

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

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- Argonne National Laboratory (ANL), Argonne, IL (V. Stamenkovic, Dennis van der Vliet, Nenad Markovic)
- Jet Propulsion Laboratory (JPL), Pasadena, CA (S.R. Narayanan, Charles Hays)

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### 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 electrode assembly (MEA) characterized by:

- total Pt group metal 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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (HFCIT 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 catalyst (NSTF) roll-good fabricated electrocatalysts and MEAs. Table 1 compares the NSTF current 2<sup>nd</sup> quarter, calendar year (CY) 2009 status with the electrocatalyst targets for 2010/2015 from Table 3.4.12 of the DOE HFCIT MYRDDP. Additional rows were added to summarize recent accelerated durability test results. All metrics were obtained with the same cathode and anode alloy catalysts. 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

- Improved baseline NSTF-MEA roll-good performance containing 0.15 mg-Pt/cm<sup>2</sup> total loading (0.1 cathode) to obtain 0.62 V at 1.5 A/cm<sup>2</sup> under 150 kPa H<sub>2</sub>/air inlet pressure at 80°C, 67% relative humidity (RH). Performance reproduced in 50 cm<sup>2</sup> single cell measurements at General Motors.
- Demonstrated inverse specific power density in a 50 cm<sup>2</sup> cell that exceeds the DOE 2015 target of 0.20 g<sub>Pt</sub>/kW at 650 mV. Similar value obtained by system integrator in a short stack with same 0.05/0.10 mg<sub>Pt</sub>/cm<sup>2</sup> loadings.
- Demonstrated a 50% increase in oxygen reduction reaction (ORR) mass activity, from 0.18 to 0.27 A/mg<sub>Pt</sub>, using the DOE protocol for activity at 900 mV, with a new PtM alloy over our standard Pt<sub>68</sub>(CoMn)<sub>32</sub>.

**TABLE 1.** Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Characteristic	Units	Targets 2010/2015	3M Status – 6/09 (mfg'd roll-good)
PGM Total Content	$g_{Pt}/kW_e$ rated in stack	0.3/0.2	<0.18 $g_{Pt}/kW$ for cell V <0.67 volts in 50 $cm^2$ cell at 150 kPa inlet. <b>0.19<math>g_{Pt}/kW</math>, 400 <math>cm^2</math> short stack</b>
PGM Total Loading	mg PGM/ $cm^2$ total	0.3/0.2	<b>0.15</b> with current PtCoMn alloy
Durability under Load Cycling	Hours, T $\leq$ 80°C Hours, T > 80°C	5,000 / 5,000 2,000 / 5,000	>7,000 hours, 0.2/0.2 mg/ $cm^2$ , mech. reinforcement, no chem. stab., ~ 5,000 hours, 0.05/0.1 mg/ $cm^2$ , no chem. stab. or reinforcement
Mass Activity (150 kPa $H_2/O_2$ , 80°C, 100% RH)	A/mg-Pt @ 900 mV, 150 kPa $O_2$	0.44 / 0.44	<b>0.18 A/mg</b> in 50 $cm^2$ w/ PtCoMn <b>0.27 <math>\pm</math> 0.04 A/mg</b> in 50 $cm^2$ with Pt $_x$ M $_y$ , both 0.1 mg $_Pt/cm^2$ on cathode.
Specific Activity (150 kPa $H_2/O_2$ at 80°C, 100% RH)	$mA/cm^2$ -Pt @ 900 mV	0.72 / 0.72	<b>1.7</b> for PtCoMn, 0.1 mg $_Pt/cm^2$ <b>2.1 <math>\pm</math> 0.3</b> for new Pt $_x$ M $_y$ , 0.1 mg $_Pt/cm^2$
Accel. Loss: 30,000 cycles, 0.7–0.9 V step, 30 sec hold at 80/80/80°C	-mV at 0.8 A/ $cm^2$ %ECSA loss	<30 mV <40% / 40%	~ 0 mV loss at 0.8 A/ $cm^2$ ~ 0 % loss of $cm^2_{Pt} / cm^2_{planar}$
Accel. Loss: 200 hr hold @ 1.2 V at 95°C, $H_2/N_2$ , 150 kPa, 80% RH	-mV at 1.5 A/ $cm^2$ % ECSA loss	<30 mV <40% / 40%	+ 25 mV gain at 1.5 A/ $cm^2$ ~ -17% loss of $cm^2_{Pt} / cm^2_{planar}$
OCV hold without PEM failure under 250/200 kPa $H_2$ /air, 90°C, 30% RH and periodic stops for ECSA, x-over meas.	Hours $mA/cm^2$	200 <20	<b>950 to 1,340 Hrs.</b> $H_2$ Crossover <20 mA/ $cm^2$ , F-ion release rate < 0.5 $\mu g/cm^2$ -day
Accel. Loss: 4,000 cycles 0.6 -1.2 V, 20 mV/sec, 95/95/95°C, 270 kPa, $H_2/N_2$	Specific Activity % ECSA loss	Not specified	-1% to+ 5% gain in $mA/cm^2_{Pt}$ -25+5% loss of $cm^2_{Pt} / cm^2_{planar}$ with 0.05/0.10 mg $_Pt/cm^2$ on anode/cathode

RH – relative humidity; ECSA – electrochemically active surface area; OCV – open-circuit voltage; T - temperature

- Using rotating disk electrode (RDE) measurements on the new NSTF PtM alloy, demonstrated the highest ORR specific activity, mass activity and half-wave potential values for any catalyst to date:  $i_{kin}$  at 0.90 V = 6.8 mA/ $cm^2$ -Pt, 1.1 A/mg-Pt, and  $E_{1/2}$  = 0.962 V, with 0.10 mg $_Pt/cm^2$  loading on the NSTF whiskers.
- Completed three designed experiments on production equipment to correlate whisker-support surface area with process conditions, that allowed development of a quantitative model of catalyst surface area and the understanding of how it depends on the whisker characteristics and growth conditions.
- Exceeded by a factor of five the 2015 OCV hold lifetime targets at 90°C (250/200 kPa  $H_2$ /air, and 30% RH) while cross-over remained below 20 mA/ $cm^2$  and F<sup>-</sup> ion release rates remained below 0.50  $\mu g/cm^2$ /day.
- Repeated over 7,000-hour lifetime under humidity load cycling lifetime tests at 80/64/64°C, (cell temperature/anode dew point/cathode dew point) with a second MEA having no ionomer chemical additives, but mechanical stabilization as reported in the CY 2008 report.
- Demonstrated 5,000-hour lifetimes of two MEAs with the same humidity load cycling lifetime test as above, but using the current “best of class” NSTF catalyst-coated membrane (CCM) having 0.05/0.10 mg/ $cm^2$  PtCoMn on the anode and cathode, respectively, and a 20 micron thick 3M 850 equivalent weight (EW) membrane that did not contain chemical additives or mechanical reinforcement.
- Demonstrated 0 to 5% gain in specific activity and -20% to -30% loss in surface area with 0.10 mgPt/ $cm^2$  cathode loading under 0.6 to 1.2 volt cyclic voltammetry (CV) cycling at 20 mV/sec under more severe conditions of 95/95/95°C (cell/dew point temperatures).
- Produced over 55,000 linear ft combined of NSTF substrate, coated catalyst, and CCM for process development, qualification and use (partially produced for the current contract).
- Identified critical protocol and materials factors having significant effects on the break-in conditioning requirements for the low loading NSTF MEAs, and initiated a new task to focus on this issue. Developed a simplified air cooling, voltage cycling protocol for conditioning that reduced break-in time from over 24 hours to less than 6 hours.
- Quantified new transient power-up issues with NSTF thin layer electrodes and established a

protocol to study them. Identified new MEA interface and GDL concepts for addressing both transient and steady-state flooding under cool wet conditions characteristic of ultra-thin electrodes.



## Introduction

State-of-the-art proton exchange membrane (PEM) fuel cell electrocatalyst technology utilized in today's prototype fuel cell vehicles are demonstrating significant 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 for attaining the above objectives builds on a 12-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 while demonstrating much lower losses due to Pt dissolution and membrane chemical attack [3,4,5,6], and has significant high volume all-dry roll-good manufacturing advantages [7].

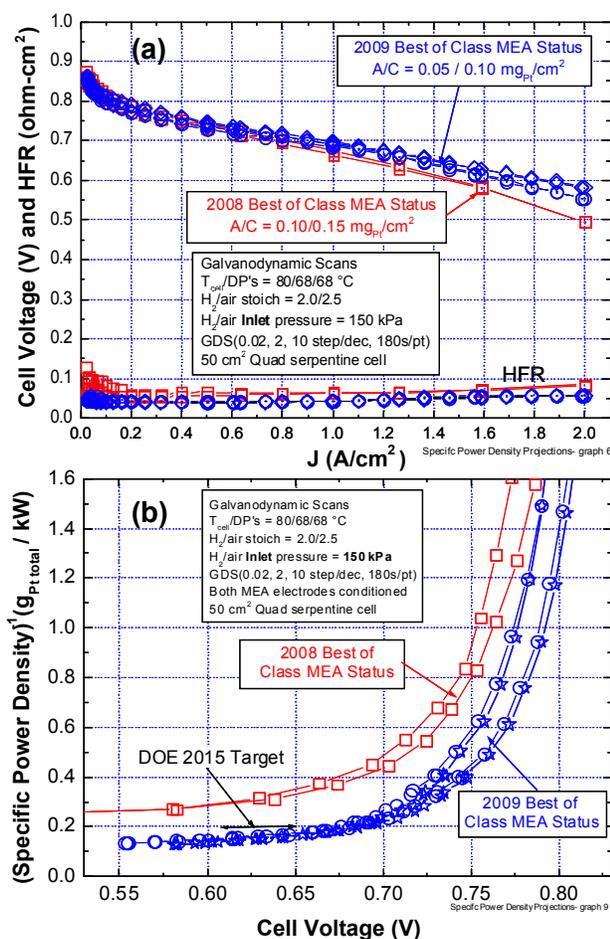
The scope of work in the first two-year budget period included extensive work at 3M to increase the NSTF catalyst support film surface area, fabrication and screening of new alloys in 50 cm<sup>2</sup> single cells, and evaluation of multiple deposition parameters to obtain increased catalyst surface 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-RDE catalyst evaluation technique with JPL. Research in the second year has continued to focus on development and characterization of GDL materials and process methods for improved cool-start and water management of the ultra-thin NSTF electrodes; application of various accelerated aging tests for membrane and catalyst durability and lifetime improvement; and catalyst/membrane integration for improved CCM performance with reduced Pt loading,

## Results

The technical accomplishments for the first year fall into six areas of research and development corresponding to Project Tasks 1.1, 1.2, 1.3, 2, 5.1, 5.2 and 6. We briefly summarize the main results from each of these areas.

In the first area (Task 5.1), the improvements in catalyst electrodes, membrane and GDL are combined to establish a current "best of class" MEA. Similar to last year, we further improved high current density performance while reducing the total Pt loading. At the start of the contract, our baseline CCM consisted of the NSTF PtCoMn ternary at a loading of 0.2 mg-Pt/cm<sup>2</sup> on both the anode and cathode sides of a 3M PEM (~35 microns, 850 EW). Last year we reduced the size of the microstructure features of the NSTF roll-good substrate, which improved mass transport to the catalyst at high current densities, and reduced the anode and cathode loadings to 0.1 and 0.15 mg/cm<sup>2</sup>, respectively. This year, we further reduced the PtCoMn catalyst loadings to 0.05 and 0.10 mg/cm<sup>2</sup>, respectively, and the membrane thickness from 32 to 20 μm with a subsequent gain in performance. Figure 1(a) illustrates galvanodynamic polarization curves under 150 kPa H<sub>2</sub>/air from the current best of class NSTF MEAs compared to last year's status, showing a 34% reduction in impedance and an 85 mV gain at 2 A/cm<sup>2</sup> while using 40% less Pt. Figure 1(b) shows the same curves from (a) plotted as inverse specific power density versus cell voltage, indicating the new results now exceed the DOE 2015 target for this metric in the peak power range. Tafel plots of the galvanodynamic scan (GDS) polarization curves from 1(a) show a 70 mV/decade slope and an ~40% reduction of the mass transport overpotential at 2 A/cm<sup>2</sup> with the new MEA constructions over last year's.

The second results area was that of Task 1.1. This is a major task focused on increasing the surface area of the NSTF whisker supported catalyst. There are two aspects to increasing the surface area, viz. increasing the surface area of the bare whisker support and increasing the surface area of the thin film catalyst coating applied to the whiskers. All the work under this task has been done with the standard NSTF PtCoMn ternary catalyst. The primary emphasis of the work at 3M in the past year has centered on completing three designed experiments conducted on pilot-scale facilities to produce NSTF whisker support particles with controlled physical characteristics of areal number density, N, whisker length, L, and diameter, d. The first of these designed experiments was introduced in last year's report and completed by the end of CY 2008. Whiskers were fabricated under 24 different process condition parameter sets using the roll-good manufacturing equipment. Two subsequent whisker area optimization experiments built on the knowledge gained from the

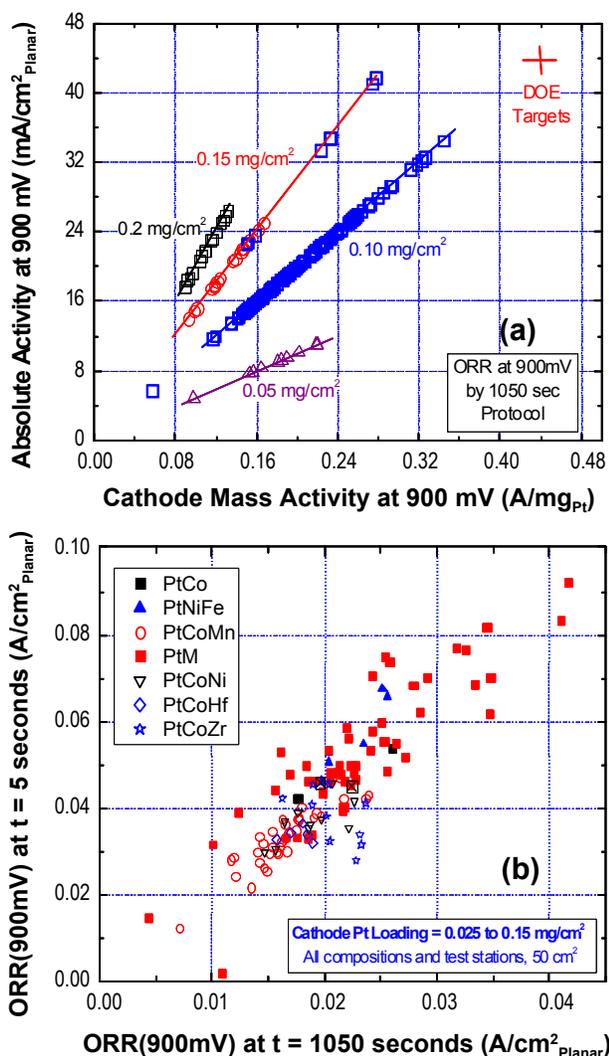


**FIGURE 1.** (a) Galvanodynamic polarization curves under 150 kPa H<sub>2</sub>/air from the current best of class NSTF MEAs compared to last year's status, showing a 34% reduction in impedance and an 85 mV gain at 2 A/cm<sup>2</sup> while using 40% less Pt. (b) The curves from (a) plotted as inverse specific power density versus cell voltage showing the DOE 2015 target is now exceeded by the current best of class NSTF MEA.

first. A primary outcome of these experiments has been the first understanding of how the measured ECSA, from  $H_{\text{upd}}$  measurements, is related to the physical characteristics of the whisker support film, the catalyst loading, and the whisker growth process conditions. This has permitted development of a quantitative model of Pt surface area as a function of the whiskers' dimensions and number density, the mass loading and alloy density, the fraction  $\alpha$  of catalyst coated onto the sides of the whiskers, and a scaling parameter  $f$  for the catalyst coating roughness factor. Using the model and generic values for the latter two parameters,  $\alpha$  and  $f$ , deduced from five whisker support types, the resultant mass activity could be calculated as a function of  $N^*L$  and the specific activity. This was then used to project that a 67% gain in  $N^*L$  and a 50% gain in specific activity would be sufficient to meet the DOE 2015 targets for mass activity at 900 mV of 0.44 A/mg<sub>Pt</sub>.

The whisker support area and the subsequent catalyst coating surface area contribute to the total surface area and are related. The understanding of how they are related is a second primary outcome of this task. The structural model for the thin film catalyst coating on the whiskers is that of the NSTF "whiskerettes" that grow epitaxially off the side planes of the crystalline whiskers [8]. From the results of the Task 1.1 work this year, we have determined that for a given alloy composition and loading, the catalyst thin film grain size (whiskerette size) and ratio of exposed Pt face-centered cubic (hkl) crystal facets (from X-ray diffraction) determine the catalyst's activity, how it varies with loading and how it depends on the support whisker surface area. The second and third whisker area optimization experiments have continued to increase our knowledge of how to obtain the required surface area increase of the whisker supports and catalyst thin film over-coating for a given loading. No substantial increase in specific surface area at the 0.1 mg/cm<sup>2</sup> loadings above 10 m<sup>2</sup>/g has been achieved in the past year, but work is continuing with two remaining whisker-growth process parameters that have not previously been investigated.

In the third results area (Tasks 1.2 and 1.3) the focus was on development of new Pt alloys to increase specific activity and durability, independent of the whisker support surface area development work of Task 1.1 discussed above. For all this work with new alloys, the standard NSTF whisker support was used and 50 cm<sup>2</sup> single cells were used. The objective is to increase the absolute and mass activities above that obtained with the standard PtCoMn. Two activity criteria that must be met are illustrated in Figure 2(a), which shows the absolute ORR activity at 900 mV plotted versus cathode mass activity. The DOE targets for 2015 are indicated. The results for standard PtCoMn on many different whisker structures investigated in Task 1.1 at loadings of 0.05, 0.1, 0.15 and 0.2 mg<sub>Pt</sub>/cm<sup>2</sup> are shown as the black squares (0.2), red circles (0.15), and purple triangles (0.05 mg/cm<sup>2</sup>). The Task 1.1 results for the 0.1 loadings are hidden under the much larger series of new catalyst alloys (blue squares) studied at 0.10 mg/cm<sup>2</sup> loadings under this Task 1.3. As seen, the new alloy work has been successful in getting much closer to the DOE targets, and the loading of 0.1 mg/cm<sup>2</sup> appears to be the shortest path. For the activity measurements in Figure 2(a), the DOE protocol at 900 mV under saturated 150 kPa H<sub>2</sub>/O<sub>2</sub> is used, in which the current density is taken 1,050 seconds after setting the cell potential at 900 mV, having been held at ~0.10 V under N<sub>2</sub> for 20 min. During this time, the Pt surface is oxidizing and the current degrades as the state of the surface changes. This raises the question of whether this is a reliable protocol to compare different alloy systems that can oxidize at different rates. Figure 2(b) shows the ORR absolute activity recorded at nominally 5 seconds after setting the potential at 900 mV versus that at 1,050 seconds,



**FIGURE 2.** (a) Plot of absolute activity versus mass activity at 900 mV for a large series of NSTF catalysts alloys, loadings and whisker support types investigated during the past year, relative to the DOE targets. (b) Absolute ORR activity for a series of different NSTF alloy catalysts, measured in 50 cm<sup>2</sup> cells at 5 seconds after setting the cell potential at 900 mV versus the value at 1,050 seconds after setting the cell potential at 900 mV.

for a wide series of the NSTF alloy compositions and loadings investigated in 50 cm<sup>2</sup> cells. Three things are apparent in Figure 2(b). First there is significant scatter, indicating different decay rates for different alloys and compositions. Second, the ORR values at 5 seconds are roughly twice the values obtained at 1,050 seconds, and most meet or exceed the DOE target values of 44 mA/cm<sup>2</sup><sub>planar</sub>. The ORR activity values at 5 seconds are indicative of the clean surface state, and therefore comparative to RDE measurements in which the catalyst is acid washed and due to the CV scan rates and directions, also representative of the clean surface state. Third, the new PtM compositions (red squares in

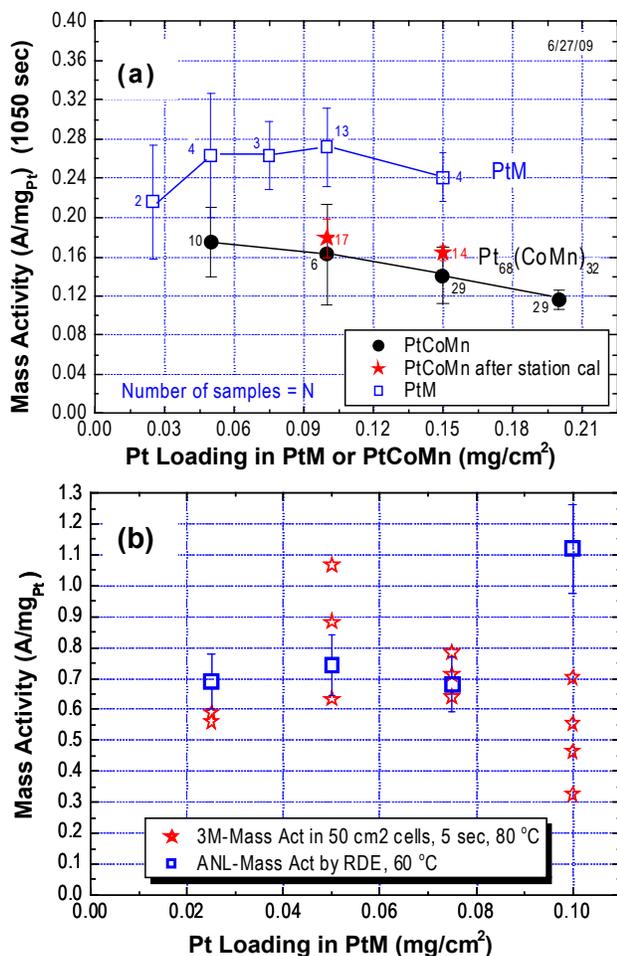
Figure 2(b)) are by far the most active and exceed those of PtCoMn at the standard composition.

Figure 3(a) shows the mass activity (1,050 sec values) versus platinum loading for the standard NSTF PtCoMn composition and the new PtM alloy at the preferred composition. PtM shows a statistically significant gain in mass activity by ~50% at the 0.10 mg/cm<sup>2</sup> loading. The commensurate kinetic performance improvement in fuel cell polarization curves is also obtained with the new PtM catalyst. However, high kinetic activity is only one necessary performance criterion for a suitable electrocatalyst, and the new PtM catalyst is not ready yet to replace the PtCoMn. We are actively working on the issues it presents for high current density and durability. This involves optimization of post fabrication process steps that have been found productive.

In Figure 3(b) we show the mass activity measured at 5 seconds versus the Pt loading for the preferred PtM composition. The 3M values in 50 cm<sup>2</sup> single cells are plotted as red stars. For comparison we show the mean values of multiple sample measurements for the same catalyst lots made by RDE at ANL (blue squares). What is remarkable is that the 50 cm<sup>2</sup> and RDE values agree quantitatively fairly well with no adjustable parameters, consistent with the point discussed above that the 5 sec fuel cell measurement is more representative of the clean surface state, as in RDE measurements. The RDE measurements are optimized for the amount of NSTF catalyst particles applied to the glassy carbon disks. By these metrics then, activity measured on the clean surface state in a fuel cell at 900 mV or by RDE, the PtM alloy activity significantly exceeds the DOE target, and in fact, the standard PtCoMn catalyst activity also meets the target. The good correlation of the RDE and fuel cell (at 5 sec) activity measurements has also been demonstrated for a series of other alloys, including PtCo, PtNiFe, PtCoMn, PtCoNi and PtCoZr.

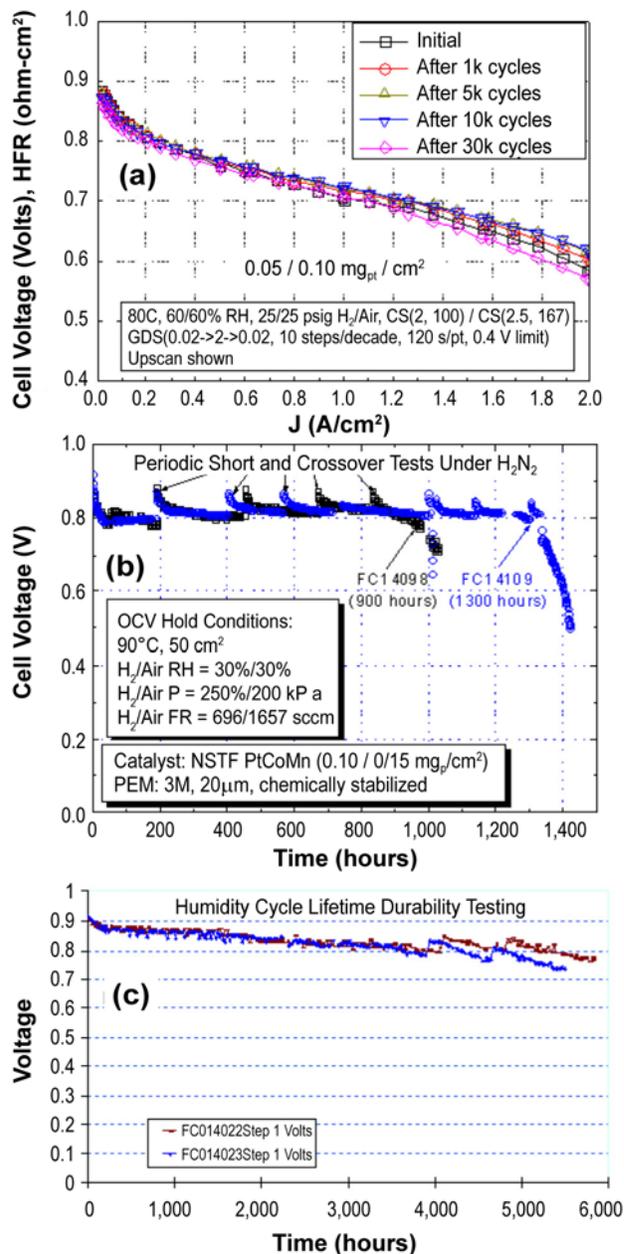
Another important outcome of this Task 1.2 work with ANL has been the successful demonstration of a post-fabrication catalyst treatment that in RDE measurements increases the mass activity by 60% over the as-received alloys. This has been born out for PtM, PtCoMn, PtNiFe, but not for pure Pt. It is believed that the surface structure composition is being affected by the post treatment. Work completed at 3M has also involved experiments to duplicate the post-fabrication treatment and identify a roll-good compatible process.

The third area of results includes all the work done with Dalhousie University to develop new catalyst compositions and structures using high-throughput compositional spread screening methods [5]. Samples comprising sixty-four electrode arrays of thin film catalysts deposited onto the NSTF whisker supports are prepared at Dalhousie University, converted into MEAs



**FIGURE 3.** (a) Plot of mass activity versus Pt loading for the new PtM alloy and the NSTF standard PtCoMn composition, measured in 50 cm<sup>2</sup> cells. (b) Mass activity at 900 mV versus Pt loading on the NSTF whiskers for the new NSTF PtM alloy composition, measured at 3M in multiple 50 cm<sup>2</sup> cells with the 5 sec protocol (red stars), compared to the values from ANL by RDE at 900 mV.

at 3M and evaluated in 64-channel cells at Dalhousie. Initial results were summarized in Figure 4 of last year’s annual progress report. Over 70 additional libraries were fabricated and tested this year, involving many different binary, ternary and quaternary material sets (over 130 to date). Extensive surface area measurements in the 64 channel cells have been correlated with the lattice parameters and grain sizes of the alloys as a function of composition. This work has led to a new patent application. The durability under high voltage CV cycling from 0.6 to 1.2 V has been determined for most libraries and continues to be a key method to survey new alloy resistance to Pt dissolution. A new methodology for doing rotating ring disc electrode tests on NSTF whiskers grown directly on glassy carbon disks has also been developed and appears to be an excellent method with very high signal to noise for studying low catalyst loadings. With this approach and the newest



**FIGURE 4.** Examples from three types of accelerated durability testing: (a) GDS polarization curves from the best of class MEA before, during and after 30,000 cycles from 0.7 to 0.9 V (30 sec hold, square wave) under 7.35 psig H<sub>2</sub>/N<sub>2</sub> and 80°C cell and dew point temperatures. (b) OCV hold test versus time with periodic measurements of crossover and F<sup>-</sup> ion release for two NSTF MEAs that contained a chemical stabilizer in the 20 μm 3M PEM. (c) Open circuit voltage versus time under an 80°C cell temperature, 64°C DP, load cycling protocol for two best of class MEAs containing the 0.05/0.10 mg/cm<sup>2</sup> loadings, a 20 μm thick 850 EW 3M PEM with neither chemical stabilizers nor mechanical reinforcement. Both achieved 5,000 hours before OCV dropped below 0.8 V.

NSTF alloys, Dalhousie is observing surface areas as high as 30 m<sup>2</sup>/g<sub>Pt</sub> and kinetic currents so high that 1.0 V is being used to fully eliminate transport effects.

This area also includes work completed with JPL to generate and screen new NSTF alloy catalysts deposited at JPL onto multi-electrode arrays of NSTF whiskers. These are then characterized both ex situ and in a novel JPL electrochemical cell with rotating electrolyte that simulates an RDE measurement. The equipment and techniques for depositing the thin film catalysts onto the NSTF support whiskers were fully implemented to fabricate 18 electrode arrays, and characterization in the novel pseudo-RDE cell was completed for several binary and ternary alloy systems at JPL. Comparison experiments to obtain the equivalent rotating disc speed of the JPL approach have been made and suggest that the equivalent RDE speed of the circulating electrolyte approach may be insufficient for in situ ORR characterization. Increased focus on catalyst alloy fabrication by two methods unique to JPL's facilities is being pursued.

In the fourth results area (Task 2) we continued to carry out five types of accelerated durability tests using both the NSTF baseline MEA from the start of the contract and the reduced loading, thinner membrane MEAs, discussed in Figure 1.

Test 1 was a 30,000 cycle, 0.7 V (30 sec hold) to 0.9 V (30 sec hold) step-wise cycling test at 80°C and saturated conditions under 7.35 psig H<sub>2</sub>/N<sub>2</sub>, with periodic interruptions for measuring catalyst surface area, activity and MEA performance. This test evaluates resistance to Pt dissolution. The target value for surface area loss was <40% and for mass activity <60% (measured at 900 mV, 150 kPa saturated H<sub>2</sub>/O<sub>2</sub>). Test results were discussed in last year's report for the 2008 best of class MEA with the 0.1/0.15 mg/cm<sup>2</sup> catalyst loadings, for which those NSTF MEAs demonstrated 0% loss in ECSA, a mass activity loss of ~13%, and a performance gain of 2 mV at 0.8 A/cm<sup>2</sup>. This gain in performance was observed at all current densities and increased with current density and after each new measurement. After 30,000 cycles, the gain in potential at 1.5 A/cm<sup>2</sup> was 19 mV. The NSTF electrodes appear to be completely stable under this accelerated test. This year the same test was applied to the 2009 best of class MEA discussed in Figure 1, with the 0.05/0.10 mg/cm<sup>2</sup> loadings and thinner PEM. A series of the DOE test protocol-required GDS polarization curves (25 psig, 80°C, 64% RH) are shown in Figure 4(a) after 0, 1K, 5K, 10K, and 30K cycles. The polarization curves increase uniformly from 0K to 10K cycles, and then show some loss between 10K and 30K cycles relative to the initial, 0K curve. At 0.8 A/cm<sup>2</sup>, the overall loss was about 10 mV after the 30K cycles. The ECSA loss after 30K cycles was -22% for each of two MEAs. Both performance and ECSA loss for the new NSTF baseline MEA with 0.05/0.10 mg<sub>Pt</sub>/cm<sup>2</sup> after the 30K cycles exceeds the DOE 2015 target but are worse than was measured for the 2008 baseline reported last year, for

which no loss of performance or ECSA was obtained (as still listed in Table I as the best result for this test).

Test 2 is a lifetime-hold at OCV at 90°C under 250/200 kPa H<sub>2</sub>/air at 30% RH. This test evaluates MEA chemical stability. Figure 2 of last year's report showed a test result in which the NSTF MEA used had the NSTF PtCoMn ternary catalyst (0.2 mg-Pt/cm<sup>2</sup>) on both anode and cathode sides of a neat (no chemical additives, or reinforced) 3M 850 EW, 35 micron thick PEM. Although the DOE test target time of 200 hours was exceeded by about a factor of four, when it was attempted to do periodic shut-downs to measure cross-over as a function of time, the MEAs typically failed. This year, we show in Figure 4(b) the results from two MEAs that had the lower anode/cathode loadings of the 2008 baseline MEA, and a 3M 850 EW 20 µm PEM that contained chemical stabilizers. As shown the MEAs were successfully operated for 900 and 1,300 hours respectively with periodic shutdowns for cross-over and F<sup>-</sup> ion release rates. The cross-over remained below 20 mA/cm<sup>2</sup> and F<sup>-</sup> ion release rates remained below 0.50 µg/cm<sup>2</sup>/day over their lifetimes.

Test 3 is a load cycling test, results of which were reported last year in Figure 3 of the Fiscal Year 2008 annual progress report. 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. OCVs (measured daily) were compared for both NSTF and conventional dispersed Pt/C based MEAs. NSTF MEAs with 0.2/0.2 mg<sub>Pt</sub>/cm<sup>2</sup> loadings on 3M 35 µm membranes containing neither chemical stabilizer nor reinforcement had mean lifetimes of ~3,500 hours, ~seven-fold longer than the conventional MEAs with the same membrane and GDL. However, when the NSTF electrodes were applied to an experimental membrane containing the same 3M ionomer that was reinforced courtesy of W.L. Gore, the lifetime exceeded 7,000 hours. In the past year, a second identical MEA also exceeded 7,000 hours prior to its OCV dropping consistently below 0.8 V (the criterion for end of life). But this year we also evaluated the current best of class NSTF CCM with the 0.05/0.10 mg/cm<sup>2</sup><sub>Pt</sub> loadings on a 3M 850 EW PEM that did not contain any chemical stabilizer or mechanical reinforcement. Under the same load cycling test protocol, the first two MEAs evaluated had lifetimes of approximately 5,000 hours before their OCV dropped consistently below 0.8V, as shown in Figure 4(c). Although this just barely meets the DOE 2015 target goal, combining the lower loading electrodes with a 3M PEM having chemical additives should be able to significantly exceed the DOE targets, (re: 3M Membrane project DE-FG36-07GO17006).

Tests 4 and 5 are high voltage cycling tests to test for Pt dissolution. In both tests 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 temperature and

100% inlet RH. For Test 4,  $T = 80^{\circ}\text{C}$ ,  $P = 0$  psig while for Test 5, the cell temperature and dew points were  $95^{\circ}\text{C}$  and pressures were 14.7 psig. Under Test 4, the current best of class MEAs, with the  $0.05/0.10 \text{ mg}_{\text{Pt}}/\text{cm}^2$  on the thinner 3M PEM, experienced  $\sim 10$  mV loss uniformly from 0.2 to  $1.6 \text{ A}/\text{cm}^2$ , -15 to -17% loss in ECSA, and minimal mass transport loss. At the more severe Test 5 conditions, the same MEAs exhibited 20 to 30% ECSA gain after 4,000 cycles, 10-21 mV of kinetic performance and some increased mass transport losses relative to the Test 4. Although there are no designated DOE targets for these tests, each of these results are no worse than were previously obtained with the higher loaded 2008 baseline NSTF MEAs, but represent an opportunity for further improvement.

The fifth area of work (Task 5.2) focused on development of GDL materials and process parameters, and fuel cell test protocols for improved water management with the ultra-thin NSTF type electrodes. Water management properties are different for the NSTF electrodes which are 20-30 times thinner than conventional dispersed catalyst electrodes. This is particularly noticeable for operation under cold-wet conditions since the rate of water generation per unit of catalyst surface area is roughly six times higher for the lower surface area/loading NSTF electrodes. This correlates very well with measured limiting currents. For example, using standard hydrophobic GDLs at  $30^{\circ}\text{C}$  the current density at 0.6 V for an NSTF cathode with  $0.1 \text{ mg}_{\text{Pt}}/\text{cm}^2$  is roughly five to six times lower than for a conventional Pt/C electrode with  $0.4 \text{ mg}_{\text{Pt}}/\text{cm}^2$ . This means that under cool, wet steady-state conditions, liquid water must be moved to compensate for the reduced vapor transport mechanism, while for fast dynamic low-to-high power transient events, sufficient surface area or volume must be available to accommodate the water of generation for the few seconds it takes for electrode heating to enable vapor transport.

Conventional GDLs are not designed to move liquid water. Modified GDL materials and electrode interfaces with the GDL and membrane are likely required to enable adequate water transport under all conditions for ultra-thin, low loading electrodes. This year three designed experiments were fully completed around the current best practices GDL carbon paper backing layer, microporous layer modifications and GDL processing. The first of these were initiated last year and included the type of carbon paper used for the electrode backing, percent and type of fluoropolymer used for wet proofing, the microporous layer coating weight and drying conditions, type and amount of fluoropolymer used in the MPL, different approaches for incorporation of hydrophilic materials into the GDL, and asymmetric anode/cathode GDLs. These experiments defined the envelope of possibility with essentially conventional all-hydrophobic GDL structures, to meet cool and

wet as well as hot and dry operating condition. No combination of GDL materials and processing were found to substantially improve the cool, wet operation over the current best practices 3M GDL. Some modest improvements were demonstrated in short stack tests with GDLs having modified MPL materials, and avenues along those material sets are being pursued. Perhaps more promising, modified electrode structures and interfaces have very recently been shown to have a substantial benefit for transient response, and this work is accelerating to define the optimum type of interface capable of satisfying low temperature as well as high temperature conditions. Finally, non-conventional GDL physical structures are being developed and evaluated for direct liquid water transport under cool, wet conditions.

Finally, the sixth and last area of work is focused on improving break-in conditioning of the NSTF MEAs. This activity has now been incorporated as a new Task 6. Significant work prior to the current project has 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 is focused on both materials effects and the protocol effects in order to significantly reduce the time and simplify the procedures for conditioning a new MEA. At this time the new test station protocol work has been successful in reducing the conditioning time with our current test stations from over 24 hours to less than six hours. From a materials perspective, we have identified catalyst alloy effects that can increase the time for break-in conditioning by nearly two orders of magnitude and post fabrication processes that can reduce that time by even more for those catalysts. There are many parameters and effects that interplay in bringing an MEA to full performance as quickly as possible and this work will continue to be a focus to target a three hour break-in conditioning time with simplified procedures for the best of class MEA materials.

## Conclusions and Future Directions

The project has met or exceeded all of the currently specified DOE electrocatalyst and MEA performance and durability targets for 2015 using the same MEA components, except for mass activity measured in a fuel cell at 900 mV by the DOE recommended protocol. If mass activity is measured from the non-oxidized catalyst surface by either RDE or in a fuel cell using a modified DOE protocol (5 sec vs 1,050 sec), then this target for 2015 has been met as well for the NSTF PtCoMn

catalyst. Further improvements in activity with new alloys and durability should be possible and work will continue in this direction. The project has increased its focus on understanding and improving the key water management issues associated with the NSTF electrodes, and simplifying and reducing the break-in conditioning time. Future work will be strongly focused on reducing these remaining gaps for a robust, durable, high performance, roll-good manufactured MEA containing no more than 0.15 mg/cm<sup>2</sup> of PGM combined on the anode and cathode.

### Water Management Improvement

- Tailor the GDL materials and physical construction for more effective electrode water transport over a wide range of operating conditions without compromising high temperature performance under dry conditions.
- Develop MEA interface improvements to improve transient response and sensitivity to operating conditions.

### Start-Up Conditioning (New Task)

- Continue to develop break-in conditioning protocols and catalyst/membrane components to reduce MEA break-in conditioning time to <3 hours for the best of class MEAs.

### Cathode Catalyst Mass Activity Gain

- Continue to fabricate and test new catalyst compositions and surface structures to exceed the target mass activity at 900 mV of 0.44 A/mg<sub>Pt</sub> using the standard (1,050 sec) fuel cell protocol and which meet all other performance and durability requirements.
- Achieve 50% gain in surface area of NSTF supports over current NSTF baseline without loss of specific activity or durability under the most severe accelerated test.

### Durability Improvement

- Reduce by 50% any losses in surface area, activity or mass transport over-potential under the more severe fast high voltage cycling protocol (e.g. 4,000 cycles, 0.6–1.2 V under H<sub>2</sub>/N<sub>2</sub> at 20 mV/sec at 95/95/95°C).

### FY 2009 Publications/Presentations

1. Arman Bonakdarpour, Tara R. Dahn, Radoslav Atanasoski, Mark K. Debe, and Jeff R. Dahn, "H<sub>2</sub>O<sub>2</sub> Release During Oxygen Reduction Reaction on Pt Nano Particles," *Electrochemical and Solid-State Letters*, **11**, B208-B211, 2008.

2. Radoslav Atanasoski and Mark Debe: "Nano-Structured Thin Film - NSTF Catalysts for PEM Fuel Cells: Fundamentals and Application" ACES Electromaterials Symposium "Nanostructured Electromaterials", University of Wollongong, NSW, Australia, 4-6 February 2009, *invited*.

3. Radoslav Atanasoski: "Fuel Cell Catalysts of Tomorrow": XX Congress of Chemist and Technologist of Macedonia Ohrid, Macedonia, September 16–21, 2008, *invited*.

4. Radoslav Atanasoski, Mark Debe and Tom Wood: "High performance platinum and non-precious metal catalysts for PEM fuel cell application" (NMES08-57), New Materials for Electrochemical Systems Symposium, Montreal, Canada, June 24–27, 2008, *invited*.

5. G. Vernstrom, A Schmoekkel, R. Atanasoski, S. Hendricks, A. Steinbach, and M. Debe, "Oxygen Reduction Activities of Nanostructured Thin Film Alloy Electrocatalysts", Fuel Cell Seminar, Oct. 13–17, 2008, Phoenix, Abst. 1365.

6. A.J. Steinbach, K. Alade-Lambo, H. Le, and M.K. Debe: "Investigation of Cation-Induced Losses in PEM Fuel Cells", Fuel Cell Seminar, Oct. 13–17, 2008, Phoenix, Abst. GHT35a-22.

7. A.J. Steinbach: "Influence of Contaminants, MEA Components, and Temperature on PEM Fuel Cell Reversible Performance Stability", Canada – USA PEM Network Research Workshop, February 16 and 17, 2009, NRC Institute for Fuel Cell Innovation, Vancouver, BC, Canada.

8. D.A. Stevens, R.J. Sanderson, A. Garsuch, S. Wang, R.E. Mar and J.R. Dahn: "High Throughput Screening of PEM Fuel Cell Catalysts", Canada – USA PEM Network Research Workshop, February 16 and 17, 2009, NRC Institute for Fuel Cell Innovation, Vancouver, BC, Canada.

9. 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," Abstract for 216<sup>th</sup> ECS Meeting, Vienna, Austria, Oct. 4, 2009.

10. Dennis van der Vliet, Dusan Strmcnik, Chao Wang, Radoslav Atanasoski, Mark Debe, Nenad Markovic and Vojislav Stamenkovic, "Multimetallic Catalysts for the Oxygen Reduction Reaction," Abstract for 216<sup>th</sup> ECS Meeting, Vienna, Austria, Oct. 4, 2009.

11. C.C. Hays, J.G. Kulleck, B.E. Haines and S.R. Narayan, "Thin Film Platinum Alloys for Use as Catalyst Materials in Fuel Cells," Abstract for 216<sup>th</sup> ECS Meeting, Vienna, Austria, Oct. 4, 2009.

12. 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," Abstract for 216<sup>th</sup> ECS Meeting, Vienna, Austria, Oct. 4, 2009.

13. 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," Abstract for 238<sup>th</sup> Am. Chem. Soc. Meeting, Washington, D.C. August 16, 2009.

14. Mark K. Debe, "Ultra-high activity electrocatalysts based on nanostructured organic films and sputtered Pt alloys," *Invited Abstract for 238<sup>th</sup> Am. Chem. Soc. Meeting*, Washington, D.C. August 16, 2009.

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8. L. Gancs, T. Kobayashi, M.K. Debe, R. Atanasoski, and A. Wieckowski, *Chem. Mater.* **20**(7), 2444-2454 (2008).