

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

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### Objectives

The objectives of this project are development of a durable, low cost (both Pt 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  $\leq 0.25$  mg/cm<sup>2</sup>,
- short-stack specific power density of  $\leq 0.3$  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,

- 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 (FCT MYRDDP):

- (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 2<sup>nd</sup> quarter, calendar year (CY) 2010 status with DOE electrocatalyst targets for 2010/2015 from Table 3.4.12 of the FCT MYRDDP. Additional rows were added to summarize recent accelerated durability test results. Unless noted otherwise, all metrics were obtained with the 2009 NSTF “best of class” catalyst-coated membrane (CCM) containing 0.10 mg-Pt/cm<sup>2</sup> on the cathode and 0.05 mg-Pt/cm<sup>2</sup> on the anode using a PtCoMn alloy catalyst. The MEAs used for the inverse specific power density values listed in the first row, PGM total content, had loadings of 0.05/0.10 mg<sub>Pt</sub>/cm<sup>2</sup> on the anode and cathode respectively. The short stack results were obtained outside the project but evaluated catalysts and gas diffusion layer (GDL) developed within the project.

### Accomplishments

Water Management for Cool/Wet Operation (Task 5.2)

- Demonstrated new paradigm for water management of thin layer electrodes based on sub-atmospheric anode pressure and high liquid water permeability anode GDLs that: a) enables steady-state current density up to 2.0 A/cm<sup>2</sup> at 30 to 35°C with NSTF MEAs in 50 cm<sup>2</sup> single cells, and b) 5 second 0 -1 A/cm<sup>2</sup> load transients at 50°C and 140% relative humidity (RH).
- Demonstrated hybrid MEA with gradient cathode catalyst construction that enables steady-state 1 A/cm<sup>2</sup> at 30°C, successful load transient 0 -1 A/cm<sup>2</sup> step at 40°C, 140% RH, and which does not reduce performance at 80°C over the standard NSTF CCM.

**TABLE 1.** Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications. (Values in red are new versus last year's report.)

Characteristic	Units	Targets 2010 / 2015	Status: Values for roll-good CCM w/ 0.15mg <sub>Pt</sub> /cm <sup>2</sup> per MEA or as stated
PGM Total Content	g <sub>Pt</sub> /kW <sub>e</sub> rated in stack	0.3 / 0.2	< 0.18g <sub>Pt</sub> /kW for cell V < 0.67 V in 50 cm <sup>2</sup> cell at 150kPa inlet, and 0.19g <sub>Pt</sub> /kW in OEM 400 cm <sup>2</sup> stack
PGM Total Loading	mg PGM / cm <sup>2</sup> total	0.3 / 0.2	0.15, A+C with current PtCoMn alloy
Durability under Load Cycling (membrane lifetime test)	Hours, T ≤ 80°C Hours, T > 80°C	5000 / 5000 2000 / 5000	> 6500 hrs, 3M PEM (20µm, 850 EW w/ stabilizers), 50cm <sup>2</sup> , 80/64/64 °C 2000 hrs (OEM short stack, 0.1/0.15)
Mass Activity (150kPa H <sub>2</sub> /O <sub>2</sub> 80°C, 100% RH, 1050 sec)	A/mg-Pt @ 900 mV, 150kPa O <sub>2</sub>	0.44 / 0.44	0.24 A/mg in 50 cm <sup>2</sup> w/ PtCoMn 0.40 A/mg in 50 cm <sup>2</sup> with new Pt <sub>3</sub> Ni <sub>7</sub>
Specific Activity (150 kPa H <sub>2</sub> /O <sub>2</sub> at 80°C, 100% RH)	µ A/cm <sup>2</sup> -Pt @ 900 mV	720 / 720	2,100 for PtCoMn, 0.1mg <sub>Pt</sub> /cm <sup>2</sup> 2,500 for new Pt <sub>3</sub> Ni <sub>7</sub> , 0.1mg <sub>Pt</sub> /cm <sup>2</sup>
Accel. Loss: 30,000 cycles, 0.7 – 0.9V step, 30 s hold at 80/80/80°C	- mV at 0.8 A/cm <sup>2</sup> % ECSA loss	< 30mV < 40% / 40 %	~ 0 mV / -10mV, Cat=0.15/0.1 mg/cm <sup>2</sup> ~ 0% / -22%, Cat=0.15/0.1 mg <sub>Pt</sub> /cm <sup>2</sup>
Accel. Loss: 200 hr hold @ 1.2 V at 95°C, H <sub>2</sub> /N <sub>2</sub> , 150kPa, 80% RH	- mV at 1.5 A/cm <sup>2</sup> % ECSA loss	< 30mV < 40% / 40%	+ 25mV gain at 1.5 A/cm <sup>2</sup> ~ - 17% loss (Cath. = 0.15 mg/cm <sup>2</sup> )
OCV hold without PEM failure under 250/200 kPa H <sub>2</sub> /air, 90°C, 30%RH	Hours mA/cm <sup>2</sup>	500 < 20	610/1200 for Cath. = 0.1/0.15mg <sub>Pt</sub> /cm <sup>2</sup> H <sub>2</sub> Crossover < 20 mA/cm <sup>2</sup> , F <sup>-</sup> ion release rate < 0.5 µg/cm <sup>2</sup> -day
Accel. Loss: 4,000 cycles 0.6 -1.2V, 20mV/sec, 95/95/95°C, 200kPa, H <sub>2</sub> /N <sub>2</sub>	Specific Activity % ECSA loss	?? ??	-14 ± 15% loss in mA/cm <sup>2</sup> <sub>Pt</sub> -23 ± 8 % loss of cm <sup>2</sup> <sub>Pt</sub> / cm <sup>2</sup> <sub>planar</sub>

### Catalyst Activity and Understanding (Task 1)

- Increased PtCoMn mass activity 30% to 0.24 A/mg and demonstrated Pt<sub>3</sub>Ni<sub>7</sub> alloy with mass activity of 0.40 A/mg and absolute activity at 900 mV of 40 mA/cm<sup>2</sup> with 0.1 mg/cm<sup>2</sup>.
- Developed a post-fabrication treatment process that is roll-good compatible and increases oxygen reduction reaction (ORR) mass activity up to 50% for as-made PtCoMn and Pt<sub>3</sub>Ni<sub>7</sub> alloys.
- Made catalyst deposition process improvement that gives NSTF pure Pt performance equal to PtCoMn with much greater Pt face centered cubic (hkl) grain sizes.

### Catalyst and MEA Durability (Task 2)

- Demonstrated MEA load cycling lifetime of >6,500 hours with 0.05/0.10 mg/cm<sup>2</sup> loaded 20 µm membrane having no reinforcement.
- Demonstrated that with chemical stabilizers in the membrane, the 500 hour DOE target for open circuit voltage (OCV) hold under H<sub>2</sub>/air is exceeded by a factor of 2X for anode/cathode loadings of 0.05/0.15 mg<sub>Pt</sub>/cm<sup>2</sup> respectively.

### Large Area Short Stack Test Durability Testing (Task 3)

- Initiated large area short stack testing with Nuvera Inc. to evaluate for the first time, the combination of the 3M NSTF electrode technology with the Nuvera

open flow field bi-polar plate technology. Three short stacks were built and initiated beginning of life testing.

### Membrane-Electrode Integration and CCM scale-up (Task 5.1)

- Produced 37,000 linear ft combined of NSTF substrate, coated catalyst supports, and CCM for process development, qualification and customer use.

### Break-In Conditioning (Task 6)

- Developed more user friendly MEA conditioning protocols that can provide 90% of full performance in 2 to 5 hours depending on the material set.



### 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. 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 13-year DOE/3M funded development of the 3M NSTF catalyst and MEA technology. The NSTF catalyst fundamentally has higher specific activity for oxygen reduction [1,2], removes all durability issues with carbon supports, demonstrates much lower losses due to Pt dissolution and membrane chemical attack [3-6], and has significant high-volume all-dry roll-good manufacturing advantages [7].

The scope of work in the three-year initial budget period included extensive work at 3M to increase the NSTF catalyst support film surface area, fabrication and screening of new alloys in 50 cm<sup>2</sup> 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 catalyst evaluation technique with JPL. Research during this third year has focused on: a) water management improvements for cool/wet operation through optimization of materials, electrode structure and operating conditions; b) continued investigation of multiple strategies for increasing NSTF support surface area, catalyst activity and durability with total loadings of  $\leq 0.25$  mg-Pt/cm<sup>2</sup> per MEA; c) continued fundamental studies of the NSTF catalyst activity for ORR in general and methods to achieve the entitlement activity for NSTF catalysts; d) more severe accelerated testing to benchmark the NSTF-MEA durability; e) development of faster, easier MEA break-in conditioning protocols; and f) work with system integrators to validate NSTF functional properties and issues in short stacks.

## Results

The technical accomplishments for the third year fall into five areas of research and development corresponding to Project Tasks 1, 2, 3, 5 and 6. We briefly summarize the main results from each of these areas.

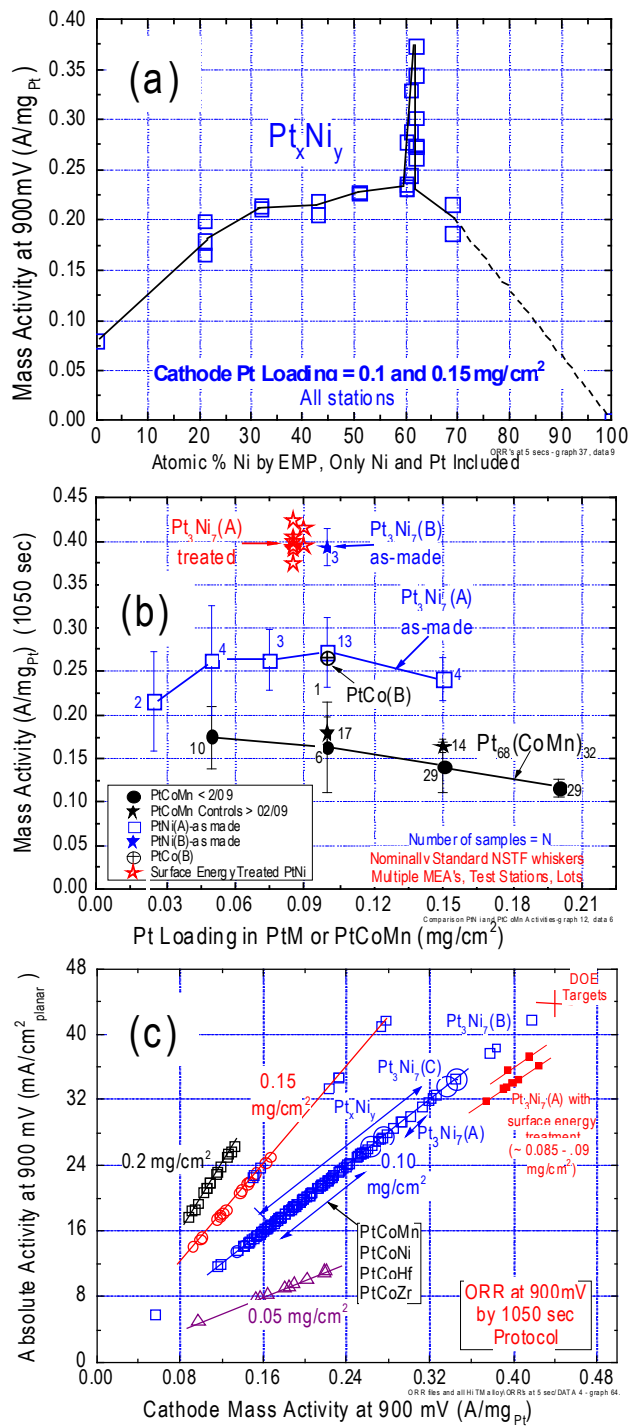
### Task 1

Work under Task 1 had three primary areas of focus this year. The first and largest effort investigated a specific PtNi alloy in greater depth. At the end of 2008 and early 2009 we were investigating a broader

compositional range for various PtM and PtMN alloys, when we noticed that for PtNi binaries, there appeared to be a significant and sharply defined increase in ORR activity around 70 at% Ni as best determined using thin film gravimetric methods. This year we fabricated many more samples over a broad range of composition with sufficient resolution to try to better reveal the peak width and composition. Although most accurate, the gravimetric measurement of the Pt/Ni content has only  $\pm 5\%$  precision so higher precision X-ray fluorescence (XRF) and electron microprobe (EMP) were also used. Both show that there is indeed a finite peak width, although it is very narrow, with the mass activities approaching 0.4 A/mg. The results for mass activity vs at% Ni by EMP is shown in Figure 1(a). The peak position by EMP occurs at 60 at% Ni. By XRF the peak appears to be at about 75% Ni [8]. Since the more accurate gravimetric peak is at 69% Ni, we are calling this a Pt<sub>3</sub>Ni<sub>7</sub> alloy composition. Once we saw this strong compositional effect with PtNi, we then investigated PtCo over a similar range of compositions, and although it also shows a sharp peak, it is not as dramatic as that for PtNi.

Figure 1(b) compares the mass activity as a function of Pt loading of the Pt<sub>3</sub>Ni<sub>7</sub> with our more standard PtCoMn composition. Specific activity and absolute activity for ORR of the Pt<sub>3</sub>Ni<sub>7</sub> and PtCoMn are shown in reference [8]. Increases in both specific activity and surface area of the Pt<sub>3</sub>Ni<sub>7</sub> contribute to its higher mass activity. There is also a process effect in the catalyst deposition that has a significant effect on the Pt<sub>3</sub>Ni<sub>7</sub> activity as indicated by the process A or process B labeled data points. The Pt<sub>3</sub>Ni<sub>7</sub> alloy by process A was made on full-scale roll-good manufacturing equipment, while process B was lab-based and limited to 50 cm<sup>2</sup> areas.

The second focus area under Task 1 was development of a surface energetic treatment for treating the catalyst to effectively anneal it. It is roll-good compatible so it can eventually be done as the catalyst is made. Many process parameter values were studied and slide 10 of reference [8] shows examples of how mass activity and surface area of the Pt<sub>3</sub>Ni<sub>7</sub> alloy made by process A and our standard PtCoMn are affected by these process parameter values. Compared to the untreated values, the activity of both catalyst types are increased by about 50% for the most effective treatment parameter values. The red stars data in Figure 1(b) are the activities from the process A-made Pt<sub>3</sub>Ni<sub>7</sub> after the surface energetic treatment with the most effective treatment parameter. The surface energetic treatment has further increased the Pt<sub>3</sub>Ni<sub>7</sub> activity made by process A to be similar to that of the Pt<sub>3</sub>Ni<sub>7</sub> made by process B. The mass activity values are now even closer to the targets. Figure 1(c) is a summary plot of absolute activity versus mass activity, updated from last year's report, for a variety of alloys we have made and



**FIGURE 1.** (a) Mass activity for a series of NSTF Pt<sub>x</sub>Ni<sub>y</sub> alloys as a function of atomic % Ni measured by EMP. The peak occurs at 69% Ni (Pt<sub>3</sub>Ni<sub>7</sub>) using gravimetrically-determined composition. (b) Mass activity versus Pt loading for PtCoMn and Pt<sub>3</sub>Ni<sub>7</sub> alloys as-made by two different processes (A and B), and after energetic surface treatment of the Pt<sub>3</sub>Ni<sub>7</sub> made by process A (red stars). (c) Absolute activity versus mass activity of various NSTF catalysts relative to the DOE targets, updated from last year's report.

characterized in the past year. Compared to last year, we have now many more candidates closer to this DOE electrocatalyst target.

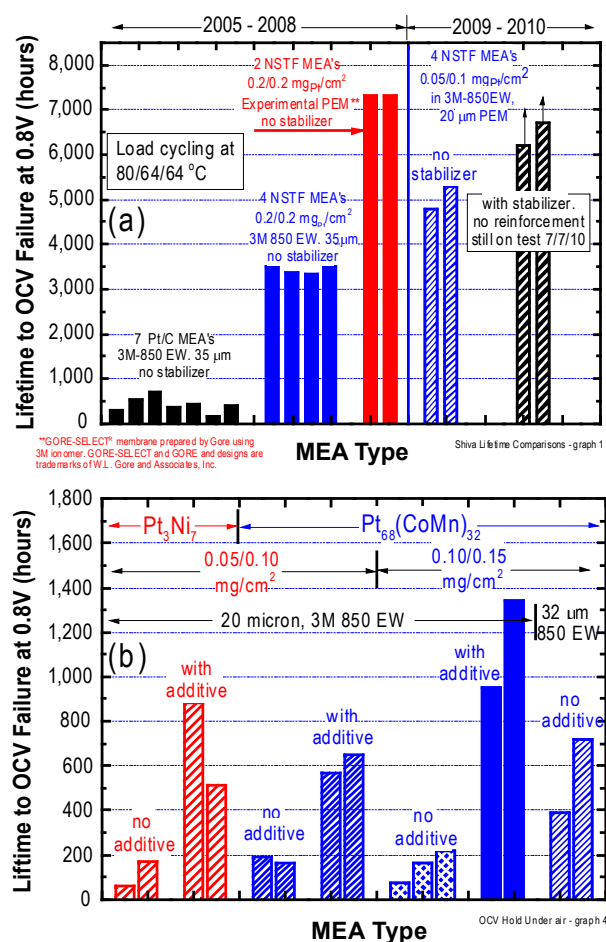
The Pt<sub>3</sub>Ni<sub>7</sub> alloy is a unique model system, but not a practical catalyst yet. The as-made composition is not stable and quickly de-alloys in situ in the working fuel cell, giving the resultant state of high activity. Although the higher mass activity translates into higher H<sub>2</sub>/air polarization curve kinetics [8], due to the excess Ni diffusing into the PEM that in turn affects cathode to anode water transport, there are severe performance limitation above 1 A/cm<sup>2</sup> from mass transport overpotential increases [8].

The final focus area under Task 1 was to revisit pure Pt with NSTF catalyst deposition process improvements in our manufacturing facility. Most notably the Pt(111) grain sizes of the Pt made by the improved process are substantially higher (8.5 nm at 0.1 mg/cm<sup>2</sup>) than those made by the standard process conditions, or those of our standard PtCoMn (5 nm at 0.1 mg<sub>Pt</sub>/cm<sup>2</sup>) [8]. The polarization curves are very similar to those from our PtCoMn with nearly the same loading. There appears to be about a 10 mV improvement in the polarization curve of the pure Pt by the new process conditions versus the standard. The impact on durability of the larger grain size of the pure Pt made by the improved process is still being determined. We will be extending these process improvements to the Pt alloys in the future.

**Task 2**

Our work under the second area (Task 2) continued this year to focus on three types of accelerated durability tests using the 2009 'best of class' NSTF MEA having 0.15 mg<sub>Pt</sub>/cm<sup>2</sup> of total loading but with a thinner membrane and MEA modifications of the latter. These three tests are load cycling, high voltage cycling and OCV hold. Figure 2(a) is an update of the load cycling tests under 80°C that we have shown results from in previous years. Cell voltages at various current densities are measured versus time under an 80°C cell temperature, 64°C dew point, constant flow load cycling protocol [8]. OCVs (measured daily) are used to determine end of life in this test (<0.8 V). At the end of last year we had obtained ~5,000 hr lifetimes with the 2009 best of class NSTF CCM with the 0.05/0.10 mg/cm<sup>2</sup><sub>Pt</sub> loadings on a 3M 850 equivalent weight PEM that did not contain any chemical stabilizer or mechanical reinforcement (blue crosshatched bars in Figure 2(a)). The set of black crosshatched bar graphs on the right side of Figure 2(a) are new results this year, and show that MEAs with our 2009 best of class CCM, with 0.05/0.1 loadings and a 20 micron 3M PEM with a chemical stabilizer, but still no reinforcement, have survived 6,500 hours without failure and are still going strong.





**FIGURE 2.** Updated chart of the lifetime to OCV failure of various NSTF MEAs, (a) under load cycling at 80°C with 64°C dew points, showing the effect of various membrane types and catalyst loadings, compared with conventional Pt/C MEAs; (b) after OCV hold under H<sub>2</sub>/air at 90°C, 30% RH, 22.1/14.7 psig. GDLs were constant, only the membranes and catalyst loadings were varied.

Cumulative results from the second type of durability test, OCV hold at 90°C under H<sub>2</sub>/air at 22.1/14.7 psig, 30%/30% RH, and 696/1,657 sccm, are shown in Figure 2(b). The bar graphs summarize the effects of a variety of different catalysts, catalyst loadings and membrane thicknesses and additives. Under this test we have found that chemical additives to the membrane are very important to enable exceeding the OCV hold targets (500 hours). Second, the Pt<sub>3</sub>Ni<sub>7</sub> alloy at the same 0.1 mg/cm<sup>2</sup> Pt loading on the cathode is slightly better than the standard PtCoMn (698±184 vs. 610 ±40 hrs). Finally higher loading helps to improve lifetime (1,145±195 hrs. for 0.1/0.15 mg/cm<sup>2</sup> vs. 610±40 hours for 0.05/0.10 mg/cm<sup>2</sup>) as does a thicker membrane. A number of combinations can exceed the new 500-hour targets for this test.

The third type of durability testing under Task 2 was testing of catalyst stability under high voltage cycling to simulate start-up and shut-down. The cathode under N<sub>2</sub> is cycled (relative to the anode under H<sub>2</sub>) 4,000 times between 0.6 and 1.2 V at 20 mV/sec at 95°C and 100% inlet RH. Slide 15 of reference [8] summarizes results with both the low loading standard PtCoMn and the Pt<sub>3</sub>Ni<sub>7</sub> under more severe conditions than we have reported previously. For this test we cycle from 0.6 to 1.2 V at 95°C and saturated inlets. Nine samples were tested with varying catalyst and membrane lots, and test cells. A key result was that the amount of surface area loss after 4,000 cycles depended on how the catalyst and CCM were made. The roll-good manufactured CCMs fared better than hand-laminated CCMs, losing 23% versus 36% surface area respectively. Fuel cell polarization curves before and after cycling for the manufactured versus hand-made MEAs show the performance loss mirrors the surface area loss, with the manufactured MEA losing less performance. A second key result is that the relative performance loss of the Pt<sub>3</sub>Ni<sub>7</sub> alloy, also at 0.1 mg/cm<sup>2</sup> loading of Pt, is less than the standard Pt<sub>68</sub>(CoMn)<sub>32</sub>. It doesn't start with as high of performance above 1 A/cm<sup>2</sup>, but after the 4,000 cycles, the Pt<sub>3</sub>Ni<sub>7</sub> performance is similar or slightly better than the PtCoMn [8].

### Task 3

Initiated about the first of this calendar year, Task 3.2 is focused on preliminary large area cell tests for performance and durability prior to starting the final stack testing under Task 5.3. An opportunity to combine the uniqueness of the 3M NSTF electrode technology with the Nuvera open flow field plate technology approach motivated going directly into full size area short stack testing of both the 2008 (0.1/0.15 mg/cm<sup>2</sup> loaded NSTF) and the 2009 (0.05/0.1 mg/cm<sup>2</sup> loaded) MEAs in 8 and 16 cell stacks at both 3M and Nuvera with the Nuvera Andromeda stack design. After just six months we are still investigating the best operating conditions to use (e.g. lower pressure and drier) and learning to marry the materials and the hardware. However fit and function went very smoothly, there does not seem to be contamination issues to any significant degree based on 3,000 hours of assembled shelf time and occasional operation. We have verified that there is a large opportunity to improve the performance by reducing the in-cell impedance that is roughly 50% larger than we expect based on single cell 50 cm<sup>2</sup> cells. Slides 16 and 41 in reference [8] compare the single cell 50 cm<sup>2</sup> test results with the first 16 cell stack tested at 3M and very preliminary 8 cell short stack performance at Nuvera. The average stack performances are roughly 75 mV below the single cell out to 2 A/cm<sup>2</sup>, while the best cell performance of the 16 cell stack reduces this to about 30 mV.

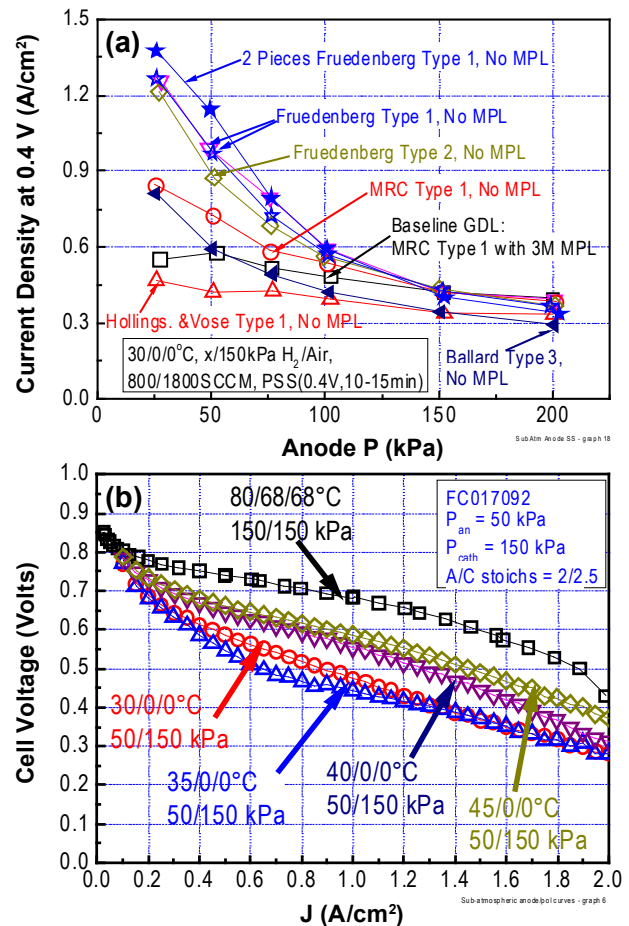
## Task 5

Task 5 embodies all work done under catalyst/membrane integration and scale up (Task 5.1) and GDL integration and water management (Task 5.2). Task 5.2 and the area of water management was our primary focus area for the year and the one with the most significant results. The NSTF electrodes are submicron in thickness and this leads to cathode flooding under cool/wet conditions if conventional water management approaches are used. This year we made significant changes in both material factors and operating conditions to demonstrate two independent paths to solve this cathode flooding issue.

## Water Management – Path 1

For the first path, based on use of sub-atmospheric anode pressure, we changed the paradigm for conventional MEA water management by removing cathode product water (liquid and vapor) out the anode instead of the cathode. This is possible with the hydrophilic ultra-thin NSTF catalyst electrode layers because they are in intimate contact with the membrane, and have high permeability for liquid water. Key material parameters to enable this include removing the hydrophobic microporous layer (MPL) from the anode GDL, use of a thinner membrane, use of anode GDL backing layers with adequate liquid water permeability and thickness, use of higher cathode pressure than anode pressure, and most effective, use of subatmospheric anode pressure. Low temperature operation is critical for rapid stack start-up from temperatures below 60°C. Figure 3(a) shows steady-state current density at 0.4 volts versus absolute anode pressure at 30°C for various combinations of anode GDL, all with no MPL except the baseline GDL (open squares). The anode absolute pressure is seen to be a very effective boundary condition for reducing cathode flooding. The Freudenberg GDL backing layers are much more effective than the baseline Mitsubishi Rayon Co. (MRC)-type GDL backing layer we had been using, improving the effectiveness of the sub-atmospheric anode pressure significantly. Over the past two-three years we had made simple liquid water permeability measurements for a whole series of difference GDL backing materials, (see slide 18 of reference [8]) and it was on this basis that we started testing the Freudenberg GDL on the anode versus the MRC baseline GDL backing layer since it had a much higher liquid water permeability (6x). The improvement in fuel cell performance is consistent with that property, but since then we have determined that that measured property is not the only factor determining the fuel cell response at 30 °C.

Figure 3(b) shows galvanodynamic scan (GDS) polarization curves as a function of 50 cm<sup>2</sup> cell temperature under 50/150 kPa anode/cathode absolute pressures of H<sub>2</sub>/air. The MEA uses the 2009



**FIGURE 3.** (a) Current density at 0.4 volts as a function of absolute anode pressure under steady-state fuel cell operation at 30°C, dry inlets and 150 kPa H<sub>2</sub>/air, for various anode GDL types, most without MPLs. (b) GDS polarization scans as a function of temperature and anode pressure for NSTF MEA containing the Freudenberg Type 1 GDL on the anode, 2009 best of class CCM and standard 3M cathode GDL.

best-of-class CCM and the as-received Freudenberg GDL backing layer on the anode (no MPL or Teflon<sup>®</sup> treatment). With the proper anode GDL and reduced anode pressure, it is possible to run the cell stably at 2 A/cm<sup>2</sup> even at 30°C. The high temperature curve at 80°C and 68°C dew points in Figure 3(b) also shows there is no impact of the anode GDL on standard higher anode pressure/temperature operation. Operating at equal anode/cathode pressures (150 kPa) or higher, the same MEA will flood out at a limiting current of <0.4 A/cm<sup>2</sup> at 30°C. But if the cathode pressure exceeds sufficiently the anode pressure, then the cell can hit 2 A/cm<sup>2</sup> even with the anode at atmospheric pressure (Reference [8], slide 19).

Load transient performance under cooler wet conditions is very important for stack operation. We find this is also significantly helped by this new water management strategy. Figure 4(a) shows 0.02 to

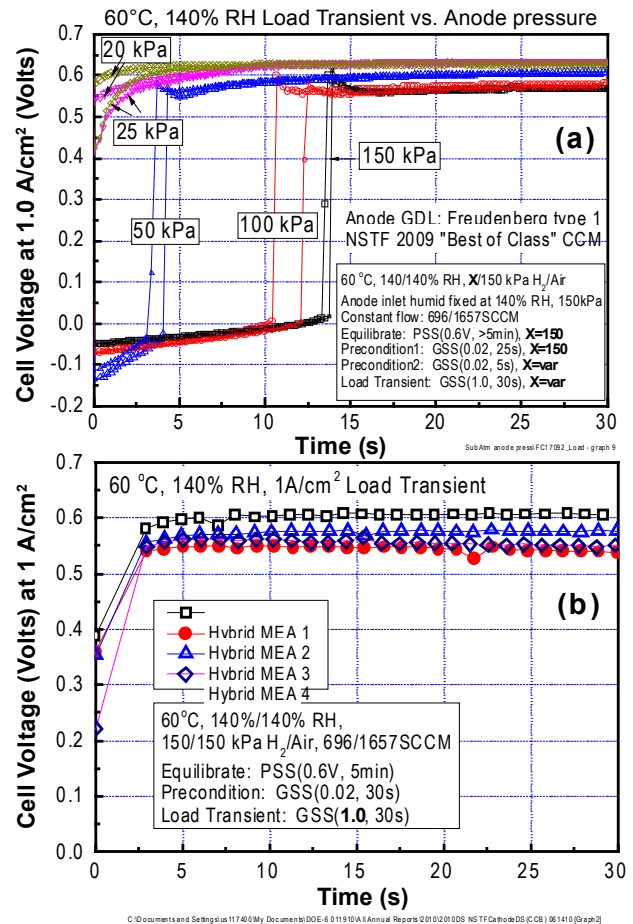
1 A/cm<sup>2</sup> load steps under 60°C and 140% RH, using the same MEA as discussed with Figure 3(b). The impact of the reduced anode pressure greatly improves load transient performance at 140% RH, and for values below 25 kPa, there is no delay in response with the 50 cm<sup>2</sup> cells. “Steady-state” (>15 seconds after the load step) performance is also improved with reduced anode pressure (+60 mV as anode pressure decreases from 100 kPa to 25 kPa.). Finally we note that reduced anode pressure also assists load transients at 50°C, 140% RH similarly [8]. Since the heat capacity of these single cells is much higher than one would have in a stack, this is a very good indicator that load transient power up in a stack will be improved even further. In summary, this approach of managing cathode flooding under cool/wet conditions by pulling the product water through the CCM and out the anode is very effective for steady state and transient operation.

### Water Management – Path 2

The second path pursued for resolving the cool-start water management issue involves using a gradient cathode catalyst such as described in reference [9], to more effectively remove water from the cathode in a more conventional manner. This involves a hybrid electrode, consisting of both an NSTF catalyst layer and a lower loading of a conventional Pt/C dispersed catalyst layer. Slides 43-45 of reference [8] show other data relative to this water management approach, and in particular, slides 44 and 45 show an alternative solution which was nearly as effective in which a small amount of additional dispersed Pt/C (< 0.05 mg/cm<sup>2</sup>) of catalyst layer is added to the cathode electrode outside the NSTF cathode. With the right choice of Pt/C catalyst, this also helps improve the steady state and transient response under cool, wet conditions without loss of high temperature performance. Figure 4(b) shows comparative load transient responses of four hybrid MEAs, each slightly different, with the same test conditions as used for 4(a) except that the anode and cathode pressures are equal at 150 kPa. These hybrid MEAs use NSTF CCMs with 0.05 mgPt/cm<sup>2</sup> anode loadings, 0.1 or 0.15 mgPt/cm<sup>2</sup> cathode loadings, the same PEM type, the as-received Freudenberg GDL discussed above, and 0.05 mg/cm<sup>2</sup> of a specific Pt/C applied to the cathode GDL. All easily make the 0.02 to 1 A/cm<sup>2</sup> load step. Such a hybrid MEA shows promise for further extending the high temperature limiting current density as well, with recent results attaining 2.4 A/cm<sup>2</sup> (at 0.55 V) with only 40 mV of mass transport overpotential below a 70 mV/decade Tafel slope, with 0.2 mg<sub>Pt</sub>/cm<sup>2</sup> total per MEA. Further optimization is underway.

### Task 6

The last area of work focused on improving break-in conditioning of the NSTF MEAs. This activity was



**FIGURE 4.** Two methods for effective load transient response under cooler, wet conditions: (a) Load transient response as a function of anode pressure under 60°C, 140% RH, of a standard NSTF MEA consisting of the CCM and MPL-free anode GDL indicated, and a standard 3M cathode GDL. (b) Similar load transient responses of new hybrid MEAs at 150 kPa H<sub>2</sub>/air, consisting of the same anode GDL and similar NSTF CCMs as in a), but with a 0.05 mg/cm<sup>2</sup> Pt/C catalyst coating applied to standard 3M cathode GDL.

incorporated last year as a new Task 6. Significant work prior to the current project had identified many MEA component materials and their processes, and test station protocols that strongly affect the time for break-in conditioning of new MEAs. These include catalyst composition, surface area, fabrication conditions, membrane processing solvents and drying conditions, and GDL types. A thermal cycling protocol with liquid water injection has been used for years to break-in new NSTF MEAs to obtain full performance. The new task focuses on both materials effects and the protocol effects in order to significantly reduce the time and simplify the procedures for conditioning a new MEA. Last year new test station protocol work was successful in reducing the conditioning time with our current test stations from over 24 hours to less than 6 hours. In the current year protocols were developed that both reduced the time



for reaching full power and were more stack friendly to implement. (Our standard protocol we call thermal cycling, requires at least 24 hours and the use of liquid water to flood the cells during the cool down periods.) Since this task started last year, over 40 new protocols were investigated. Slide 20 in reference [8] shows a recent fast conditioning protocol that produces nearly the same performance break-in as the standard thermal cycling, but requires 4-5 hours and operates with completely dry input gases. The same slide also shows a graph demonstrating a material effect, that is the Pt<sub>3</sub>Ni<sub>7</sub> alloy conditions faster than our standard PtCoMn with the standard thermal cycling protocol.

## Conclusions and Future Directions

This project has met or exceeded the currently specified DOE electrocatalyst and MEA performance and durability targets for 2015 using the same MEA component set in 50 cm<sup>2</sup> cell tests. Furthermore, the NSTF catalyst based MEAs used outside this project in original equipment manufacturer 400 cm<sup>2</sup> (>20 cell) short stacks have generated specific power densities of <0.2 g<sub>Pt</sub>/kW, successful 10°C cold and -20°C freeze-start [8], and lifetimes of 2,000 hours under various automotive system relevant cycling. Significant improvements in ORR activity with new alloys and processing methods were demonstrated and further improvements are anticipated. Probably the most significant advances this past year were understanding and improving major water management issues associated with the ultra-thin NSTF electrodes. Future work will be strongly focused on down-selecting and incorporating these advanced components into a robust, durable, high-performance, roll-good manufactured MEA containing no more than 0.2 mg/cm<sup>2</sup> of PGM total for the final stack testing-deliverable. Specific future directions include:

### Water Management Improvement

- Continue to combine the improvement factors now identified that significantly enhance cool operation and load transient start-up; determine best synergistic combinations towards the 2010 best of class MEA for final stack testing.

### Cathode Catalyst Mass Activity Gain

- Down-select the final catalyst and configuration to be scaled up for the final stack testing.
- Optimize fabrication processes for the down-selected catalyst.

### MEA Integration

- Down-select the final 2010 best-of-class MEA (catalysts for each electrode, membrane, GDLs for

each electrode, processes, etc.) under Task 5, for final stack testing.

### Stack testing

- Continue Task 3 short stack evaluations with 2009 best-of-class MEA, upgrading to 2010 best of class MEA.
- Identify original equipment manufacturer stack for final stack testing under Subtask 5.3.

### Start-up conditioning and reversible stability

- Continue to develop simplified break-in conditioning protocols and catalyst/membrane components to reduce MEA break-in conditioning time to <3 hours for full performance.

## FY 2010 Publications/Presentations

1. Gary C-K Liu, R.J. Sanderson, G. Vernstrom, D.A. Stevens, R. T. Atanasoski, M.K. Debe and J.R. Dahn, "RRDE measurements of ORR activity of Pt<sub>1-x</sub>Ir<sub>x</sub> (0<x<0.3) on high surface area NSTF-coated GC disks," Presentation at 216<sup>th</sup> ECS Meeting, Vienna, Austria, Oct. 4, 2009.
2. Dennis van der Vliet, Dusan Strmcnik, Chao Wang, Radoslav Atanasoski, Mark Debe, Nenad Markovic and Vojislav Stamenkovic, "Multimetallic Catalysts for the Oxygen Reduction Reaction," Presentation at 216<sup>th</sup> ECS Meeting, Vienna, Austria, Oct. 4, 2009.
3. Dusan Strmcnik, Dennis van der Vliet, Chao Wang, Radoslav Atanasoski, Mark Debe, Nenad Markovic and Vojislav Stamenkovic, "Catalysts with Multifunctional Active Sites: From well-defined to nanoscale surfaces," Presentation at 216<sup>th</sup> ECS Meeting, Vienna, Austria, Oct. 4, 2009.
4. A.J. Steinbach, H. Le, K Alade-Lambo, C.V. Hamilton Jr., M.J. Kurkowski and M.K. Debe, "Reversible Performance Stability of Polymer Electrolyte Membrane Fuel Cells," Presentation for 238<sup>th</sup> Am. Chem. Soc. Meeting, Washington, D.C., August 16, 2009.
5. Mark K. Debe, "Ultra-high activity electrocatalysts based on nanostructured organic films and sputtered Pt alloys," Invited presentation for 238<sup>th</sup> Am. Chem. Soc. Meeting, Washington, D.C., August 16, 2009.
6. Mark K. Debe, "Update of the activity, performance, durability and water management of the 3M NSTF catalyst based MEA's for PEM fuel cell," Invited, MEA Fuel Cell Modeling and Characterization Workshop, NRC Institute for Fuel Cell Innovation, Vancouver, BC, Canada, Nov. 12-13, 2009.
7. D. Stevens, S. Wang, R. Sanderson, A. Garsuch, M. Debe, S. Hendricks, R. Atanasoski and J. Dahn, "Assessing the Pt<sub>upd</sub> surface area stability of Pt<sub>1-x</sub>M<sub>x</sub> (M=Re,Nb,Bi) solid solutions for PEM fuel cells," Journal of the Electrochemical Society **157**(5), B737-B743(2010).



8. Gary C-K Liu, R.J. Sanderson, G.Vernstrom, D.A. Stevens, R.T. Atanasoski, M.K. Debe and J.R. Dahn, "RRDE measurements of ORR activity of Pt<sub>1-x</sub>Ir<sub>x</sub> (0<x<0.3) on high surface area NSTF-coated GC disks," *Journal of the Electrochemical Society* **157**(2), B207-B214 (2010).
9. A. Garsuch, D. Stevens, R. Sanderson, S. Wang, R. Atanasoski, S. Hendricks, M. Debe and J. Dahn, "Alternative Catalyst Supports for Proton Exchange Membrane Fuel Cells," *Journal of the Electrochemical Society* **157**(2), B187-B194 (2010).
10. D. Stevens, A. Bonakdarpour, R. Sanderson, S. Wang, R. Atanasoski, M. Debe and J. Dahn, "Development of Multi-component PEM Fuel Cell Catalysts for Enhanced Stop-Start Protection", 217<sup>th</sup> ECS meeting, Vancouver, BC, Canada, April 28, 2010.
11. Mark K. Debe, Project review at the DOE 2010 Vehicle Technologies and Hydrogen Programs Annual Merit Review, June 8, 2010, Washington, D.C., number FC 001.
12. Radoslav Atanasoski (invited) and Mark Debe, "Nanostructured thin film-NSTF catalysts for PEM fuel cells: focus on durability," Ulm ElectroChemical Talks 2010 and 2015 Technologies on Batteries and Fuel Cells, Ulm, Germany, June 16, 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<sub>1-x</sub>M<sub>x</sub> [M = Ni, Co] (0 <x <1) catalysts and impact on surface area enhancement," Extended Abstract for 218<sup>th</sup> ECS meeting.
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<sub>1-x</sub>Ni<sub>x</sub> (0 <x <1) on high surface area NSTF-coated GC disks," Abstract for 218<sup>th</sup> ECS meeting.
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17. M.K. Debe, A. Steinbach, G. Vernstrom, S. Hendricks, R. Atanasoski, P. Kadera, "Extraordinary ORR activity of Pt<sub>3</sub>Ni<sub>7</sub>," Extended Abstract for 218<sup>th</sup> ECS meeting.
18. M.K. Debe, Abstract for invited presentation "Nanostructured Catalyst Developments," 2<sup>nd</sup> CARISMA Conference, Montpellier, France, Sept. 2010.

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7. M. Debe, A. Hester, G. Vernstrom, A. Steinbach, S. Hendricks, A. Schmoekkel, R. Atanasoski, D. McClure and P. Turner, in proceedings of the 50<sup>th</sup> Annual Technical Conference of the Society of Vacuum Coaters, Louisville, KY, May 1, 2007.
8. Mark K. Debe, Project review at the DOE 2010 Vehicle Technologies and Hydrogen Programs Annual Merit Review, June 8, 2010, Washington, D.C., number FC 001.
9. US patent 6,238,534.