

V.C.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 (MTU), Houghton, MI
- Lawrence Berkeley National Laboratory (LBNL), 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: February 29, 2016

Overall Objectives

- Demonstrate a durable, low-cost, and high performance membrane electrode assembly for transportation applications, characterized by:
 - Total platinum (Pt) group metal loadings of ≤ 0.125 mg/cm² of membrane electrode assembly (MEA) area
 - Performance at rated power of $\geq 1,000$ mW/cm²
 - Performance at $\frac{1}{4}$ power (0.8 V) of ≥ 0.3 A/cm²
 - Durability of $\geq 5,000$ hours under cycling conditions
 - Q/ ΔT of ≤ 1.45 kW/ $^{\circ}$ 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) 2015 Objectives

- Improve operational robustness via material optimization, characterization, and modeling
- Optimize post-processing of 3M Pt₃Ni₇/NSTF oxygen reduction reaction (ORR) cathode electrodes for improved MEA activity, durability, and rated-power capability
- Integrate ultra-low platinum group metal (PGM) nanostructured thin film (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

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 MEAs (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 (March) Best of Class (BOC) MEA, tested in duplicate and described at the bottom of Table 1. This MEA has achieved the DOE 2020 Q/ ΔT and performance at 0.8 V characteristics, and is within 15% of the performance at rated power and 7% of the PGM total loading characteristics. Durability with cycling status under the prescribed protocol is not available, but the MEA does pass the DOE membrane chemical durability test.

TABLE 1. Status against Technical Targets

Characteristic	Units	2020 Targets	3M 2015 Status*
Q/ΔT	kW/°C	1.45	1.45
Cost	\$/kW	7	5 (PGM only @ \$35/g _{Pt})
Durability with cycling	hours	5,000	NA
Performance @ 0.8 V	mA/cm ²	300	304
Performance @ rated power	mW/cm ²	1,000	855
PGM total content (both electrodes)	g/kW (rated)	0.125	0.155
PGM total loading	mg PGM/cm ² electrode area	0.125	0.133

*3M Status with 2015 (March) Best of Class MEA: 0.015 mg_{PGM}/cm² PtCoMn/NSTF anode electrode, 0.102 mg_{PGM}/cm² Pt₃Ni₇(TREATED)/NSTF + 0.015 mg_{PGM}/cm² Pt/C interlayer cathode electrode, 14 μ 725EW 3M supported PEM, 3M "X2"/2979 Anode/Cathode GDLs, Optimized Flow Fields, 90°C, 150 kPa hydrogen/air (outlet), 2.0/2.5 hydrogen/air Stoichiometry 84°C Dewpoints (J > 0.4 A/cm²), 68°C Dewpoints (J < 0.4 A/cm²)
Rated power defined at 0.692 V.
NA – not applicable; GDL – gas diffusion layer

FY 2015 Accomplishments

- Cathode catalyst dealloying method validated in continuous pilot production trials. Trial-to-trial reproducibility was established and 50' continuous roll-good was generated.
- Cathode interlayer with high durability developed that maintains improved NSTF MEA operational robustness and performance after the DOE Support cycle accelerated stress test (AST) and through most of the DOE Electrocatalyst cycle AST.
- MTU's GDL Pore Network Model and LBNL's MEA Continuum models were successfully integrated. The combined model accurately predicts performance temperature sensitivity of NSTF MEAs with different anode gas diffusion layers.
- The 2015 (March) BOC MEA was integrated with improved performance, cost, and operational robustness over 2014 status.
- 3M validated that rated power degradation of NSTF MEAs is caused by perfluorosulfonic acid (PFSA) PEM decomposition. An improved PEM was developed that decreased rated power degradation 30% compared to baseline.



INTRODUCTION

While significant progress has been made, state-of-the-art polymer electrolyte 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 platinum nanoparticle catalysts currently incorporate precious metal loadings that 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

This project optimizes 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

We previously reported an improved chemical dealloying method developed at Johns Hopkins University that resulted in a ca. 20% increase in hydrogen/air limiting current density of Pt₃Ni₇/NSTF cathodes over the pre-project baseline dealloying method [1]. Work this year has focused on process development to optimize dealloying conditions to maximize performance and enable continuous roll processing. Figure 1A shows that after batch dealloying, the platinum mole fraction increases substantially, which depends upon dealloying time and temperature. Resultant MEA mass activity and hydrogen/air performance also vary strongly with treatment conditions, and peak hydrogen/air performance and mass activity occur at ca. 40–42 at% Pt. Dealloyed catalyst generated in continuous process trials showed good agreement between target and actual catalyst composition and very good trial-trial reproducibility (Figure 1B), and hydrogen/air performance was substantially improved over non-dealloyed (Figure 1C).

Historically, one challenge of NSTF 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 backing can have an extraordinarily large positive influence [2], but the mechanism was unclear. Last year, we reported that spatial variation in anode GDL backing carbon paper density was a key material factor enabling improved low

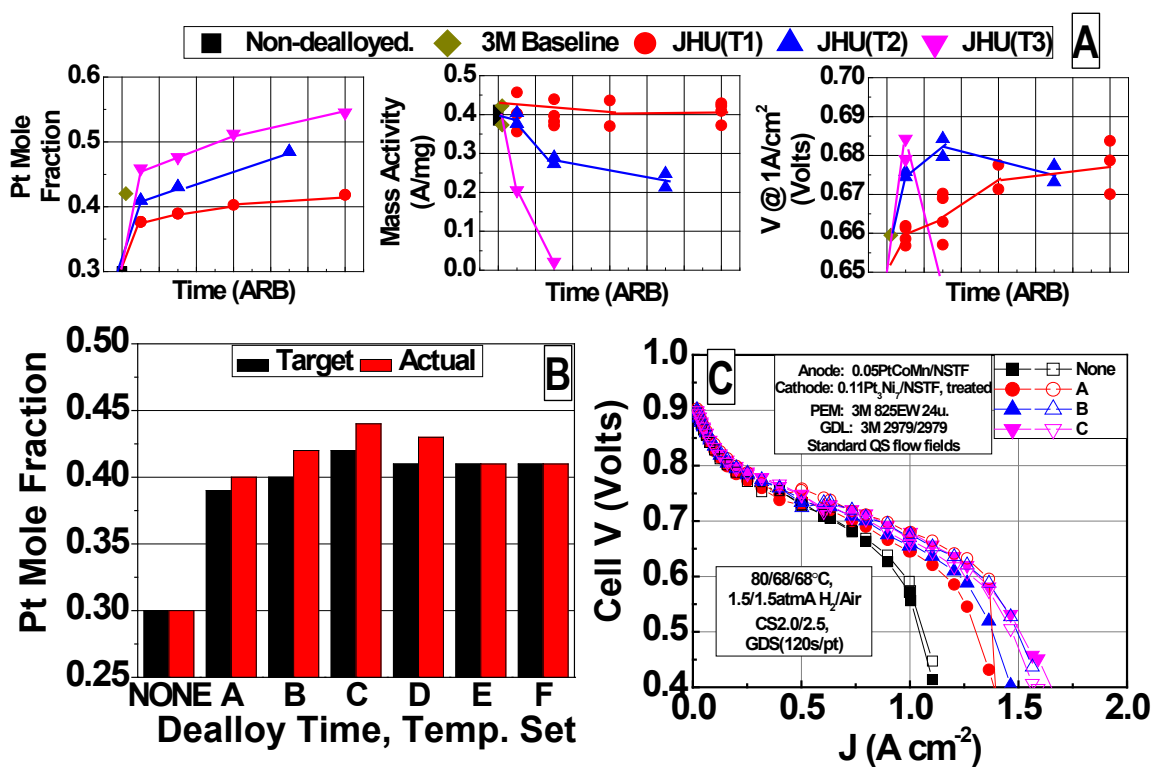


FIGURE 1. Cathode activity, hydrogen/air performance and composition vs. batch dealloy process conditions (A). Continuous dealloying process control (B) and resultant hydrogen/air performance (C).

temperature performance of NSTF MEAs [1]. These so-called “banded” GDLs enabled higher anode liquid water removal rates in MEAs, reducing cathode flooding. Pore network modeling at MTU suggested possibly higher gas and liquid permeability due to preferential liquid water transport in low density regions. This year, X-ray computed tomography studies at LBNL confirmed that as liquid pressure increases, liquid water preferentially fills low density regions while maintaining reduced saturation in the high density region (Figure 2A). Additionally, significant work focused on integration of MTU’s pore network models of 3M GDLs with LBNL’s continuum MEA model, and the resultant combined model accurately predicts NSTF MEA performance sensitivity to temperature with two anode GDL types (Figure 2B).

In addition to the improvements demonstrated with the anode GDL, we have previously shown that integration of a cathode interlayer (low-loaded Pt/C electrode between NSTF cathode and GDL) substantially improves NSTF MEA’s ability to withstand load transients (step increases in current density to 1 A/cm²) under condensing conditions [1]. One concern with the approach is that conventional dispersed Pt/C electrocatalysts may not be sufficiently durable due to well-known degradation modes such as platinum agglomeration and dissolution and carbon corrosion. This year, we have optimized the cathode interlayer for improved durability while maintaining improved operational

robustness demonstrated previously [1]. Figure 3 shows that when an NSTF MEA with the improved interlayer was evaluated under the DOE Support Cycle AST, hydrogen/air performance at rated power improved substantially, mass activity and specific area losses were modest, steady state performance at low temperatures improved substantially, and load transient performance was largely maintained.

MEA integration work this year has focused on incorporation of several improved components towards improved performance, cost, and operational robustness. Figure 4A compares the hydrogen/air performance of the 2015 (March) BOC MEA to the pre-project 2012 BOC MEA. The 2015 BOC MEA incorporates many improved components over 2012 status, including a reduced PGM anode, improved performance, reduced-PGM dealloyed PtNi/NSTF cathode, a higher conductivity mechanically-stabilized 3M PFSA PEM, an optimized anode gas diffusion layer and a cathode interlayer that enable improved operational robustness, and optimized flow fields. The 2015 BOC has substantially improved performance and reduced PGM loading, resulting in a 48% increase in specific power at the DOE Q/ΔT heat rejection target of 1.45 kW/°C. Figure 4B shows that the operational robustness of the 2015 BOC MEA is substantially improved over 2013 status, where the stable operating temperature window for 1 A/cm² operation was increased from 70–80°C to 40–80°C and is within 10°C of targets.

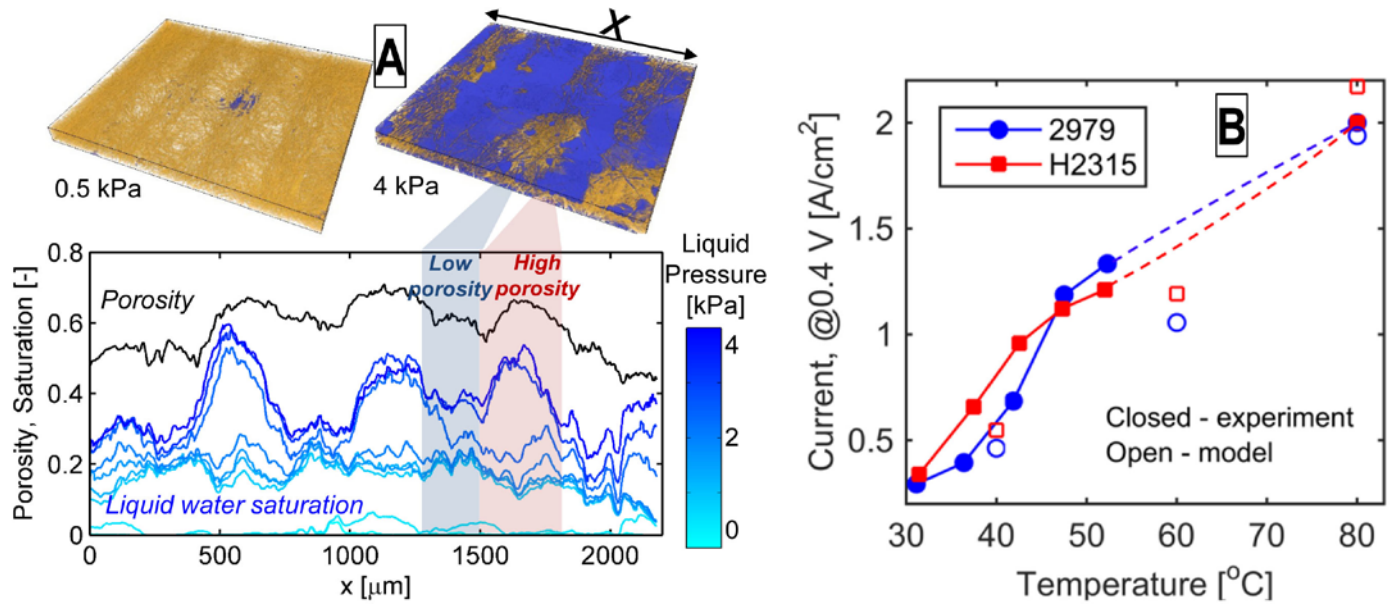


FIGURE 2. X-Ray computed tomography analysis of spatial water saturation in anode GDL (A). Integrated MTU-LBNL model prediction of NSTF MEA temperature sensitivity with two anode GDLs (B).

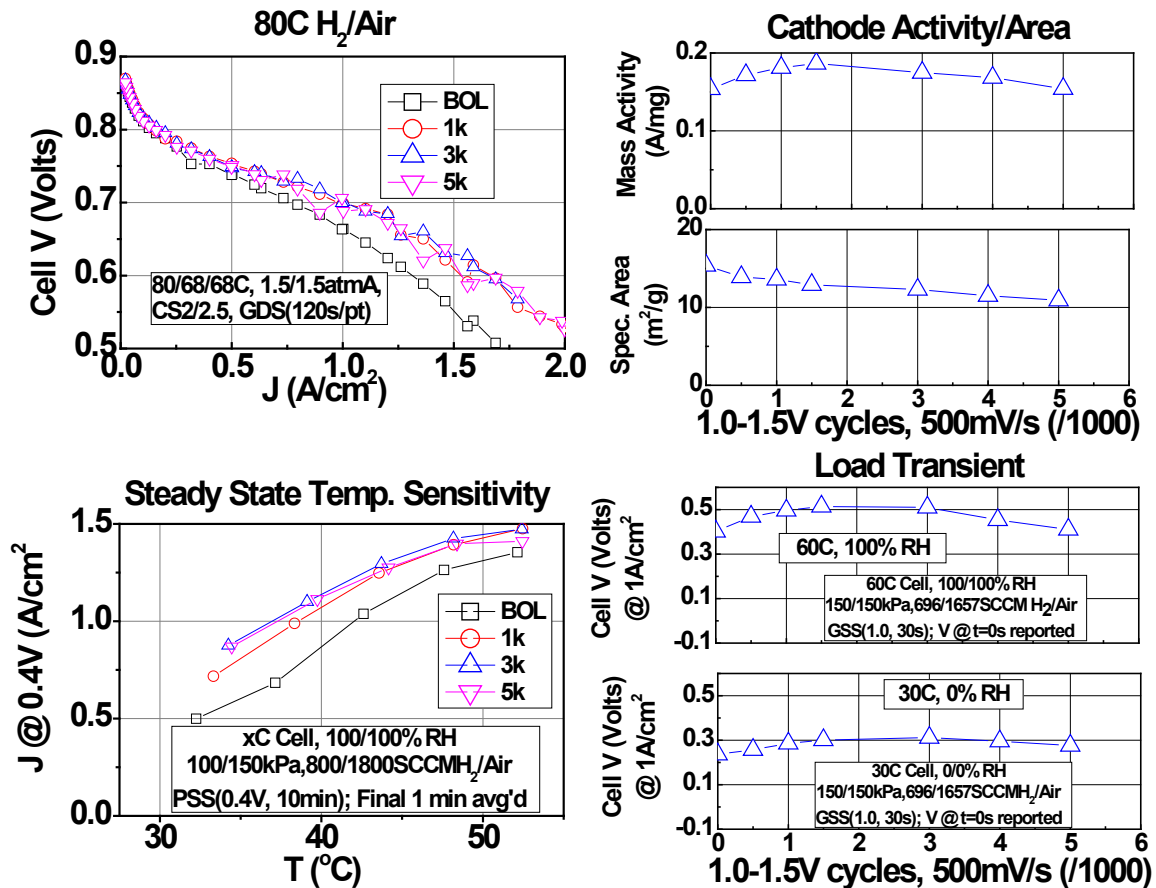


FIGURE 3. Evolution of hydrogen/air performance, cathode activity, and operational robustness of NSTF MEA with cathode interlayer during the DOE Support Cycle AST.

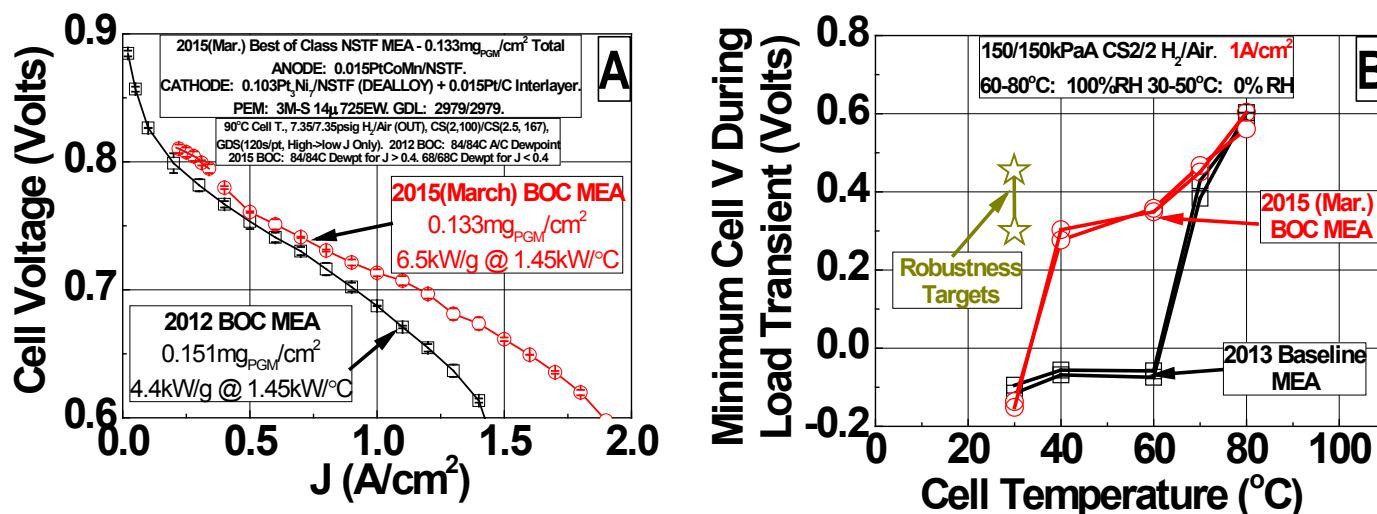


FIGURE 4. 3M NSTF 2015 (March) Best of Class MEA Hydrogen/air performance (A) and operational robustness (B).

Work has continued this year to understand the factors influencing rated power durability of NSTF MEAs, and work has been initiated to improve the durability. Last year, we reported key results and our assessment that rated power degradation was correlated to the loss of ORR absolute activity due to the irreversible adsorption of one or more unidentified PFSA PEM decomposition products [1]. This year, experiments were conducted to validate this hypothesis and to analyze the relationship between performance loss and PEM decomposition. Figure 5A shows that when baseline PtCoMn/NSTF MEAs are held at 90°C cell temperature at different fixed cell voltages, the performance loss rate increases over 3x as cell voltage is decreased from 0.90 to 0.30 V and F^- emission rates increase substantially. We have previously shown that NSTF MEA performance loss at both low and high current density appears to be explained entirely by absolute ORR activity loss [1] and this was found to also be the case here (Figure 5B). The ORR activity loss in this testing was determined to be due to two factors: loss of cathode surface area as a function of test time and loss of cathode specific activity due to PEM decomposition as determined by cumulative F^- generation (Figure 5C). Based on this work, a new experimental 3M PEM was developed that reduced the voltage decay rate by 30% and substantially reduced ORR activity losses (Figure 6).

CONCLUSIONS AND FUTURE DIRECTIONS

Significant progress has been made towards improvement of NSTF MEA performance, cost and operational robustness, and all relevant DOE 2020 targets have been reached or substantially approached. Durability of rated power remains a primary concern, but the confirmed hypothesis linking NSTF MEA rated power loss to PFSA PEM decomposition has provided clear directions towards

improvement, including development of novel PEMs and integration of NSTF cathodes with higher surface area and activity. Primary future directions for the current project include:

- 2015 (March) BOC MEA evaluation in short stacks for performance and operational robustness.
- Development of material and operational mitigation approaches to reduce rated-power degradation.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. A. Kusoglu, C. Blake, F. Allen, A. Crothers, A.Z. Weber, *Understanding Conduction and Structure in PFSA Membranes*, 17th Solid State Protonic Conductors, Seoul, Korea, September 14–19, 2014.
2. A.J. Steinbach, project presentation to USCAR Fuel Cell Tech Team, October 15, 2014, Southfield, MI.
3. V. Konduru, E.F. Medici, and J.S. Allen, *Modeling Thermal Transport in Heterogeneous Porous Media of PEM Fuel Cells Using Pore Network Model*, Trans. of the 226th Electrochemical Society Meeting, October 2014, Cancun, Mexico.
4. A.J. Steinbach and D. van der Vliet, project presentation to DOE, November 4, 2014, St. Paul, MN.
5. I.V. Zenyuk, A. Santamaria, P.K. Das, A. Steinbach, R. Mukundan, R.L. Borup, A.Z. Weber, *Water Management with Thin-Film Catalyst Layers*, CARISMA, South Africa, Dec. 1, 2014.
6. I.V. Zenyuk, D.Y. Parkinson, G. Hwang, A.Z. Weber, *Understanding Water Transport in Compressed Gas Diffusion Layers of Polymer-Electrolyte Fuel Cells Using X-ray Computed Tomography*, 2015 MRS Spring Meeting & Exhibit, April 9, 2015.
7. D.A. Cullen, M. Lopez-Haro, P. Bayle-Guillemaud, L. Guetaz, M.K. Debe, and A.J. Steinbach, *Linking Morphology with Activity in Novel PtNi Nanostructured Thin Film Catalysts*, J. Mat. Chem. A 3 11660, 2015.

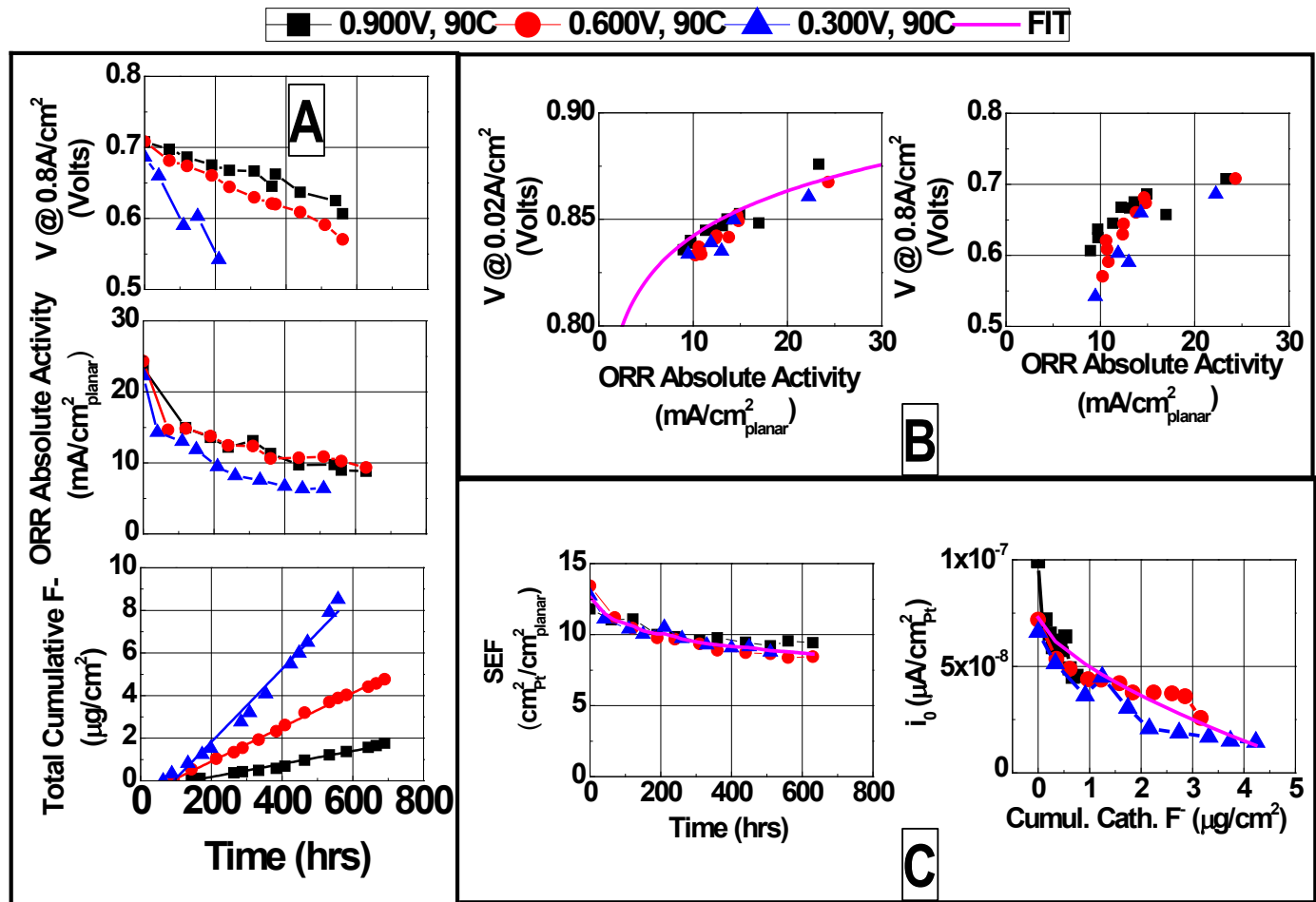


FIGURE 5. Cell voltage, cathode absolute ORR activity, and cumulative F⁻ emission over time vs. cell voltage (A). Hydrogen/air performance loss due to ORR activity loss (B). ORR activity losses due to cathode surface area loss and specific activity loss (C).

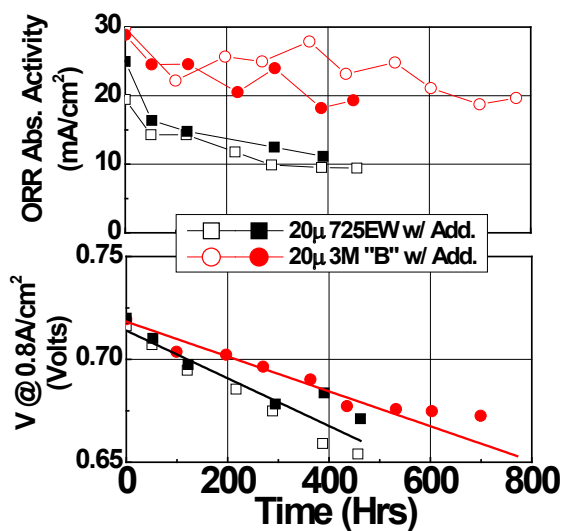


FIGURE 6. Improved ORR activity retention and 30% decrease in cell voltage loss rate with improved experimental 3M PEM "B".

8. I. Zenyuk, E.F. Médecin, J.S. Allen, and A.Z. Weber, *Coupling Continuum and Pore Network Models in Polymer Electrolyte Fuel Cells*, 7th International Conference on Porous Media, May 2015, Padova, Italy.
9. V. Konduru, J.S. Allen, J. Pharaoh, *Multiscale modeling of water transport in porous transport layers (PTL) of PEM fuel cells using combined pore network and finite volume modeling*, 7th International Conference on Porous Media, May 2015, Padova, Italy.
10. A.J. Steinbach, *High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation Applications*, Presentation FC104, 2015 DOE Annual Merit Review, Washington, DC, June 2015.
11. A.J. Steinbach, *High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation Applications*, IEA Annex 34 - Fuel Cells for Transportation, June 24, 2015, Jülich, Germany.
12. R.K. Ahluwalia, X. Wang, and A.J. Steinbach, *Performance of Advanced Automotive Fuel Cell Systems with Heat Rejection Constraint*, J. Power Sources, 2015, submitted.

13. A.J. Steinbach and D. van der Vliet, project presentation to DOE, July 16, 2015, St. Paul, MN.

14. I.V. Zenyuk, E.F. Médiçi, 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.