

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

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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
- Argonne National Laboratory, Argonne, IL (collaborator)
- Los Alamos National Laboratory, Los Alamos, NM

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 (PGM) 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, and
 - 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) 2014 Objectives

- Improve operational robustness via material optimization, characterization and modeling.
- Optimize post-processing of 3M Pt₃Ni₇ nanostructured thin film (NSTF) oxygen reduction reaction (ORR) cathode electrodes for improved MEA activity, durability, and rated-power capability.
- Integrate ultra-low 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, with a primary focus on maintenance of rated power performance.

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 Multi-Year Research, Development and Demonstration Plan. The project status values are provided by results from the 2014 (March) Best of Class MEA, tested in duplicate and described at the bottom of Table 1. This MEA has achieved 91% of the performance at rated power and 42% of the performance @ 0.8 V characteristics, and PGM total content and Q/ΔT are higher than the allowable target by 3.2 and 5.5%, respectively. An estimate of total MEA cost is not available, but the PGM catalyst cost is estimated to be \$5/kW. Durability with cycling status is not available.

FY 2014 Accomplishments

- Improved NSTF MEA operational robustness via development and integration of a durable, low PGM Pt/C interlayer which provides a 20°C improvement in minimum operating temperature for fast load transients up to 1 A/cm². Confirmed that the primary mechanism by which the anode GDL influences cold-startup

TABLE 1. Status against Technical Targets

Characteristic	Units	2017 Targets	3M 2014 Status*
Q/ΔT	kW/°C	1.45	1.53
Cost	\$/kW	9	5 (PGM only @ \$35/g _{Pt})
Durability with cycling	hours	5,000	Not available
Performance @ 0.8 V	mA/cm ²	300	125
Performance @ rated power	mW/cm ²	1,000	907
Platinum group metal total content (both electrodes)	g/kW (rated)	0.125	0.143
PGM total loading	mg PGM/cm ² electrode area	0.125	0.129

*3M Status with 2014 (March) Best of Class MEA: 0.019 mg_{PGM}/cm² PtCoMn/NSTF anode, 0.110 mg_{PGM}/cm² Pt₃Ni₇(TREATED)/NSTF cathode, 20μ 825 equivalent weight (EW) 3M PEM, 3M 2979 gas diffusion layers (GDLs), optimized flow fields. 90°C, 150 kPa H₂/air, 84°C dewpoints, 2.0/2.5 H₂/air stoichiometry. Performance @ rated power, Q/ΔT characteristics calculated at 1.34 A/cm², 0.675 V.

capability of NSTF MEAs is its ability to influence MEA water balance.

- Developed chemical dealloying method for Pt₃Ni₇/NSTF cathodes which results in a 20% increase in MEA limiting current density over the baseline dealloying method. Demonstrated a 43% increase in rated power output per unit PGM (0.675 V) over 2012 pre-project status with the 3M 2014 (March) Best of Class MEA, directly reducing cost.
- Developed hypothesis that rated power degradation of NSTF MEA is most likely caused by generation of perfluorosulfonic acid (PFSA) PEM decomposition products which appear to irreversibly adsorb to the cathode electrode, leading to decreased ORR activity and electrode utilization.



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

One challenge of NSTF electrode MEA integration into automotive stacks has been its higher performance sensitivity

to operating conditions than traditional thick dispersed electrode MEAs, especially at cool and wet conditions applicable to automotive startup. In previous work, we had shown that variation of the anode GDL can have an extraordinarily large positive influence [1], but the mechanism was unclear. This year, through combined materials characterization and modeling studies at 3M, Michigan Technological University and Lawrence Berkeley National Laboratory, several relevant factors have been identified. Spatial variation in the anode backing fiber density appears beneficial, possibly leading to higher limiting liquid water flux under cold-startup conditions (Figure 1A), higher retention of gas phase permeability (Figure 1B), both likely due to formation of preferential liquid/gas transport pathways and/or decreased water droplet detachment force [2], which ultimately results in decreased water content within the cathode electrode [3]. Based on these findings, anode backing optimization experiments with Freudenberg FCCT are currently in progress. In addition, we have also previously reported that integration of an interlayer (low-loaded Pt/C electrode between the NSTF cathode electrode and cathode GDL) improves NSTF MEAs' ability to rapidly transition from low- to high-current density under cool and wet operating conditions. This year, interlayer optimization studies have significantly improved the load transient capability at low temperature (passes at 30°C cell temperature with interlayer vs. 50°C without interlayer), with <0.02mg_{PGM}/cm² of interlayer loading [4]. The interlayer performance benefit has proven to be relatively durable. After 3,000 accelerated stress test voltage cycles up to 1.2 V, the mass activity was unchanged, the H₂/Air performance increased, and the load transient response improved (Figure 2).

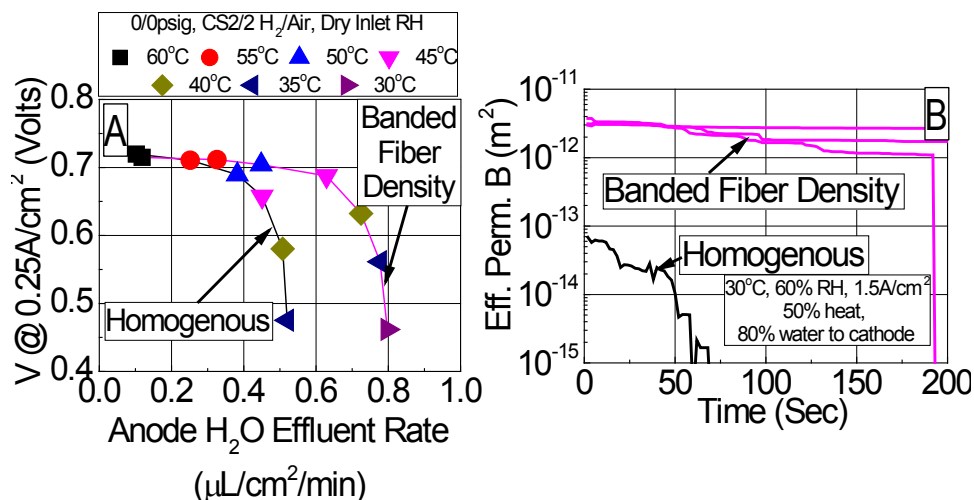


FIGURE 1. Influence of Anode GDL on Measured MEA Water Balance (A) and Modeled Gas Permeability (B) Under Cold-Startup Relevant Conditions

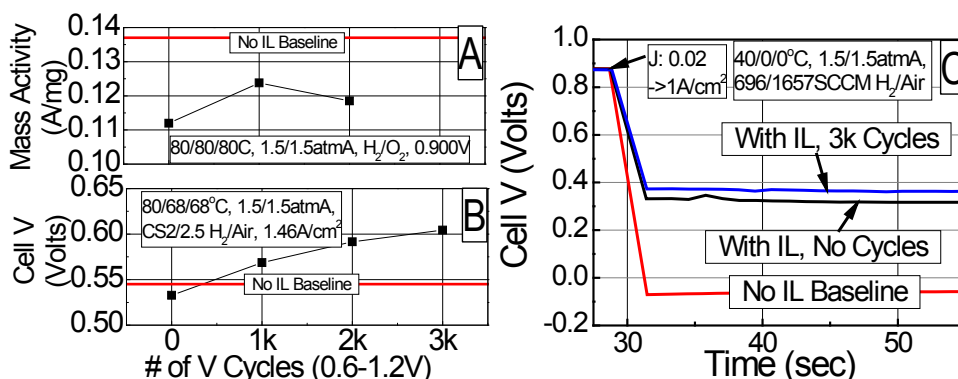


FIGURE 2. Performance of MEAs with Interim Downselected Cathode Interlayer as a Function of Number of Accelerated Stress Test Voltage Cycles (A): ORR Mass Activity. (B): Cell Voltage at 1.46 A/cm², 150 kPa H₂/Air. (C): Stepwise Load Transient from 0.02 to 1.0 A/cm², at 40°C Cell Temperature. Accelerated Stress Test Cycles: 0.6-1.2 V vs. Reference Hydrogen Electrode, 20 mV/s, 70°C Cell Temperature.

Work has continued this year to improve the activity and rated power capability of Pt₃Ni₇/NSTF ORR cathode catalysts, through optimization of annealing and dealloying methods. Over the past year, development of an improved dealloying method at Johns Hopkins University has resulted in a ca. 20% increase in the H₂/air limiting current density over the baseline method [4]. High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy characterization at Oak Ridge National Laboratory has revealed that the dealloying transforms the Pt₃Ni₇/NSTF surface from NiO_x - to Pt-rich and forms nanoporosity [4]. HAADF STEM has also confirmed that annealing improves the process by which in situ nanoporosity develops during fuel cell operation, leading to 30% higher mass activity [4]. The dealloying development has enabled a significant improvement in rated power coincident with a PGM loading

reduction. Figures 3A and 3B show measured polarization curves and PGM content per unit power output, respectively, for the pre-project baseline MEA (March 2012), the project Best of Class (BOC) MEA from last year (March 2013), and a further improved March 2014 BOC MEA. Compared to the pre-project baseline MEA, the March 2014 BOC MEA achieved a 60 mV gain in cell voltage at 1.41 A/cm² and reduced PGM content 14.5%, resulting in a 43% gain in power output per unit PGM at 0.675 V. Mass activity has been maintained at 0.38 A/mg. In addition, work has also been conducted to develop Pt₃Ni₇/NSTF cathode ORR kinetic and MEA performance models in collaboration with Argonne National Laboratory.

Extensive work has continued towards understanding the key factors which influence the durability of rated power performance with project MEAs. This year, additional

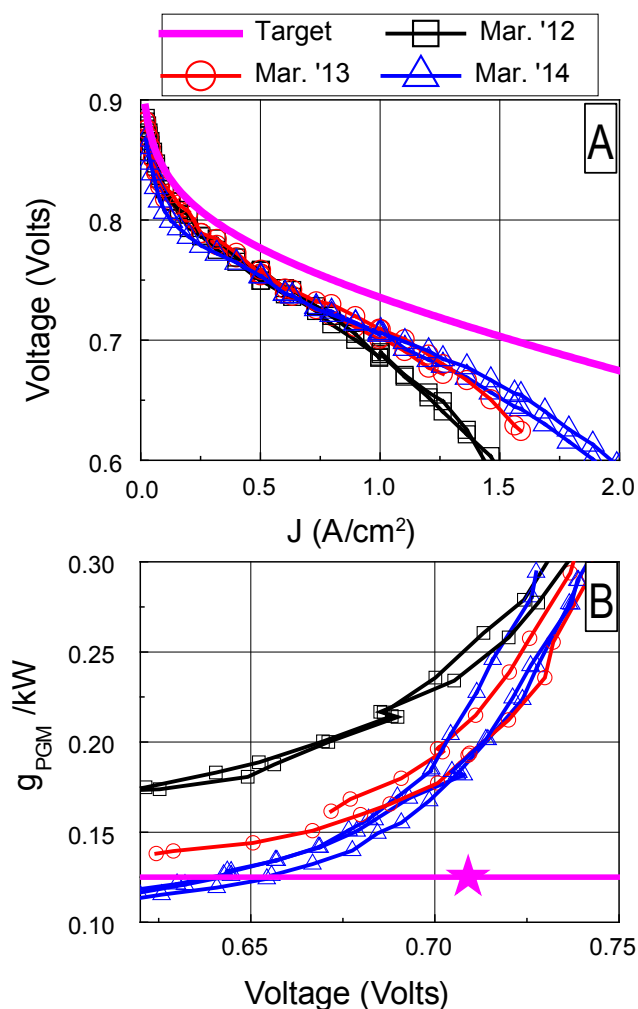


FIGURE 3. Performance Progression over Project for Integrated Project MEAs (A): Measured Polarization Curves. (B): PGM Content per Unit Power Output. Conditions: 90/84/84°C Cell/Anode/Cathode, 150/150 kPa H₂/Air, Stoichiometry 2.0/2.5.

diagnostic experiments have been conducted, efforts have been expanded to include studies at Los Alamos National Laboratory, and a primary hypothesis for the mechanism has been generated. Along with the operating temperature and PFSA EW effects noted last year [1], this year we have shown that presence of an ionomer chemical degradation mitigating agent decreases degradation rates 10x as compared to when the agent was not present in the MEA [4]. Cathode cyclic voltammetry indicates a correlation between performance degradation extent and the degree of cathode contamination by a (likely) anionic contaminant [4]. A correlation was identified between the H₂/Air cell voltage at 1 A/cm² and the cathode ORR activity, where the cell voltage decreases ca. 130 mV per decade of ORR absolute activity loss (Figure 4). With all factors taken into account, our hypothesis is that the loss of rated power performance is due to the (apparently) irreversible adsorption of PFSA PEM decomposition

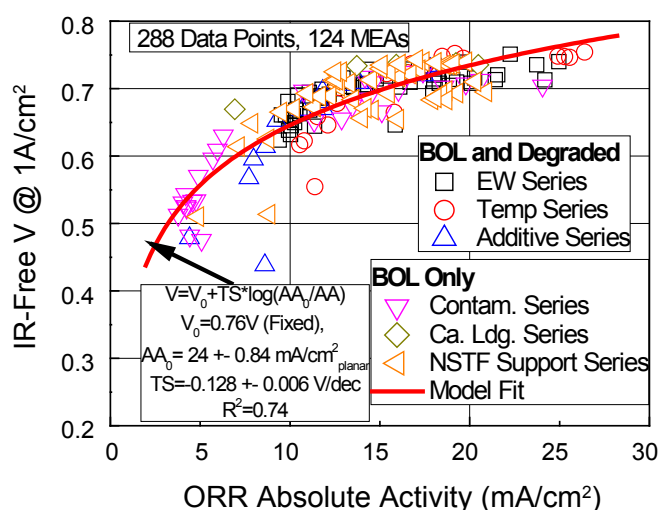


FIGURE 4. Relationship between H₂/Air Performance and ORR Absolute Activity for NSTF MEAs at Beginning of Life or After Degradation Due to Durability Testing—Conditions (H₂/Air): 80/68/68°C Cell/Anode/Cathode, 150/150 kPa H₂/Air, Stoichiometry 2.0/2.5. Conditions (ORR Activity): 80/80/80°C Cell/Anode/Cathode, 150/150 kPa H₂/O₂; After 17.5 minute hold at 0.900 V_{MEAS}.

product(s) on the cathode electrocatalyst, resulting in substantial loss of ORR absolute activity and rated power.

Work has continued to integrate next generation PEMs with NSTF anode and cathode electrodes, including PEMs comprising mechanical supports and new ionomer types. In addition to the PEM-induced MEA areal-utilization losses noted last year [1], a factor was identified this year which resulted in substantial ORR activity and H₂/Air performance reduction with certain supported PFSA PEMs. Through extensive in-situ and ex situ diagnostic experiments, the loss mechanism was identified and the issue was resolved, leading to demonstration of expected performance. Additional work to integrate PEMs based on next generation 3M perfluoroimide acid and alternative PFSA ionomers, as well as the influence of PEM processing, is in progress.

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:

- Demonstrate scale up feasibility of downselected Pt₃Ni₇ dealloying method, and incorporate best practice catalyst annealing for optimal MEA rated power and kinetic performance.
- Continue efforts towards improving NSTF MEA operational robustness, including materials optimization, characterization, and modeling of the anode gas

diffusion layer and further optimization of the cathode interlayer.

- Integrate advanced, thinner supported PEMs to increase performance and durability, and to reduce cost.
- Develop material and operational mitigation approaches to reduce rated-power degradation.

FY 2014 PUBLICATIONS/PRESENTATIONS

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