

V.D.1 Advanced Cathode Catalysts and Supports for PEM Fuel Cells

Mark K. Debe (Primary Contact),
Andrew J. Steinbach, Susan M. Hendricks,
Michael J. Kurkowski, George D. Vernstrom,
Amy E. Hester, Eric Iverson, Sean Luopa,
Paul Kadera, and Radoslav T. Atanasoski

Fuel Cell Components Program, 3M Company
3M Center, Building 201-2N-19
St. Paul, MN 55144-1000
Phone: (651) 736-9563
Email: mkdebel@mmm.com

DOE Managers

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

GO: David Peterson
Phone: (303) 275-4956
Email: David.Peterson@go.doe.gov

Technical Advisor

Thomas Benjamin
Phone: (630) 252-1632
Email: Benjamin@cmt.anl.gov

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Subcontractors and Federally Funded Research and Development Centers:

- Dalhousie University, Halifax, Nova Scotia, Canada (Jeff Dahn, David Stevens)
- Argonne National Laboratory (ANL), Argonne, IL (V. Stamenkovic, Dennis van der Vliet, Nenad Markovic)
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- GM Global Research and Development, Honeoye Falls, NY (E. Thompson, stack testing)

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- Durability sufficient to operate at $>80^{\circ}\text{C}$ for 2,000 hours, $\leq 80^{\circ}\text{C}$ for 5,000 hours, with cycling for transportation applications
- High prospects for 40,000 hours durability under operating conditions for stationary applications
- High volume manufacturability

Technical Barriers

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

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

Technical Targets

This project is focused on improving the performance and durability of the 3M nanostructured thin film (NSTF) roll-to-roll fabricated electrocatalysts and MEAs. Table 1 compares the NSTF catalysts/MEA status as of the second quarter, 2012, with DOE electrocatalyst targets for 2017 updated from Table 3.4.12 of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan. Changes from last year's annual report reflect recent gains in mass activity and performance with post-processed NSTF- Pt_3Ni_7 alloys (quotation marks " Pt_3Ni_7 " imply the exact composition is changed from as-deposited), and accelerated durability test results with NSTF- $\text{Pt}_{68}(\text{CoMn})_{32}$. The MEAs used for the inverse specific power density values listed in the first row, PGM total content, had catalyst loadings of $0.03/0.12 \text{ mg}_{\text{Pt}}/\text{cm}^2$ on the anode and cathode respectively with NSTF- PtNi cathodes fabricated by improved roll-to-roll deposition, de-alloying and annealing processes. These same materials exhibited the improved mass and specific activities listed in Table 1 as measured at General Motors (GM) using both 3M and GM oxygen reduction reaction (ORR) test protocols. The improved 30,000 cycle durability results were obtained with PtCoMn catalysts containing $0.05 \text{ mg}_{\text{Pt}}/\text{cm}^2$ on the anode and $0.15 \text{ mg}_{\text{Pt}}/\text{cm}^2$ on the cathode that were fabricated for full size short stack testing.

Fiscal Year (FY) 2012 Objectives

The objectives of this project continue to be development of a durable, low-cost (both precious group metal [PGM] content and manufacturability), high-performance cathode electrode (catalyst and support), which is fully integrated into a proton exchange membrane electrode assembly (MEA) characterized by:

- Total PGM loading per MEA of $\leq 0.25 \text{ mg}/\text{cm}^2$
- Short-stack specific power density of $\leq 0.3 \text{ g}/\text{kW}$ at rated power

TABLE 1. Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications
(Values in blue are new targets/results this year)

Characteristic	Units	Targets 2017	Status: Values for roll-good CCM w/ 0.15mg _{Pt} /cm ² per MEA or as stated
PGM Total Content	g _{Pt} /kW _e rated in stack	0.125	0.14 - 0.18 g _{Pt} /kW for cell 0.6 < V < 0.65 at 80 °C and 150kPaa to 250 kPaa outlet. Pt ₃ Ni ₇ , 50 cm ² cell w/ 0.15 mg/cm ² total Pt.
PGM Total Loading	mg PGM / cm ² total	0.125	0.15 to 0.20, A+C with PtCoMn alloy 0.15 A+C with Pt/Pt ₃ Ni ₇
Mass Activity (150kPa H ₂ /O ₂ , 80°C, 100% RH, 1050 sec)	A/mg-Pt @ 900 mV, 150kPa O ₂	0.44	0.24 A/mg in 50 cm ² w/ PtCoMn 0.47 – 0.67 A/mg in 50 cm ² with Pt ₃ Ni ₇
Specific Activity (150 kPa H ₂ /O ₂ at 80°C, 100% RH)	mA/cm ² -Pt @ 900 mV	0.720	2.1 for PtCoMn, 0.1mg _{Pt} /cm ² 2.7-3.0 for R2R Pt ₃ Ni ₇ , 0.125 mg _{Pt} /cm ²
Durability: 30,000 cycles 0.6 -1.0V, 50mV/sec, 80/80/80°C, 100kPa, H ₂ /N ₂	- mV at 0.8 A/cm ² -% ECSA loss -% Mass activity	< 30mV < 40% < 40%	10±7mV loss at 0.8 A/cm ² 16±2% loss ECSA, PtCoMn 37±2% loss mass activity
Durability: 1.2 V for 400 hrs. at 80°C, H ₂ /N ₂ , 150kPa, 100% RH	- mV at 1.5 A/cm ² % ECSA loss % Mass activity	< 30mV < 40% < 40%	10 mV loss at 1.5 A/cm ² 10% loss ECSA 10 % loss mass activity
Durability: OCV hold for 500 hrs. 250/200 kPa H ₂ /air, 90°C, 30%RH	H ₂ X-over mA/cm ² % OCV loss	< 20 < 20 %	13 ± 4 mA/cm ² at 500 hrs (5 MEAs) 12 ± 5 % OCV loss in 500 hrs
Durability under Load Cycling (membrane lifetime test)	Hours, T ≤ 80°C Hours, T > 80°C	5000 5000	9000 hrs, 3M PEM (20µm, 850 EW w/ stabilizers), 50cm ² , 80/64/64 °C 2000 hrs (OEM short stack, 0.1/0.15)

CCM – catalyst-coated membrane; RH – relative humidity; OEM - original equipment manufacturer

FY 2012 Accomplishments

New catalyst activity and understanding; annealing and process scale up (Task 1.3)

- Extended the enhanced catalyst deposition process improvement (P1) from pure Pt and PtCoMn to Pt₃Ni₇, obtaining same dramatic gains in Pt(hkl) grain size with a simpler, more cost-effective coating process.
- Screened over 100 different ex situ de-alloying conditions in batch processes for impact on fuel cell performance. Down-selected to one de-alloying condition that is 240 times faster than initial nitric acid bath conditions.
- Successfully transferred faster ex situ dealloy process to a roll-to-roll pilot-scale process that maintained the 240-fold increased dealloying rate:
 - Applied 240x roll-to-roll dealloying and surface energy treatment (SET, annealing) processes to 0.12 mg-Pt/cm² loaded as-made Pt₃Ni₇ that generated cathode mass activities in 50-cm² cells at GM ranging from 0.47 A/mg to 0.67 A/mg depending on 3M's MEA membrane cleaning process and ORR protocol used by GM.
 - Achieved 0.14–0.18 g_{Pt}/kW over 0.6 to 0.65 V, at 80°C and 150–250 kPa using 0.15 mg/cm² total Pt in the MEA.

Met 2017 cyclic voltammetry (CV) cycling and open circuit voltage (OCV) targets with MEA type used in short-stack testing (Task 2)

- 30,000 CV cycle test: Demonstrated 10±7 mV loss at 0.8 A/cm², 16±2% loss of electrochemical surface area, and 37±2% loss of mass activity w/MEA used in the second short-stack tests.
- Met 3M OCV hold test: 570 hours with OCV loss = 13% under 50 kPa H₂ overpressure.

Membrane-electrode integration and catalyst-coated membrane (CCM) scale up (Task 5.1)

- Produced over 60,000 linear ft combined of NSTF substrate, coated-catalyst supports, and catalyst-coated membrane for process development, short stack and customer use.

Short-stack testing with PtCoMn-based NSTF electrodes (Task 5.3)

- Completed first 29-cell rainbow short stack performance testing at GM to down-select the MEA configuration from 6 to 1 configuration for a final second durability short-stack test.

- Initiated durability cycling tests with second short stack (20 cells with one type of 3M MEA), however tests were not completed before end of project.



Introduction

State-of-the-art proton exchange membrane (PEM) fuel cell electrocatalyst technology utilized in today's prototype fuel cell vehicles reveals limitations with respect to general durability and robustness under start-stop cycling, adequate performance with low PGM loadings, and low-cost manufacturability. To a large degree, these deficiencies are traceable to properties of the conventional carbon supported dispersed Pt catalysts in use today and issues with membrane integration. The research and development of this project are focused on overcoming these three most critical barriers for fuel cell MEA automotive deployment by using an alternative catalyst support and deposition method.

Approach

The approach to achieve the above objectives builds on a fifteen-year DOE/3M-funded development of the 3M NSTF catalyst and MEA technology. The NSTF catalyst fundamentally has higher specific activity for oxygen reduction [1-11], removes all durability issues with carbon supports, demonstrates much lower losses due to Pt dissolution and membrane chemical attack [12-15], and has significant high volume all-dry roll-good manufacturing advantages [16].

The scope of work in the initial three-year budget period included extensive work at 3M to increase the NSTF catalyst support film surface area, fabrication and screening of new alloys in 50-cm² single cells, and evaluation of multiple deposition parameters to obtain increased catalyst surface area and utilization. Complementary to this work at 3M, collaborative work included high throughput fabrication and characterization of new multi-element Pt alloys (ternaries and quaternaries) with Dalhousie University, fundamental catalyst characterization studies with ANL, and development and evaluation of a pseudo-rotating disk electrode (RDE) catalyst evaluation technique with JPL. Research last year (the fourth year) focused at 3M on continued studies of water management improvements for cool/wet operation via optimization of materials, electrode structure and operating conditions; catalyst fabrication process improvements for increased catalyst performance and production efficiency; in-depth MEA component screening to down-select final configurations for the final short-stack testing; continued accelerated testing to benchmark the NSTF-MEA durability with each generation of MEA components; and initial fabrication of roll-good materials for initial stack testing by the GM fuel cell laboratory.

This final year the focus was on a) completing the first year short stack testing to down-select a final MEA type for a second (durability) stack; b) resolving specific production and MEA integration issues related to the final stack MEAs; c) second stack durability protocol development and initial testing; d) extension of the improved, more cost effective P1 deposition process to the as-made NSTF-Pt₃Ni₇ catalysts; and e) development of fast roll-to-roll capable de-alloying and annealing processes for the NSTF "Pt₃Ni₇" catalysts.

Results

The technical accomplishments for the fifth and final year fall roughly into three areas of research and development corresponding to project tasks 1, 2, and 5.3. We briefly summarize the main results from each of these areas.

Task 1

The NSTF-Pt₆₈Co₂₉Mn₃ catalyst has been the workhorse cathode and anode of choice for a number of years. As indicated last year, with it we have been able to exceed the previous DOE 2015 target of 0.2 g-Pt/kW in a full-size short stack with 0.05 mg/cm² of PGM on the anode and 0.1 mg/cm² on the cathode [17]. More recent work has focused on improving the NSTF-catalyst roll-to-roll process so that the support whiskers and sputter deposited catalyst alloy can be applied simultaneously on the moving substrate web in a single step. This new process, called P1, offers greater simplicity and more cost-effective coating than the standard process called P4. In last year's report we showed the positive impact on PtCoMn crystallite size and surface smoothness for loadings between 0.054 and 0.184 mg_{Pt}/cm² produced by using the improved P1 process, as well as small fuel cell performance benefits. As indicated in our 2011 annual report, to reach the new more rigorous DOE 2017 target for cathode catalyst inverse mass specific power density of 0.125 g-Pt/kW, a new catalyst alloy will be required, and the NSTF-Pt₃Ni₇ as-made alloy [18] was the best candidate. We also pointed out the important effects of two post-processes, ex situ dealloying and SET "annealing", that when applied to the as-made NSTF-Pt₃Ni₇ significantly improved the mass activity and helped with the limiting current density issue that comes with excess Ni going into the PEM. This past year we have applied the P1 process to the as-made NSTF-Pt₃Ni₇ with similar benefits as seen with the PtCoMn (see slide 30, in reference 19), and put significant effort into developing and scaling up the dealloying and SET post-processes.

A broad series of batch process experiments were completed to investigate the effects of both electrochemical and passive chemical dealloying, with acid bath composition, concentrations, time and temperature as parameters. These were applied to various catalyst material factors, including Pt₃Ni₇ loading (0.075 to 0.15 mg-Pt/cm²), alloy homogeneity (P1 vs. P4), and the SET annealing process. The objective was

to try and optimize the process both to improve the limiting current density without loss of ORR activity, and to find conditions suitable for roll-to-roll processing at reasonable web speeds. Over 100 different combinations of the acid bath conditions, catalyst fabrication and process parameters were screened and tested in 50-cm² fuel cells in duplicate. Conditions were found that allowed speeding up the rate of dealloying by a factor of 240 over the baseline nitric acid bath soak. Using existing facilities at 3M, full-width roll-to-roll dealloying was developed with the faster process conditions. Sixteen ORR relevant kinetic and performance metrics were extracted from the fuel cell potentiodynamic and galvanodynamic polarization curves and correlated with materials and proprietary process parameters. Without disclosing proprietary process information, a total of 38 global scatter-plots can be generated to illustrate how critical metrics vary with two basic catalyst properties, surface area and loading. Figure 1(A) shows one such global metric plot of ORR absolute activity at 900 mV under 150 kPa saturated oxygen, versus the surface area enhancement factor in cm² of Pt per cm² of planar surface area. The inset graph in Figure 1(A) illustrates the conditions and protocol used for the ORR measurement; for the MEA ORR activity measurement the total current density is recorded 1,050 seconds after setting the potential at 900 mV. The current density, in mA/cm²_{planar} is decreasing as the Pt is oxidizing, so the ORR activity is measured on an oxidized surface in contrast to most RDE measurements [9]. The slope of the scatter plot in Figure 1(A) gives an indication of the high specific activity of the Pt₃Ni₇ derived catalysts, ~3.6 mA/cm²-Pt, which is somewhat higher than an average of the actual values measured for each sample. Figure 1(B) is a similar scatter plot showing that roll-to-roll dealloying and annealing conditions were found which generated mass activities of 0.44 A/mg-Pt using the 3M ORR protocol above, equivalent to the DOE 2017 target. These were obtained at higher loadings than demonstrated in last year's report for SET batch treated as-made Pt₃Ni₇ catalysts with loadings below 0.09 mg/cm² that did not give high absolute fuel cell performance at either low or high current densities. Other such plots (see slides 21 and 23 in reference 19) show that mass specific surface areas of 15 to 20 m²/g were common for the dealloyed/SET annealed catalysts with the highest mass activities. The increased surface area and specific activity both contributed to the improved mass activity.

CCMs made with P1 fabricated, roll-to-roll dealloyed and SET treated Pt₃Ni₇ alloy cathodes at loadings of 0.121±0.003 mg-Pt/cm² were tested at GM using both their own and 3M's ORR mass activity protocols. These CCMs were made at 3M with 3M membranes that were either as-made or cleaned using both nitric acid and peroxide baths. Table 2 summarizes the results from the GM measurements in which the standard treatment refers to the usual NSTF thermal cycling for break-in conditioning. The last column in Table 2 shows that a proprietary GM additional pretreatment

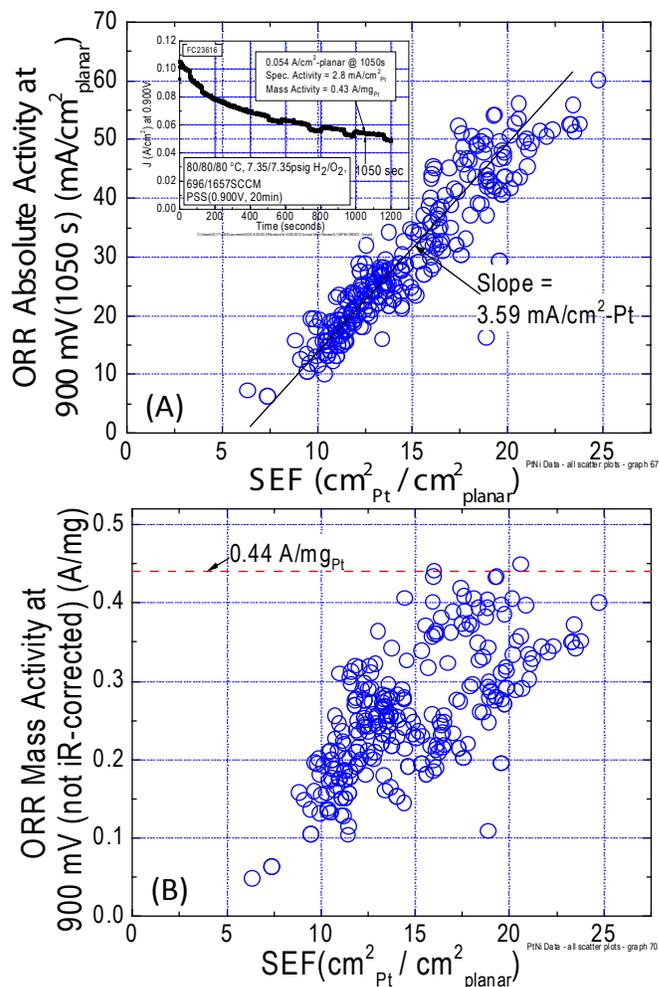


FIGURE 1. (A) ORR absolute activity as a function of surface area enhancement factor for over 100 different NSTF-PtNi cathodes derived from the as-deposited Pt₃Ni₇ catalysts for various loading, dealloying and SET post-process parameters. (B) Mass activity as a function of surface area enhancement factor for the same MEA cathodes as in (A).

TABLE 2. Mass activities measured at GM of 3M CCMs having NSTF Pt₃Ni₇ roll-to-roll dealloyed and SET treated cathodes laminated to either cleaned or as-made 3M PEMs. Cathode loadings were 0.121±0.003 mg-Pt/cm².

Sample membrane used in CCM	Protocol used for measurement	Standard Treatment (A/mg)	With Additional Pretreatment (A/mg)
As-made PEM	GM	0.45	0.47
As-made PEM	3M	0.52	0.67
Cleaned PEM #1	GM	0.41	0.54
Cleaned PEM #1	3M	0.23	0.65
Cleaned PEM #2	GM	0.41	0.58
Cleaned PEM #2	3M	0.21	0.62

process can further substantially increase the apparent mass activities over the standard treatment, which now cover the ranges of 0.47 to 0.58 A/mg by the GM ORR protocol and 0.62 to 0.67 A/mg using the 3M protocol.

To test the best overall performance possible with these roll-to-roll dealloyed/annealed Pt/Ni cathode catalysts, 50-cm² CCMs were prepared with Pt₃Ni₇ cathode loadings of 0.121±0.003 mg-Pt/cm², pure NSTF-Pt anodes with 0.030 mg/cm², and 3M 24 micron, 850 equivalent weight non-supported membrane, as-made. GDLs were the 3M standard 2979, and testing was done with quad-serpentine flow fields. Figure 2(A) shows galvanodynamic scan (GDS) polarization curves at three pressures and the conditions indicated in the legend. The inset graph shows that the higher kinetic performance expected from the high mass activity is realized in the MEAs at 0.8 V (quarter peak power point), with 0.21 to 0.31 A/cm² at 0.8 V obtained over a 150 to 250 kPa outlet pressure range. Even though the limiting current densities are still not as high as they should be, there is a substantial improvement over that obtained with the as-made Pt₃Ni₇ catalysts (about 0.8 A/cm², as shown in [17] and reasonable current densities are being realized at 650 mV. Figure 2(B) shows the inverse specific power density plots for the three polarization curves shown in Figure 2(A). These advanced PtNi cathodes with the lower anode loading on a 24-micron thick membrane exhibit values of 0.14 to 0.18 g-Pt/kW over 0.6 to 0.65 V and the 150 to 250 kPa operating range at 80°C. There is little temperature sensitivity over the 80 to 95°C range (see slide 34 in reference 19). Further improvements in understanding and controlling the dealloying and SET treatment processes are required to take advantage of thinner membranes which should further improve their performance towards the 0.125 g-Pt/kW target for 2017.

Task 5.3 – stack 1

The other major effort over the past year has been to prepare for, fabricate roll-good CCMs and execute independent short-stack testing of MEAs comprising catalysts and process advancements developed under this project through early 2011. The stack testing has been provided by GM's fuel cell facilities at Honeoye Falls, NY. Last year's annual report summarized work done in 2010/2011 towards MEA component down-selection for initial and final stack testing. Two stack tests were planned. The first was a 29-cell "Rainbow" stack, one "color" for each MEA type, for initial beginning of life operation under various automotive relevant test protocols. This first stack was to enable down-selecting to the final MEA type to be tested in a second stack under an accelerated durability protocol. The first stack compared the six MEA configurations shown in Table 3.

The stack 1 performance was a surprise in that it significantly underperformed what we expected based on 50-cm² single cells. Figure 3(A) compares polarization curves from the four configuration-1 MEAs in stack 1 with what we and GM had previously measured in 50-cm² single cells for similar MEAs under similar conditions.

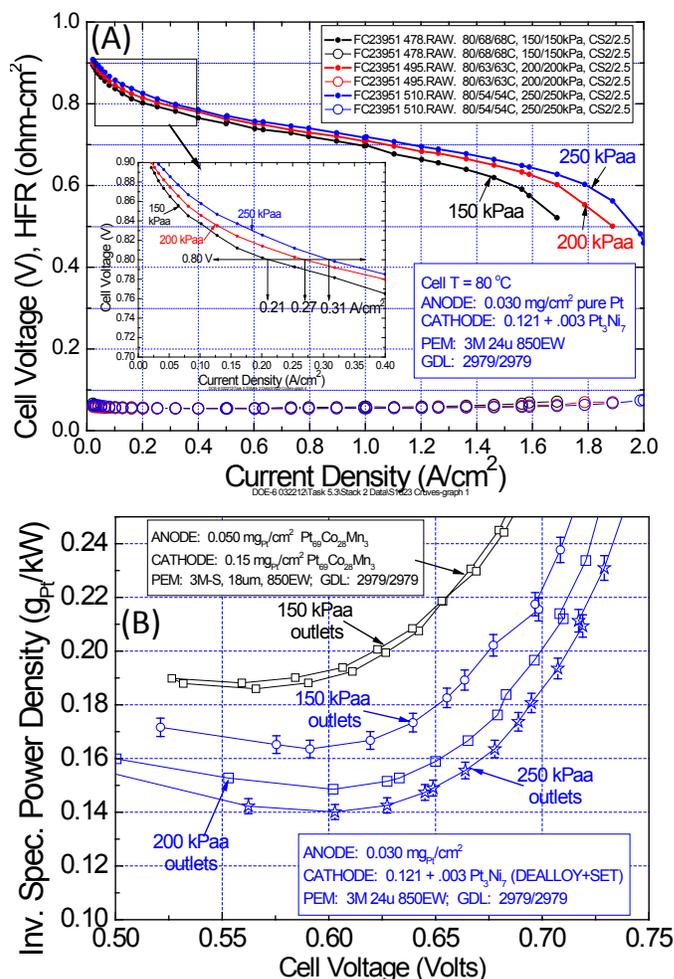


FIGURE 2. (A) GDS polarization curve performances for the 2012 "best of class" MEA based on the roll-to-roll dealloyed and SET "annealed" NSTF-Pt₃Ni₇ cathodes. The MEA contained a total PGM loading of 0.15 mg-Pt/cm². (B) Inverse specific power density versus cell voltage for the three GDS polarization curves shown in (A).

Significant effort was spent by both 3M and GM to "debug" the low performance over a 2.5-month period. A number of confounding issues contributed, including test station water purity, properties or contamination of the ionomer used for the membrane lots used to fabricate the CCMs, and more effective break-in conditioning that is possible with single cells versus large area stacks. Further tests revealed the catalyst ORR metrics and surface areas were as expected, stack compression was nominal, but 50-cm² CCMs made in the lab with the same membrane lots as used in roll-to-roll fabrication of the CCM for stack 1 also underperformed what was expected. CCMs from the same roll-to-roll lots were also tested in a 3M short stack (5 cell, 312 cm²) and found to underperform the single cell results at ambient pressure but give similar results at 22 psig, and slightly better than the GM stack at a similar pressure (see slide 8 in reference 19). Still the GM stack 1 tests were successful in clearly being

TABLE 3. Definition of six MEA configurations evaluated in Stack 1, a 29-cell “rainbow” stack

CCM ID	PEM	Anode	Cathode	S1622 Cells
Config. 1	3M-24um (w/add. 2)	0.05 P1 PtCoMn	0.15 P4 PtCoMn + SET	9-12
	3M-24um (w/add. 1)	0.05 P1 PtCoMn		
Config. 2	3M-24um (w/add. 2)	0.05 P1 PtCoMn	0.10 P1 PtCoMn	5-8, 22-25
Config. 3	3M-S	0.05 P1 PtCoMn	0.15 P1 PtCoMn	13-16
		0.05 P1 PtCoMn		
Config. 6	3M-X	0.05 P1 PtCoMn	0.15 P1 PtCoMn	17,18
Config. 7		0.05 P1 PtCoMn	0.10 P1 PtCoMn	19-21
Config. 8	3M-24um (w/add. 1)	0.05 P1 PtCoMn	0.15 P1 PtCoMn	1-4, 26-29

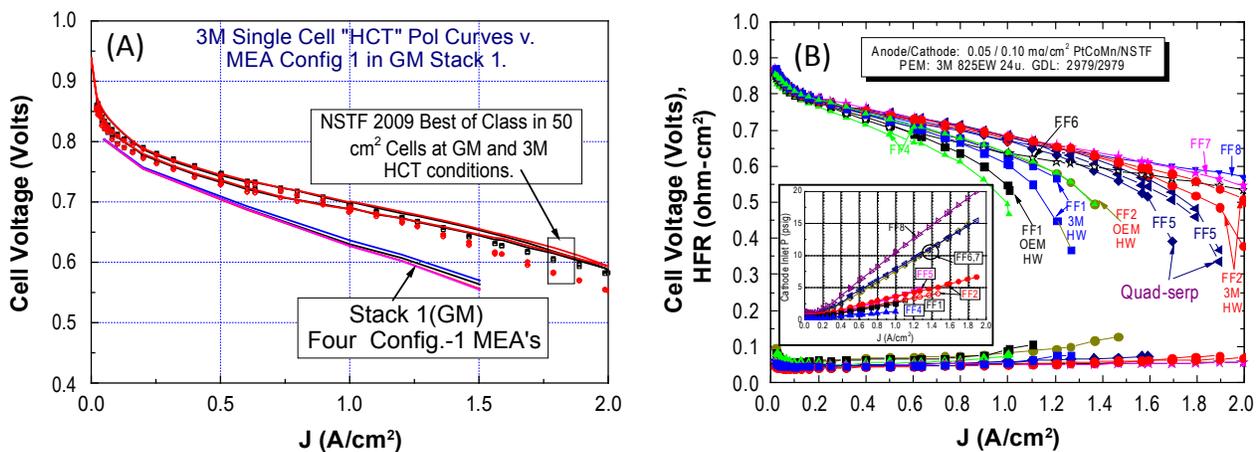


FIGURE 3. (A) Comparison of the polarization curves obtained from the four configuration 1 MEAs in stack 1, with the expected performance based on 50-cm² single-cell tests measured both at 3M and GM. (B) Comparison of single cell (50 cm²) GDS polarization curves from the standard quad serpentine flow field (FF5) with six alternative flow fields: FF1 = 6 serpentine channels, 2 loops, 2 mm channel width, 2 mm land width, ~0.3 mm channel depth; FF2 = 24 serpentine channels, 2 loops, 0.5 mm channel width, 0.5 mm land width, ~0.25 mm channel depth; FF4 = 9 serpentine channels, 4 loops, 1 mm channel width, 0.6 mm land width, 1 mm channel depth; FF5 (quad-serpentine) = 4 serpentine channels, 10 loops, 0.8 mm channel width, 0.8 mm land width, 1 mm channel depth; FF6 = single channel 3M Zig-Zag (21); FF7 = 2 serpentine channels, 21 loops, 1 mm channel width, 1 mm land width, 1 mm channel depth; FF8 = single serpentine, 43 loops, 0.8 mm channel width, 1.0 mm land width, 1.5 mm channel depth.

able to delineate the performance order of the six MEA configuration types, with MEA configuration 1 being the best and down-selected MEA for the eventual stack 2 durability testing (see slide 7 in reference 19). Figure 4 shows a pressure-series of polarization curves, comparing the 4-cell average stack performance of the configuration-1 MEAs with six, 50-cm² single-cell tests (done at 3M) having the identical type MEA. (The test conditions used for the data in Figure 4 were those supplied by the systems modeling group at ANL, Ahluwalia et al., and used by 3M for generating other MEA data requested by that group.) Performance improves with

pressure similarly in single cells and the stack, consistent with mass transport issues. The stack 1, MEA type 1 performance average underperforms the single-cell tests at all conditions, but not by too much as long as the current density is below ~1.5 A/cm². At higher current densities the stack 1 performance falls considerably short of the small single cells.

There is still a question of the possible impact of flow field differences between the quad-serpentine 50-cm² cells used at 3M and the flow field of the GM stack. Flow fields

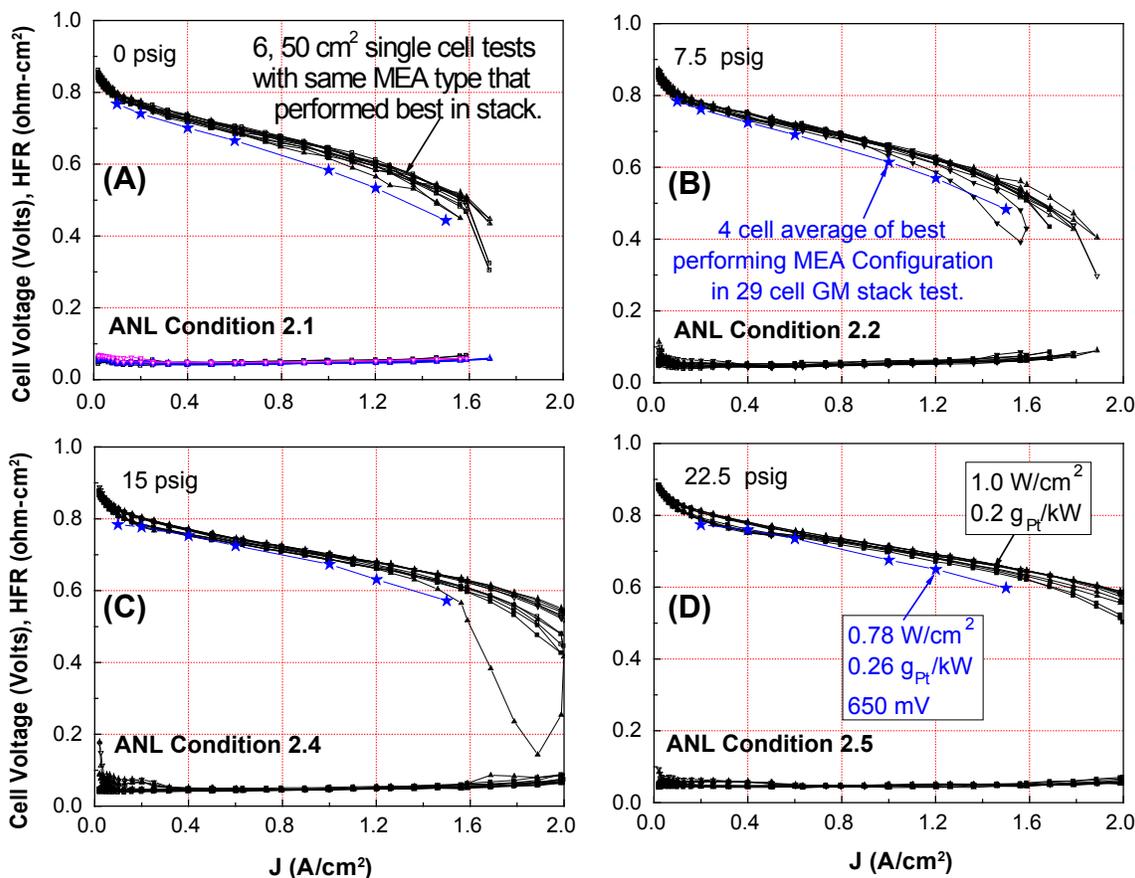


FIGURE 4. (a) GDS polarization curve comparisons at four pressures, of the 4-cell average GM stack 1 performance (configuration-1 MEAs) with six, 50-cm² single-cell tests (at 3M) having the identical type MEA. GDS polarization scan: 0.02->2->0.02 A/cm², 10 steps/decade, 120 s/pt, 0.4 V limit, 0.1 max current density step. The test conditions used for the data in Figure 4 were those supplied by the systems modeling group at ANL (Ahluwalia et al.) and used by 3M for generating other MEA data requested by that group:

ANL Condition 2.1 = 80/73/73°C, 1/1 atm H₂/Air, CS(2,100)/CS(2.0, 200)

ANL Condition 2.2 = 80/70/70°C, 1.25/1.25 atm H₂/Air, CS(2,100)/CS(2.0, 200)

ANL Condition 2.4 = 80/56/56°C, 2.0/2.0 atm H₂/Air, CS(2,100)/CS(2.0, 200)

ANL Condition 2.5 = 80/40/40°C, 2.5/2.5 atm H₂/Air, CS(2,100)/CS(2.0, 200)

have never been systematically optimized for the NSTF type ultra-thin electrodes yet can clearly have a strong effect that might not be considered an issue with conventional thick layer electrodes. To establish a baseline of these effects we initiated tests of NSTF MEAs having a similar construction as MEA configuration 1 (but nominally non-contaminated PEM lot) in a series of nine alternative flow field designs. The 50-cm² flow field graphite blocks were all tested in one set of 3M cell hardware or one set of OEM cell hardware (OEM HW). Figure 3(B) compares the GDS polarization curves from six alternative flow fields with the standard quad-serpentine (FF5), completed at the end of this project. As shown there is a huge impact of the flow field type on the limiting current density, and several that perform better than our standard quad serpentine. The HFR differences are small and not responsible for the differences when the graphite blocks are all in the same set of 3M Al cell hardware (3M HW). Cathode pressure drop was also measured for

the different flow fields, and can explain the high current density performance gain with the single channel flow fields FF7 and FF8 relative to the standard FF5. However, the FF2 flow field blocks used in the 3M Hardware significantly out-performed the standard with similar or slightly lower pressure drops. This suggests that the smaller (0.5 mm) channel and land width dimensions of the FF2 are key to improved performance and a guide to optimizing the flow field for NSTF MEAs.

Task 5.3 – stack 2

The down-selected MEA configuration type 1 in Table 3 from the stack 1 tests was intended to be the sole MEA type used in the second stack, slated for accelerated durability testing. Due to various issues, this exact MEA configuration 1 did not end up being the final MEA type used in stack 2, as a different membrane was ultimately

used. Factoring into the decision were NSTF CCM-production issues with available standard, non-supported PEM lots, which made it attractive to move to the newer generation membrane. This gave the opportunity to switch the membrane type from a standard, non-supported membrane to a new, 3M experimental supported membrane, which previous data had indicated helped improve certain accelerated MEA durability tests. There was risk associated with this decision as these were still experimental PEMs and optimized integration with the NSTF had not been completed. Work related to resolving these issues required an additional 9 month no-cost extension of the project. The final MEA stack 2 catalysts used were the same as that used in configuration 1 in Table 3. We subsequently discovered that performance in 50-cm² single cells was again much worse than expected. Once the final CCM roll-goods were fabricated, and shortly after shipment to GM, the reason for the underperformance was tracked to the inadvertent production release of an experimental PEM lot to make the CCMs that had been put on hold due to suspected contamination of its ionomer. Due to lack of time and funding to make further MEAs, the decision was made to continue with the stack 2 testing with these CCMs. Figure 5(A) compares 50-cm² single-cell beginning of life performances at 7.5 psig H₂/air from MEAs using the same CCM lots as used in stack 2, with that from MEAs using CCMs made with the same catalyst lots but with normally performing experimental 3M-supported membrane (best 3M-S) at 7.5 and 22 psig H₂/air. In addition to the dramatic loss of limiting current density with the contaminated PEM, the ORR activities were slightly depressed, while the catalyst electrochemical surface areas and MEA HFR were normal. Surprisingly however, as the stack 2 type MEA was tested in a single 50-cm² cell using the same cycling durability protocol discussed below for stack 2, but with periodic recovery, the MEA performance continuously improved for nearly 400 hours and approached that of the best 3M-S curves shown in Figure 5(A).

Despite these issues with beginning of life performance, Figures 5(B) and 5(C) show that the MEAs using CCMs from the same lots as in the stack 2 MEAs, passed both the DOE OCV hold tests and the CV cycling tests. The objective of the OCV hold test is assessment of the whole MEA/membrane durability at OCV at 90°C under 30% RH, 250/200 kPa H₂/air. The target is 500 hours with less than 20% loss of OCV. This MEA went 570 hours with a 13% loss under the 50 kPa H₂ overpressure. The CV cycling accelerated stress test characterizes the resistance of the catalyst to dissolution, agglomeration or loss of activity due to high voltage cycling. The protocol involves cycling the cathode between 0.6 and 1.0 volts and back again at 50 mV/sec under 100/100 kPa H₂/N₂ at 80°C cell and dew points. The target is to have after 30,000 cycles, less than 40% loss of surface area and ORR mass activity and a polarization curve loss of less than 30 mV at 0.8 A/cm².

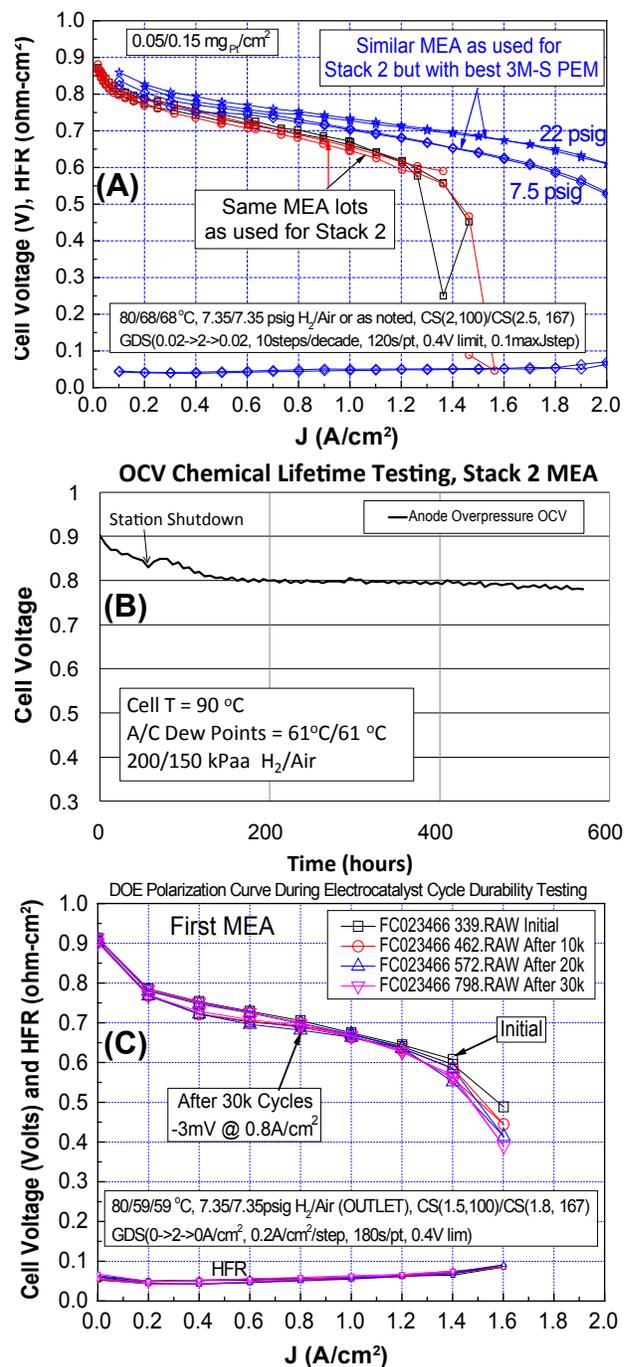


FIGURE 5. (A) Single-cell 50-cm² GDS polarization curves at 7.5 psig from MEAs taken from the same lot as used for stack 2, compared with a similar MEA that used a known non-contaminated 3M-S membrane, at both 7.5 and 22 psig. (B) OCV hold versus time durability test for an MEA identical to that used for stack 2. (C) GDS polarization curve and HFR impedance for an MEA identical to that used for stack 2 before, during and after 30,000 CV cycles from 0.6 to 1 volt.

The stack 2 lot of MEAs (two were tested) demonstrated a 10±7 mV loss at 0.8 A/cm², 16±2% loss of surface area, and 37±2% loss of mass activity. This is the first time we have

TABLE 4. Conditions used for beginning of life tests of stack 2

Stack Cond.	T (°C)	An/Ca St.	An RH in (%)	Can RH out (%)	Pressure
1	~ 82	~1.5/1.8	25	82	Variable
2	~ 75	~1.5/1.8	30	85	Variable
3	~ 65	~2 /1.8	30	≥100	Variable
4	~ 78	~1.5/1.8	20	65	Variable
5	~ 78	~2.0/1.8	≥100	≥100	Variable

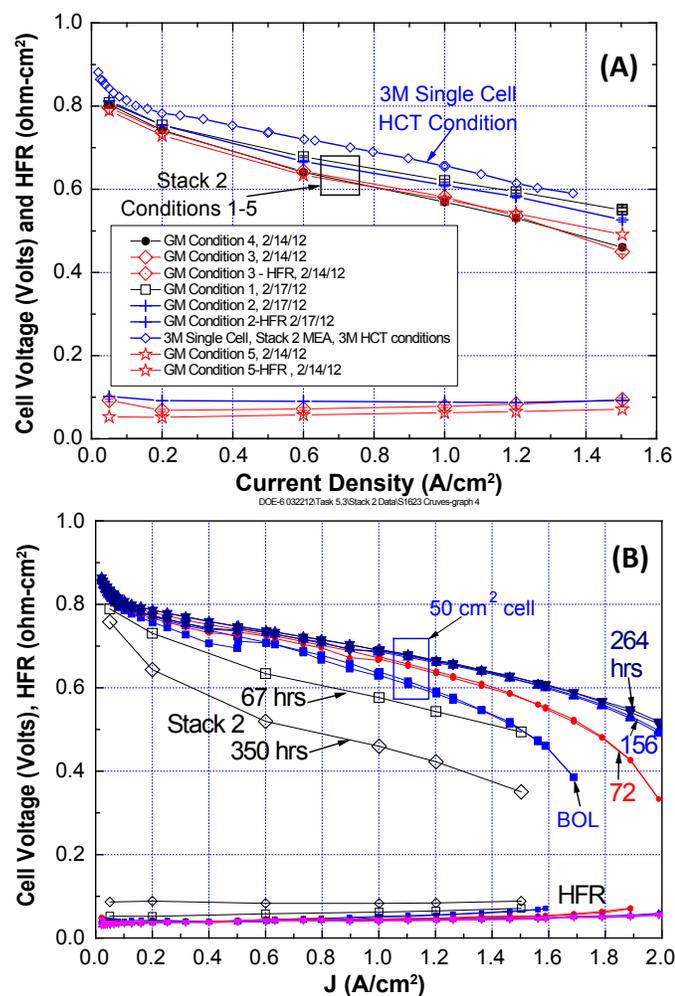


FIGURE 6. (A) Average MEA beginning-of-life performance in stack 2 at the five conditions shown in Table 3, compared to the 50-cm² single-cell test under GDS high current test conditions of: 80/68/68°C cell temperature/anode/cathode dew points; 150 kPa H₂/air; and anode/cathode stoichiometric flows of 2/2.5. GDS polarization curve conditions are same as in Figure 3. (B) Comparison of stack 2 performance change after 4 sets of 1,500 load cycles (~300 hours) with the performance change of the same MEA type in a 50-cm² single-cell (at 3M) after 200 hours of a similar load cycle, interspersed with periodic recovery shutdowns every 12 or 24 hours. Procedure Loop: 1) 5 thermal cycles, 2) polarization curves, 3) 12- or 24-hr cycling under following procedure - 3a) 80/83/83°C, H₂+N₂/Air, 0/0psig, PSS(x,30s); x=0.85, 0.60 V - 3b) 80/53/53°C, H₂+N₂/Air, 0/0psig, GSS(x,30s); x=0.02, 0.10 A/cm.

been able to demonstrate meeting all the targets with this accelerated stress test.

The stack 2 beginning of life performance was evaluated under five different sets of operating conditions as in Table 4. Consistent with the single-cell tests, the beginning of life stack 2 MEA performances were much lower than expected and lower than single-cell tests with the same MEA lot, but did not vary significantly from the driest to the wettest conditions, see Figure 6(A). Average cathode surface areas were approximately normal at 8.2 m²/g, while in-stack shorting resistances were lower than the standard GM baseline MEAs used as end-cells in the 29-cell short stack.

The objective of stack 2 was to conduct a load-cycling protocol representative of an accelerated stress test for lifetime durability. The protocol chosen was close to that recommended by the U.S. Drive Fuel Cell Tech Team with some modifications to adapt it to the under-performing MEA and the slower cool-wet transient behavior of the thin-layer NSTF electrodes with the GDLs used (see reference 20 for impact of anode GDL type on this behavior). Higher pressure, controlled current ramp rate, and minimum voltage control were the main modifications to the protocol. After four sets of 1,500 cycles, ~350 hours of operation, the following observations were made: two point (beginning and end) performance decay rates were much higher than expected (by factors of 3x to 8x); cross-over leak rates and hydrogen take-over in the cells were high; high frequency resistance increased with time but could not account for the lost performance; there were significant fluctuations in performance between each of the 4-cycle sets. Figure 6(B) shows the beginning-of-life performance (67 hours, open squares) of the stack and that after 350 hours (open diamonds) of cycling, showing extreme decay. Also shown in 6(B) are the performances of the same stack 2 type MEA tested in a 50-cm² single cell at 3M at beginning of life and after 72 hours (red circles), 156 hours (up triangles) and 264 hours (down triangles) with nominally the same load cycling protocol. One key difference in the single cell tests and the stack tests is that the single cell was recovered periodically (12- or 24-hour period) by stopping the load cycling and doing five thermal cycles before resuming the load cycling. Thermal cycling is the typical break-in conditioning protocol used for NSTF MEAs and the large improvement in performance of the single-cell MEA seen with the load cycling is consistent with removal of impurities in the vicinity of the electrodes. The performance of the single-cell MEA in Figure 6(B) continued to improve or stabilized depending on current density for nearly 400 hours, after which its performance started to decay and by 580 hours it had failed due to edge failure of the CCM. This MEA did not have subgasket edge-protection which would be expected to improve lifetime significantly. Low performing cells in the stack 2 prevented going to high current densities and necessitated replacing MEAs and rebuilding the stack on two occasions. It was observed that the shorting resistance

for every cell, including the GM baseline cells, would significantly worsen (drop in value) after each such rebuild. It was eventually determined that further work with the stack would not be instructive and testing was discontinued just prior to the 6/30/12 end of this project.

Conclusions and Future Directions

The encouraging work with the NSTF Pt₃Ni₇ dealloying, annealing and membrane integration development will be continued in part in a follow-up DOE/3M project “High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation Applications,” that is just beginning. Stack testing and GDL/MEA component integration will be a significant part of that effort and will hopefully identify the sources for some of the impedance, shorting, and contamination issues plaguing the stack testing in this project, as well as further understand the importance of the flow field design for optimum performance with ultra-thin electrodes.

FY 2012 Publications/Presentations

Publications

1. M.K. Debe, R.T. Atanasoski, and A.J. Steinbach, “Nanostructured Thin Film Electrocatalysts – Current Status and Future Potential,” *ECS Trans*, **41**(1) 937-954 (2011).
2. A. Steinbach, M. Debe, M. Pejsa, D. Peppin, A. Haug, M. Kurkowski and S. Maier-Hendricks, “Influence of Anode GDL on PEMFC Ultra-thin Electrode Water Management at Low Temperatures,” *ECS Trans*, **41**(1) 449-457 (2011).
3. Dennis van der Vliet, Chao Wang, Mark Debe, Radoslav Atanasoski, Nenad M. Markovic and Vojislav R. Stamenkovic, “Platinum-alloy Nanostructured Thin Film Catalysts for the Oxygen Reduction Reaction,” *Electrochim. Acta*, **56** 8695-8699 (2011).
4. Mark K. Debe, “Effect of Electrode Structure Surface Area Distribution on High Current Density Performance of PEM Fuel Cells,” *J. Electrochem. Soc* **159**(1) B54-B67 (2011).
5. Mark K. Debe, “Electrocatalyst Approaches and Challenges for Automotive Fuel Cells,” invited review article, *Nature*, **486**(9401) 43-51(2012).
6. Mark K. Debe, “Nanostructured Thin Film Electrocatalysts for PEM Fuel Cells – A Tutorial on the Fundamental Characteristics and Practical Properties of NSTF Catalysts,” *ECS Transactions* **45**, (2) 47-68 (2012).
7. M.K. Debe, S.M. Hendricks, G.D. Vernstrom, M. Meyers, M. Brostrom, M. Stephens, and Q. Chan, Jason Willey, Monjid Hamden, and Cortney K. Mittelsteadt, Christopher B. Capuano, Katherine Ayers and Everett Anderson, “Initial Performance and Durability of Ultra-low Loaded NSTF Electrodes for PEM Electrolyzers,” *J. Electrochem. Soc.*, **159**(6) K165-K176 (2012).
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11. Mark K. Debe et al., “Advanced Cathode Catalysts and Supports for PEM Fuel Cells,” DOE Hydrogen and Fuel Cells Program, FY 2011 Annual Progress Report, page 697-705.

Presentations

1. M. Debe, S.M. Hendricks, G. Vernstrom, J. Wiley, M. Hamden, C. Mittelsteadt, C. Capuano, K. Ayers and E. Anderson, “Initial Performance and Durability of Ultra-low Loaded NSTF Electrodes for PEM Electrolyzers,” Abs. #694, 220th ECS Meeting, Boston, MA, Oct., 2011.
2. M.K. Debe, Project review at the DOE Hydrogen Program 2012 Annual Merit Review, Washington, D.C., May 15, 2012, presentation FC001.
3. M.K. Debe (Invited), R.T. Atanasoski, and A.J. Steinbach, “Nanostructured Thin Film Electrocatalysts – Current Status and Future Potential,” 220th ECS Meeting, Boston, MA, Oct. 2011.
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7. X. Wang, R.K. Ahluwalia, A.J. Steinbach, and M.K. Debe, “Dynamic Performance of Automotive Fuel Cell Systems with Low Platinum Loadings,” 220th ECS Meeting, Boston, MA, Oct. 2011.
8. M.K. Debe (Invited plenary), “PEM Fuel Cell Performance Factors Determined by Electrocatalyst Structure Characteristics,” Zing International Hydrogen and Fuel Cell Conference, Riviera Maya, Mexico, Dec. 1, 2011.
9. Mark K. Debe, (Invited), “A New Generation of Catalysts and Electrode Designs for PEM Water Electrolysis: Fundamentals and Practical Examples,” Hydrogen Production and Water Electrolysis Short Course, North-West University, Potchefstroom, South Africa, April 18–19, 2012.

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