Advanced Cathode Catalysts and Supports for PEM Fuel Cells

2007 DOE Hydrogen Program Annual Merit Review

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3M Company
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DOE Hydrogen Program

Project ID FCP25

Overview

Timeline

- Project start : April 1, 2007
- Project end : March 30, 2011
- 2% Complete

Budget

- Total Project funding **$10.43MM**
  - $8.34 MM DOE
  - $2.09 MM Contractor share
- Received in FY06: $0
- Received in FY07: $0 million

Partners

- Dalhousie University (J. Dahn)
- JPL (S. R. Narayanan)
- ANL (N. Markovic)
- Project Management – 3M

Barriers

A. Electrode and MEA Durability

B. Stack Material & Mfg Cost

C. Electrode and MEA Performance

DOE Technical Targets

Electrocatalyst/ MEA	2010	2015
Lifetime Hrs, > 80°C	2000	5000
Mass Activity(A/mg)	0.44	0.44
PGM, (g/KW rated)	0.3	0.2
Performance, @ Rated (W/cm^2), @ 0.8V	1 0.25	1 0.25

Overall Contract Objectives

Development of a durable, low cost, high performance cathode electrode (catalyst and support), that is fully integrated into a fuel cell membrane electrode assembly with gas diffusion media, and that is characterized by:

- total Pt group metal loading per MEA of $\leq$ 0.25 mg/cm^2,
- short-stack specific power density of < 0.5 g/kW at rated power,
- durability sufficient to operate at > 80^{o}C for 2000 hours, or $\leq$ 80^{o}C for 5000 hours, with cycling for transportation applications,
- high volume roll-good manufacturability, and
- high prospects for 40,000 hours durability under operating conditions for stationary applications.

Project Approach

Unique Aspect of Approach:

Development of advanced cathode catalysts and supports will be based on 3M's nanostructured thin film (NSTF) catalyst technology platform, which has already demonstrated catalyst specific activity and durability significantly higher than conventional Pt/Carbon catalysts.

Task 1.0 NSTF Catalyst Activity

1.1 NSTF surface area increase
1.2 Fundamentals of NSTFC activity
1.3 New alloys to increase activity

Task 2.0 Durability Improvements

2.1 Stabilization against dissolution
2.2 Grain size stabilization

Task 3.0 Full Size (> 250 cm^2) Single Cell Performance and Durability Tests

Task 4.0 Durability Understanding

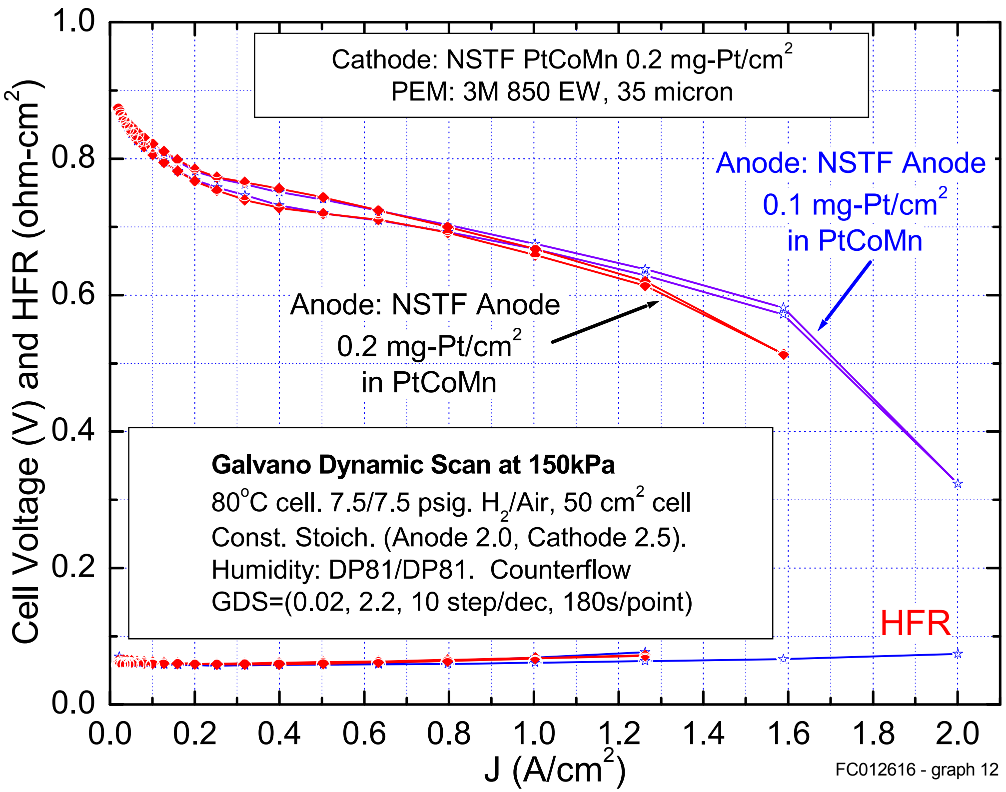
4.1 Durability tests of new NSTF supports
4.2 Durability tests of new conventional catalyst supports
4.3 Degradation model development

Task 5.0 Scale-up and Stack Testing

5.1 NSTF catalyst / PEM optimization
5.2 Optimized anode and cathode GDL's
5.3 Short stack testing (> 10 cells, > 250 cm^2)

Technical Progress to Date

The focus of this project is development of advanced cathode catalysts and supports based on 3M's NanoStructured Thin Film (NSTF) catalyst technology platform, which has already demonstrated catalyst specific activity and durability significantly higher than conventional carbon supported Pt catalysts. The scope of work includes fundamental catalyst studies, high throughput fabrication and characterization of new multi-element Pt alloys (ternaries and quaternaries), investigation of alternative catalyst support particles, extensive fuel cell testing in 50-cm² single cells and large area short stacks, integrated MEA development using advanced 3M membranes, and GDL's specific to the water management properties of ultra-thin layer electrodes.



Recent result with reduced anode loading and improved water management: **80mV gain at 1.6 A/cm².**

Technical Progress to Date (cont.)

- Implementation of strategic approach defined in original proposal
- Review of technical literature specific to how catalyst ORR activity is related to catalyst surface and electronic structure, water management
- Definition of specific experimental plans for each subtask
  - Criteria for materials selection for increasing catalyst surface area, specific activity, grain stabilization, water management
  - Interactive input from Collaborators
- PtCoMn coated NSTF whisker supports provided to ANL and JPL for baseline analyses; GDL and NSTF whisker support roll-good materials supplied to Dalhousie
- Magnetron sputtering-target materials purchased for Tasks 1.1 and 1.3
- Working Kick-off meeting held April 23, at 3M with all collaborators participating
- Required equipment modifications initiated at JPL and Dalhousie
- At 3M: Fabrication of roll-good NSTF support substrate for contract needs; Coater maintenance and upgrade check-outs completed; In-depth analyses of 45 ft CCM roll-good and continued evaluation of impurity induced reversible and irreversible stability, both as part of Task 5.2; Verified performance gain with reduced anode loading.

FY07 and FY08

Subtask 1.1 NSTF surface area optimization

The purpose of this subtask is to increase the surface area of the NSTF catalysts by increasing the surface area of the catalyst support system. The NSTF catalyst support system consists of a monolayer of oriented, high aspect ratio (length-to-width) crystalline whiskers, ~ 1 microns in length, with area number densities exceeding 3 billion whiskers/cm^2. The expected outcome will be an increase in the specific surface area of the NSTF catalysts by a factor of 2x to 3x from the current ~ 10 m^2/g-Pt.

NSTFC Rev 1 Catalyst Coated Whiskers

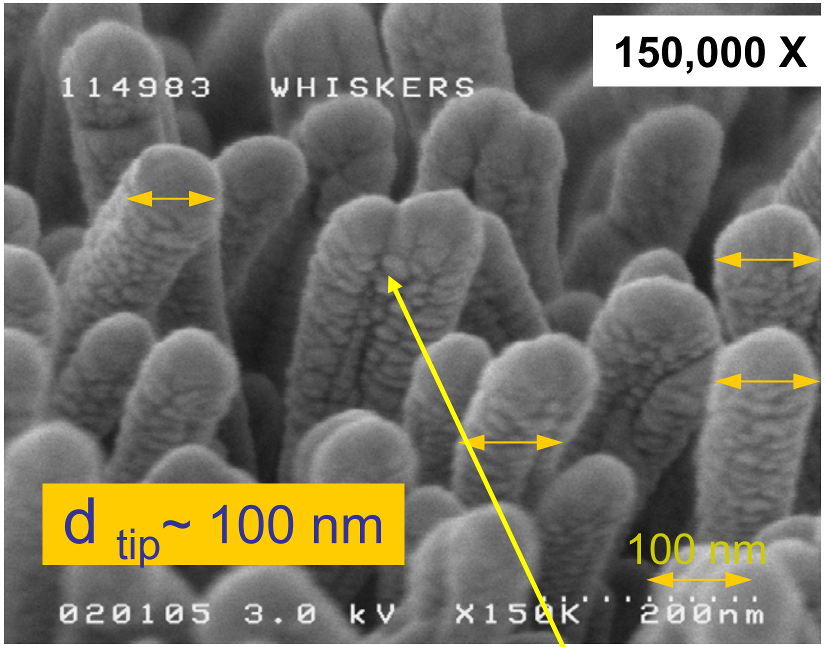
First order approximation of geometric Surface Area :

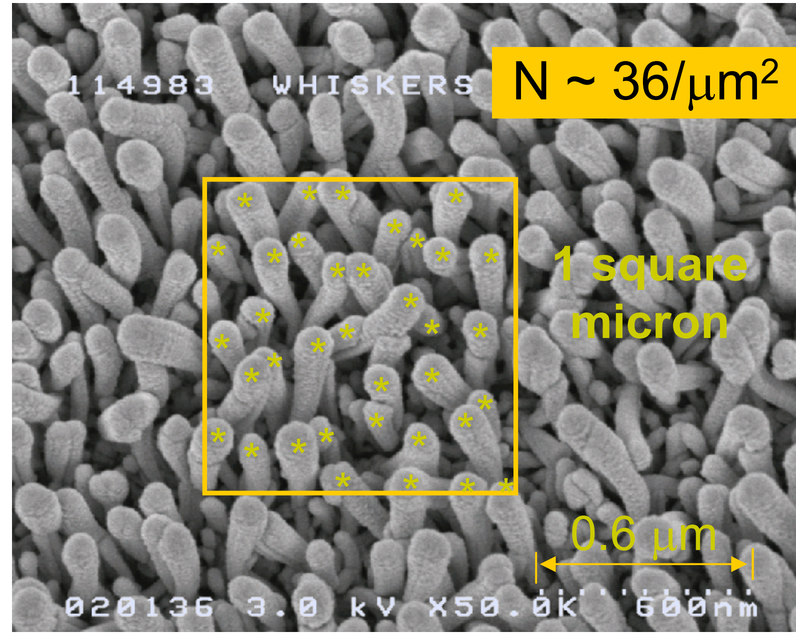
$$\text{Surface Area Geo.} = 1.414 \times N[\pi d_{av}L+\pi(d_{tip}^2/2)]r_f$$

$N \sim 36/\mu m^2$; $d_{av} \sim 0.075\mu m$;
$d_{tip} \sim 0.1\ \mu m$; $L \sim 0.7\mu m$; $r_f \sim 1.5$ to 2

Geometric Surface Area = 13 to 17.4 $\mu m^2 / \mu m^2$

Subtask 1.1 NSTF surface area optimization





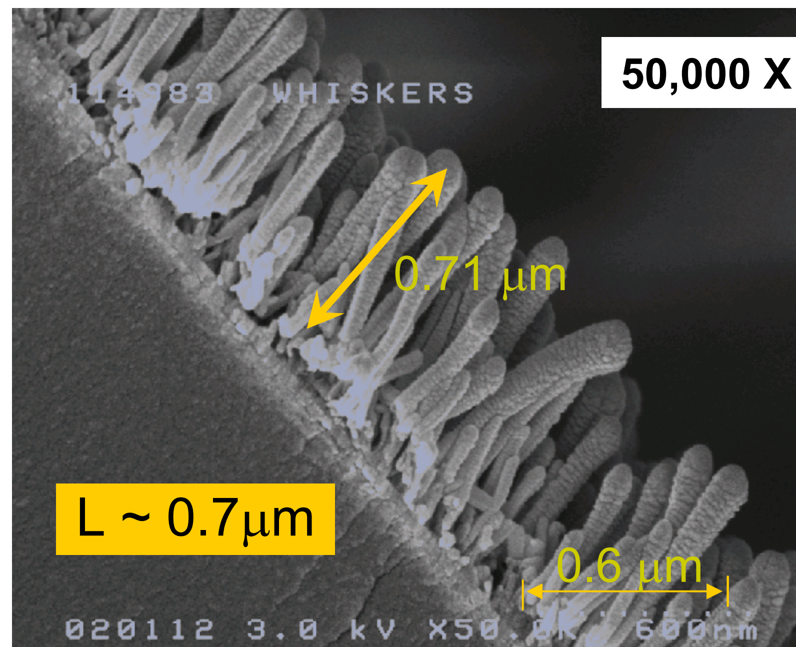
Surface Roughness Factor

may be : r_f ~ 1.5 to 2 ?

Tip diameter : d_{tip}~ 100 nm

Base diameter : ~ 50nm of bare whisker

Mean diameter over length taken as average of base and tip: d_{av} ~ 75nm



Future Work: FY07 and FY08 (cont.)

Subtask 1.2 Fundamental studies of NSTF catalysts

The purpose of this subtask is to obtain a better understanding of the fundamental oxygen reduction reaction pathways on the NSTF ternary catalysts in order to elucidate the source of the well documented 10x gain in specific activity that NSTFC demonstrates over conventional dispersed Pt/Carbon electrocatalysts. An expected outcome of this subtask will be an understanding of the most important material parameters for obtaining further gains in NSTF electrocatalyst specific activity.

Subtask 1.3 New multi-element catalysts to increase activity and reduce impedance

The purpose of this subtask is to obtain further increases in the NSTF catalyst specific activity (A/cm^2-Pt) for ORR by fabrication, characterization and screening of new Pt alloys. The approach will use well established methods at 3M and its collaborators for rapid throughput fabrication and characterization of new multi-element alloy catalyst compositions and constructions. An expected outcome of this subtask is a further increase in stable alloy specific activity by 50% or more over the current best PtCoMn ternary.

Future Work: FY07 and FY08 (cont.)

Subtask 2.1 NSTF catalyst stabilization against dissolution

The purpose of this subtask is to down-select the new catalyst compositions from Task 1 for improved stability against Pt corrosion at high potentials, high temperatures or under conditions of voltage transients or stop/start cycling. The approach will use well-documented methods, by 3M and one of its collaborators, for *ex situ* and *in situ* evaluation of catalyst durability and stability. The outcome will be a subset of the higher performing catalysts which demonstrate, using these tests, increased resistance to Pt dissolution over the current PtCoMn state-of-the-art NSTF electrocatalyst.

Subtask 2.2 NSTF catalyst grain size stabilization

The purpose of this subtask is to fabricate and test new catalyst compositions, many from Task 1, specifically for improved stability of the thin film catalyst grain size. Grain size can change under fuel cell operation due to various grain growth mechanisms, which can adversely affect catalyst activity and durability. As for Subtasks 1.3 and 2.1, this subtask will use high throughput fabrication and screening of the new catalyst compositions by well-established methods at 3M and its subcontractors. The expected outcome is a subset of the compositions from Subtask 2.1 that further exhibit stable grain size.

Future Work: FY07 and FY08 (cont.)

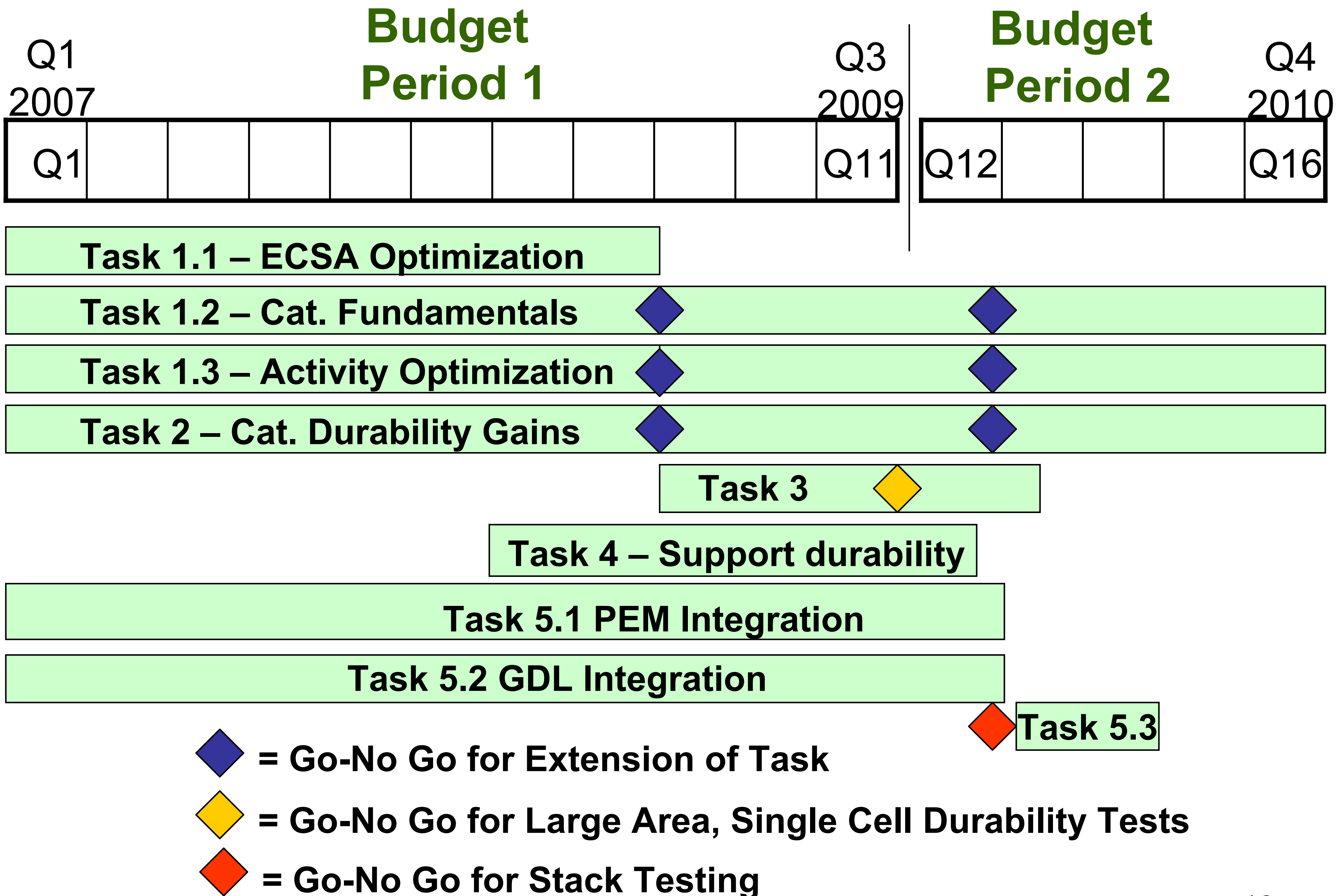
Subtask 5.1 NSTF catalyst / low EW membrane interface

The purpose of this subtask is to optimize the pilot scale fabrication of catalyst coated membrane (CCM) roll-goods using the advanced cathode catalysts and supports from Tasks 1-4 in combination with new, lower equivalent weight 3M membranes developed (outside of this project) to have enhanced durability and water management properties.

Subtask 5.2 Optimized anode and cathode GDL's

The purpose of this subtask is to select the anode and cathode GDL's for best overall water management and high current density performance under automotive conditions, in combination with the CCM's from Subtask 5.1. The approach will include evaluating available roll-good fabricated electrode backing materials having various water proofing and microporous layer coatings. The expected outcome is a GDL configuration that best matches the CCM and stack flow field in which the integrated MEA will be tested for performance and durability.

Future Work and Project Time-line



Project Summary

Relevance: Directly addresses the top three most critical barriers for use of H_2/air MEA's in fuel cell vehicle commercialization.

Approach: Builds on 10 year DOE/3M funded development of NSTF catalyst and associated MEA technology that has already demonstrated order of magnitude gains in activity and accelerated durability.

Technical Accomplishments and Progress:
Project has been formally initiated with all collaborators. Sample materials, sample fabrication processes, characterization methods (*ex situ* and *in situ*) and test protocols are defined for each task for first year.

Technology Transfer/Collaborations:
Catalyst performance and durability advances will be implemented in 3M commercialized MEA's. Strong collaborations with leading university and two national laboratories.

Future Research: Complete all project tasks.

NSTF Catalyst Characteristics vs DOE Targets

Table 3.4.12. Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2010/2015 Stack Targets	3M 2007 Status (volume mfg'd 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 $\leq$ 80°C At operating T > 80°C	Hours	 5000 / 5000 2000 / 5000	**> 3500 hrs** (single cell load cycling, 80°C)	> 5000
Mass Activity (150kPa H_2/O_2 80°C. 100% RH)	A/mg-Pt @ 900 mV	0.44 / 0.44	**0.18 – 0.25** ($\leq$ 0.2 mg/cm^2)	> 0.5
Specific Activity (150 kPa H_2/O_2 at 80°C, 100% RH)	mA/cm^2-Pt @ 900 mV	720 / 720	**2,930** (0.2 mg/cm^2)	> 5000
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

Relevant Prior Work

- 3M/DOE Cooperative Agreement No. DE-FC02-97EE50473
  "High Performance, Low Cost Membrane Electrode Assemblies for PEM Fuel Cells"
- 3M/DOE Cooperative Agreement No. DE-FC02-99EE50582
  "High Performance, Matching PEM Fuel Cell Components and Integrated Pilot Manufacturing Processes"
- 3M/DOE Cooperative Agreement No. DE-FC36-02AL67621
  "Advanced MEA's for Enhanced Operating Conditions"

Recent Publications

- Debe, M. K.; Schmoeckel, A.; Hendricks, S.; Vernstrom, G.; Haugen, G.; Atanasoski, R., *ECS Transactions* **1**(1), 51 (2006).
- Debe, M. K.; Schmoeckel, A. K.; Vernstrom, G. D.; Atanasoski, R., *Journal of Power Sources* **161**, 1002 (2006).
- Steinbach, A.J.; Noda, K.; Debe, M. K., *ECS Transactions* **3**(1) 835 (2006).
- 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).
- Bonakdarpour, A.; Wenzel, J.; Stevens, D. A.; Sheng, S.; Monchesky, T. L.; Lobel, R.; Atanasoski, R. T.; Schmoeckel, A. K.; Vernstrom, G. D.; Debe, M. K.; Dahn, J. R., *Journal of The Electrochemical Society* **152**, A61(2005).