

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

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- high prospects for 40,000 hours durability under operating conditions for stationary applications, and
- 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
- (D) Water Transport within the Stack

Technical Targets

This project is focused on improving the performance and durability of the 3M nanostructured thin film (NSTF) roll-good fabricated electrocatalysts and MEAs. Table 1 compares the NSTF current 2nd quarter, calendar year (CY) 2011 status with DOE electrocatalyst targets for 2010/2015 updated from Table 3.4.12 of the DOE Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan to reflect recent accelerated durability test results. The MEAs used for the inverse specific power density values listed in the first row, PGM total content, had PtCoMn catalysts with loadings of 0.05/0.10 mg_{PGM}/cm² on the anode and cathode, respectively deposited by 3M's standard P4 process. The short stack results were obtained outside the project but evaluated catalysts and gas diffusion layers (GDLs) developed within the project. The updated accelerated stress test results were obtained with PtCoMn catalysts containing 0.05 mg_{Pt}/cm² on the anode and 0.15 mg_{PGM}/cm² on the cathode deposited by the new P1 process discussed in the following.

Fiscal Year (FY) 2011 Objectives

The objectives of this project are 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 (PEM) electrode assembly (MEA) characterized by:

- total Pt group metal loading per MEA of ≤ 0.25 mg/cm²,
- short-stack specific power density of ≤ 0.3 g/kW at rated power,
- 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,

FY 2011 Accomplishments

Water Management for Cool/Wet Operation (Task 5.2)

- Developed key strategy for reducing cathode flooding at cool temperatures by taking product water out the anode, the "water-out-anode" mode.
 - Demonstrated that anode GDL was most critical component for water-out-anode strategy. Significantly improved cool/wet performance at ambient pressure.
 - Developed cathode gradient catalyst hybrid construction that also dramatically helps water management at low temperature as well as high temperature.

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

Characteristic	Units	Targets 2015	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	< 0.18 g _{Pt} /kW for cell V < 0.67 V in 50 cm ² cell at 150kPa inlet. 0.19 g _{Pt} /kW, 400 cm ² GM short stack
PGM Total Loading	mg PGM / cm ² total	0.125	0.15 – 0.20, A+C with current PtCoMn alloy
Mass Activity (150 kPa 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 > 0.43 A/mg in 50 cm ² with SET Pt ₃ Ni ₇
Specific Activity (150 kPa H ₂ /O ₂ at 80°C, 100% RH)	μ A/cm ² -Pt @ 900 mV	720	2,100 for PtCoMn, 0.1 mg _{Pt} /cm ² 2,500 for new Pt ₃ Ni ₇ , 0.1 mg _{Pt} /cm ²
Durability: 30,000 cycles 0.6 -1.0 V, 50mV/sec, 80/80/80°C, 100 kPa, H ₂ /N ₂	- mV at 0.8 A/cm ² - % ECSA loss - % Mass activity	<30mV <40% <40%	- 40 mV loss at 1.5 A/cm ² - 18% loss ECSA - 48 % loss mass activity
Durability: 1.2 V for 400 hrs. at 80°C, H ₂ /N ₂ , 150 kPa, 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	5,000 5,000	9000 hrs, 3M PEM (20μm, 850 EW w/ stabilizers), 50 cm ² , 80/64/64°C 2000 hrs (OEM short stack, 0.1/0.15)

RH – relative humidity; ECSA – electrochemical surface area ; OEM - original equipment manufacturer; EW - equivalent weight; CCM - catalyst coated membrane; GM - General Motors; OCV - open circuit voltage

New Catalyst Activity and Understanding; Annealing and Process Scale-Up (Task 1.3)

- Extended enhanced catalyst deposition process improvement (P1) from pure Pt to PtCoMn and obtained same dramatic gains in Pt(hkl) grain size and surface smoothing with simpler, more cost-effective coating process.
- Scaled up Surface Energy Treatment (SET) process for roll-to-roll catalyst annealing. Significantly improves oxygen reduction reaction (ORR) activity of some alloys, more than others.
- Demonstrated Pt₃Ni₇ alloy catalyst mass activities in 50 cm² cells ranging from 0.35 ± 0.06 A/mg to 0.59 ± 0.08 A/mg at 3M and GM depending on lab, protocol and loading measurement. Gain in ORR activity derived from SET catalyst annealing process.
- Validated Pt₃Ni₇ alloy peak composition in compositional spread rotating disk electrode (RDE) measurements on NSTF whiskers (Dalhousie).
- Obtained first confirmation of Pt₃Ni₇ composition at nm scale of whiskerettes and Pt enrichment of whiskerette tips (JPL).

Catalyst and MEA Durability with Preliminary 2010 “Best of Class MEAs” (Task 2)

- OCV Hold: Demonstrated 12 ± 5% OCV voltage loss after 1,400 hours at 250/200 kPa H₂/air, 90°C, 30%RH, and met cross-over targets.
- 1.2 V hold: Demonstrated 10 mV loss at 1.5 A/cm², 10% loss of ECSA and 10% loss of mass activity after 400 hr at 1.2 V at 80°C, 150 kPa, 100% RH.
- 30,000 Cyclic Voltammetry (CV) cycles: Demonstrated 40 mV loss at 1.5 A/cm², 18% loss of ECSA, and 48% loss of mass activity under 30,000, 0.6-1.0-0.6 V cycles at 50 mV/sec and 80/80/80°C.
- Demonstrated load cycling lifetimes of 9,000 hours with 2009 “Best of Class” catalyst loadings (0.05/0.10 mg/cm²) in non-supported 3M PEM with chemical stabilizers.

Membrane-Electrode Integration and CCM Scale Up (Task 5.1)

- Produced 50,000 linear ft combined of NSTF substrate, coated catalyst supports, and CCM for process development, qualification and customer use.

2010 “Best of Class” MEA Down-Selection for Final Stack Testing (Task 5.3)

- Defined and implemented major screening programs for down-selection and integration of all MEA components for 2010 best of class MEA for final stack testing.
- Final short stack testing activities initiated at GM.



Introduction

State-of-the-art 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. The research and development of this contract 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 14-year DOE/3M funded development of the 3M NSTF catalyst and MEA technology. The NSTF catalyst fundamentally has higher specific activity for oxygen reduction [1-8], removes all durability issues with carbon supports, demonstrates much lower losses due to Pt dissolution and membrane chemical attack [9-12], and has significant high volume all-dry roll-good manufacturing advantages [13].

The scope of work in the previous three-year 1st 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-RDE catalyst evaluation technique with JPL. Research during the fourth year has focused at 3M on: a) continued water management improvements for cool/wet operation via optimization of materials, electrode structure and operating conditions; b) catalyst fabrication process improvements for increased catalyst performance and production efficiency; c) in-depth MEA component screening to down-select final configurations for the final short-stack testing; d) continued accelerated testing to benchmark the NSTF-MEA durability with each generation of MEA components; and e) fabrication of roll-good materials for stack testing by the GM fuel cell laboratory.

Results

The technical accomplishments for the fourth year fall roughly into five areas of research and development corresponding to Project Tasks 1, 2, 5.1, 5.2 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. 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 [14]. More recent work has focused on improving the NSTF-PtCoMn 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. The key is to make sure it does not reduce performance and hopefully improves it. An example of its effectiveness is shown in a series of PtCoMn loadings deposited by the P1 process at 0.054, 0.103, 0.146 and 0.184 mg_{Pt}/cm². They were coated in the production equipment and evaluated for structural differences by X-ray diffraction (XRD), scanning electron microscopy (SEM)/transmission electron microscopy (TEM) and fuel cell performance. SEM indicated no substantial differences at 40,000 magnification, but the TEM and XRD results showed significant changes. Figure 1(a) (left) shows that whereas the face-centered cubic (fcc) Pt[hkl] grain sizes by the standard process P4 are essentially independent of loading and 4 to 6 nm in size, the P1 process produces grain sizes that increase with loading and are larger, 6 to 12 nm. Consistent with this are the TEM images, Figure 1(a) (right), that show the catalyst coatings on the whiskers are smoother than those obtained by the P4 process, which produces highly oriented whiskerettes growing off the sides of the underlying whisker core, as discussed at length in reference [15]. This can be understood since aspects of the P1 process provide annealing like conditions.

Fuel cell performance of the P1 deposited PtCoMn is also generally the same as with the P4 process, as shown in Figure 1(b). With the conditions shown in the inset of Figure 1(b), in the same 50 cm² cell with quad-serpentine flow fields, using the same station and production lots of PEMs and GDLs, the P1 processed anodes and cathodes (0.1 to 0.184 loadings) show very similar performance to each other and to P4 processed 0.10 mg_{Pt}/cm² PtCoMn cathode. The galvanodynamic scans with the 0.054 mg/cm² cathodes are substantially lower (black open and closed squares) but at least as good if not better than historical results with P4 cathodes at these loadings. More careful inspection of the curves in Figure 1(b), show the P1 process yields about a 10 mV improvement at 0.32 A/cm² and 5 mV at 1 A/cm² over the P4 process, but very similar performance

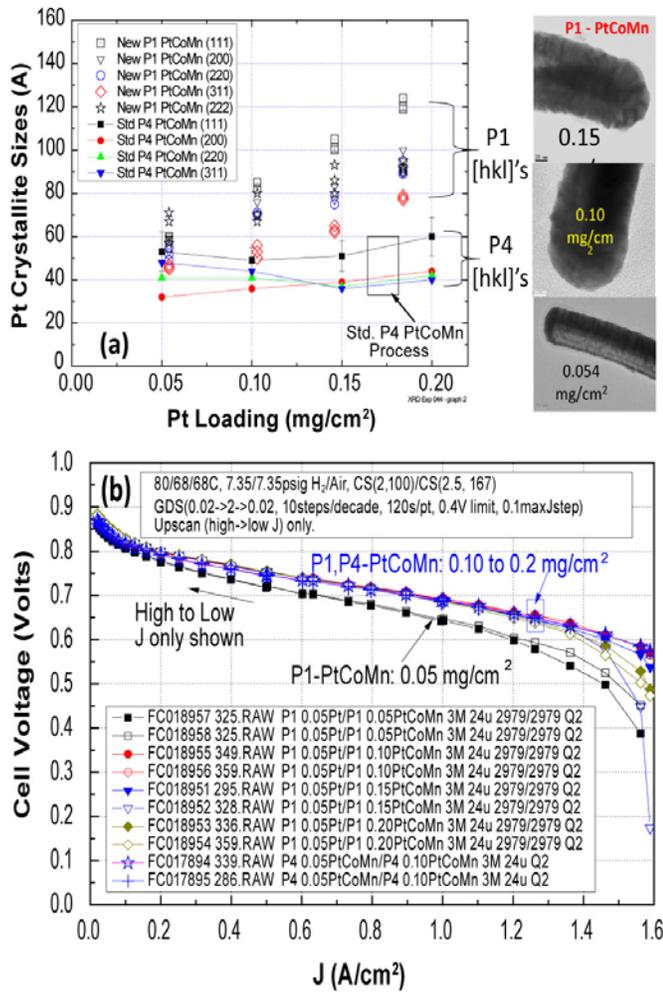


FIGURE 1. (a) Left: PtCoMn fcc[hkl] grain sizes by XRD as a function of Pt loading for catalysts sputter coated by new process P1 versus the standard process P4. Right: TEM images of the PtCoMn coated whiskers using new deposition process P1. At all three loadings the catalyst coating is smoother than by the standard P4 process that produces whiskerettes as discussed in reference [15]. (b) Polarization curves for PtCoMn deposited by the P1 process at ca. 0.05, 0.10, 0.15 and 0.20 mg_{Pt}/cm², and the P4 process at 0.10 mg_{Pt}/cm², under 80°C cell temperature, 68°C dew points and 150 kPa H₂/air. 3M-24 μm, 850 EW PEM. 3M standard GDLs, all 50 cm². Actual Pt loadings of the cathodes are 0.054, 0.103, 0.146 and 0.184 mg_{Pt}/cm².

at very low (0.025 A/cm²) and high (1.5 A/cm²) currents. Measurements of the absolute and specific activities at 900 mV under 150 kPa H₂/O₂ are very similar for both processes, although the P1 cathodes have slightly higher surface area than the P4 deposited materials. In conclusion, there are slight performance benefits and no penalties for the simpler, faster P1 process for depositing the NSTF alloys.

The recently revised 2015 DOE target of 0.125 g-Pt/kW (down from 0.2 g-Pt/kW for 2015) with a total of 0.125 mg/cm² of PGM per cm² of MEA will require further work and probably a new NSTF alloy

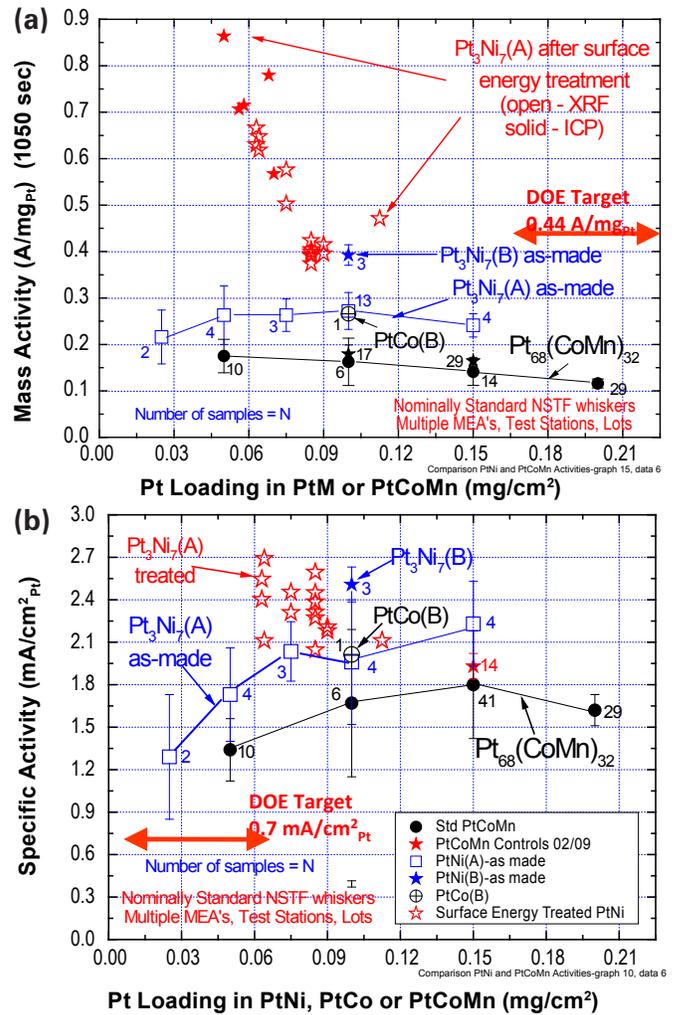


FIGURE 2. Summary of NSTF alloy ORR mass (a) and specific activity (b) as a function of Pt loading, comparing PtCoMn and Pt₃Ni₇ as-made and after surface energy treatment. Pt₃Ni₇ (A) was roll-good production fabricated at 3M. Pt₃Ni₇ (B) was lab coated at Dalhousie University with extremely thin alternating layers compared to (A).

material. This will likely be based on a Pt_xNi_y alloy, such as the unique NSTF- Pt₃Ni₇ introduced in last year’s annual report on this project and discussed in detail in reference (16). Figure 2 summarizes the ORR mass (a) and specific activities (b) measured in 50 cm² MEAs for both the PtCoMn and as-made PtNi systems. The open squares show the improvement of the as-made Pt₃Ni₇ alloy over the Pt₆₈Co₂₉Mn₃ alloy. Much higher activities are possible, however, by post-processing the as-made Pt₃Ni₇ using another process improvement we have been implementing. This process we refer to as a SET process that effectively anneals the as-made NSTF catalyst layers prior to their incorporation into a CCM. This past year it was further scaled up to allow roll-to-roll treatment.

The SET process improves the activities of both the PtCoMn and the PtNi systems, but the latter benefits much

more. SET treated production fabricated Pt_3Ni_7 (type A) cathodes are shown by the stars in Figure 2 and show there is a dramatic improvement of the measured activities over the open squares. The examples in Figure 2 were batch processed and it was necessary to re-measure the loading of the catalysts after the SET treatment in order to get accurate mass activities, as there was some loss of catalyst from the 0.1 mg/cm^2 as-made loadings. This measurement was done by both X-ray fluorescence (XRF) and inductively coupled plasma (ICP) as indicated by the solid and open stars in Figure 2. These values now indicate the promise for significantly exceeding the nominal 2015 DOE electrocatalyst target for mass activity at 900 mV of 0.44 A/mg . To further validate the SET treated Pt_3Ni_7 activities, a multi-sample set of 50 cm^2 MEAs were produced and measured at both 3M and GM using slightly different ORR activity protocols inherent to each lab. The mass loadings were also measured independently by both labs. Table 2 summarizes the results which range from 0.35 to 0.59 A/mg depending on the protocols used and confirm that the activity values are very near the DOE targets.

TABLE 2. Mass activities of surface energy treated Pt_3Ni_7 NSTF alloys measured at 3M and GM using independently measured loadings and ORR activity protocols. 50 cm^2 MEAs. Lab refers to the place of measurement. ORR protocol refers to the source of the protocol.

Loading Measurement Method	Lab/ORR Protocol	Mass Activity (A/mg-Pt) at 900 mV
3M XRF/ICP	3M/3M	0.59 ± 0.08
3M XRF/ICP	GM/3M	0.51 ± 0.06
3M XRF/ICP	GM/GM	0.43 ± 0.06
GM ICP	GM/3M	0.42 ± 0.08
GM ICP	GM/GM	0.35 ± 0.06

Fuel cell performance under H_2/air in the kinetic region with the Pt_3Ni_7 alloy mirrors the gain in mass activity. However a major issue with the current constructs is that the dealloying of the excess Ni into the membrane severely attenuates the high current density performance above about 0.8 A/cm^2 , as shown in reference [14]. Proper ex situ dealloying methods are being investigated but ultimately, the structure and composition of the catalyst surface as it actually ends up in the working electrode is what we must make initially to mitigate any complex processing requirements.

Task 2

Any new electrocatalyst alloy must have the requisite durability and stability, so we continuously test our new MEA component compositions and process improvements against the DOE recommended accelerated stress tests. Below are summarized the results of three DOE defined accelerated stress tests (AST) for support, catalyst and MEA durability.

1.2 V Hold: In this test the MEA cathodes are held at 1.2 V vs. the reference hydrogen electrode (RHE) for nominally 400 hours under 150 kPa H_2/N_2 at 80°C . It effectively measures the stability of the catalyst support particle against corrosion. The DOE targets are that ORR activity and surface area will each drop $\leq 40\%$, and the performance at 1.5 A/cm^2 will drop less than 30 mV from initial levels. Figure 3(a) shows the series of polarization curves (DOE conditions) measured periodically over a total of 435 hours at 1.2 V, for an MEA having the P1 processed PtCoMn on the anode (0.05 mg/cm^2) and cathode (0.15 mg/cm^2). The MEA used a 3M made 3M-supported membrane with a chemical additive. It is apparent that the test had only a small effect on performance. Surface area loss was 10%, specific activity was unchanged, and the

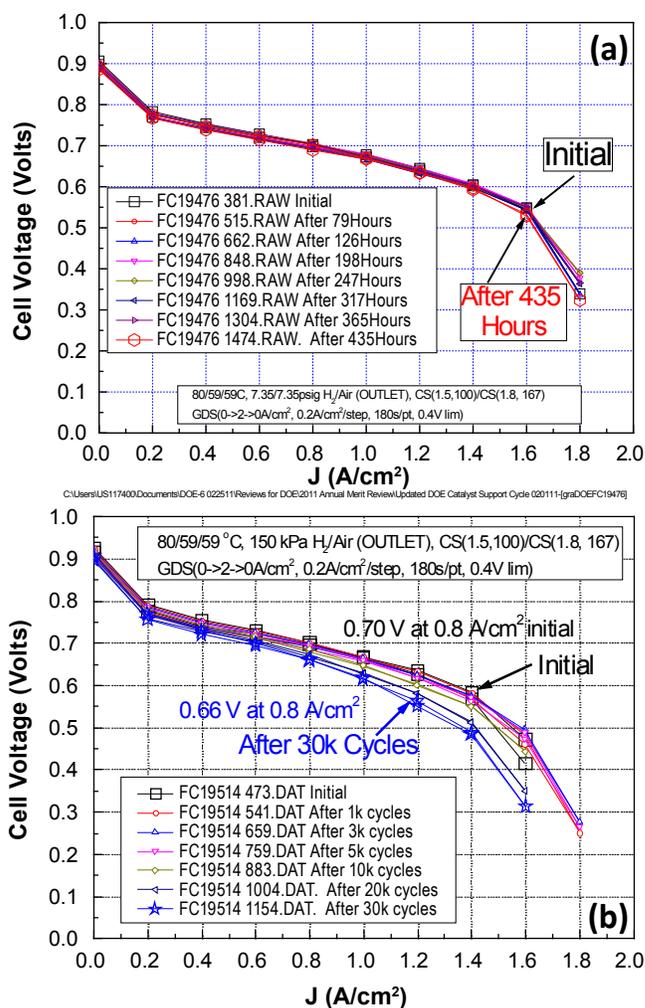


FIGURE 3. (a) Polarization curves versus time during the DOE 1.2 V hold durability test protocol. (b) Polarization curves versus time during the DOE CV cycling durability test protocol, 0.6 - 1.0 - 0.6 V, 50 mV/sec under 100/100 kPa H_2/N_2 . Anode /cathode catalysts were all PtCoMn made by the P1 process at $0.05/0.15 \text{ mg}_p/\text{cm}^2$ loadings; 3M-supported PEM with additive; standard 3M GDLS.

performance at 1.5 A/cm² dropped only 10 mV, so all targets were met and repeated with a second MEA.

OCV Hold: The objective of this 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. Using similar or the same MEA construction as in the 1.2 V hold test, six MEAs met the 500 hour limit and cross-over targets before stopping the tests. Two MEAs were allowed to go further and have exceeded 1400 hours with ~12% loss of OCV and acceptable H₂ cross-over.

CV Cycling: This AST 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 activity and a polarization curve loss of less than 30 mV at 0.8 A/cm². This test was applied to the same MEA type as used for the previous two ASTs. The surface area loss of 18% met and exceeded the DOE target. The mass activity loss was 48% and therefore did not meet the target of ≤40%. Figure 3(b) shows the polarization curves before and after 30,000 cycles. The loss of cell voltage at 0.8 A/cm² was 40 mV, and therefore also did not meet the ≤30 mV loss target. Further results are given in reference [14], but improvements in stability under this test are required.

Task 5

Task 5 embodies all work done under catalyst/membrane integration and scale up, GDL integration and water management, and MEA component down-selection for final stack testing.

Water Management: MEAs utilizing the ultra-thin (<1 μm) 3M NSTFC technology have several demonstrated advantages compared to MEAs comprising conventional, relatively thick (~10 μm) carbon-supported catalyst, as noted in the introduction. However, the low temperature (0-50°C) steady state limiting current density of typical NSTFC MEAs with standard GDLs under usual operating conditions is substantially lower than that of many conventional catalyst MEAs (0.3 v. 1.6 A/cm² at 30°C, air cathode). This reduced low temperature performance can be attributed to the NSTFC's much higher water generation rate per unit catalyst volume and to a hydrophilic electrode pore structure that is more susceptible to water condensation. Recent studies have been conducted to better understand water management differences between NSTF and Pt/C electrode MEAs. In one study, the product water effluent rate out the cathode was evaluated at several conditions where NSTF MEAs typically show reduced performance due to flooding. By calculating the fraction of water exiting the cathode in the liquid phase and plotting against the performance loss from 80°C reference performance, reasonably quantitative

agreement is observed for both NSTF and Pt/C electrode MEAs. A primary conclusion from this study is that liquid phase product water removal out the cathode is detrimental to performance for both electrode types, but, at a given set of conditions, the total water effluent rate out the cathode is less for Pt/C electrodes than NSTF electrodes. It also stresses that taking water out the anode rather than the cathode is a most desirable strategy if possible.

In light of these results, a logical path forward was based upon the premise of minimizing liquid product water removal out the cathode GDL, which is accomplished by maximizing liquid product water removal out the anode GDL. One such method found to be effective towards this premise is decreasing the total anode pressure to enable both enhanced liquid and vapor phase product water removal out the anode GDL. This concept was introduced in last year's annual report. Decreasing the anode pressure from 200 to 25 kPa resulted in nearly a three-fold gain in the current density at 30°C cell temperature, while the limiting current density increased from 0.4 to over 2 A/cm² as the anode pressure was reduced from 150 to 50 kPa at 30°C.

A less system dependent and probably more practical method for improving the low temperature performance of NSTF MEAs is through materials development. This year we have focused on screening the anode GDL backing and microporous layer (MPL) properties. Several different vendor supplied anode GDL backings were evaluated to determine their impact on low temperature response. Figure 4(a) shows results from four tests where the anode GDL backing was varied; all GDLs contained similar hydrophobic treatments and MPLs applied by 3M. Under Test I, the MEAs with GDLs MRC A and Freudenberg A yielded similar performance whereas the MEA with MRC C had lower performance at high current density, due to higher high-frequency resistance (HFR). Under Test II, a pseudo-system startup transient, Freudenberg A GDL provided a short burst of higher performance than MRC A, but the current density dropped to the MRC A level within ~15 s. MRC C, which had lower performance than the other GDLs under Test I, yielded transient current densities which were 50% higher than Freud A and a steady-state current density approximately 3x that of the other two GDLs. Under Test III, MEAs with either MRC A or Freudenberg A GDL had similarly low performances at 30°C. As the cell was heated, the performance with both GDLs improved, with Freudenberg A having better performance at 40°C than MRC A. MRC C, which performed well under Test II, also performed well at low temperatures under Test III. As the cell temperature exceeded 50°C, all three MEAs performed similarly. Under Test IV, MEAs with either Freudenberg A or MRC C performed similarly as the current density was stepped up from 0.02 to 1 A/cm² when the cell temperature was 70°C, but at 60°C, Freud A was unable to provide a positive cell voltage at 1 A/cm² whereas MRC C only showed a slight loss relative to 70°C. These results show anode GDL properties are the most promising and effective component variable we have identified for solving low temperature

cathode flooding with ultra-thin electrodes. Exactly which properties of the GDL are most critical for this function are still unclear and something we are trying to determine.

We have also explored gradient cathode electrode options that can also provide some benefit, using hybrid combinations of NSTF and thin Pt/C dispersed layers as discussed in last year’s annual report. The ratio of benefits to added Pt loading and processing costs are not nearly as favorable as with just anode GDL optimization, and the benefit of selecting the correct anode GDL properties appears larger. This is illustrated in Figure 4(b) which is a larger summary of several GDL responses to the pseudo-system startup transient Test II discussed above, including anode GDLs comprising the MRC C (GDL C in 4(b)) with and without MPLs, the Freudenberg A type and 3M standard GDLs. Also shown in Figure 4(b) is the impact of the gradient or hybrid CCB used on the cathode with either a standard GDL on the anode or Freudenberg A or MRC C on the anode. The top three responses curves in 4(b) are obtained with the MRC C on the anode with or without an MPL and a standard cathode GDL. This combination would seem to be the best solution to the low temperature performance issue with ultra-thin electrodes, but there is still a high temperature issue with the MRC C type due to the HFR that remains to be solved as noted in Figure 4(a) test I.

MEA component down-selection: A primary focus of this project for most of the year has been the screening process for down-selecting the final MEA component sets for the final stack testing. Much of the GDL development work, P1 vs P4 catalyst deposition and SET process work discussed above were all directed at this objective. The MEA component sets investigated in this process included these bulleted items:

- Cathode catalyst: composition, loading, deposition process, post process
- Anode catalyst: composition and deposition process (finalized)
- PEM: thickness, supported vs un-supported, chemical additive levels, etc.
- Anode GDL: Backing layer type, MPL properties
- Cathode GDL: Backing layer type and MPL properties, interfacial coatings

The down-selection process itself involved evaluation of hundreds of MEAs in duplicate covering two dozen or more specific component/process parameter experiments. The results are too extensive to discuss here but more information and some examples can be found in reference [14]. The end result is that for the first short stack test we defined six MEA component configurations with three different membrane options, and three cathode catalyst options. Different GDLs were used for the anodes and cathodes, but only one type of each. The anode catalyst was fixed at NSTF-0.05 mgPt/cm² of the P1 processed PtCoMn. These six MEA types were fabricated as roll-goods and used to

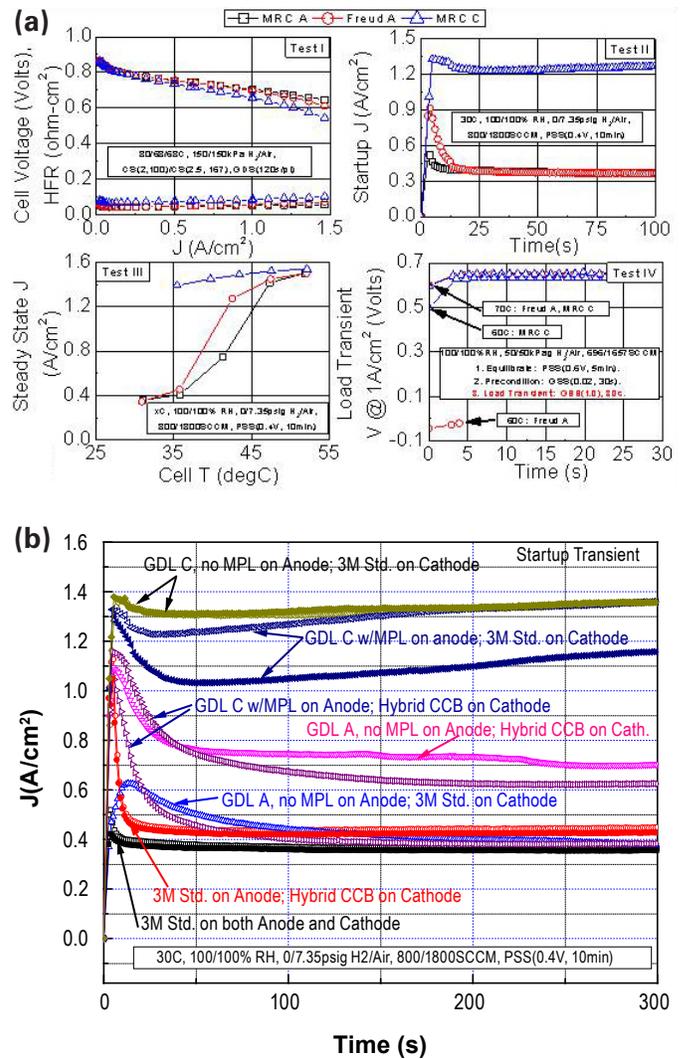


FIGURE 4. (a) Comparison of the 50 cm² cell response to four different test protocols sensitive to water management: Test I is steady-state high temperature performance; Test II is a pseudo-system startup transient at 30°C; Test III is steady-state current density at 0.4 V versus temperature; Test IV is a load transient current density step up from 0.02 to 1 A/cm² at 60 or 70°C. (b) Comparison of the 50 cm² cell response to a start-up transient (OCV to 0.4 V) at 30°C and 100% RH for different anode and cathode GDL combinations. H₂/air pressures are 100/150 kPa. GDL type C performance with or without an MPL is far superior in transient and steady-state operation to the 3M standard GDL.

populate a 29 cell “Rainbow” stack (i.e., term used by stack manufacturers to refer to different MEA configurations used in the stack metaphorically similar to the different colors seen in a rainbow), one “color” for each MEA type, for initial beginning of life operation under various automotive relevant test protocols for beginning of life testing to enable further down-selection for a second stack that will be used for longer durability studies. At the time of this report preparation the first stack is still under test.

Conclusions and Future Directions

Last year we were able to claim that this project had met or exceeded the then currently specified DOE electrocatalyst and MEA performance and durability targets for 2015 using the same MEA component set in 50 cm² cell tests. Recent tightening of the DOE 2015 targets for performance (gPt/kW) and durability has reintroduced new challenges that we must demonstrate. Significant improvements in ORR activity with NSTF-PtNi alloys and improved processing methods were demonstrated and further improvements should be possible but may not be reached by the end of this project. Continued advances this past year were made in understanding and improving low temperature water management behavior associated with the ultra-thin NSTF electrodes, particularly by identifying the importance of the anode GDL backing properties. Significant effort focused on screening and down-selecting all MEA component materials and process options for integration into an advanced robust, durable, high performance, roll-good manufactured MEA containing no more than 0.2 mg/cm² of PGM total for the final stack testing-deliverable. At this time, the stack testing has been initiated in a rainbow short stack, and performance criteria are being evaluated and compared to past short stacks and single cell results for six different MEA configurations. Specific future work will include:

- Selecting the final one or two MEA configurations for long-term testing in a second stack.
- Fabricating final MEAs sufficient for final stack(s).
- Delivering MEA media for stack integration and executing the testing plan.
- Continuing effort on one or two key issues related to anode GDLs for water management and understanding long term irreversible voltage decay.
- Exploring ex situ dealloying optimization of Pt₃Ni₇ system to achieve high current density (A/cm²).

FY 2011 Publications/Presentations

1. D.A. Stevens, S. Wang, R.J. Sanderson, G.C. K. Liu, G.D. Vernstrom, R.T. Atanasoski, M.K. Debe and J.R. Dahn, "A combined rotating disk electrode/X-ray diffraction study of Co dissolution from Pt_{1-x}Co_x Alloys," *J. Electrochem. Soc.* **158**(8) B899-B904 (2011).
2. Gary Chih-Kang Liu, D.A. Stevens, J.C. Burns, R.J. Sanderson, G.D. Vernstrom, R.T. Atanasoski, M.K. Debe and J.R. Dahn, "Oxygen reduction activity of dealloyed Pt_{1-x}Ni_x catalysts" *J. Electrochem. Soc.* **158**(8) B919-B926 (2011).
3. D.A. Stevens, R. Mehrotra, R.J. Sanderson, G.D. Vernstrom, R.T. Atanasoski, M.K. Debe and J.R. Dahn, "Dissolution of Ni from high Ni content Pt_{1-x}Ni_x alloys," *J. Electrochem. Soc.* **158**(8) B905-B909 (2011).
4. M.K. Debe, A.J. Steinbach, G.D. Vernstrom, S.M. Hendricks, M.J. Kurkowski, R.T. Atanasoski, P. Kadera, D.A. Stevens, R.J. Sanderson, E. Marvel and J.R. Dahn, "Extraordinary oxygen reduction activity of Pt₃Ni₇," *J. Electrochem. Soc.* **158**(8) B910-B918 (2011), and *ECS Trans.*, **33** 143 (2010).
5. S.K. Deppe, S.M. Hendricks, and E.M. Fischer, "A New Paradigm for PEMFC Ultra-Thin Electrode Water Management at Low Temperatures," *ECS Trans.*, **33**(1), 1179-1188 (2010).
6. 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," Abstract #781, 220th ECS Meeting, Boston, MA, Oct. 9-14, 2011.
7. M. K. Debe, R. T. Atanasoski and A. J. Steinbach, Invited presentation "Nanostructured Thin Film Electrocatalysts – Current Status and Future Potential," Abstract #805, 220th ECS Meeting, Boston, MA, Oct. 9–14, 2011.
8. Mark K. Debe, Project review at the DOE 2011 Vehicle Technologies and Hydrogen Programs Annual Merit Review, May 10, 2011, Washington, D.C., number FC 001.
9. M.K. Debe, Invited presentation, "Nanostructured Catalyst Developments," 2nd CARISMA Conference, La Grande Motte, France, Sept. 19–22, 2010.
10. Radoslav Atanasoski, Invited presentation, "Fundamental and practical aspects of Nano-structured thin film - NSTF catalysts for PEM fuel cells: Durability under Transient Conditions," 61st ISE – Electrochemical Energy Conversion and Storage, Nice, France, Sept. 2010.
11. D.A. Stevens, Invited presentation, T.D. Hatchard, R.J. Sanderson, R.T. Atanasoski, M.K. Debe and J.R. Dahn, "PEMFC Electrocatalyst Development," Presentation at the 218th ECS meeting, Las Vegas, NV, Oct. 11, 2010.
12. M.K. Debe, A. Steinbach, G. Vernstrom, S. Hendricks, R. Atanasoski, P. Kadera, "Extraordinary ORR activity of Pt₃Ni₇," Presentation at the 218th ECS meeting, Las Vegas, NV, Oct. 12, 2010.
13. Gary Chih-Kang Liu, R.J. Sanderson, D.A. Stevens, G. Vernstrom, R.T. Atanasoski, M.K. Debe and J.R. Dahn, "De-alloying of Pt_{1-x}M_x [M = Ni, Co] (0 < x < 1) catalysts and impact on surface area enhancement," Presentation at the 218th ECS meeting, Las Vegas, NV, Oct. 12, 2010.
14. Gary Chih-Kang Liu, R. Sanderson, D.A. Stevens, G. Vernstrom, R.T. Atanasoski, M.K. Debe and J.R. Dahn, "RRDE measurements of ORR activity of Pt_{1-x}Ni_x (0 < x < 1) on high surface area NSTF-coated GC disks," Poster paper at the 218th ECS meeting, Las Vegas, NV, Oct.13, 2010.
15. D.A. Stevens, S. Wang, R.J. Sanderson, G.C.K. Liu and J.R. Dahn, G.D. Vernstrom, R.T. Atanasoski and M.K. Debe, "A Combined Rotating Disk Electrode/X-Ray Diffraction study of Co Dissolution from Pt_{1-x}Co_x alloys," Poster paper at the 218th ECS meeting, Las Vegas, NV, Oct. 13, 2010.
16. A. J. Steinbach, M.K. Debe, J.L. Wong, M.J. Kurkowski, A.T. Haug, D. M. Peppin, S. K. Deppe, S. M. Hendricks and E.M. Fischer, "A New Paradigm for PEMFC Ultra-Thin Electrode Water Management at Low Temperatures," Presentation at the 21^{8th} ECS meeting, Las Vegas, NV, Oct. 14, 2010.
17. M.K. Debe, Invited presentation, "NanoStructured Thin Film Catalysts -15 (or is it 28?) Years on an Alternative Path for PEM Fuel Cell Electrocatalysts," Fuel Cell Seminar and Exposition R&D Award presentation, San Antonio, TX, Oct. 19, 2010.

18. M.K. Debe, Invited presentation, “Nanostructured Thin Film Catalysts for PEM Fuel Cells: Status and Path Forward to Meet Performance, Durability and Cost Targets for High Volume Automotive Applications,” Workshop on PEM Fuel Cell Catalyst & MEA Preparation and Characterization, HySA Catalysis Competence Center and University of Cape Town, Cape Town, Rondebosch, South Africa, March 28-29, 2011.

19. M.K. Debe, Invited presentation, “NSTF Catalyst Technology for Energy Applications,” Northwest University, Potchefstroom, South Africa, March 25, 2011.

20. M.K. Debe, Invited presentation, “A General Introduction to Nano-Structured Thin Film Catalyst (NSTFC) Technology for Hydrogen and Fuel Cell Applications,” Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa, March 24, 2011.

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