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

Andrew Steinbach (Primary Contact), Amy Hester, Cemal Duru, Andrei Komlev, Darren Miller, Mike Yandrasits, Andrew Haug, John Abulu, 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:

Dimitrios Papageorgopoulos
Phone: (202) 586-5463
Email: Dimitrios.Papageorgopoulos@ee.doe.gov

Greg Kleen
Phone: (240) 562-1672
Email: Gregory.Kleen@ee.doe.gov

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Subcontractors:

- Johns Hopkins University, Baltimore, MD
- Michigan Technological University, Houghton, MI
- Lawrence Berkeley National Laboratory, Berkeley, CA
- General Motors (GM) 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, 2016

## 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/cm$^2$ of MEA area.
  - Performance at rated power of ≥1,000 mW/cm$^{2.}$
  - Performance at ¼ power (0.8 V) of ≥0.3 A/cm$^{2.}$
  - Durability of ≥5,000 hours under cycling conditions.
  - Q/ΔT of ≤1.45 kW/°C.
  - Cost of $5/kW-$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) 2016 Objectives

- Fabricate project Best of Class (BOC) MEAs and constituent components via pilot-scale production processes.
- Validate performance and operational robustness of pilot scale BOC MEAs in single cell and short stack formats.
- Evaluate BOC MEA performance under wide range of operating conditions to generate data to support performance and cost modeling at Argonne National Laboratory and Strategic Analysis, Inc.

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(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 2015 (September) Best of Class MEA, described at the bottom of Table 1. This MEA has met the DOE 2020 Q/ΔT and performance @ 0.8 V characteristics, is within 11% of the performance at rated power characteristic, and is within 5% of the PGM total loading characteristic. Status of durability with cycling to 10% voltage loss is estimated to be between 656–1,864 h at 0.8 A/cm$^2$, based on a single 3M durability test at 80°C, significantly less than the 5,000-hour target.

## FY 2016 Accomplishments

- Generated all final project BOC components on pilot scale equipment. Resultant BOC MEA, evaluated in single cell at 3M, yielded improved ultimate performance (5% improved specific power [kW/g]) and operational robustness (33% improved current density at 40°C cell temperature) over last year's status.

**TABLE 1.** Status against Technical Targets

| Characteristic | Units | 2020 Targets | 3M 2016 Status* |
|---|---|---|---|
| Q/ΔT | kW/°C | 1.45 | 1.45 |
| Cost | $/kW | 7 | 8.62** |
| Durability with Cycling | hours | 5,000 | 656–1,864 |
| Performance @ 0.8 V | mA/cm$^2$ | 300 | 310 |
| Performance @ Rated Power | mW/cm$^2$ | 1,000 | 891 |
| Platinum Group Metal Total Content (Both Electrodes) | g/kW (rated) | 0.125 | 0.147 |
| Platinum Group Metal Total Loading | mg PGM/cm$^2$ Electrode Area | 0.125 | 0.131 |

*3M Status with 2015 (September) Best of Class MEA: 0.019 $mg_{PGM}/cm^2$ PtCoMn/NSTF anode electrode, 0.096 $mg_{PGM}/cm^2$ $Pt_3Ni_7$ (TREATED)/NSTF + 0.016 $mg_{PGM}/cm^2$ Pt/C interlayer cathode electrode, 14 µm 725 EW 3M supported PEM, 3M "X3"/2979 Anode/Cathode GDLs, "FF2" Flow Fields. Performance assessed at 90°C, 150 kPa $H_2$/air (outlet), 2.0/2.5 $H_2$/air Stoichiometry, 84°C Dewpoints (J > 0.4 A/cm$^2$), 68°C Dewpoints (J < 0.4 A/cm$^2$); rated power defined at 0.692 V, which achieves Q/ΔT = 1.45 kW/°C.

"Best of Class" refers to the currently-determined optimal combination of components. Durability with cycling evaluated in single 50cm$^2$ cell under 3M 80°C load/RH cycle and assessed at 0.8A/cm$^2$, 1.5 atmA $H_2$/air.

**MEA cost estimated by Strategic Analysis, Inc. at 500,000 systems/year volume [1].

PEM – Polymer electrolyte membrane; GDL – Gas diffusion layer; RH – Relative humidity; NSTF – Nanostructured thin film; EW – Equivalent weight

- Conducted extensive evaluation (>200 tests) of BOC MEAs to support generation of performance and cost models at Argonne National Laboratory and Strategic Analysis, Inc. Resultant models predicted 25% higher stack power density and 16.8% lower stack cost as compared to 2015 status.
- Conducted 80°C load/RH cycle durability evaluation of BOC MEAs in 50 cm$^2$ single cell format. Single cell has operated for >3,000 hours with 10 µV/h and 15 µV/h degradation rates at open circuit voltage (OCV) and 0.2 A/cm$^2$, respectively, but time to 10% voltage loss at 0.8 A/cm$^2$ is estimated between 656–1,864 h.
- BOC MEAs were integrated into two 3-cell and one 28-cell rainbow short stacks at General Motors. Resultant performance and operational robustness was substantially below single cell results obtained at 3M and GM. Diagnostic experiments indicated issue was largely due to anode hydrogen oxidation reaction deactivation, and a new anode activation method was developed which is believed to be stack-compatible.

## INTRODUCTION

While significant progress has been made, state-of-the-art proton exchange membrane 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 nanostructured thin film (NSTF) anode and cathode catalysts with 3M's state-of-the-art polymer electrolyte membranes (PEM), 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 perfluosulfonic acid (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

This year, a first focus area was generation of project BOC MEAs on pilot-scale fabrication processes, of sufficient quality and quantity to enable evaluation in short stacks. This included fabrication of catalyst coated membrane (CCM) comprising NSTF anode catalyst, dealloyed PtNi/NSTF cathode catalyst, and 3M 725 EW supported membrane, 3M "X3" anode GDL, and 3M "2979" cathode GDL with type "B" interlayer. More than 30 m of each was produced and validated with multiple lab-scale fuel cell tests. Figure 1 compares the performance and operational robustness of the final project 2015 (September) BOC MEA to the previous 2015 (March) BOC MEA, and Table 2 summarizes the MEA construction and key performance metrics. The September BOC MEA yielded modestly higher performance than the March BOC MEA. Specific power at 0.692 V (which meets the DOE Q/ΔT target of 1.45 kW/°C) increased from 6.5 kW/g to 6.8 kW/g, and performance at 0.80 V increased from 0.304 A/cm$^2$ to 0.310 A/cm$^2$. Figure 1B summarizes performance under a load transient test conducted at several cell temperatures, a measure of operational robustness. The 2015 (September) BOC MEA had similar operational range as the 2015 (March) BOC MEA, but yielded higher cell performance between 40–80°C cell temperature.

Figure 2 summarizes specific power progression over the course of the project at 150, 200, and 250 kPaA $H_2$/air reactant pressures. As compared to the 2012 (March) pre-project baseline MEA, specific power of the final 2015 (September) BOC MEA increased 57% at 150 kPaA, and

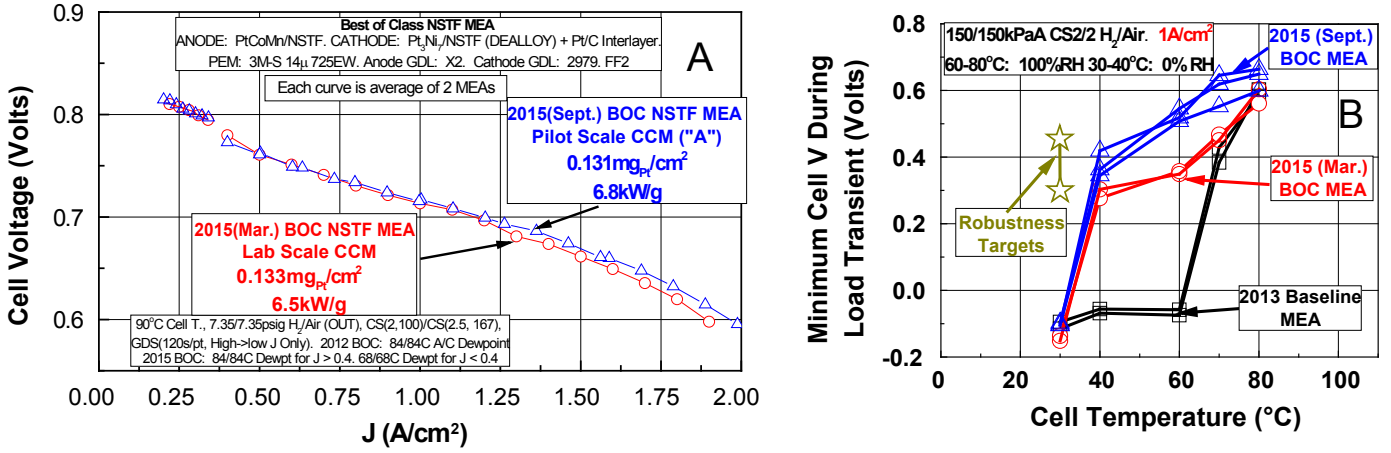


**FIGURE 1.** 2015 (September) Best of Class MEA performance (A) and operational robustness (B)

**TABLE 2.** Best of Class MEA Construction and Performance (90°C, 1.5 atmA $H_2$/air)

| MEA | Anode Catalyst | PEM | Cathode Catalyst | Anode GDL / Cathode GDL+IL | PGM Total Loading (mg/cm$^2$) | Spec. Power @ 0.692 V (kW/g) | Performance @ 0.80 V (A/cm$^2$) |
|---|---|---|---|---|---|---|---|
| 2015 (Mar.) | PtCoMn/ NSTF 15 μg/cm$^2$ | 3M-S 725EW 14 μm w/add. | Dealloyed PtNi/NSTF, 0.103 mg/cm$^2$ | "X2"/ 2979 + "A" (15 μg/cm$^2$) | 0.133 | 6.5 | 0.304 |
| 2015 (Sept.) | PtCoMn/ NSTF 19 μg/cm$^2$ | | Dealloyed PtNi/NSTF, 0.096 mg/cm$^2$ | "X3"/ 2979 + "B" (16 μg/cm$^2$) | 0.131 | 6.8 | 0.310 |

IL – Ionic liquid; w/ – With

the DOE target of 8 kW/g was exceeded when operated with 200 kPaA reactant pressures or higher.

The 2015 (September) BOC MEA was evaluated for performance sensitivity to a wide range of operating conditions to generate datasets to be used for performance and cost modeling. Tests were conducted on an MEA with a 5 cm$^2$ active area in a 50 cm$^2$ test cell with relatively high reactant flows, allowing operation in "differential" mode. Figure 3 summarizes polarization curve performance as a function of cathode oxygen concentration, reactant total pressure, cell temperature, and reactant relative humidity. Performance sensitivity to the above operational variables were largely as expected, and the limiting current density at 80°C, 1.5 atmA $H_2$/air approached 3 A/cm$^2$. The resultant dataset was provided to Argonne National Laboratory and Strategic Analysis, Inc. for performance and cost modeling. The model analysis indicated that as compared to 2015 status, the power density increased 25% and stack cost was decreased by $4.32/kW, a decrease of 16.8% [2].

2015 (September) BOC MEAs were evaluated for durability under a 3M load/RH cycle test conducted at 80°C cell temperature and 1.5 atmA $H_2$/air reactant pressures. Three 50-cm$^2$ MEAs were evaluated. Two MEAs completed <200 h prior to unanticipated or uncontrolled shutdowns due to facility issues, after which performance was irreversibly

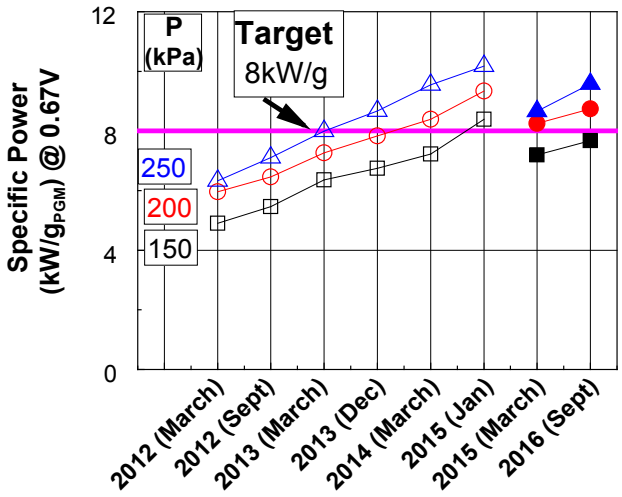


**FIGURE 2.** Best of Class MEA specific power progression over project

changed and testing was halted. The remaining MEA completed over 3,000 h of testing. Figure 4 summarizes the $H_2$/air performance and cathode $F^-$ emission rates of the remaining MEA, and the timing of all shutdowns (controlled and uncontrolled). Performance change over time is due

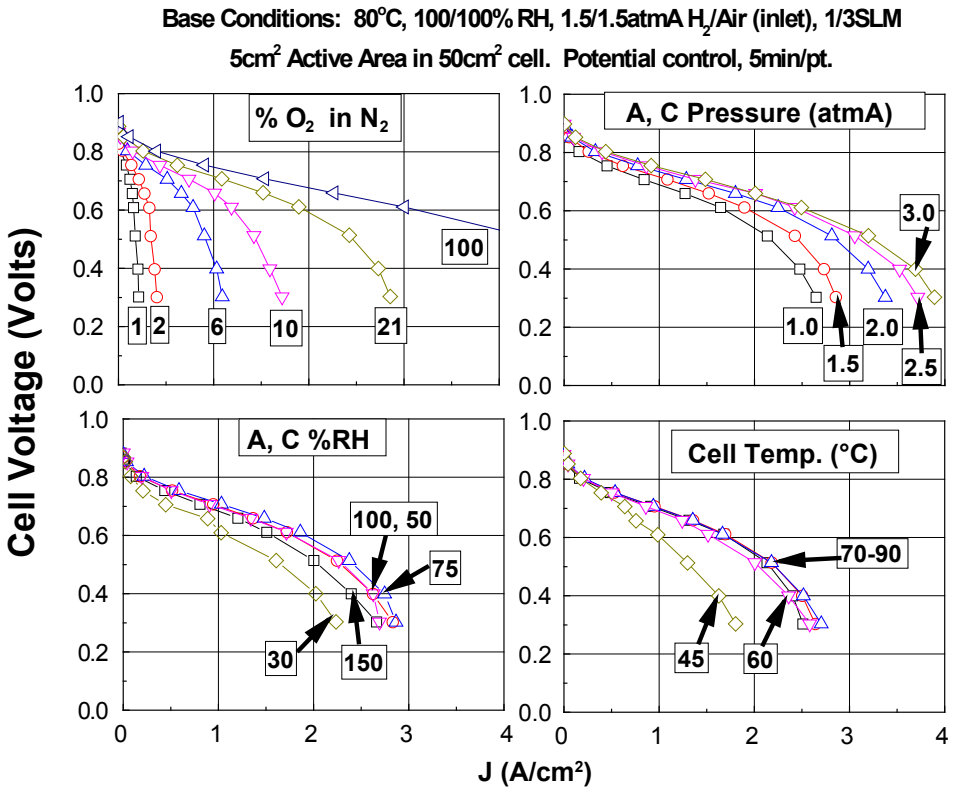


**FIGURE 3.** 2015 (September) Best of Class MEA performance sensitivity testing in 5 $cm^2$ differential cell format

to both reversible and irreversible loss factors and due to partial recoveries consistent with shutdowns. The cell voltage at OCV and 0.2 A/$cm^2$ was relatively steady with decay rates of -9.7 ± 0.4 µV/h and -15.2 ± 0.4 µV/h, respectively, estimated by linear regression fits. Performance at 0.8 A/$cm^2$ decreased at a higher rate than at lower current densities. After a shutdown at 656 h of operation, performance decreased 53 mV as compared to beginning of life (-81 µV/h average) and after a shutdown at 1,864 h of operation, total performance loss was 88 mV (-47 µV/h average). 10% voltage loss at 0.8 A/$cm^2$ (70 mV) was estimated to occur between 656 h and 1,864 h, or 13–37% of the 5,000-hour DOE 2020 target.

Based on previous project work, two key performance degradation modes with BOC NSTF MEAs are expected. The first performance degradation mode is further dealloying of the PtNi/NSTF cathode catalyst, leading to reduced mass activity and rated power loss due to $Ni^{2+}$ contamination of the PFSA PEM. A second primary degradation mode is deactivation of the cathode catalyst due to PFSA decomposition, which correlates to $F^-$ emission rate and rated power loss [2]. Analysis of the first degradation mode may occur once testing is complete, while the second degradation mode is assessable by cathode $F^-$ emission. Figure 4 shows that cathode $F^-$ emission was low and relatively constant over the period of measurement, averaging 7.3 ± 1.8 ng/$cm^2$/h

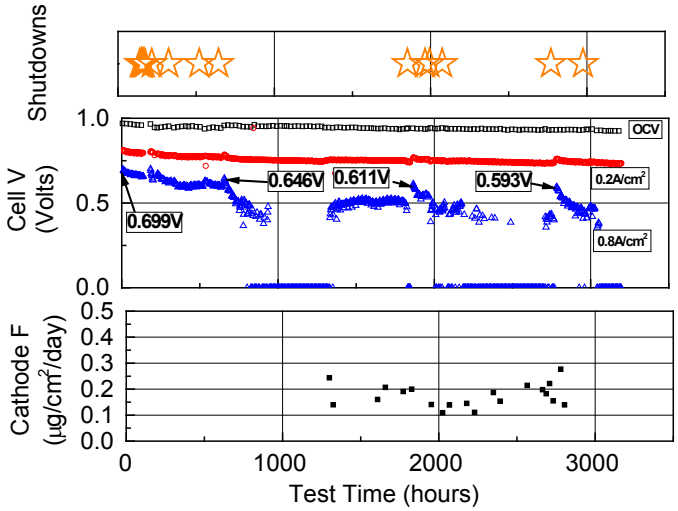


**FIGURE 4.** 2015 (September) Best of Class MEA performance during 3M load/RH cycling testing, conducted at 80°C cell temperature and 1.5/1.5 atmA $H_2$/air

which was largely within expected values and consistent with the observed performance decay.

Pilot scale baseline and project BOC MEAs were provided to GM for evaluation for performance and

operational robustness in automotive short stacks. Integration work consisted of numerous 50 $cm^2$ single cells, two 3-cell stacks, and one 28-cell rainbow stack. Figure 5A summarizes performance of a 3M baseline MEA and 3M BOC MEAs, relative to a GM baseline MEA. Performance of the 3M MEAs was substantially below expectation, based on single cell results. Figure 5B summarizes performance of the MEAs under load transient testing, a measure of operational robustness. The BOC MEAs failed under this testing, as indicated by a negative cell voltage at 1 $A/cm^2$, whereas all other MEAs passed, including GM baseline MEAs and other NSTF MEAs.

During this work, it was determined that in single cells, the 2015 (September) BOC MEAs require extensive hours of conditioning (>100 h) to achieve expected performance and robustness, and the conditioning method used in single cells is difficult to implement at stack level. Figure 6 shows that $H_2$/air performance between 30–90°C cell temperature is substantially improved after activation of the MEA anode in single cell. A substantial fraction of the relatively low BOC MEA performance and operational robustness in short stack was attributed to insufficient anode conditioning, caused by incompatibility of the single cell method with short stack operation. This strong requirement for substantial anode activation is likely a consequence of contamination

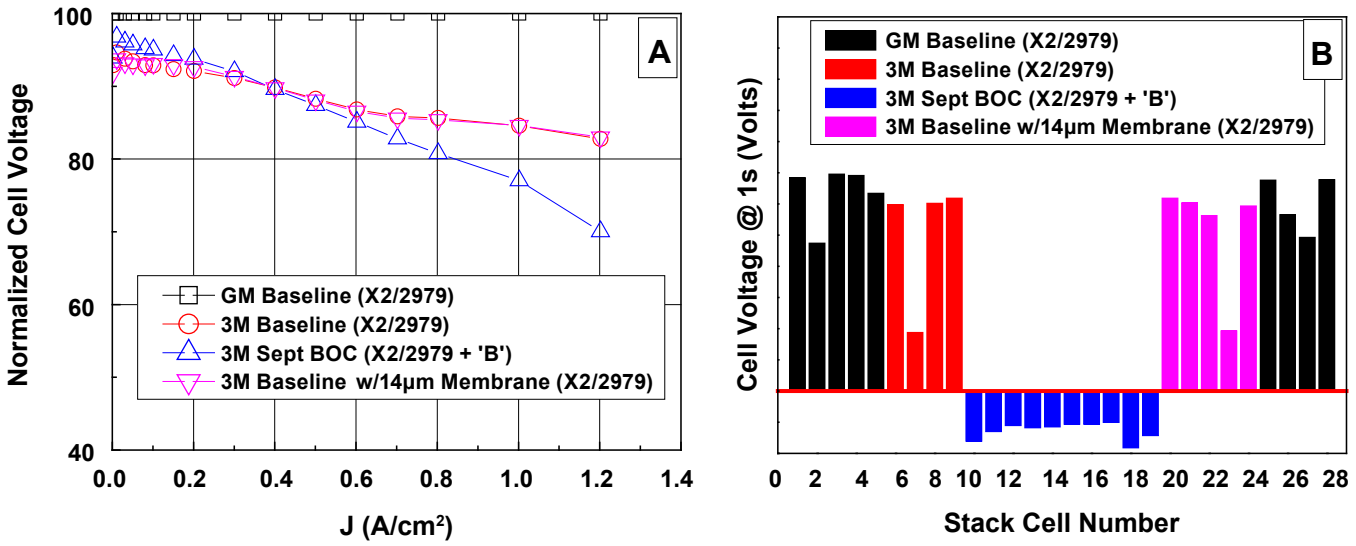


**FIGURE 5.** Relative performance and operational robustness of 2015 (September) BOC MEAs, 3M baseline MEA, and GM baseline MEA in 28-cell rainbow short stack

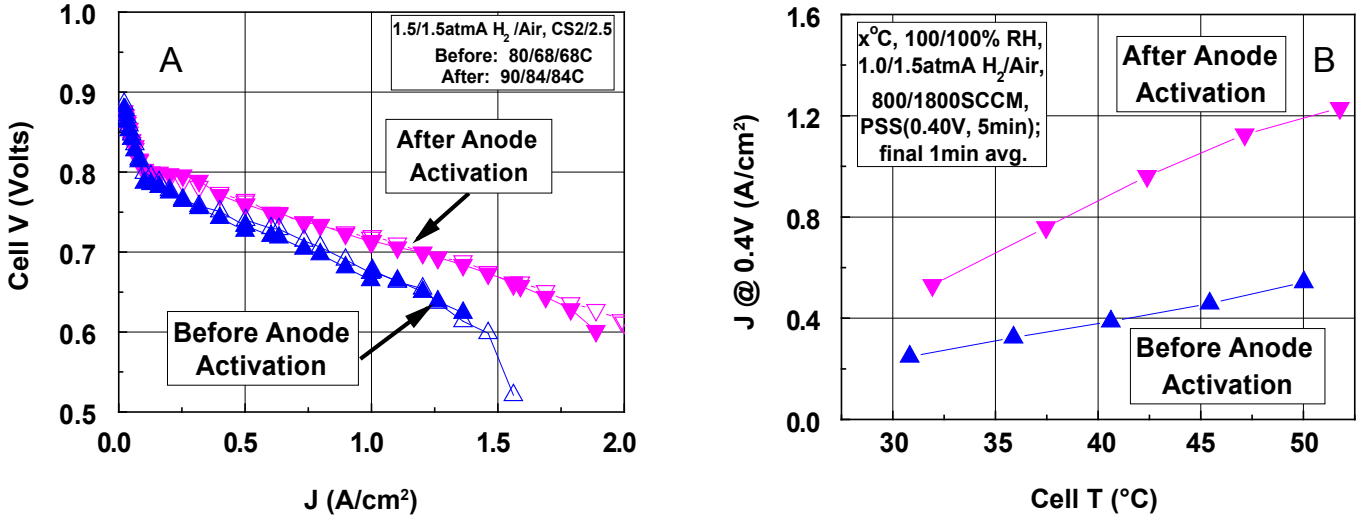


**FIGURE 6.** Impact of anode electrode conditioning on $H_2$/air rated power performance (A) and operational robustness (B)

of the low-loading (0.02 $mg_{Pt}/cm^2$), low specific area (<20 $m^2/g$) electrode. Work to develop a robust, stack-friendly conditioning method has been conducted at both 3M and GM and is planned to be implemented in short stack testing to occur over the remainder of the project.

## CONCLUSIONS AND FUTURE DIRECTIONS

Significant progress has been made towards improvement of NSTF MEA performance, cost and operational robustness, and all but one relevant DOE 2020 targets have been reached or substantially approached. High performance, low cost, operationally robust MEAs have been fabricated via continuous, scalable pilot processes, indicative of feasibility of several project approaches. Key future work within this project is implementation of improved BOC MEA activation methods at short stack scale and to allow demonstration of anticipated performance and operational robustness.

Development of NSTF MEAs with improved rated power durability and activation will continue beyond the end of this project. Durability of rated power performance remains a primary challenge, but factors which cause this degradation mode are now reasonably understood and will require new material development to first partially, then fully mitigate. A second primary concern is the long and complex activation required for activation of ultra-low loading electrodes to achieve full performance and robustness. While some factors are understood, significant future work is needed to implement improved operational and material solutions.

## FY 2016 PUBLICATIONS/PRESENTATIONS

**1.** A.J. Steinbach, "Challenges and Opportunities with 3M Nanostructured Thin Film (NSTF) Ultra-low PGM ORR Electrocatalysts," Challenges towards zero platinum for oxygen reduction, September 15, 2015, Le Grande Motte, France; *invited*.

**2.** A.J. Steinbach, D.F. van der Vliet, A.E. Hester, J. Erlebacher, C. Duru, I. Davy, M. Kuznia, and D.A. Cullen, "Recent Progress in Nanostructured Thin Film (NSTF) ORR Electrocatalyst Development for PEM Fuel Cells," 228th Meeting of the Electrochemical Society, October 13, 2015, Phoenix, AZ USA; *invited*.

**3.** A.J. Steinbach, D.F. van der Vliet, A.E. Hester, J. Erlebacher, C. Duru, I. Davy, M. Kuznia, and D. A. Cullen, "Recent Progress in Nanostructured Thin Film (NSTF) ORR Electrocatalyst Development for PEM Fuel Cells," *ECS Trans.* 2015 **69**(17): 291–301.

**4.** I.V. Zenyuk, E.F. Médici, J.S. Allen, and A.Z. Weber, "Coupling Continuum and Pore- Network Models in Polymer-Electrolyte Fuel Cells," European Fuel Cell 2015 – Piero Lunghi Conference, Naples, December 16–18, 2015.

**5.** A.J. Steinbach, "High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation Applications," Presentation to USCAR Fuel Cell Tech Team, February 17, 2016.

**6.** R.K. Ahluwalia, X. Wang, and A.J. Steinbach, "Performance of Advanced Automotive Fuel Cell Systems with Heat Rejection Constraint," *J. Power Sources* **309** 178–191 (2016).

**7.** E. Medici, I.V. Zenyuk, D.Y. Parkinson, A.Z. Weber, J. Allen "Understanding Water Transport in Polymer-Electrolyte Fuel Cells Using Coupled Continuum and Pore-Network Models," *Fuel Cells* (2016). DOI 10.1002/fuce.201500213.

**8.** E.F. Medici and J.S. Allen, "A Quantitative Technique to Compare Experimental Observations and Numerical Simulations of Percolation in Thin Porous Materials," *Transport in Porous Media* (2016). DOI 10.1007/s11242-016-0672-4.

## REFERENCES

**1.** B. James, Presentation FC018, 2016 U.S. Department of Energy Hydrogen and Fuel Cells Annual Merit Review, June 2016, Washington, D.C.

**2.** R.K. Ahluwalia, Presentation FC017, 2016 U.S. Department of Energy Hydrogen and Fuel Cells Annual Merit Review, June 2016, Washington, D.C.