

V.C.1 High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation Applications

Andrew Steinbach (Primary Contact),
Dennis van der Vliet, Andrei Komlev,
Darren Miller, Sean Luopa, Amy Hester,
James Sieracki, Mike Yandrasits, and Matthew Pejsa

3M Company, Fuel Cell Components Program
3M Center, Building 201-2N-19
St. Paul, MN 55144-1000
Phone: (651) 737-0103
Email: ajsteinbach2@mmm.com

DOE Managers

Kathi Epping Martin
Phone: (202) 586-7425
Email: Kathi.Epping@ee.doe.gov

Gregory Kleen
Phone: (720) 356-1672
Email: Gregory.Kleen@go.doe.gov

Technical Advisor

John Kopasz
Phone: (630) 252-7531
Email: kopasz@anl.gov

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Subcontractors:

- Johns Hopkins University, Baltimore, MD
- Michigan Technological University, Houghton, MI
- Lawrence Berkeley National Laboratory, Berkeley, CA
- General Motors Co., Pontiac, MI (in negotiation)
- Argonne National Laboratory, Argonne, IL (collaborator)

Project Start Date: September 1, 2012

Project End Date: August 31, 2015

Overall Objectives

- Demonstrate a durable, low-cost, and high-performance membrane electrode assembly (MEA) for transportation applications, characterized by:
 - total platinum (Pt) group metal loadings of ≤ 0.125 mg/cm² of MEA area
 - performance at rated power of $\geq 1,000$ mW/cm²
 - performance at ¼ power (0.8 V) of ≥ 0.3 A/cm²
 - durability of $\geq 5,000$ hours under cycling conditions
 - Q/ΔT of ≤ 1.45 kW/°C
 - cost of \$5-\$9/kW, projected at high volume

- Improve operational robustness to allow achievement of transient response, cold-startup, and freeze-startup system targets.

Fiscal Year (FY) 2013 Objectives

- Optimize post-processing of 3M Pt₃Ni/nanostructured thin film (NSTF) oxygen reduction reaction (ORR) cathode electrodes for improved MEA activity, durability, and rated-power capability.
- Integrate ultra-low platinum-group metal (PGM) NSTF anode catalysts, NSTF cathode catalysts, and next-generation supported 3M polymer electrolyte membranes (PEMs) for improved MEA performance, durability, and cost.
- Identify key factors influencing NSTF MEA durability, including Pt₃Ni/NSTF electrocatalyst durability and maintenance of rated power.
- Improve operational robustness via anode gas diffusion layer optimization.

Technical Barriers

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project is focused on development of a durable, high-performance, low-cost, and robust MEA for transportation applications. Table 1 lists current project status against the DOE Technical Targets for Membrane Electrode Assemblies (Table 3.4.14) and a subset of Electrocatalyst Targets (Table 3.4.13) from the 2012 Multi-Year Research, Development and Demonstration Plan. The project status values are provided by results from the 2013 (March) Best of Class (BOC) MEA, tested in duplicate and described at the bottom of Table 1. This MEA has achieved 84% of the performance at rated power and 68% of the performance at 0.8 V characteristics, and PGM total content and Q/ΔT are higher than the allowable target by 31 and 5.5%, respectively. An estimate of total MEA cost is not available, but the PGM catalyst cost is estimated to be \$6/kW. Durability with cycling status is not available.

TABLE 1. Status against Technical Targets

Characteristic	Units	2017 Targets	3M 2013 Status
Q/ΔT	kW/°C	1.45	1.53
Cost	\$/kW	9	6 (PGM only @ \$35/g _{Pt})
Durability with cycling	hours	5,000	NA
Performance @ 0.8 V	mA/cm ²	300	203
Performance @ rated power	mW/cm ²	1,000	837
PGM total content (both electrodes)	g/kW (rated)	0.125	0.164
PGM total loading	mg PGM/cm ² electrode area	0.125	0.137

*3M Status with 2013(March) Best of Class MEA:

- 0.02 mg_{PGM}/cm² PtCoMn/NSTF anode, 0.117 mg_{PGM}/cm² Pt₃Ni₇(TREATED)/NSTF cathode, 24μ 825 equivalent weight 3M PEM, 3M 2979 gas diffusion layers, optimized flow fields.
- 90°C, 150 kPa H₂/air, 84°C dewpoints, 2.0/2.5 H₂/air stoichiometry.
- Performance at rated power, Q/ΔT characteristics calculated at 1.24 A/cm², 0.675 V.

NA - not available

FY 2013 Accomplishments

- Demonstrated a 25% increase in rated power output per unit PGM over 2012 pre-project status with the 3M 2013 (March) BOC MEA, directly reducing cost.
- Demonstrated annealed Pt₃Ni₇/NSTF cathode catalyst with ORR mass activity of 0.52 A/mg (30% increase over unannealed), and dealloyed Pt₃Ni₇/NSTF catalyst with peak power of 1 W/cm² at 0.60 V, (41% gain over 2012 status), potentially leading to improved cost, performance at 0.80 V, and performance at rated power.
- Completed multi-month PEM-cathode catalyst integration study which identified two performance-influencing factors caused by PEM-catalyst interactions.
- Demonstrated anode catalyst PGM reduction of 33% from 2012 status, and identified possible pathways for further PGM and cost reduction.
- Improved cold-startup robustness via development of an improved anode gas diffusion layer (GDL), leading to an 88% gain in 40°C performance compared to the 2012 baseline.
- Initiated substantial project to evaluate and improve component and MEA durability.



INTRODUCTION

While significant progress has been made, state-of-the-art PEM fuel cell MEAs utilized in today's prototype automotive traction fuel cell systems continue to suffer from significant limitations due to high cost, insufficient durability, and low robustness to off-nominal operating conditions. State-of-the-art MEAs based on conventional carbon-supported Pt nanoparticle catalysts currently incorporate precious metal loadings which are significantly above those needed to achieve MEA cost targets; performance, durability and/or robustness decrease significantly as loadings are reduced. This project focuses on integration of 3M's state-of-the-art NSTF anode and cathode catalysts with 3M's state-of-the-art PEMs, advanced and low-cost GDLs, and robustness-enhancing interfacial layers. At significantly lower precious metal content, the NSTF catalyst technology platform has several significant demonstrated benefits in performance, durability, and cost over conventional catalysts.

APPROACH

Optimize integration of advanced anode and cathode catalysts with next generation PFSA PEMs, gas diffusion media, and flow fields for best overall MEA performance, durability, robustness, and cost by using a combined experimental and modeling approach.

RESULTS

Significant work has been conducted to improve rated-power performance coincident with anode and cathode PGM loading reduction. Figure 1(A) shows measured polarization curves and Figure 1(B) shows PGM content per unit power output for the pre-project baseline MEA (March 2012), an improved MEA just after project commencement (Sept. 2012), and a further improved March 2013 BOC MEA. Compared to the pre-project baseline MEA, the March 2013 BOC MEA achieved a 49 mV gain in cell voltage at 1.41 A/cm² and reduced PGM content 10%, resulting in a 25% gain in power output per unit PGM at 0.675 V.

We have previously reported many of the unique properties of the highly active Pt₃Ni₇/NSTF ORR cathode catalyst [1], the benefit of annealing for further improved activity [2] and the requirement of dealloying for improved rated power [1]. In current annealing optimization work, mass activity was increased from 0.40 (unannealed) to 0.52 A/mg, a 30% increase, and also identified that the activity gain is sensitive to annealing process variables and correlates with a measured catalyst structure parameter. Development of an optimized dealloying method is occurring at Johns Hopkins University (JHU). After application of a JHU electrochemical dealloying method, the Pt₃Ni₇/NSTF MEA's current density at 0.60 V increased 80% compared to non-dealloyed and 42% compared to 3M best-practice

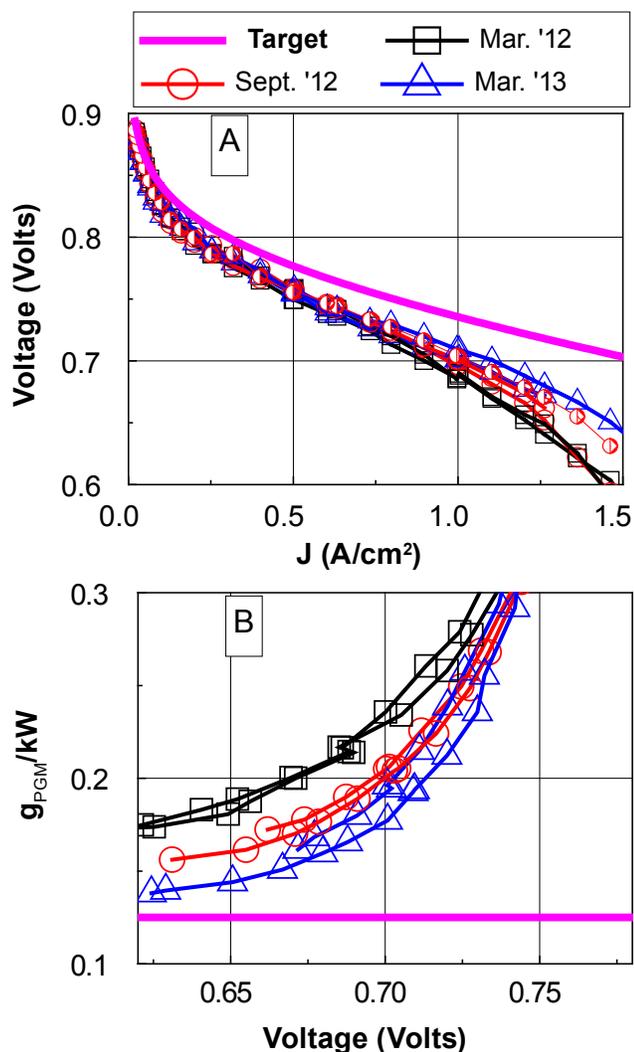


FIGURE 1. Performance Progression during FY 2013 for Integrated Project MEAs. (A): Measured Polarization Curves. (B): PGM Content per Unit Power Output. Conditions: 90/84/84°C Cell/Anode/Cathode, 150/150 kPa H₂/Air, Stoichiometry 2.0/2.5.

dealloying (Figure 2), and exhibited an ORR mass activity of 0.4 A/mg. The JHU electrochemical dealloying method used is not amenable to high volume production, but provides a near-term entitlement result and a structural/compositional target for volume-capable dealloying process development. High-angle annular dark-field scanning transmission electron microscopy characterization of annealed and/or dealloyed materials is occurring at Oak Ridge National Laboratory, and has revealed that a significant portion of the high mass activity of the Pt₃Ni₇/NSTF cathode is due to substantial porosity development during MEA conditioning.

In an integration study, we evaluated the influence of basic PFSA PEM variables (equivalent weight [EW], thickness, support) on performance with MEAs containing either the 2013 (March) BOC cathode or a 0.10 mg_{PGM}/cm²

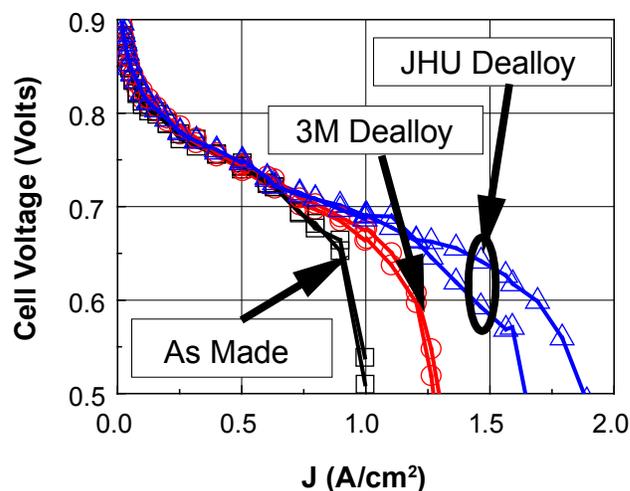


FIGURE 2. Pt₃Ni₇/NSTF Dealloying Development during FY 2013. Conditions: 80/68/68°C Cell/Anode/Cathode, 150/150 kPa H₂/Air, Stoichiometry 2.0/2.5.

PtCoMn/NSTF cathode [3]. PEM integration work with the BOC cathode revealed that the MEA limiting current density decreased as the PEM effective EW increased above ca. 900, and results with the PtCoMn/NSTF cathode suggested that the observed performance variation was consistent with PEM-induced decreased MEA areal-utilization [4].

Significant work to reduce MEA cost via PGM-content minimization of the NSTF hydrogen oxidation reaction anode catalyst revealed that sufficient performance was maintained with as little as 20 μg_{PGM}/cm², and possible further reduction is possible with NSTF support optimization [3]. In a study with Argonne National Laboratory, the surface-specific hydrogen oxidation reaction activity of a fully-conditioned PtCoMn/NSTF anode was found to be ca. 10x higher than Pt/C [5].

Significant improvement in NSTF MEA operational robustness was also demonstrated. Figure 3 shows the performance sensitivity to operating temperature of a representative 3M NSTF MEA was dramatically improved when the baseline anode GDL was replaced with a newly-developed anode GDL. With the new GDL, the current density at 40°C was 88% higher than with the baseline anode GDL. Work conducted at Michigan Technological University (MTU) and Lawrence Berkeley National Laboratory has focused on understanding the mechanism(s) by which the anode GDL influences NSTF MEA low-temperature performance via a combined materials characterization and modeling approach. Characterization of three different 3M anode GDLs, which induce a ca. three-fold variation in NSTF MEA low-temperature performance, is nearly complete and included evaluation of capillary pressure, static and dynamic contact angles, and studies of material structure by X-ray tomography. In addition, MTU has conducted pore network modeling studies to determine the transient thermal and mass

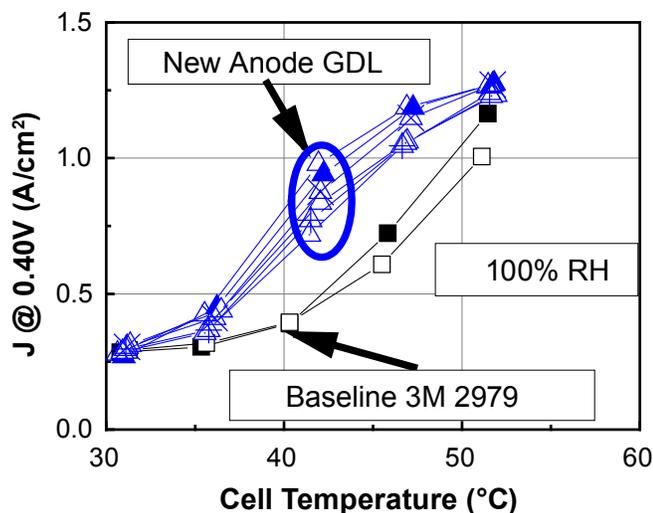


FIGURE 3. Performance Sensitivity to Operating Temperature as a Function of Anode GDL. Conditions: 100/100% Anode/Cathode Relative Humidity (RH), 100/150 kPa H_2 /Air, 800/1800 SCCM, Potentiostatic Hold at 0.40 V.

transport characteristics which occur during cold-startup and sensitivity studies to GDL solid phase distributions, both done in preparation for model incorporation of project material sets.

Extensive evaluation of MEA and component durability has also been conducted. The March 2013 BOC MEA passed the 500-hour MEA chemical durability [6] test with only 2% voltage loss, as compared to the 20% target-allowable loss. Evaluation of the March 2013 BOC MEA's cathode under an electrocatalyst durability test [6] indicated a severe 66% loss in mass activity, larger than the allowable 40% target and also much larger than the 38% loss exhibited by our previous baseline PtCoMn/NSTF cathode [7]. Substantial efforts were also initiated to improve the maintenance of MEA rated-power performance after the MEA is degraded by load cycling, starting with experiments aimed at mechanism determination via sensitivity studies. We have confirmed strong sensitivities to load cycle operating temperature, PFSA PEM type, and NSTF cathode alloy type. Figure 4 shows that as the load cycling temperature increased from 80 to 100°C, the performance loss rate increased modestly at 0.02 A/cm² but substantially at 1.0 A/cm².

CONCLUSIONS AND FUTURE DIRECTIONS

While significant progress has been made, considerable additional work is needed to achieve project performance, cost and durability targets and to improve operational robustness of NSTF MEAs. Primary future directions include:

- Continue cathode annealing and dealloying development for further performance improvement and PGM reduction, with a significant focus on scalable dealloying processes.

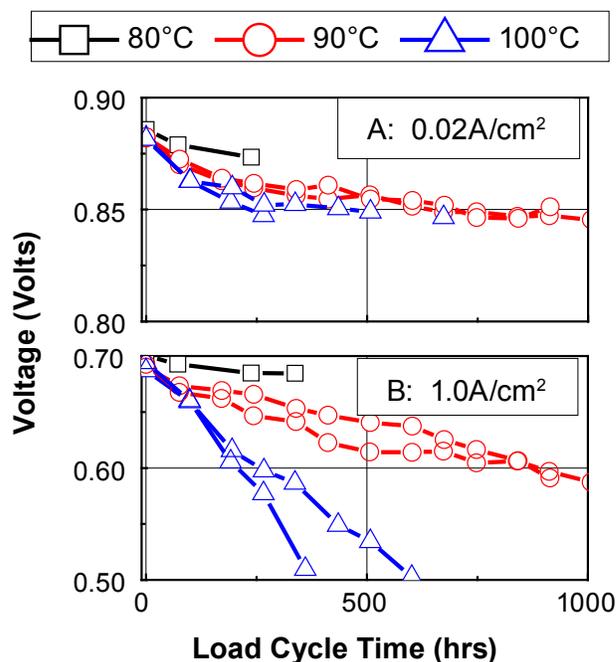


FIGURE 4. Influence of Load Cycle Operating Temperature on MEA Performance Durability. MEA Construction: 0.05/0.15 mg_{PGM}/cm² PtCoMn/NSTF Anode/Cathode, 3M 24μ 825EW PEM, and 3M 2979 GDLs. Performance Check Conditions: 80/68/68°C Cell/Anode/Cathode, 150/150 kPa H_2 /Air, Stoichiometry 2.0/2.5. (A) 0.02 A/cm² and (B) 1.0 A/cm².

- Increase focus towards improving NSTF MEA operational robustness, including materials optimization, characterization, and modeling of the anode GDL.
- Develop mechanistic understanding of rated-power degradation via continued sensitivity and diagnostic studies, followed by materials-based mitigation development.
- Improve the 2013 BOC MEA cathode electrocatalyst durability via evaluation of various proprietary approaches (developed outside this project).

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Andrew Steinbach, Project Kickoff Presentation to DOE, Sept. 2012, St. Paul, MN.
2. X. Wang, R.K. Ahluwalia, and A.J. Steinbach, "Kinetics of Hydrogen Oxidation and Hydrogen Evolution Reactions on Nanostructured Thin-Film Platinum Alloy Catalyst", *J. Electrochem. Soc.*, **160**(3) F251-F261 (2013).
3. Project Update Presentation to DOE, Feb. 2013, Golden, CO.
4. Andrew Steinbach, "High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation Applications", Presentation FC104, 2013 DOE Annual Merit Review, May 2013, Washington, D.C.

REFERENCES

1. Debe et al., “Extraordinary Oxygen Reduction Activity of Pt₃Ni,” *J. Electrochem. Soc.*, **158** B910 (2011).
2. Mark K. Debe, Presentation FC001, 2011 Annual Merit Review, DOE Hydrogen and Fuel Cell Vehicles Technology Programs, May 2011, Washington, D.C.
3. Andrew J. Steinbach, Presentation FC104, 2013 Annual Merit Review, DOE Hydrogen and Fuel Cell Vehicles Technology Programs, May 2013, Washington, D.C.
4. Steinbach et al., “Polymer Electrolyte Membrane Fuel Cell Active Area Utilization Dependence on Relative Humidity Measured via AC Impedance High Frequency Resistance”, *ECS Trans.*, Submitted.
5. Wang et al., “Kinetics of Hydrogen Oxidation and Hydrogen Evolution Reactions on a Nanostructured Thin-Film Platinum Alloy Catalyst”, *J. Electrochem. Soc.*, **160**(3) F251 (2013).
6. U.S. Drive Partnership, Fuel Cell Technical Team, “Cell Component Accelerated Stress Test and Polarization Curve Protocols for Polymer Electrolyte Membrane Fuel Cells”, Rev. Dec. 16th, 2010. http://www.uscar.org/commands/files_download.php?files_id=267.
7. Mark K. Debe, Presentation FC001, 2012 Annual Merit Review, DOE Hydrogen and Fuel Cell Vehicles Technology Programs, May 2012, Washington, D.C.