of 0.08 mg/cm² directly onto a gas diffusion layer for use as an anode (see Figure 1). These low loaded anodes were tested at Nuvera Fuel Cell's site with short stacks comprised of 500 cm² elements. We found no loss in performance due to the ultra-low loaded anode. DuPont advanced the stability and

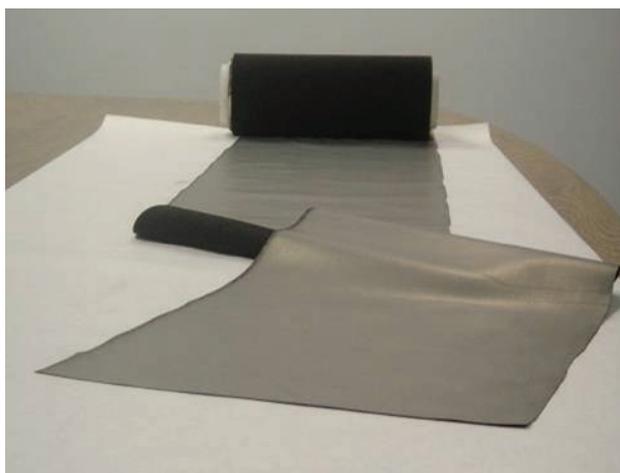


FIGURE 1. Roll-to-Roll Ion Beam Coating - Pt on ELAT GDL, Standard Gradient, 0.08 mg/cm², 30 linear meters, Pt variation < +/-3%

performance of two prime new membranes that were developed in this project. One of these new materials was forwarded to E-TEK to fabricate MEAs.

Prior to scaling up the improved platinum alloys discovered in this project, we investigated the fundamental chemistry used to prepare the platinum precursor. This investigation resulted in an improvement in the base platinum catalyst. Figure 2 shows the chronological improvement. Immediately obvious is the difference between the “start of project catalyst” (top trace, diamonds, pre-DOE) and the first generation developed early in the project (second trace, squares, DOE-2003). One notes a fundamental decrease in platinum crystallite size, which leads to an increase in surface area for electrochemical reactions. The advancement developed during this last year is shown as the third and lowest trace (circles, DOE-2005). Now one can see the largest crystallite being ca. 3.7 nm, and more importantly, the crystallite size or agglomeration is almost independent of the loading on the carbon support. While a small platinum crystallite is important, it is not the ultimate goal – indeed, some believe that for platinum, too small a size will inhibit oxygen reduction. However, the next step of formation of alloys often requires high temperatures, and it is during this step that the alloy crystallite grows too large in size. Therefore, creating these small initial sizes provides a path for small and potent alloys. The ability to create small starting platinum crystallites can aid efforts to develop more durable catalysts on graphitic and thus low surface area supports.

We have presented advances in MEA performance and a decrease in precious metal loading due to the fine gradient approach. We have evaluated the impact of gas diffusion layer design on durability, especially

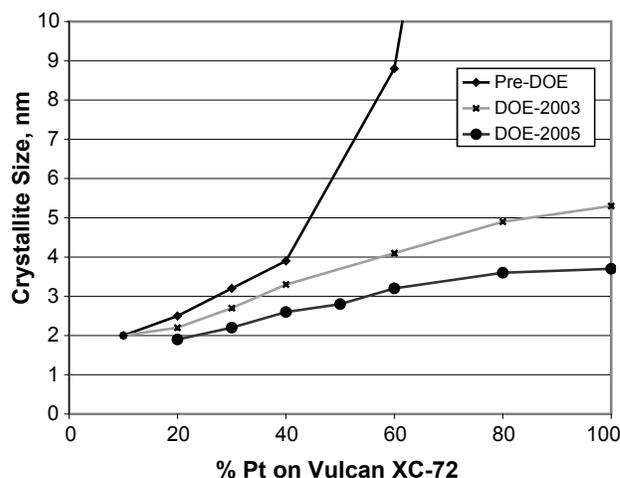


FIGURE 2. Improved Catalyst Chemistry - Crystallite Size vs. Weight Loading of Platinum on Vulcan XC-72 (100% represents platinum black)

when operating in highly flooding conditions such as at high power output or fully humidified cathodes. For a standard gradient GDL as a baseline, we typically observe a decay of 58 uV/hr at constant current. This great loss in performance is largely recovered if the MEA is subjected to dry air. This recovery indicates that the large decay rate could be partially due to water accumulation in the GDL. An alternative gradient in the GDL was designed, and we demonstrated under the same conditions as the baseline a 16 uV/hr decay rate, whereby very little improvement is seen after the dry air regimen. While GDL water accumulation is not the only mechanism behind performance decay, it can contribute under certain operating conditions. Lastly, MEAs containing low PM using fine gradient configurations or hybrid designs of both fine gradient cathodes and IBAD anodes (0.39 mg/cm² or less) have been evaluated in the Nuvera Fuel Cell 500 cm² stack; the best of these has shown a decay rate of 0.7 uV/hr over 1,000 hours (constant current mode).

A large part of our efforts is directed toward designing electrode or electrode-membrane interfaces that can perform at either low RH or low RH and high temperature (>100°C) with the specially developed membranes of DuPont. Figure 3 indicates the interim progress we have achieved by constructing an electrode that can retain water under the dryer conditions. In comparing Gradient A or Gradient C to the Standard (Base) Gradient one notes an improvement of over 100 mV at either 0.4 A/cm² or 0.6 A/cm² when operating under 30% RH.

In this period, the DuPont team continued to submit additional “high temperature” membranes to the E-TEK group for design of a high temperature interface as part of the electrode structure. Other efforts included work

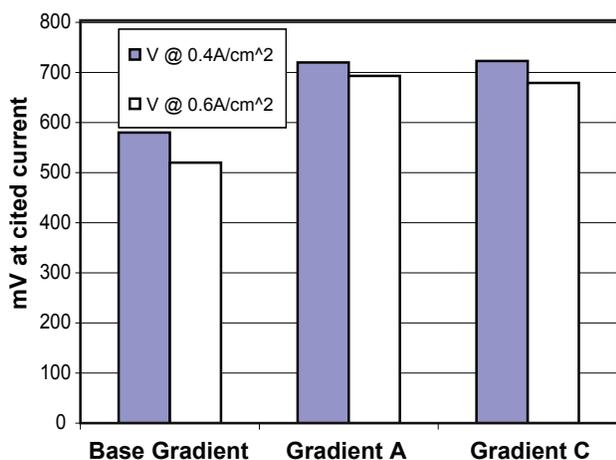


FIGURE 3. MEAs for Low RH Operation - Cell mV at Cited Current Density (Cell temperature 70°C, inlet RH=50% at anode and cathode, H₂/air, 1.5/2.0 stoichiometry, 1 mg/cm² total Pt, Nafion® 112)

on AE-type polymer electrolytes. One goal is to increase the molecular weight (MW) and also insolubilize the AE-type polymer electrolyte. Three variations of AE-type membranes were prepared (BL, BN, BP) whereby film-forming molecular weights were obtained. All three met conductivity targets at 95% RH, one met thermal stability and 25% RH conductivity targets, but all three dissolved or gave unacceptable swelling at either 22°C or 100°C. 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 continues.

The BA membrane is the front-runner in the high temperature membrane campaign. Through December 2005, DuPont identified that incompletely oxidized functional groups led to a decrease in thermal stability. A systematic study of oxidants identified one candidate that delivered less than 0.1% unreacted residual groups. Improved membranes using this methodology were delivered to E-TEK for MEA fabrication and testing. For comparison, the conductivity of BA is 24 to 30 mS/cm at 120°C and 25% RH (~3X Nafion) and 23 mS/cm for a humidified membrane at -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 DuPont's first membrane candidate that combines low-RH conductivity significantly higher than Nafion®, thermal stability, and water insolubility.

Conclusions and Future Directions

- Key milestones for electrode kinetics, lifetime in stacks with low precious metal, and high temperature membranes have been met or exceeded during this period.
- We have exceeded target kinetic activities for the IBAD system by >100%, showing promise for 2010 goals.
- The DuPont team has identified polyelectrolyte systems greatly exceeding the Nafion® benchmark at both sub-zero and high temperature/low RH.
- Remaining milestones include operation of a short-stack using MEAs derived from low RH/high temperature materials or demonstration of a stack meeting DOE power goals with 0.3 mg/cm² total PM. We will address these milestones by:
 - Reducing PM loading to 0.3 mg/cm² through a combination of IBAD anodes and fine gradient cathodes.
 - Constructing high temperature MEAs using membrane V and membrane BA; if membrane V assemblies approach DOE goals, we will construct stack-scale fabrications and submit to Nuvera for validation and additional lifetime studies.

- Using fine gradient ELATs, IBAD (via cathode improvement through GDL design), or a combination of both.

FY 2006 Publications/Presentations

1. V. Gurau, M. Bluemle, Jr., E. S. De Castro, Y. M. Tsou, J. A. Mann, T. A. Zawodzinski: "Characterization of Transport Properties In Gas Diffusion Layers for PEMFCs 1. Wettability (Internal Contact angle to water and surface energy of GDL fibers)", Accepted in Journal of Power Sources, 2006.
2. "High performance polymer electrolyte fuel cells with ultra-low Pt loading electrodes prepared by dual ion-beam assisted deposition." - M. Saha, A. Gullá, R. Allen, S. Mukerjee; *Electrochimica Acta*, 2006.
3. "Towards Improving the Performance of PEM Fuel Cell by Using Mix Metals Electrodes Prepared by Dual IBAD." - A. Gullá, M. Saha, R. Allen, S. Mukerjee; *Journal of the Electrochemical Society*, 2006.
4. "Dual Ion Beam Assisted Deposition as a Method to Obtain Low Loading-High Performance Electrodes for PEMFC's" - A. Gullá, M. Saha, R. Allen, S. Mukerjee; *Electrochemical and Solid-State Letters*, 2005.
5. "Enhancing the Performance of Low Pt Loading Electrodes Prepared by Dual Ion Beam Assisted Deposition in PEM Fuel Cells." - A. Gullá, R. Allen, M. Saha, S. Mukerjee; presented at the 208th Symposium of the Electrochemical Society in Los Angeles, CA, 2005.
6. "Peroxide Yield on New Materials for Oxygen Reduction in Acid Media" - A. Gullá, R. Allen, C. Urgeghe, Y. Garsany, S. Mukerjee; presented at the 207th Symposium of the Electrochemical Society in Quebec City, Canada, 2005.
7. "High Performance of Electrode with Very Low Pt Loading Prepared by Dual Ion-Beam Assisted Deposition in PEM Fuel Cells" - A. Gullá, R. Allen, M. Saha, S. Mukerjee; presented at the 207th Symposium of the Electrochemical Society in Quebec City, Canada, 2005.
8. Emory S. De Castro, Yu-Min Tsou, Lixin Cao and Chien Hou "New ELAT Interface Designs through Manufacturing Practices", Fuel Cell Seminar, Palm Springs, Nov. 2005.
9. Y. Tsou, L. Cao, E. De Castro, "Factors Affecting Activities of Nano-sized Fuel Cell Catalysts and Diagnosis Methods", 208th ECS Meeting, LA, Oct. 2005, abstract# 907.
10. Y. Tsou, E. De Castro, Chien Hou, Zhiyong Zhu, "Impact of Machine Coating GDE/MEA on Commercialization of Fuel Cells or Electrolyzers, 208th ECS Meeting, LA, Oct. 2005, abstract #1025.