

IV.A.3 Advanced MEAs for Enhanced Operating Conditions

Mark K. Debe (Primary Contact), Steven J. Hamrock, Radoslav T. Atanasoski

3M Company

3M Center, Building 0201-01-N-19

St. Paul, MN 55144-1000

Phone: (651) 736-9563; Fax: (651) 575-1187; E-mail: mkdebel@mmm.com

DOE Technology Development Manager: Amy Manheim

Phone: (202) 586-1507; Fax: (202) 586-9811; E-mail: Amy.Manheim@ee.doe.gov

Technical Advisor: Thomas Benjamin

Phone: (630) 252-1632; Fax: (630) 252-4176; E-mail: Benjamin@cmt.anl.gov

Subcontractors:

VAIREX Corporation, Boulder, CO; Case Western Reserve University, Cleveland, OH; Dalhousie University, Halifax, N.S., Canada; University of Illinois, Urbana, IL; University of Miami, Miami, FL; University of Minnesota, Minneapolis, MN

Objective

Develop high-performance, lower-cost membrane electrode assemblies (MEAs) that

- meet demanding system operating conditions of higher temperature and little or no humidification,
- use less precious metal than current state-of-the-art constructions, and
- are made by processes amenable to high-volume manufacturing.

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:

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

Approach

- Develop advanced cathode catalysts that have less precious metal and can be made by high-volume-compatible processes, building on the knowledge gained in the preceding 3M/DOE project.
- Develop new membranes based on 3M's perfluorinated sulfonic acid (PFSA) ionomer to obtain enhanced oxidative stability under hotter, drier operating conditions. Optimize matching MEA components, flow field, and air management for the temperature range of $85 < T < 120^{\circ}\text{C}$.
- Develop high-temperature non-aqueous electrolyte membranes, stable catalyst constructions, optimized catalyst/membrane interfaces, and matching gas diffusion layer (GDL) and flow field components for an operating range of $120 < T < 150^{\circ}\text{C}$ and nearly dry operation.
- Scale up and optimize MEA component fabrication processes amenable to high-volume, high-quality, low-cost production for selected components from the above tasks.
- Characterize selected MEAs in full-scale, short stacks.

Accomplishments

- Documented five-fold gain in specific activity of 3M Nanostructured Thin Film (NSTF) catalysts over Pt/carbon by two methods at 3M and a third method at Lawrence Berkeley National Laboratory (LBNL).
- Identified two new NSTF Pt_xB_y constructions with enhanced specific activity over Pt.
- Determined NSTF electrode characteristics that eliminate mass transport losses under H₂/air at 2 A/cm².
- Determined stable phases of PtM and PtAB constructions in acid baths and fuel cells, and demonstrated electrochemical and high temperature stability of NSTF surface areas.
- Identified path for GDL/catalyst improvements to reach 2010 DOE performance targets.
- Documented 100-fold reduction in F⁻ ion release of 3M's PFSA ionomeric membrane compared with standard cast Nafion™ or Nafion 112 membrane.
- Identified five additives that enhance the 3M proton exchange membrane (PEM) oxidative stability based on tests showing that they reduced or eliminated mass loss in H₂O₂ soak tests and also reduced F⁻ release rates in fuel cell tests by one to two orders of magnitude. Found that two of these additives increased MEA lifetime in accelerated durability tests of single cells.
- Prepared membranes that exhibit 2 to 5 times greater conductivity than the Nafion control at temperatures from 80°C to 120°C with 80°C dew point gasses.
- Tested new inorganic/polymer composite membranes that exhibit conductivity >10 mS/cm at 120°C bone dry.

Future Directions

- 85 < T < 120°C MEA: Execute down-selection process for PEM, catalyst and GDL component selection; complete stack testing; and initiate pilot-level scale-up to demonstrate high-volume capability with down-selected materials.
- T > 120°C MEA: Continue fundamental studies and screening measurements of non-aqueous proton-conducting electrolytes, down-select membrane matrix formation and filling methods, and initiate studies of electrolyte/catalyst interface effects for oxygen reduction reaction (ORR).

Introduction

In order for proton exchange membrane fuel cells (PEMFCs) to be commercially viable for automotive and distributed stationary applications, several issues must be addressed, including efficiency, durability, and cost. The efficiency of a fuel cell is directly related to the cell operating voltage. The higher the current and power density, the smaller the stack size and cost can be. These factors are primarily affected by polarization of the cathode catalyst and stability of catalyst activity and surface area. Therefore, higher-performing and more stable cathode catalysts are required to achieve the goals of increased performance with less precious metal catalyst. From a system perspective, operation at higher temperatures reduces thermal management constraints, thereby increasing overall efficiency and reducing cost. Greater tolerance of fuel impurities at

high temperatures can also contribute to performance increases. Designing MEAs for hot, dry, reactant conditions requires development of new membranes, catalysts and GDLs that are stable and durable under those conditions. The components must be matched to each other and integrated with a flow field design and air management strategy. Membranes that are stable against peroxide-induced decomposition and catalysts with stable surface areas under the demanding operating conditions are critical requirements for meeting the DOE long-term technical targets for durability. In addition, the processes for making the MEA components must be consistent with high-volume production to meet the quality and cost targets. This project is directed toward development of MEAs that meet demanding system operating conditions of higher temperature and little or no humidification, use less precious metal than current state-of-the-art constructions,

have the required stability and durability, and are made by processes amenable to high-volume manufacturing.

Approach

The approach to higher-temperature MEAs involves the development of components for two sets of temperature ranges: $85^{\circ}\text{C} < T < 120^{\circ}\text{C}$, and at or above 120°C . For the lower temperature range, PEMs are being developed based on modifications of 3M's novel PFSA-type membrane that still utilizes water for proton conduction. The 3M PEM's T_g is 25°C higher than that of Nafion of equivalent weight, and the modulus is over ten times higher at 120°C , dry. The modifications include incorporation of functionalized additives to facilitate peroxide decomposition for better oxidative stability and enhanced water retention for higher conductivity under low humidification. The upper operating temperature for an MEA made from a PFSA membrane is about 120°C due to performance and stability considerations. For the higher temperature range, new membrane materials and low-water based proton conduction methods are being investigated which utilize 3M perfluorinated acids, various proprietary liquids, and various inorganic additives. Work includes understanding how to incorporate those materials into polymer matrices to form effective membranes.

The approach to the development of advanced cathode catalysts that have less precious metal than current state-of-the-art constructions is based on the novel 3M NSTF catalyst support and deposition system [1]. The approach builds on previous work in which multi-element cathode catalysts were found that significantly outperformed pure Pt-coated NSTF supports. The NSTF process easily generates new compositions and structures via a dry, roll-goods process amenable to high-volume manufacturing [1,2,3]. These catalysts exhibit unique electronic features and increased surface area. The 3M NSTF supports (carbon free) show less susceptibility to oxidation and loss of catalyst surface area under highly oxidative conditions than commercially available carbon-supported dispersed catalysts. Methods for generating new catalyst constructions include pilot-line production of large-area catalyst formulations and a combinatorial method for

generating and characterizing a wide latitude of binary, ternary and quaternary compositions and structures (with subcontractor Dalhousie University).

A suite of critical property measurements is employed to guide development and down-selection of component materials. These include methods to measure the ionic and proton conductivity of the membranes, electrochemical impedance spectroscopy, chemical stability, PEM physical and mechanical properties, catalyst electrochemical surface areas and activities, and fuel cell tests under various protocols. Finally, methods to form effective interfaces of the catalysts with the new membranes and GDLs are necessary for optimum MEA performance.

Results

This past year, 40 new NSTF Pt-based ternary cathode catalyst constructions were fabricated on large-area, roll-good-capable, pilot-line equipment and evaluated by various fuel cell tests for performance and stability (93 total). The catalysts differ by composition, non-noble metal type, and a structure factor tied to the catalyst deposition process. All had a controlled Pt loading of 0.1 mg/cm^2 . We previously reported [4] that the NSTF catalysts have a 4x to 5x higher area specific activity for ORR than Pt/carbon dispersed catalysts, based on two methods of measurement in 50-cm^2 fuel cells. A key result this year was validation of that gain by fundamental rotating ring disc electrode (RRDE) studies of the NSTF catalysts at LBNL [3]. See Figure 1.

Seventeen large-area combinatorial library arrays of ternary thin film catalysts prepared on NSTF supports were fabricated and characterized at Dalhousie and evaluated in segmented fuel cell tests at 3M, with the result that two candidate materials were identified having increased specific activity over Pt. In addition, an extensive series of measurements was completed to evaluate stability of NSTF binary and ternary catalysts in both acid baths and fuel cell environments. Highly detailed and consistent maps were obtained showing lattice constant and atomic composition changes over 50-cm^2 sample areas. Results for PtNi are shown in Figure 2. Surprisingly, both acid baths and fuel cell

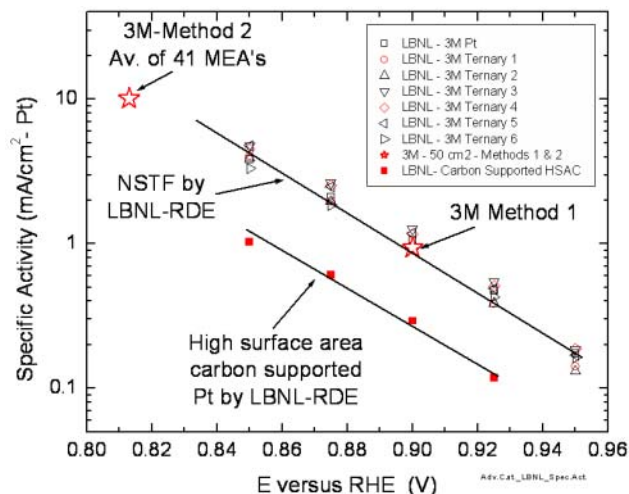


Figure 1. Summary plot of the specific activity versus potential of seven NSTF Pt ternary and pure Pt catalysts measured by the RRDE method at LBNL and compared to similar measurements by LBNL of high-surface-area carbon-supported Pt. The stars indicate specific activity measurements at 3M using two different methods in 50-cm² cells, averaged over dozens of NSTF samples [4].

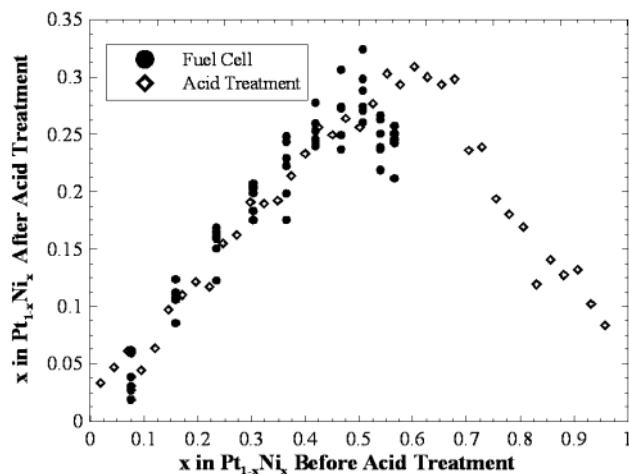


Figure 2. Plot of the effects of acid bath treatment (1M H₂SO₄, 10 days, 80°C) and fuel cell testing on the composition of PtNi binary catalysts fabricated on NSTF supports at Dalhousie U. as a 50-cm² combinatorial gradient array. Both treatments produce the same stable phases.

testing yielded the same stable compositions for multiple binary and ternary catalysts. Since the acid

bath and fuel cell exposures are so different, the resulting catalysts are believed to be highly stable.

Obtaining high current density is important for increasing power density and reducing stack volume. This period, we identified a key NSTF electrode property that allows eliminating mass transport losses under H₂/air at 2 A/cm². Figure 3(a) shows a series of constant current, constant stoichiometric polarization curves from an NSTF ternary with 0.1 mg/cm² of Pt on the cathode. Figure 3(b) shows an IR-corrected Tafel plot from the 80°C curve, illustrating that the measured IR loss and an assumed 70-mV/decade Tafel slope can account for all the overpotential, implying essentially zero mass transport loss at 2 A/cm².

Stability of the catalyst surface area and its support against loss by agglomeration and oxidation, respectively, are key requirements for higher-temperature operation. We reported last year on surface area stability measurements of the NSTF catalysts at 120°C over 90 hours [2]. This period, more extensive stability measurements of surface area have been completed by two methodologies. The first used an electrochemical stress test by polarizing the cathode at 1.2 V for 5-hour periods, followed by electrochemical surface area (ECSA) measurements. The NSTF surface areas were stable, ±10%, over 50 hours, versus an 80% loss of surface area for standard Pt/C catalyst. The second methodology is operating the fuel cell at 120°C under water balance conditions and taking surface area measurements daily. Multiple MEA tests are revealing a consistent picture of reversible (daily) loss of surface area that is associated with catalyst poisoning, while the recovered surface area values are stable over hundreds of hours to within a few percent.

A key result this period was identification of the critical pathway to achieve the 2010 DOE MEA performance targets with the NSTF electrodes. The high-frequency impedance (HFR) of the NSTF MEAs using matched GDLs for high-current-density performance produces approximately double the HFR obtained with other GDL types. Preserving the mass transport properties but reducing the impedance in half will permit a 100-mV gain at 2 A/cm². An additional 20-mV gain can potentially be harvested by combining the enhanced specific activity of the

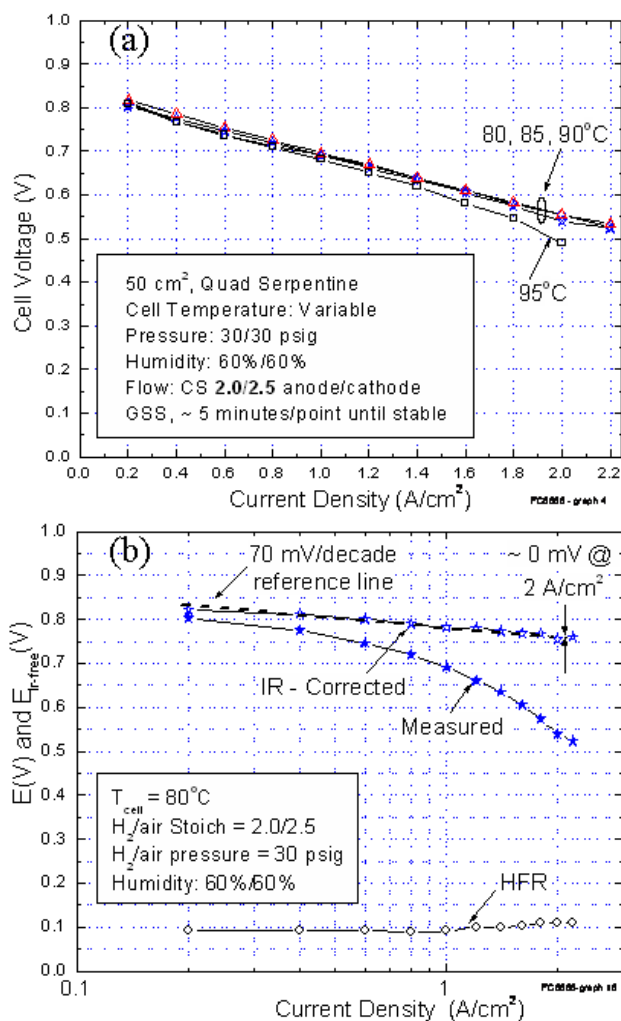


Figure 3. (a) Series of galvanodynamic, constant stoichiometric polarization curves at 80, 85, 90 and 95°C, 60% RH and 30 psig on both anode and cathode, with 0.1 mg-Pt/ cm^2 in an NSTF PtAB ternary on the cathode. (b) IR-corrected Tafel plot of the 80°C curve from (a), showing that a 70-mV/decade reference line can completely account for the IR-corrected overpotential, implying no mass transport loss out to 2 A/cm^2 .

optimized ternary, discussed above, with optimized NSTF support whiskers for better surface area. Together, using 0.05 mg-Pt/ cm^2 on the anode and the 0.1 mg-Pt/ cm^2 -containing ternary on the cathode, it should be possible to obtain less than 0.2 g-Pt/kW for cell voltages below 0.75 V.

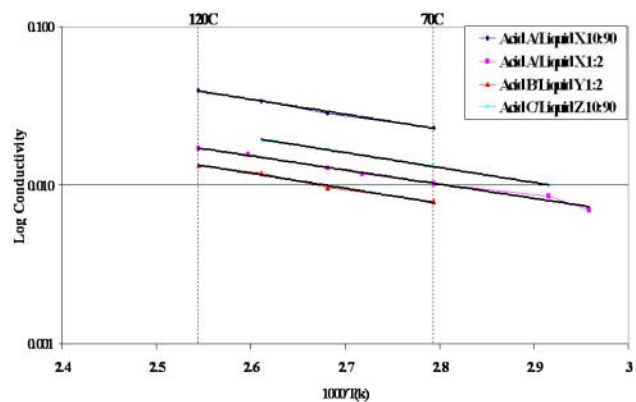


Figure 4. Conductivity of several acid additive/liquid combinations. Experimentally derived $E_a = \sim 0.2$ eV.

Good progress towards development of a high-temperature membrane (120°C or greater) that exhibits high levels of proton conduction with substantially lower levels of humidification has been realized. The proton transport of several combinations of fluorinated liquids and acids has been studied using a hydrogen/hydrogen liquid cell. Plotting conductivity as a function of temperature gives a linear relationship yielding an activation energy (E_a) of about 0.2 eV (Figure 4). This is in good agreement with values of about 0.3 eV generated through *ab initio* calculations using one liquid/acid combination by Professor J. W. Halley (subcontractor, University of Minnesota). The ionic conductivity of some of these acids incorporated into membranes has also been tested. Figure 5 shows AC impedance spectroscopy-derived conductivity of a membrane comprising one of the acids and Nafion 1000. Measurements at temperatures from 80°C to 120°C show 2 to 5 times higher ionic conductivity for the acid-containing membrane than a Nafion control and conductivity higher than a PBI-phosphoric acid control at temperatures below 100°C. In addition, these acids are stable and non-volatile at temperatures up to 250°C, and preliminary tests show them to be stable to “washing out” in MEAs run at 70°C with humidification levels well over 100% relative humidity (RH).

Additional work has been done in the area of inorganic/polymer composite membranes, and new

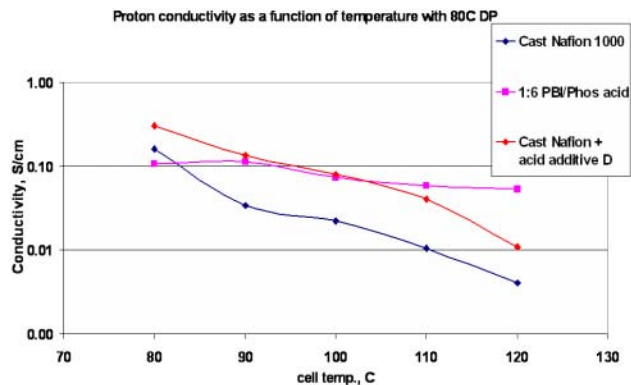


Figure 5. Conductivity of proprietary Acid D/cast Nafion membrane compared with Nafion 1000 and PBI-6 Phosphoric Acid.

membranes with good mechanical properties have been prepared which exhibit conductivity >10 mS/cm at 120°C **bone dry**. In addition, they are stable in boiling water for >7 hours.

As part of the effort to develop a more stable PEM for temperatures up to 120°C , a series of over two dozen additives to enhance the 3M PEM oxidative stability was tested in H_2O_2 soak tests. In all but a very few cases, these additives had no impact on membrane conductivity or fuel cell performance. Five candidates reduced or eliminated mass loss under these conditions. Some of these materials had significant stabilizing ability even at loadings as low as 0.01 weight percent. Fuel cell testing of membranes comprising these materials demonstrated that all five additives reduced F^- release rates in the effluent water by one to two orders of magnitude compared to multiple controls of the neat 3M PEM (Figure 6). The 3M ionomer has been demonstrated to give substantially lower rates of fluoride evolution in fuel cell effluent water compared to either cast or extruded Nafion membranes [5]. In accelerated lifetime testing on single cells, the two additive-containing membranes tested so far both increase MEA lifetime by 2 to 3 times.

Conclusions

The NSTF catalyst system has a five-fold higher specific activity compared to Pt/carbon. The 3M nanostructured catalyst process and combinatorial

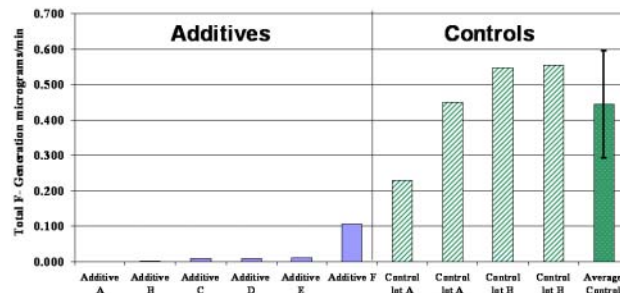


Figure 6. Fluoride release for membrane additives: 90/60/60 $^{\circ}\text{C}$, load cycled from 0 to 0.5 A/cm 2 , 50-cm 2 cell, dispersed catalyst, 0.4/0.4 Pt/Pt, 800/1800 SCCM, 7/0 psig H_2/air .

approach to development of new catalysts are continuing to yield catalyst constructions having improved performance with lower loadings. The oxidative chemical stability and high-temperature electrochemical surface area stability of 3M nanostructured catalysts and supports are superior to commercial carbon-black-supported Pt catalysts. Mass transport overpotential losses in the NSTF electrodes can be reduced to zero at 2 A/cm 2 .

The 3M PFSA ionomeric membrane has improved mechanical properties compared to membranes made with current commercial PEM ionomers and much lower levels of fluoride in the effluent water in fuel cells. The dramatically reduced F^- release rates measured in accelerated fuel cell tests with the additive-modified 3M PFSA ionomeric membranes are very encouraging that the required lifetimes for automotive applications will be obtained under realistic operating conditions $<120^{\circ}\text{C}$. An MEA materials development path utilizing the NSTF catalysts has been identified to reach the DOE 2010 performance targets.

For higher temperature ranges (120°C or above), the approach to development of new membranes using perfluorinated acids plus liquid additives is promising, based on actual proton conductivity results and membrane conductivity tests. Key issues will revolve around forming useful membranes and effective catalyst/electrolyte interfaces with these new materials.

“Nafion” is a registered trademark of DuPont.

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