

V.E.4 Advanced Cathode Catalysts and Supports for PEM Fuel Cells

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Subcontractors and Federally Funded Research
and Development Centers:

- Dalhousie University, Halifax, Nova Scotia, Canada
- Jet Propulsion Laboratory (JPL)
- Argonne National Laboratory (ANL)

Project Start Date: April 1, 2007
Projected End Date: March 31, 2011

Technical Barriers

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

- (A) Durability
- (B) Cost
- (C) Performance
- (D) Water Transport within the Stack

Technical Targets

This project is focused on improving the performance and durability of the 3M nanostructured thin film (NSTF) roll-good fabricated electrocatalysts and MEAs. Table 1 compares the NSTF current 1st quarter, CY 2007 status with the electrocatalyst targets for 2010/2015 from Table 3.4.12 of the DOE HFCIT MYPP. The major changes from a similar table used in the 2006 annual report of the predecessor contract to the present one, are that the values in Table 1 are for large area roll-good fabricated MEAs and durability data is from a 22-cell, 5 kW, 312.5 cm² (0.2 mg/cm² PtCoMn ternary on both anode and cathode) short stack still under test at the time of this writing.



Objectives

The objectives of this project are development of a durable, low cost (both precious group metal [PGM] content and manufacturability), high performance cathode electrode (catalyst and support), which is fully integrated into a proton exchange membrane (PEM) electrode assembly (MEA) characterized by:

- Total Pt group metal loading per MEA of ≤ 0.25 mg/cm²,
- Short-stack specific power density of < 0.5 g/kW at rated power,
- Durability sufficient to operate at $> 80^\circ\text{C}$ for 2,000 hours, $\leq 80^\circ\text{C}$ for 5,000 hours, with cycling for transportation applications,
- High prospects for 40,000 hours durability under operating conditions for stationary applications, and
- High volume manufacturability.

Approach

State-of-the-art PEM fuel cell electrocatalyst technology utilized in today's prototype fuel cell vehicles and commercialized stationary systems are demonstrating significant limitations with respect to general durability and robustness under start-stop cycling, adequate performance with low PGM loadings, wide temperature and humidity operating windows, and low-cost manufacturability. To a significant degree, these deficiencies are traceable to properties of the conventional cathode catalysts in use today.

The focus of this project is continued development of advanced cathode catalysts and supports based on 3M's NSTF catalyst technology platform, which has already demonstrated catalyst specific activity [1] and durability [2,3,4] significantly higher than conventional carbon-supported Pt catalysts. The scope of work includes fundamental catalyst studies with ANL, high throughput fabrication and characterization of new multi-element Pt alloys (ternaries and quaternaries) with Dalhousie [5] and JPL, and investigation of optimized NSTF catalyst support films [6] for increased surface area and catalyst

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

Characteristic		2010/2015 Stack Targets	3M 2007 Status (volume manufactured roll-good)	Project Goal
PGM Total Content	g/kW rated in stack	0.3 / 0.2	0.47 (in 22 cell stack)	0.25
PGM Total Loading	mg PGM/cm ² electrode area	0.3 / 0.2	0.25 – 0.4	0.25
Durability with cycling At operating T ≤80°C At operating T >80°C	Hours	5,000 / 5,000 2,000 / 5,000	<20 μV/hr-cell non- reversible loss over 550 hrs (5 kW stack, 3,380 load cycles at 90°C). Testing ongoing.	>5,000
Mass Activity (150 kPa H ₂ /O ₂ 80°C, 100% RH)	A/mg-Pt @ 900 mV	0.44 / 0.44	0.18 – 0.25 (≤0.2 mg/cm ²)	>0.5
Specific Activity (150 kPa H ₂ /O ₂ at 80°C, 100% RH)	μA/cm ² -Pt @ 900 mV	720 / 720	2,930 (0.2 mg/cm ²)	>5,000
ECSA loss by Stop/Start	% ECSA loss	<40 / 40	<30	<10
Electrochemical support loss at high potentials	mV after 100 hrs @ 1.2 V	<30 / 30	<10	~0

utilization. Research in the first budget period will rely heavily on high throughput sample fabrication and compositional spread evaluation for screening new multi-element thin film materials for higher specific activity and resistance to Pt dissolution. At 3M, the thin film catalyst deposition process parameters will be explored in depth, and extensive fuel cell testing in 50-cm² single cells will be conducted for integrated catalyst coated membrane (CCM) development with advanced 3M membranes optimized for NSTF catalysts. Gas diffusion layers (GDLs) optimized specifically for water management with the ultra-thin NSTF-based electrodes is a major subtask as well.

Accomplishments

- Strategic approach defined and implemented with Dalhousie, ANL and JPL collaborators to improve NSTF catalyst activity and durability towards project goals in Table 1.
 - Criteria for materials selection for increasing catalyst surface area, specific activity and catalyst stabilization were defined.
 - NSTF-whisker-support deposition onto JPL multi-electrode arrays, and subsequent catalyst coating at JPL has been demonstrated, along with initial electrochemical surface area and the oxidation reduction reaction (ORR) measurement feasibility at JPL was also demonstrated.
 - Six multi-element compositional spreads on NSTF whisker-support films were fabricated at Dalhousie University, with extensive materials characterization and evaluation of the impact on catalyst surface area.
- The ORR specific activity gains of ~250% for NSTF-PtCoMn over NSTF-Pt validated at ANL in rotating ring disk electrode measurements with multiple samples and temperatures.
- “Start-of-Contract” baseline performance and durability testing completed or initiated using NSTF catalyst-based MEAs:
 - DOE accelerated stress tests initiated per Appendix D of DOE solicitation DE-P36-06GO96017 and HFCIT MYPP of August, 2006, using baseline NSTF-PtCoMn-based MEAs: a) 0.7-0.9 V cycling, b) 1.2 V hold, c) steady-state open circuit voltage. All tests underway.
 - Demonstrated 80 mV gain at 1.6 A/cm² by reducing anode NSTF-ternary loading to 0.1 mg-Pt/cm² (see Figure 1), reducing anode dry-out from electro-osmotic drag.
 - Determined and compared the reversible and non-reversible performance and surface area losses from controlled chloride ion exposure on NSTF versus Pt/C catalysts.
 - Extensive screening and designed experiments completed to explore the GDL coating and process windows for improving the water management behavior of NSTF MEAs at low temperature, using baseline commercial carbon paper.
 - Completed in-depth statistical analyses of 13 fuel cell performance and material characteristics from a 50-ft CCM NSTF roll-good, dissected and evaluated in 6-inch increments prior to the contract start. Performance factors correlated to membrane thickness and catalyst loading.

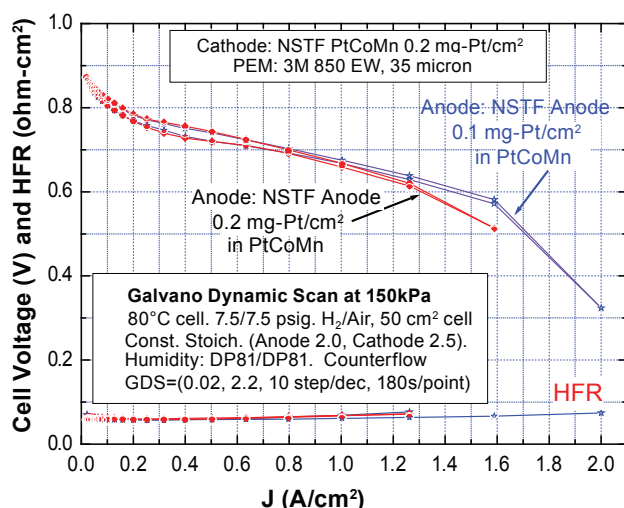


FIGURE 1. Improvement in polarization curve performance at high current density using reduced NSTF anode loading. This reduces the anode drying from electro-osmotic drag at high currents.

FY 2007 Publications/Presentations

1. K. Noda, A. J. Steinbach, and M. K. Debe, "Start-Stop Durability Testing of 3M's Nanostructured Thin Film Catalysts for PEM Fuel Cells," 210th ECS Meeting, Cancun, Mexico, Nov. 2, 2006.
2. A. K. Schmoeckel, G. D. Vernstrom, A. J. Steinbach, S. M. Hendricks, R. T. Atanasoski and M. K. Debe, "Nanostructured Thin Film Ternary Catalyst Activities for Oxygen Reduction," 2006 Fuel Cell Seminar, Honolulu, Hawaii, Nov. 13–17, 2006.
3. M. K. Debe, "Status and Prospects of PEFC Electro-catalysts: Meeting the Requirements for Automotive Fuel Cells with Nanostructured Thin Film Electrodes," in Proceedings of the 3rd International Hydrogen and Fuel Cell Expo, Session FC-8, p.1, Tokyo, Japan, Feb. 7–9, 2007. (Invited)
4. R. Atanasoski: "Low platinum and non-precious metal catalysts for PEM fuel cell application", 233rd Am. Chem. Soc. Meeting, Nanoscale Inorganic Catalysis Session, Chicago, March 2007. (Invited)

5. M. Debe, A. Hester, G. Vernstrom, A. Steinbach, S. Hendricks, A. Schmoeckel, R. Atanasoski, D. McClure and P. Turner, "NanoStructured Thin Film Catalysts for PEM Fuel Cells by Vacuum Web Coating," 50th Annual Technical Conference of the Society of Vacuum Coaters, Louisville, KY, May 1, 2007. (Invited)
6. M. K. Debe, 2007 DOE Hydrogen Program Review, Washington, D.C., May 17, 2007. Poster # FCP 25.
7. M. K. Debe, "Next Generation Catalyst Technology with Enhanced Performance and Durability for Automotive Fuel Cell Requirements," Institute for Research in Materials, Dalhousie University, Nova Scotia, June 25, 2007. (Invited)

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1. A. K. Schmoeckel, G. D. Vernstrom, A. J. Steinbach, S. M. Hendricks, R. T. Atanasoski and M. K. Debe, "Nanostructured Thin Film Ternary Catalyst Activities for Oxygen Reduction," 2006 Fuel Cell Seminar, Honolulu, Hawaii, Nov. 13–17, 2006.
2. Debe, M. K.; Schmoeckel, A.; Hendricks, S.; Vernstrom, G.; Haugen, G.; Atanasoski, R., *ECS Transactions* 1(1), 51 (2006).
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4. Steinbach, A.J.; Noda, K.; Debe, M. K., *ECS Transactions* 3(1) 835 (2006).
5. Bonakdarpour, A.; Lobel, R.; Atanasoski, R. T.; Vernstrom, G. D.; Schmoeckel, A. K.; Debe, M. K.; Dahn, J. R., *Journal of The Electrochemical Society* 153, A1835 (2006).
6. M. Debe, A. Hester, G. Vernstrom, A. Steinbach, S. Hendricks, A. Schmoeckel, R. Atanasoski, D. McClure and P. Turner, in proceedings of the 50th Annual Technical Conference of the Society of Vacuum Coaters, Louisville, KY, May 1, 2007.