

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 less than 100°C that allow a significant reduction of precious metal (PM) without loss in performance
- Develop a durable membrane for fuel cell operation at higher temperature and low water vapor pressure (>120°C, <25% relative humidity, >5000 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 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

- Fabricate highly controlled fine gradient gas diffusion layers through machine coating methods; exploit a new structure-function approach to designing improved catalysts and catalyst alloys; combine the gas diffusion layers and the improved catalysts to create enhanced electrode structures

- Synthesize and evaluate small-molecule organic electrolytes to test functional groups; incorporate promising functional groups into polymeric electrolytes and evaluate
- Develop new machine-based or ion beam coating methodologies to create ultra-low loaded precious metal MEAs

Accomplishments

- Introduced a lower-cost method for preparing a more active platinum on carbon black compared to standard commercial preparations
- Elucidated details on the structure-activity relationship behind the platinum alloy's enhanced activity for oxygen reduction
- Demonstrated proof-of-principle of the fine gradient ELAT[®] gas diffusion electrode (GDE) fabricated on a developmental coating machine (20% increase in current density at 0.6 V)
- A combination of new catalyst and improved control of gradient on an experimental carbon cloth has shown a 50% decrease in cathode platinum needed per kilowatt power output in machine fabricated structures
- Verified 10-30% increase in power density of new improved cathode materials in a Nuvera short stack
- Determined specific organic electrolyte functionalities that provide conductivity at low relative humidity (RH)
- Synthesized ionomers with conductivity significantly improved vs. benchmark Nafion[®] and evaluated their thermal stability

Future Directions

- Achieve lower total PM loadings through ion beam assisted deposition (IBAD) on membrane
- Use new GDE structures to lower metal load
- Adapt new understanding on conductivity and thermal stability to increase the number of candidate ionomers; develop membranes from these candidate ionomers

Introduction

A continuing challenge for PEMFC technology is 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 due to the cathode half reaction, which can be addressed through both improved catalysts and the electrode structure around the catalyst. In addition, there is a significant incentive to increase the operating temperature, the advantages being a) smaller radiators in transportation applications, b) more efficient use of by-product heat in stationary applications (e.g. hot water generation), c) potential for faster oxygen reduction kinetics at the cathode, d) increased

tolerance to CO in reformed-hydrogen feed streams, and e) better kinetics for methanol oxidation in direct methanol fuel cells (DMFCs). For higher temperature operation, the need to limit the total stack pressure to 1 to 1.5 bar places a limit of ~0.5 bar on the water partial pressure, which corresponds to only 25% RH at 120°C – a significant challenge in designing new membrane materials.

During this report period, we have focused on new platinum catalysts, elucidation of structure-activity relationships for alloys, new GDE structures, and new high temperature polyelectrolytes. Our work on new electrolytes that provide the requisite conductivity at high temperature and low RH has identified candidates with improved conductivity over the benchmark.

Approach

In the last report, we identified a series of innovative catalyst preparation techniques and described linking electrochemical activity to detailed bulk structural information derived from spectroscopic determinations. During this report period, we have focused on the most promising preparation methodologies and exploited these methodologies to produce highly active platinum on carbon black, as well as prepare alloy structures that led to additional insights on the structural properties that control catalytic oxygen reduction.

Our program proposed the “fine gradient” ELAT[®] as a new design for the GDE or gas diffusion layer (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. All these structures are fabricated on a sophisticated developmental coating machine so they are readily assessed for suitability towards high volume manufacturing. Lastly, the most promising structures were advanced to Nuvera Fuel Cell for short stack testing/verification.

For higher temperature membranes, a wide variety of organic functional groups were explored and small molecule model compounds synthesized. The model electrolytes were examined for their ability to conduct protons at low RH, by dint of either “holding on” to more water than Nafion[®], or by

having a different conduction mechanism that does not require as much water in the electrolyte. The scope at this point included some seven different types of acid groups with aromatic or fluorinated substrates. After discovering/identifying promising small-molecule electrolytes, the next step was to prepare polymeric electrolytes that “tie-down” the molecules, a necessity to reach the goal of no leachable components. At this point the thermal stability of the new polymers is evaluated using a thermo-gravimetric method. As of June 2003, we are about 60-80% finished with making the candidate polymers and evaluating conductivity and stability. The next step is to fabricate membranes from the new polyelectrolytes. We anticipate using cross-linking and/or composite membrane approaches to improve their mechanical properties and control water swelling and hydrogen crossover. Finally, MEAs will be fabricated and tested in single cells. In parallel with these efforts are smaller ones to benchmark the fuel cell performance of Nafion[®] and Nafion[®] inorganic composites at 120°C.

Results

Progress on developing higher power catalysts is summarized in Table 1. Generally, catalysts with smaller crystallite sizes are preferred. This preference is due to the much higher surface area inherent in what are essentially nanoparticles. However, electrochemical activity is more important than surface area, and the actual electrochemical surface area is a more effective measure of

Table 1. Comparison of Commercial Platinum Catalyst to New Platinum Catalyst

%wt Pt/C(on Vulcan XC-72)	Crystallite Size (X-ray diffraction, nm)		Electrochemical Surface Area (CO stripping, m ² /g)	
	Commercial Catalyst (E-TEK sm)	New Catalyst	Commercial Catalyst (E-TEK)	New Catalyst
10	2.0	-	-	-
20	2.5	2.2	-	-
30	3.2	2.5	32	53
40	3.9	2.8	-	39
60	8.8	3.7	-	28
80	25	4.9	-	-

electrochemical activity. In comparing our findings for 30% Pt, one sees not only a significant decrease in crystallite size, but a large gain in electrochemical surface area. The commercial prep has 36% of the total platinum area electroactive, while the new prep has 47% of total area electroactive. Thus, we have created a catalyst with a greater proportion of active crystal faces.

Extensive research of the oxygen reduction reaction (ORR) on platinum has shown that water activation by platinum produces surface species such as metal-OH that inhibit the ORR (1). Through efforts at Northeastern University, we have shown that the inhibition is highly dependent on structural features within a single alloy. These structural features are strongly determined by the method of preparation. Evaluation of the alloy's performance for ORR in electrolyte solvents that contain low amounts of water helps mimic how these catalysts would perform in high temperature fuel cells. In analytical experiments, we show there is very little difference between platinum and platinum alloys for ORR in low water environments.

Having established more facile control of deposition of the microporous layer, and applying this methodology to building the electrode layer, we systematically varied the porosity and hydrophobicity throughout the structure during a multi-layer build. We established a true fine gradient of porosity, whereby the total range of porosity (gas feed to electrode) was three orders of magnitude. For

example, this contrasts with intermediate structures that achieved a porosity range of just under two orders of magnitude. The initial proof-of-principle for machine-made fine gradient ELAT[®] structures demonstrated a 25% increase in current under mass transport limited conditions (0.6 V, 70°C, H₂/air, 1.5 atm total).

The fine gradient approach has also allowed us greater flexibility in converting new web materials such as carbon cloth. Table 2 summarizes results formalized as the key technical target "grams of platinum per kilowatt of power," whereby a combination of different carbon cloth webs, new improved catalyst, and more facile control of the gradient demonstrates our current status for reducing platinum content at the cathode. For comparison, a standard assembly containing commercially available components uses 1.8 g platinum at the cathode per kW of power when operating at 400 mA/cm². By changing the underlying carbon cloth and incorporating a high definition microporous layer, we are able to reduce the amount of platinum needed per kilowatt power output to 1.29 g/kW. Our current best is 0.89 g/kW, whereby we gain the greater activity of the new platinum catalyst plus aspects of the fine gradient structure on a new carbon cloth substrate. Samples of various structures and improved catalyst have been evaluated at Nuvera Fuel Cell in short stacks (each MEA > 200 cm², 70°C, 1.5 atmospheres total). Relative gains in performance from 10-30% were realized, depending on the operating current density, thus verifying single cell test results.

Table 2. Impact of Base Material and More Facile Control of the Gradient

Cloth Web	Cathode	Cathode	Total Pt	Total Pt
	@ 100mA/cm ²	@ 400mA/cm ²	DOE goal 2005	DOE goal 2010
	g/kW	g/kW	g/kW	g/kW
Standard (st. Pt/C)	6.40	1.80	0.6	0.2
Type 1 (st. Pt/C)	3.73	1.29		
Type 2 (new Pt/C)	3.11	0.89		
Type 3 (st. Pt/C)	6.69	2.50		

(single cell, 70°C, 1.5 atm. absolute, Air/C 1.5/2 stoich., Nafion 112)

During the investigation of different types of organic acid electrolytes, the attempts to synthesize water-less electrolytes mostly failed to exceed mS/cm conductivity. Only one electrolyte functionality was discovered which, when incorporated in two different compounds (candidates U and AB), gave 20 - 40 mS/cm proton conductivity at 125 to 180°C with either no water or at RH < 10%. Though promising, this electrolyte type had inferior conductivity to several others which still relied on water. Thus, several other *small-molecule* compounds were identified that had better conductivity relative to Nafion. In the last year, these electrolyte groups have now been successfully incorporated into *polymeric* electrolytes. The ionic conductivities of three of these candidate polymers are compared with that of benchmark Nafion in Figure 1. The conductivity is still decreasing with relative humidity, though the “rapid drop-off cliff” has been pushed to lower RH. Note that the mechanical properties of these polymers must be improved, e.g. by crosslinking or making composites, to arrive at thin membranes suitable for fuel cells.

New polymer electrolytes are being screened for thermal stability using a thermal gravimetric analysis

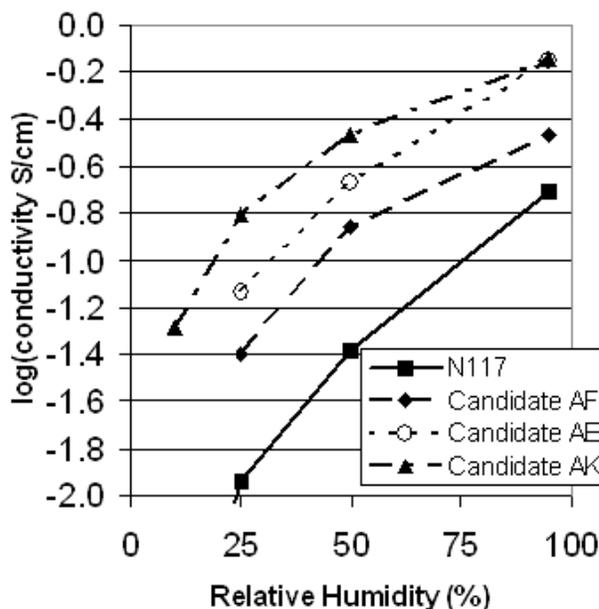


Figure 1. Ionic Conductivity of Benchmark Nafion® N117 and Three Experimental Ionomers at 120°C vs. Relative Humidity

(TGA) kinetic method (2). TGAs are performed under air humidified at 22°C and heating rates between 1 and 10°C/min. From this data, the activation energy for the first stage of thermal decomposition may be determined, and an upper limit on the lifetime of the polymer at the intended use temperature of 120°C could be extrapolated (Table 3).

Table 3. Thermal Stability for Nafion® and Experimental Polymer Electrolytes; Activation Energy, Preexponential Factor, and an Upper Limit to Life, in hours, Extrapolated to 120°C, Based on 10% of the First Stage of Decomposition to Be Completed

Sample	Activation Energy (Ea) (kJ/Mol)	Log (A min ⁻¹)	Upper Limit to Life @ 120°C (hr)
Candidate AE	290	24.3	4.0 X 10 ¹¹
Candidate AN	210	16.1	3.0 X 10 ⁹
Candidate AM	190	17.3	1.8 X 10 ⁵
Nafion® N112	160	12.9	1.3 X 10 ⁵
Candidate AF	40	14.0	1.4 X 10 ²
Candidate Z	80	7.4	2.0 X 10 ⁰

Caveats are that this test does not address electrochemical stability, nor does it detect degradation which does not result in weight loss (e.g. backbone scission), and the effect of the very low RH used has not yet been determined. The test can only alert one to a potential problem with the new polymers. Nafion® N112 has a predicted upper limit due to thermal degradation at 120°C of 1.3 X 10⁵ hr, which exceeds the lifetime goals of 5 to 40 X 10³ hr. Experimental polymers have been found to have a wide range of upper limits, with examples significantly higher, and several lower, than that of Nafion.

Conclusions

- Approach to structure-activity has yielded a more active platinum catalyst on carbon black with smaller platinum crystallite sizes and greater electrochemical surface areas.

- Full potentials of the alloy catalysts are not realized in the “low temperature” fuel cell with the current electrode structure; under conditions of temperature above 100°C (low water), the ability for an alloy to inhibit poisoning due to absorption of oxygenates is no longer relevant, and these alloys may not realize the gain observed at lower temperature (high water) conditions.
- The fine gradient ELAT[®] methodology provides a pathway to construct structures previously not attainable and will be used to recover some of the unrealized platinum alloy activity; this approach has also aided in reduction of the precious metal content in the cathode.
- Using functional groups different from perfluorosulfonic acid ionomers, it is possible to make ionomers with significantly increased conductivity over that of Nafion[®] at 25% RH.
- Ionomers can be made that pass a screening test for thermal stability.
- Achieving both conductivity and thermal stability in the same ionomer is even more challenging, but is likely possible also.

References

1. S. Mukerjee, S. Srivanasan, M.P. Soriaga and J. McBreen, *Electrochem. Soc.* 142(1995) 1409 and references therein.
2. J.H. Flynn and L.A. Wall, *Polymer Letters*, 4 (1966) 323.

FY 2003 Publications/Presentations

1. “Integrated Manufacturing for Advanced Membrane Electrode Assemblies,” E.S. De Castro and M.G. Roelofs, DOE 2003 Merit Review and Peer Evaluation Meeting, May, 2003, Berkeley, CA.
2. “Reducing Overpotential Losses for Oxygen Reduction Reaction with Pt Based Alloys: a RRDE Investigation” - V. Srinivasamurthi, C. Urian, and S. Mukerjee (Northeastern University), 203rd Electrochemical Society Meeting, Paris, France, 2003. Abstract No.1208.
3. “Oxygen Reduction Kinetics on Pt and Pt Alloys under Lower Humidity, Rotating Disk Electrode Experiments,” V. Srinivasimurti and Sanjeev Mukerjee; in preparation for the *Journal of the Electrochemical Society*.
4. “A Systematic Investigation of the Shift of H₂O Binding Energy of Pt and Pt Alloys; Changes in the On-Set Potential of Oxygen Reduction,” A. F. Gullá and Sanjeev Mukerjee; in preparation for the *Journal of the Electrochemical Society*.