

V.A.2 Advanced MEAs for Enhanced Operating Conditions

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 Dalhousie University, Halifax, N.S., Canada
 University of Illinois, Urbana, IL
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Objectives

- 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.
 - Are made by processes amenable to high volume manufacturing.

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 (HFCIT) Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

Tables 1 and 2 summarize, respectively, the status of the electrocatalyst and membrane properties developed under this project towards the 2010 and 2015 targets as outlined in the HFCIT Multi-Year RD&D Plan.

Accomplishments

- Down-selected nanostructured thin film (NSTF) ternary Pt_{Cx}Dy catalyst for best performance and durability and demonstrated mass activity of 0.25 A/mg-Pt (at 900 mV) when loading and NSTF whisker-support particle surface areas were better matched.
- NSTF catalysts shown to have significantly enhanced stability against surface area loss from Pt dissolution when compared to conventional Pt/C dispersed catalysts under both accelerated cyclic voltammogram (CV) cycling from 0.6 to 1.2 V and real time, air/air, start-stop durability cycles.

TABLE 1. Progress Towards Meeting Technical Targets for Electrocatalysts for Transportation Applications

Characteristic	Unit	2010/2015 Stack Target	3M 2006 Status (50 cm ² cell)
PGM Total Content	g/kW rated in stack	0.5 / 0.4	0.33 for V < 0.72 volts
PGM Total Loading	mg P GM/cm ² electrode area	0.3 / 0.2	0.21
PGM Cost	\$/kW @ \$15/g	8 / 6	6
Durability with cycling At operating ≤80°C At operating >80°C	Hours	5,000 2,000	TBD under specified conditions
Mass Activity (150 kPa H ₂ /O ₂ 80°C. 100% RH)	A/mg-Pt @ 900 mV	0.44 / 0.44	0.25
Specific Activity (150 kPa H ₂ /O ₂ 80°C. 100% RH)	μA/cm ² -Pt @ 900 mV	720 / 720	2,470 (0.08 mg-Pt/cm ²)

TABLE 2. Progress Towards Meeting Technical Targets for Membranes for Transportation Applications

Characteristic	Units	2010/2015 Target	3M 2006 Status (50 cm ² cell)
Membrane Conductivity at: Operating Temp.	S/cm	0.10/0.10	>0.10 @ 120°C w/ 80°C DP, 250 kPa,
Room Temperature -20°C	S/cm S/cm	0.07/0.07 0.01/0.01	0.12 saturated TBD
Operating Temperature	°C	≤ 120	≤ 120
Inlet water vapor partial pressure	kPa (absolute)	1.5/1.5	TBD
Oxygen cross-over	mA/cm ²	2/2	Expected to be similar to PFSA
Hydrogen cross-over	mA/cm ²	2/2	<2 @ 70°C, saturated
Durability with load cycling	Hours, T ≤ 80°C	5,000	>5,000
	Hours, T > 80°C	2,000/5,000	>4,000

- NSTF catalyst support-whiskers shown to have total resistance to corrosion when held at potentials up to 1.5 V for 3 hours.
- 3M proton exchange membrane (PEM) demonstrated over 5,000 hour lifetime under automotive operating conditions with load cycling at 80°C, and 64°C dew points.
- 3M PEM (730 equivalent weight, EW) demonstrated >100 mS/cm conductivity at 120°C, 80°C dew point (DP), and 250 kPa.
- 3M PEM (840 EW) and NSTF catalyst have been integrated for improved performance, durability and start-up, using all roll-good fabricated pilot-scale processing.
- MEA having NSTF catalyst and 3M PEM operated for 1,000 hours with cycling from 0.1 to 2.0 A/cm², and mean current density of 1 A/cm², under totally dry H₂/O₂, at 200 kPa and 65-70°C, with minimal permanent loss of performance.

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, specifically performance (efficiency and peak power), 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. Designing MEAs for hot, dry, reactant conditions requires development of new membranes, catalysts and gas diffusion layers (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 which produce less peroxide and have stable surface areas under 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 low 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 involved the development of full-size MEAs for the temperature range of 85°C < T < 120°C and investigation of new electrolytes for operation at or above 120°C. For the lower temperature range, MEAs were developed using PEMs based on modifications of 3M's novel perfluorinated sulfonic acid (PFSA) type membrane and catalysts based on the 3M nanostructured thin film (NSTF) catalyst and deposition system. The 3M PEM modifications included incorporation of functionalized additives to facilitate peroxide decomposition for better oxidative stability and enhanced water retention for higher conductivity under low humidification. The NSTF catalysts developed were thin film ternary alloy catalysts having much enhanced specific activities and stability under high voltage and temperature conditions. High volume capable roll-good processes are used to fabricate the 3M PEM and NSTF ternary alloy catalysts and integrate them into rolls of 3-layer catalyst coated membrane.

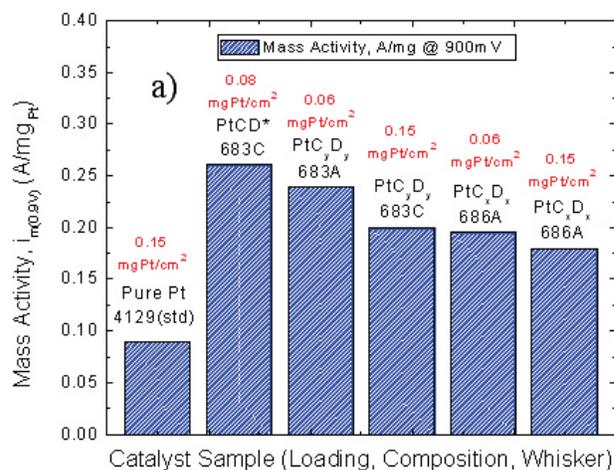
For the higher temperature range, new membrane materials and low-water based proton conduction methods were investigated, which utilize 3M perfluorinated acids, various proprietary liquids, and various inorganic additives. Work included understanding how to incorporate those materials into polymer matrices to form effective membranes.

Results

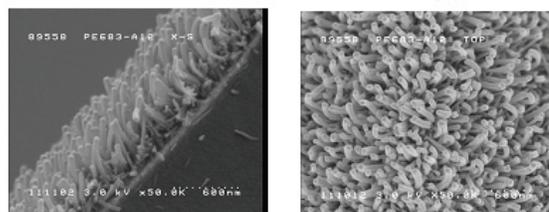
This past year, the focus of the NSTF Pt-based ternary cathode catalyst development was on investigation of ways to optimize mass activity, durability testing of MEAs containing the down-selected PtCxDy ternary alloy, qualification of the roll-good processes for fabrication of large-area, catalyst-coated 3M membranes, and preparation for stack tests of those MEAs. Load cycle durability testing of the 3M membranes with functionalized additives for enhanced stability was also completed.

The mass activity for any catalyst depends on the surface area of the support particle and how well the catalyst is distributed over it. Early this year, we completed an initial study showing that matching the catalyst loading to the surface area of the non-carbon whisker support particles can increase the NSTF catalyst mass activity. Figure 1 illustrates the measured mass activities for various NSTF ternary catalyst loadings applied to four different whisker support films that vary in areal number density and length of the average whiskers. In Figure 1(b) the scanning electron microscope (SEM) images show two of the four controlled whisker support types. PE683A contains shorter whiskers with higher number density and PE686A contains longer whiskers with lower areal number density. The mass activities were all measured 15 minutes after setting the cell potential at 900 mV under 150 kPa saturated H₂/O₂. As seen in Figure 1(a), depending on the catalyst loading and whisker support structure, mass activities of 0.25 A/mg-Pt were obtained with Pt loadings in the 0.06-0.08 mg/cm² range, significantly higher than that from the NSTF pure Pt catalyst and equivalent to those reported from high surface area dispersed alloy PtCo/Carbon catalysts. Further gains should be possible by optimizing the whisker support films for a given loading and alloy composition.

Durability studies of the NSTF catalyst-based MEAs, begun in FY 2004 and discussed in last year's annual report, were again significantly extended this year. Accelerated stop/start tests based on CV cycling between 0.6 and 1.2 V at 20 mV/sec under saturated H₂/N₂ were applied to a series of NSTF pure Pt and dispersed Pt/C based MEAs. The tests were done to simulate the loss of catalyst surface area due to agglomeration, Pt dissolution and support oxidation. In these experiments, the cycling was done at different temperatures, which allowed application of a first order kinetic rate model to describe the loss of surface area for the two types of electrocatalyst systems. Figure 2(a) compares the change in the normalized surface area as the number of CV cycles increases from the NSTF-Pt (0.15 mg/cm²) and Pt/C (0.4 mg/cm²) catalyst MEAs. The same 3M membrane and GDLs, test cells and station were used for both sets of measurements.



PE683A NSTF whisker supports



b)

PE686A NSTF whisker supports

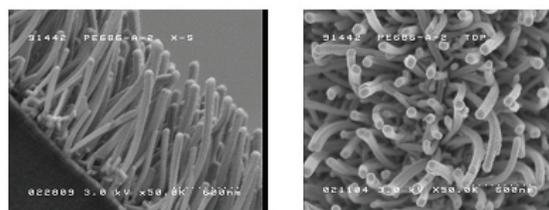


FIGURE 1. a) Mass activities at 900 mV (150 kPa saturated H₂/O₂) from various combinations of NSTF ternary catalysts and support whiskers shown in b). Better matching of catalyst loading to the surface area of the whisker supports can increase the mass activity.

The NSTF surface areas decreased about 33% and stabilized at S_{min} , whereas the dispersed MEA cathode surface areas degraded over 90% in many fewer cycles. Treatment of the data with a first order kinetic rate model, in which the rate of surface area loss with number of cycles is proportional to the remaining non-stable surface area, allowed extraction of an activation energy for surface area loss by all acting mechanisms [1]. From the Arrhenius plot in Figure 2(b), the activation energy for surface area loss by the NSTF catalysts is approximately twice that of the dispersed catalyst based MEAs. Thus, there are two aspects contributing to the enhanced NSTF stability under stop-start cycling, viz. the larger fraction, S_{min} , of stable surface area and the

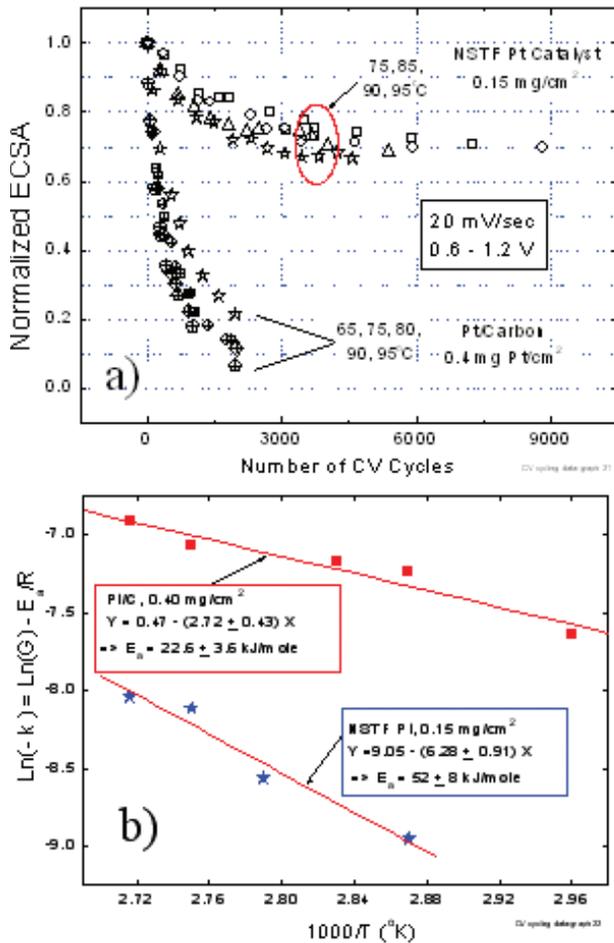


FIGURE 2. a) Normalized electrochemical surface areas, for both NSTF and Pt/C based MEA's, plotted as a function of the number of CV cycles from 0.6 to 1.2 V under H₂/N₂ at 20 mV/sec and varying temperatures. b) Application of a first order kinetic rate model to the surface area data shown in a) to extract an activation energy describing the overall surface area loss mechanisms.

larger activation energy causing the surface area loss to approach this minimum value at a slower rate.

A second type of durability test specifically targeted the corrosion resistance of the catalyst support particle. In this test, the MEA was polarized for various lengths of time at 1.5 V under H₂/N₂. Pt strongly corrodes conventional carbon support particles under these conditions. Figure 3 (top) shows the measured electrochemical surface area after periods of 30, 60, 90 and 180 minutes. There was no statistically significant change in the measured NSTF catalyst surface area over the 3 hour period. Figure 3 (bottom) shows there was also no change in the 50-cm² fuel cell H₂/air performance. In sharp contrast, the control Pt/C based MEA, with 0.4 mg/cm² of 50 wt% Pt/Ketjen Black and the same 3M membrane and GDL, lost two-thirds of the cathode surface area in just 30 minutes, with dramatic

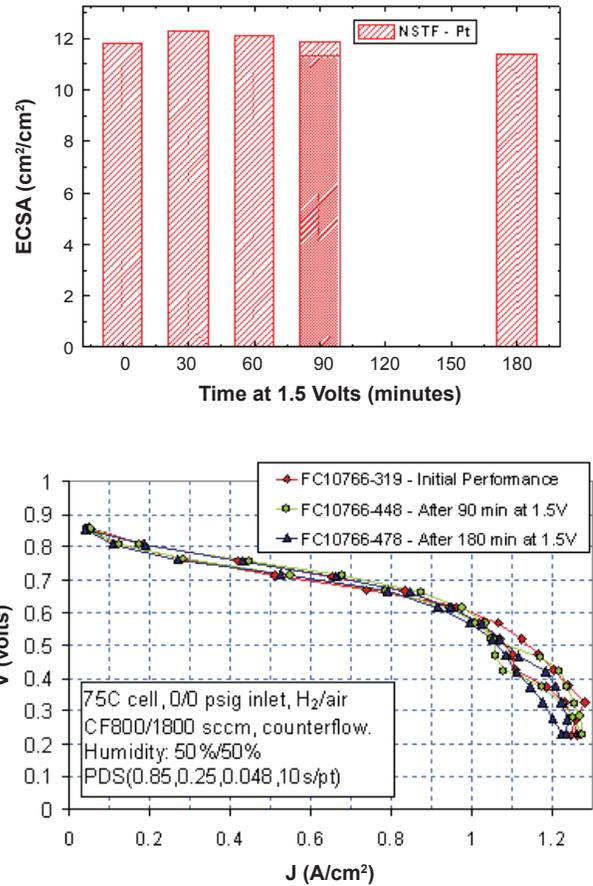


FIGURE 3. Effect on NSTF MEA electrochemical surface area (top) and fuel cell polarization curve (bottom) of polarizing the NSTF MEA to 1.5 V for the times indicated. Three hours at 1.5 V has no deleterious effect on the cathode surface area or performance. The double bar after 90 minutes shows two ECSA measurements.

losses of performance greater than what could be accounted for by loss of surface area [2].

Pilot scale fabrication of roll-good catalyst-coated membranes (CCMs) using the NSTF ternary alloy catalysts and the 3M 800 EW PEM was demonstrated in multiple runs, successfully identifying the critical parameters for most effective catalyst transfer. Fuel cell performance of the best pilot scale fabricated CCMs outperform the hand fabricated samples in 50-cm² tests. MEAs with 360 cm² active areas and integrated gaskets and GDLs were fabricated for stack testing, and preliminary 4-cell stack testing is achieving the expected results.

Development of 3M's new PFSA membrane has been discussed in prior annual reports. Many of its advantageous characteristics were discussed in the FY 2005 annual report, including the results of conductivity measurements of the 3M PFSA's having various equivalent weights and the benefits of adding stabilizing additives and reducing the number of carboxylate

end groups in the polymer to obtain substantially improved oxidative stability. This past year, load cycling durability tests were completed and 120°C conductivity measurements completed. Figure 4(a) illustrates that the modified 3M PEM can successfully sustain over 5,000 hours of load cycling whereas MEA's made with 3M-cast Nafion® membrane fail in substantially shorter times. These load-cycling tests utilized a 10-cell test station in which identical cells are cycled through the same protocol involving eight different test conditions. The current density is made to cycle non-monotonically through 0.02, 0.2, 0.8 and 1 A/cm², at 80°C cell temperature, 64°C/64°C inlet dewpoints and 175 kPa outlet pressures, with varying durations at each condition. The test results in Figure 4(a) show the cell voltages from four 3M PEM based MEAs at the 2nd test point condition of 0.02 A/cm², stoichiometry of 15 and 20 minute duration. Cell failure is defined as when this voltage falls below 800 mV.

The 2010 DOE target for membrane conductivity at 120°C is 0.1 S/cm. Figure 4(b) illustrates the measured conductivities at 120°C of 3M PEMs having nominal EWs of 730 and 830, as well as a standard Nafion® 112 membrane. At a pressure of 250 kPa, the lower EW

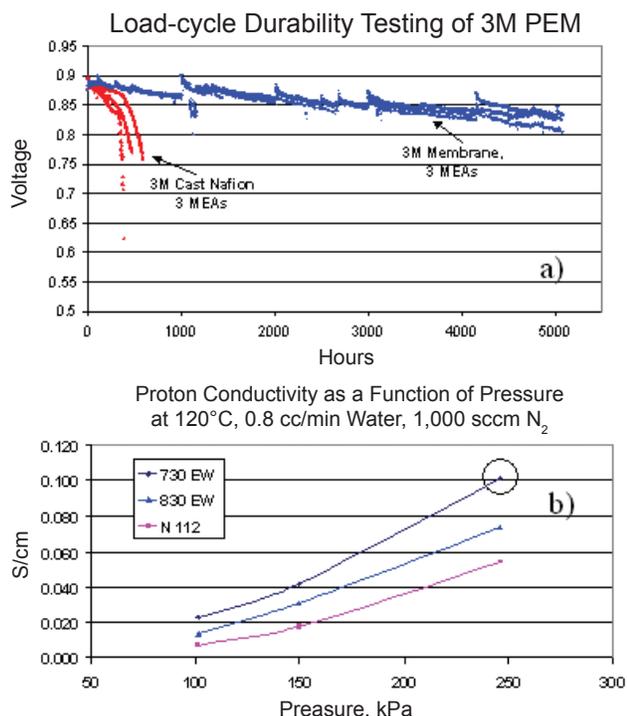


FIGURE 4. a) Comparison of load-cycling durability testing of the 3M 840 EW membrane based MEA's and MEA's made with 3M-cast Nafion membranes (both using dispersed Pt/C catalysts with 0.4/0.4 mg-Pt/cm²). b) Comparison of membrane conductivity of two different equivalent weights of 3M PEM with Nafion 112 membrane as a function of pressure at 120°C. The 730 EW PEM meets the DOE 2010 target for conductivity at 250 kPa.

PEM meets this 2010 target. Fuel cell performance with the lower EW membranes under hot, dry conditions is also improved due to better water management characteristics of these membranes. Stable fuel cell performance, in which the high frequency impedance remains on the order of 0.1 ohm-cm², is possible with the 730 EW ionomer based membrane at 120°C, 250 kPa and only 10% inlet relative humidity.

"Nafion" is a registered trademark of DuPont.

Conclusions and Future Directions

In the past year, down-selected NSTF catalysts and 3M membranes were integrated into roll-good fabricated CCMs and shown in single cell tests to meet or exceed the DOE targets for 2010. The CCM processes have been extensively advanced and significant quantities of roll-good materials fabricated. The final task of this contract is to demonstrate the performances and durability in short stack tests of ~5 kW size with large area MEAs. These stack tests, with MEAs having over 300-cm² active area, are currently underway at 3M in preparation for shipment to Argonne National Laboratory for DOE's testing.

Special Recognitions & Awards/Patents Issued

1. 2006 DOE Hydrogen Program R&D Award, presented to Mark Debe in recognition of this project team's outstanding achievement in fuel cell R&D.

FY 2006 Publications/Presentations

1. "Advanced MEA's for Enhanced Operating Conditions," 2005 Hydrogen Program Annual Report, Oct. 2005, page 672.
2. M. K. Debe, A. K. Schmoekkel, G. D. Vernstrom and R. Atanasoski, "High Voltage Stability of NanoStructured Thin Film Catalysts for PEM Fuel Cells," J. Power Sources, (in press) 2006, and presented 2005 Fuel Cell Seminar, Palm Springs, CA, Nov. 14-18, 2005.
3. M. K. Debe, A. K. Schmoekkel, S. M. Hendricks, G. D. Vernstrom, G. M. Haugen and R. T. Atanasoski, "Durability Aspects of Nanostructured Thin Film Catalysts for PEM Fuel Cells," presented at Symposium on Durability and Reliability of Low-Temperature Fuel Cell Systems, 208th ECS meeting, Oct. 16-21, 2005, Los Angeles, CA, ECS Transactions 1(8) 51-56 (2006).
4. J. McBreen, M. Balasubramanian, W.-S. Yoon, K. Y. Chung, H. S. Lee, and X. Q. Yang, R.T. Atanasoski, A.K. Schmoekkel, G.D. Vernstrom, and M.K. Debe, "PEM Fuel Cells: Materials Issues," Fifth International Symposium on Proton Exchange Membrane Fuel Cells, In Honor of Dr. Subramanian Srinivasan, 208th ECS Meeting, Los Angeles, CA, Oct. 16-21, 2005, ECS Transactions 1 (6) 149 (2006).

5. J.R. Dahn, D.A. Stevens, A. Bonakdarpour, E.B. Easton, M.T. Hicks, G.M. Haugen, R.T. Atanasoski and M.K. Debe, "Development of Durable and High-Performance Electrocatalysts and Electrocatalyst Support Materials," Symposium on Durability and Reliability of Low-Temperature Fuel Cell Systems, 208th ECS meeting, Oct. 16-21, 2005, Los Angeles, CA.
6. F. Meng, S. Dec, M. Frey, S. Hamrock, J. Turner, and A. Herring, "Spectroscopic Studies of Heteropoly Acid doped 3M Perfluorinated Sulfonic Acid Polymer Membranes," 208th Meeting of the Electrochemical Society, Los Angeles, CA, Oct. 18, 2005, ECS Transactions 1(6) 255 (2006).
7. S. Hamrock, "The Development of New PEM Fuel Cell Membranes at 3M," Golden Gate Polymer Forum, 25th Anniversary Symposium, Oct. 23, 2005, San Francisco, CA.
8. A. M. Herring, J. A. Turner, S. F. Dec, F. Meng, J. Horan, N. Aieta, R. J. Stanis, "The Use of Heteropoly Acids in the Production of High Performance PEM Fuel Cell Components," 2005 Fuel Cell Seminar, Nov. 15, Palm Springs, CA.
9. S. Hamrock, "New PFSA membranes with Improved Durability," Pacific Polymer Conference IX, Maui, HI, Dec. 12, 2005.
10. M. K. Debe, "Advanced Catalyst and Membrane Technology with Enhanced Performance and Durability for Automotive Requirements," at 4th International Fuel Cell Workshop 2005, Kofu, Japan, Sept. 23-24, 2005.
11. A. Herring, J. Turner, S. Dec, J. Malers, F. Meng, J. Horan and N. Aieta, "The Use of Heteropoly Acids in Composite Membranes for Elevated Temperature or Low Humidity PEM Fuel Cell Operation," 2nd International Conference on Polymer Batteries and Fuel Cells, Las Vegas, NV, June 13, 2005.
12. M. A. Yandrasits, "Mechanical Property Measurements of PFSA Membranes at Elevated Temperatures and Humidities," 2nd International Conference on Polymer Batteries and Fuel Cells, Las Vegas, NV, June 14, 2005.
13. M. K. Debe, "Prospects and Challenges for PEM Fuel Cells with a Focus on MEA Development for Automotive Applications," Invited Plenary Lecture, 2005 Annual Meeting of the North American Membrane Society, Providence, RI, June 15, 2005.
14. 2006 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting, May 15-19, 2006, Arlington, VA, Presentation FC-19.

References

1. M. K. Debe, A. K. Schmoekkel, G. D. Vernstrom and R. Atanasoski, "High Voltage Stability of NanoStructured Thin Film Catalysts for PEM Fuel Cells," J. Power Sources, *in press*.
2. M. K. Debe, A. K. Schmoekkel, S. M. Hendricks, G. D. Vernstrom, G. M. Haugen and R. T. Atanasoski, in ECS Transactions 1(8) 51-56 (2006) - Durability and Reliability of Low-Temperature Fuel Cell Systems, 208th ECS meeting, Oct. 16-21, 2005, Los Angeles, CA.