

## V.D.2 Highly Dispersed Alloy Catalyst for Durability

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### Subcontractors:

- Johnson Matthey Fuel Cells, Sonning Commons, UK
- Texas A&M University, College Station, TX
- Brookhaven National Laboratory, Upton, NY

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### Fiscal Year (FY) 2011 Objectives

- Develop structurally and compositionally advanced supported alloy catalyst system with loading  $\leq 0.3$  mg platinum group metal (PGM)/cm<sup>2</sup>.
- Optimize catalyst performance and decay parameters through quantitative models.
- Demonstrate 5,000 cyclic hours below 80°C with less than 40% loss of electrochemical surface area and catalyst mass activity.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (section 3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Durability
- Cost
- Performance

### Technical Targets

**TABLE 1.** DOE 2011 Technical Targets for Electrocatalysts and the Current Status of this Project

Electrocatalyst Targets	Units	Current Status	DOE 2010 Target	DOE 2015 Target
PGM (total content)	g/kW	0.50	0.3	0.2
PGM (total loading)	mg/cm <sup>2</sup>	0.40 <sup>a</sup>	0.3	0.2
Mass Activity @ 900 mV	A/mg <sub>PGM</sub> at 900 mV (iR-free)	0.20 (in MEA) 0.30 (in liquid cell)	0.44	0.44
Specific Activity	μA/cm <sup>2</sup> at 900 mV (iR-free)	940 (in MEA) 612 (in liquid cell)	720	720
Cyclic Durability At T ≤ 80°C	h	1,450 <sup>b,c</sup>	5,000	5,000
At T > 80°C	h		2,000	5,000
Electrochemical Area (ECA) Loss	%, percent	30 <sup>d</sup>	<40	<40
Cost	\$/kW at \$51.55/g	~26 <sup>e</sup>	5	3
Electrocatalyst Support mV after 400 hours @ 1.2 V	mV	92 <sup>f</sup>	<30	<30

<sup>a</sup> Based on current scaled-up 30% Pt<sub>2</sub>IrCr/C membrane electrode assembly (MEA); anode/cathode loading – 0.1/0.3 mg/cm<sup>2</sup> (PGM).

<sup>b</sup> Under an accelerated vehicle drive cycle protocol in a short stack; 40% mass activity loss under UTCP-defined accelerated single-cell test after 270 hours at 70°C and 120 hours at 80°C.

<sup>c</sup> Short stack durability test is on-going.

<sup>d</sup> Durability data measured after 30,000 cycles under UTC-defined accelerated test protocol.

<sup>e</sup> Five-year average PGM price \$51.55/g (Pt = \$1,234.33/Troy Oz; Ir = \$369.06/troy oz); costs not projected to high volume production.

<sup>f</sup> 40 mV internal resistance (iR)-free O<sub>2</sub> performance loss at 1.5 A/cm<sup>2</sup> after 360 hours at 1.2 V.

T - temperature

### FY 2011 Accomplishments

- Completed the scale up and MEA optimization of down-selected dispersed catalyst, 30% Pt<sub>2</sub>IrCr/C for performance in a full-size fuel cell. A mass activity of 0.2 A/mg(PGM) was achieved compared to the previous status of 0.14 A/mg(PGM).
- Completed the durability testing of 30% Pt<sub>2</sub>IrCr/C in a full-size MEA was completed under an accelerated protocol which showed 400 hrs of stability at 70°C. Currently testing performance and durability of the 30% Pt<sub>2</sub>IrCr/C in a short stack.
- Durability testing of 30% Pt<sub>2</sub>IrCr/C in a short stack is in progress under an accelerated vehicle drive cycle

protocol. The stack has accumulated 1,450 hours of uninterrupted operation at 70°C in H<sub>2</sub>/air.

- Scaled up a 20% Pt<sub>2</sub>IrCr alloy on the down-selected durable carbon, C4, and completed preliminary optimization of MEA for subscale fuel cell performance and stability testing in a porous plate subscale fuel cell under the DOE catalyst support corrosion protocol. A 40 mV iR-free O<sub>2</sub> performance loss at 1.5 A/cm<sub>2</sub> was observed after only 360 hours of potential holds at 1.2 V.
- A No-Go decision was made for core-shell catalysts based on extensive physical characterization and durability studies. Activity and stability of Pt<sub>ML</sub>/Pd<sub>3</sub>Co core-shell catalysts prepared using scalable chemistries were evaluated using both rotating disk electrode (RDE) and subscale fuel cell tests. Higher temperature and more concentrated electrolyte contributes to Pd dissolution and is substantially more damaging than room temperature RDE testing.



## Introduction

For the proton exchange membrane fuel cell (PEMFC) technology to become commercially viable, the cost of the components in a fuel cell must be reduced and, more importantly, the durability of the MEA must be improved. This project focuses on two distinct approaches to the DOE 2010 durability and performance targets. The first approach is the development of conventional but high performance highly dispersed Pt alloy catalyst on a carbon support. The second system utilizes a novel “Pt monolayer (ML) core-shell” approach capable of achieving very high Pt mass activities [1-3]. Under this latter concept, the main objectives are to improve the durability of the cathode catalyst by further optimizing the core material selection, shell thickness of the ML, and the particle size of the cores and to develop scalable fabrication methods.

## Approach

To achieve the objectives on this project, UTCP has teamed with Brookhaven National Laboratory (BNL), Texas A&M University (TAMU) and Johnson Matthey Fuel Cells (JMFC). The research focus and the role of all partners were reported previously [4]. BNL's role on the project focuses on the development of Pt ML “core-shell” systems on various cores including ideal surfaces such as single crystals. In addition, BNL leads our efforts to understand the effect of electronic properties, crystal structure and particle size on activity and durability of this class of electrocatalysts. TAMU focuses on development of computational atomistic models to study parameters that influence the activity and durability of core shell and dispersed catalyst systems. The overall scope of JMFC activities in the project encompasses

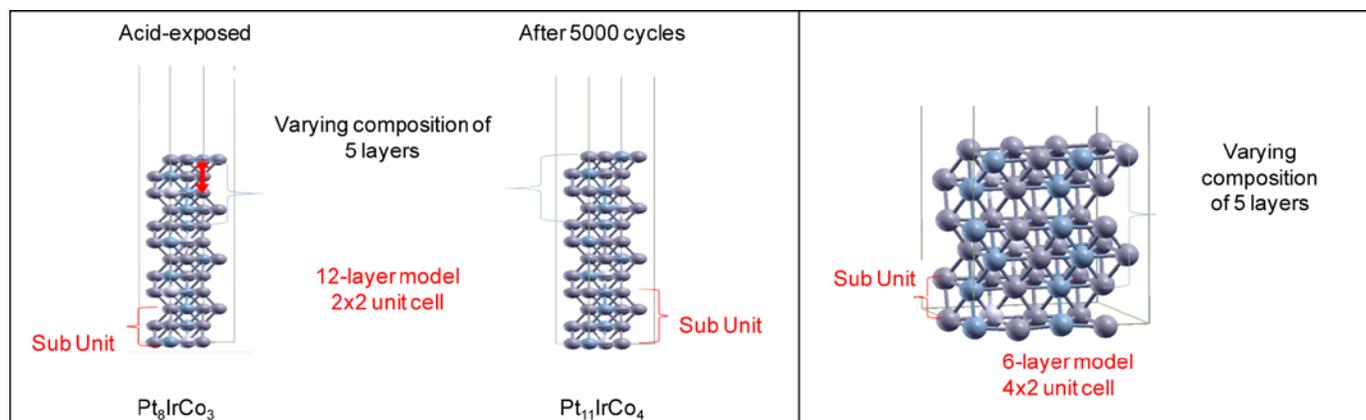
development of (i) dispersed Pt alloy catalysts including scale-up on conventional and advanced carbon supports, (ii) novel synthesis methodologies to scale up Pt ML core-shell catalysts, and (iii) MEA optimization and fabrication. Apart from overall project management, UTCP primarily focuses on the development of advanced dispersed Pt-based binary and ternary alloy catalysts. UTCP activities also include electrode modeling for MEA optimization, carbon support corrosion studies, fuel cell testing on single-cell level and fabrication and testing of a 20-cell short stack for verification.

## Results

### Molecular Modeling

It was previously reported that incorporating Ir into the bimetallic Pt<sub>3</sub>M alloy increases the tendency of Pt-skin formation and enhances the stability of the alloy systems [4]. The main topic that was studied this year was calculation of activity and stability of PtIrM ternary alloys based on experimentally found structures including surface segregation trends, Bader charge and D-band center analysis of Pt. Previously, the change in the composition of the Pt, Ir and Co in a 30% Pt<sub>7</sub>IrCo<sub>7</sub>/C as a function of cycling and the corresponding mass activity from RDE experiments were reported. A substantial loss of Co and Ir within the first 5,000 potential cycles results in a composition equivalent to that of a Pt<sub>3</sub>IrCo. The role of Ir and Co on the surface properties of two structures: Pt<sub>8</sub>IrCo<sub>3</sub> (that resulted after acid exposure) and Pt<sub>11</sub>IrCo<sub>4</sub> (composition obtained after 5,000 cycles) alloys were studied by density functional theory calculations.

The role of Ir and Co on the surface properties of PtIrCo alloys was studied by a comparative analysis for the Pt<sub>8</sub>IrCo<sub>3</sub> and Pt<sub>11</sub>IrCo<sub>4</sub> systems using two different 5-layer distribution structure models as shown in Figure 1. The results show that the most stable structures for Pt<sub>8</sub>IrCo<sub>3</sub> are the structures with one layer of Pt skin surface followed by the two-layer Pt skin surfaces. In both cases, the Pt-skin layers are more stable than the un-segregated structure. However, differences among different structures also depend critically on the subsurface composition. For example, the most stable one-layer Pt skin surface has a second layer of Pt<sub>3</sub>Co which is slightly more favorable than a PtCo in the second layer. Similar results were obtained for the Pt<sub>11</sub>IrCo<sub>4</sub> system where the most favorable second layer composition is PtCo, followed by Pt<sub>3</sub>Co, and the movement of Ir from fourth to the third layer does not affect the results. In summary, for the cycled and acid-treated structures, the single-layer Pt-skin surfaces are the most stable. However, the two-layer Pt-skin surfaces may be formed and are thermodynamically more favorable than the non-segregated structures. Co atoms tend to be in the second and third layers, and Ir atoms tend to be in the core, together with fourth and fifth layer Pt atoms that do not show a trend to segregate towards the top surface.



**FIGURE 1.** (a) 2x2 and (b) 4x2, slab model used to study segregation in  $Pt_8IrCo_3$  and  $Pt_{11}IrCo_4$  systems. The first five layers are used to study atomic redistribution after leaching. The optimized lattice constants are 3.853 Å for  $Pt_8IrCo_3$  and 3.851 Å for  $Pt_{11}IrCo_4$ .

The activity and stability of the 30%  $Pt_7IrCo_7/C$  after potential cycling were studied and Table 2 shows the electrochemical stability values for the  $Pt_{11}IrCo_4$  (composition after 5,000 cycles) structure in vacuum which shows that the stability of the cycled alloy surface is higher than that of the two-layer skin from  $Pt_2IrCo$  and comparable to that of the single-layer skin of  $Pt_3Co$  surfaces as shown by their electrochemical potential relative to a Pt (111) surface.

**TABLE 2.** Electrochemical Stability of Pt Surface Atoms Pt Surface Atoms in Two-Layer Alloy Relative to Clean Pt (111) Surfaces

System	$\mu_{Pt}$ (eV)	$\Delta\mu$ (eV)	$\Delta U$ (V)
Pt(111)	-6.98	0	0
$Pt_3Co$ (111) Single-layer Pt-skin	-7.22	-0.24	0.12
$Pt_2IrCo$ (111) two-layer Pt-skin	-7.12	-0.14	0.07
$Pt_{11}IrCo_4$ (111) two-layer Pt-skin	-7.23	-0.25	0.13

The average charge (based on a Bader charge analysis) of the first four layers of the  $Pt_{11}IrCo_4$  indicates a charge transfer from the Co subsurface atoms to the Pt atoms in the second layer and to the Ir atoms in the third layer and that the charge of the surface Pt atoms remains very similar to that on the pure Pt (111) surface suggesting an increased activity of the  $Pt_{11}IrCo_4$  surface. Similar results are also obtained from the analysis of the density of states calculations which suggest enhanced reactivity of the surface Pt layer (d-band center shifted in the direction of the Fermi level). Weak adsorption of O and OH intermediates are also observed compared to Pt (111) surfaces which confirms the higher activity of the  $Pt_{11}IrCo_4$  alloy surface. Furthermore, the electrochemical stability values for the  $Pt_{11}IrCo_4$  structure with 0.25 ML of adsorbed oxygen (Table 3) shows a decrease in surface stability of the cycled alloy surface. However, the stability is still comparable to those on pure

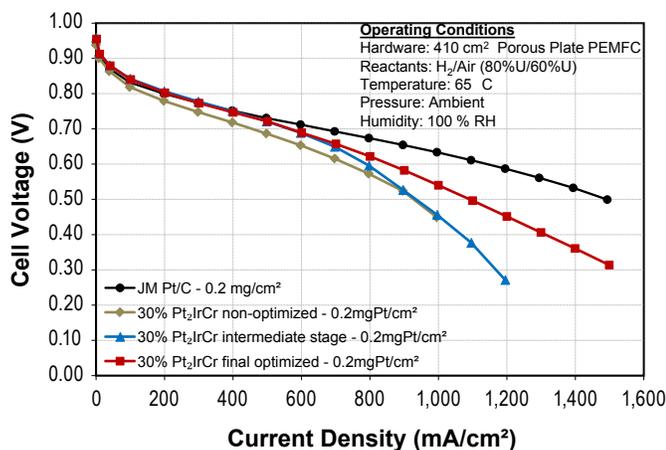
Pt (111) surfaces. These findings support the activity and stability of the 30%  $Pt_7IrCo_7/C$  observed experimentally [5].

**TABLE 3.** Electrochemical Stability of Pt Surface Layer Under 0.25 ML of Adsorbed O in Two-Layer Alloy Surface shown in Table 1 Relative to Pure Pt(111) Surfaces

System	$\mu_{Pt}$ (eV)	$\Delta\mu$ (eV)	$\Delta U$ (V)
Pt(111)	-6.26	0	0
$Pt_3Co$ (111) Single-layer Pt-skin	-6.55	-0.29	0.15
$Pt_2IrCo$ (111) two-layer Pt-skin	-6.32	-0.06	0.03
$Pt_{11}IrCo_4$ (111) two-layer Pt-skin	-6.14	0.12	-0.06

### Dispersed Pt Alloy Catalyst

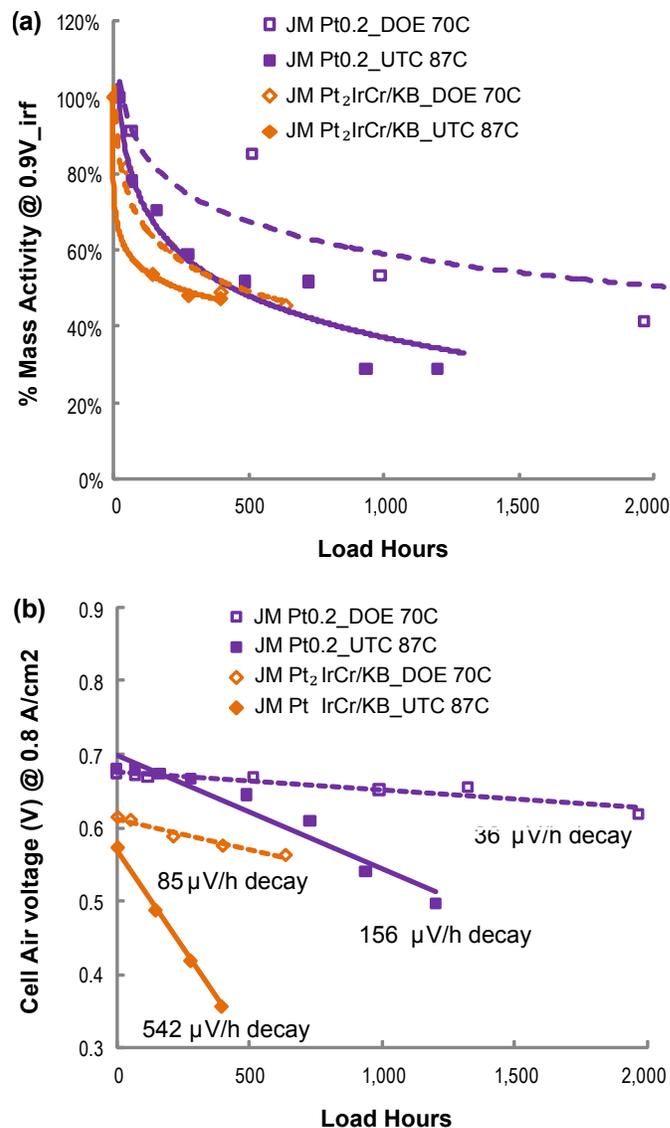
Many factors such as structure, particle dispersion, particle size, type of carbon support etc, influence the electro-catalytic activity of Pt and Pt alloy nanoparticles. Previously, within this project, a 30 wt%  $Pt_2IrCr$  cathode ( $0.3 \text{ mg}_{PGM}/\text{cm}^2$  loading) showed higher durability in both ECA and mass activity (MA) under potential cycling. This catalyst showed much lower loss (~30% ECA and MA) compared to the standard Gore Pt/C ( $0.4 \text{ mg}_{PGM}/\text{cm}^2$  loading) which showed ~50% loss and was down-selected for further development and scale up into full-size MEAs [4]. In the past year, a significant amount of effort was focused towards development and optimization of the cathode catalyst layer in an MEA with 30%  $Pt_2IrCr$  alloy catalyst to improve the catalyst utilization in electrodes keeping low PGM loading and enabling good performance at high current densities. This involved an elaborate investigation to identify key parameters such as catalyst ink formulations and ionomer content, to produce an optimum cathode catalyst layer capable of achieving good fuel cell performance in wide range of current densities.



**FIGURE 2.** Fuel cell polarization curves in  $H_2$ /air at 65°C in a water transport plate (WTP) fuel cell at 100% relative humidity (RH) and ambient pressure for an optimized, intermediate stage and un-optimized 30%  $Pt_2IrCr/C$  ternary alloy catalyst MEA compared to JMFC Pt/C ( $0.2mg_{Pt}/cm^2$ ) MEA.

Figure 2 shows the fuel cell performance curves in  $H_2$ /air at different stages of the optimization process for the 30%  $Pt_2IrCr/C$  MEA in a full size ( $410\text{ cm}^2$ ) WTP fuel cell compared to a baseline JMFC Pt/C MEA. The initial mass activity obtained for the alloy catalyst in the optimized MEA were  $0.14\text{ A}/mg_{PGM}$  compared to a MA of  $0.19\text{ A}/mg_{PGM}$  observed for the JMFC Pt/C MEA. This low activity is attributed to the low utilization of the catalyst in the MEA as seen by the low ECA of  $\sim 30\text{ m}^2/g$  (vs. liquid cell ECA of  $45\text{ m}^2/g$  from RDE). However, a clear evidence of improvement for high current density performance on  $H_2$ /air in a WTP fuel cell is observed from these catalyst layer optimization steps. Our results show that lower catalyst loading of  $0.3\text{ mg}_{PGM}/cm^2$  in the MEA can achieve high initial performances, although lower than the pure Pt/C. Extensive investigation into MEA fabrication process suggests that specific ink formulations significantly increase either mass transport properties or kinetic performance of alloy catalysts. This increase is attributed to the concentration of the ionomer in the ink formulations which results in the leaching of the Cr atoms from the catalyst surface to different concentrations and concurrently affects the kinetic and high current density performance in an MEA.

Figure 3 shows the (a) MA loss and (b) cell voltage at  $0.8\text{ A}/cm^2$  on  $H_2$ /air for the 30%  $Pt_2IrCr/C$  and the JMFC Pt/C in a WTP fuel cell under two durability protocols. A higher rate of MA and performance loss is observed for the Pt-alloy compared to the pure Pt at both operating temperatures. This higher rate is attributed to the lower stability of the transition metal in the Pt-alloy which results in the higher rate of MA loss. Additionally, any Cr leaching into the MEA would result in higher iR losses as observed by the cell voltage drop in the high current density region during cycling. Higher MA and cell voltage loss are



**FIGURE 3.** (a) Percentage mass activity and (b) cell air voltage at  $0.8\text{ A}/cm^2$  for the optimized 30%  $Pt_2IrCr/C$  MEA and JMFC Pt ( $0.2\text{ mg}_{Pt}/cm^2$ ) MEA in a full-size WTP cell under two durability protocols at 70°C and 87°C, respectively.

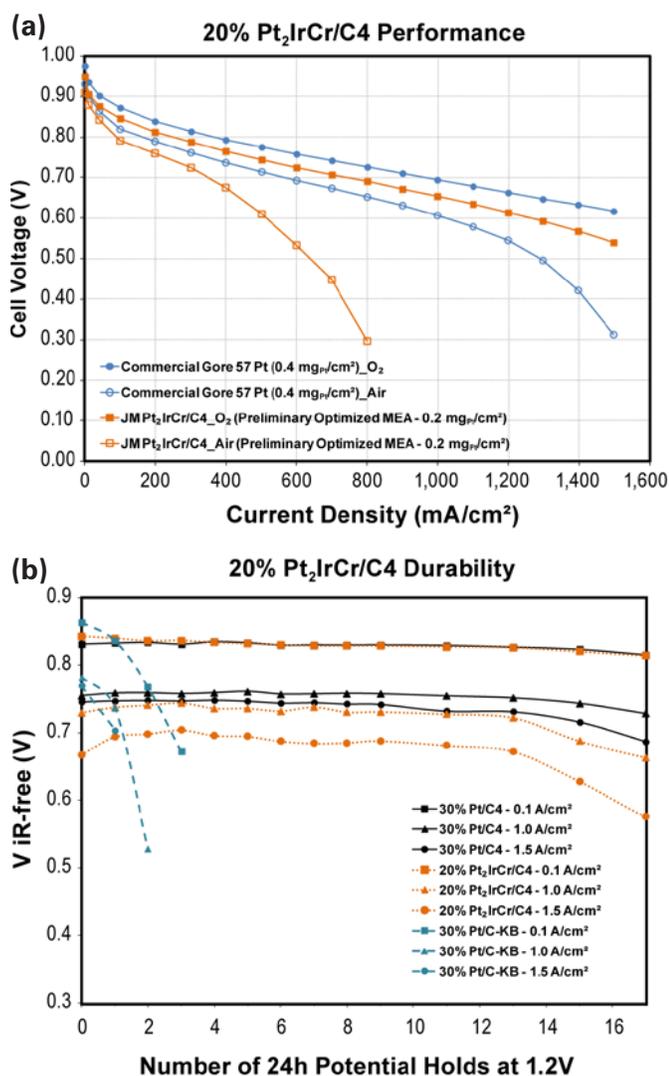
observed with increase in operating temperature of the fuel cell for both Pt and Pt-alloy. This observation suggests that the rate of degradation of the catalyst is highly dependent on the operating temperature of the fuel cell and the cycling protocol. Due to insufficient data available in the literature on the durability of alloy catalysts under real life conditions, a short stack containing the Pt-alloy was built and its durability under an accelerated vehicle drive cycle protocol will be evaluated.

### Durable Carbon Support

The main focus of this task was to explore alternate durable carbon supports capable of withstanding high

voltage spikes relevant for automotive applications. In the past year, a scaled-up batch (200 g) of 20% Pt<sub>2</sub>IrCr on the down-selected stable carbon (C4) was prepared by JMFC and optimized for performance in sub-scale size (25 cm<sup>2</sup>) WTP cells. The effect of cathode catalyst layer compositions including ionomer equivalent weight and ratio of ionomer to carbon were extensively investigated using subscale fuel cell testing. Figure 4a shows performance curves for a preliminary optimized MEA compared to a commercial Gore 57 Pt/C in subscale size WTP fuel cells operating at 80°C, 100% RH, 0 kPa backpressure. The Pt-alloy/C4 performance at high current operations is still poor mainly due to the low surface area and poor mass transport

properties of the carbon support C4. Figure 4b shows the iR-free cell voltages at various current densities (0.1, 1 and 1.5 A/cm<sup>2</sup>) for a 0.2 mgPt/cm<sup>2</sup> 30% Pt/C4 and 20% Pt<sub>2</sub>IrCr/C4 compared to a 30% Pt/C MEA obtained from a 25 cm<sup>2</sup> WTP fuel cell testing at 80°C, 100% RH under H<sub>2</sub>/O<sub>2</sub> at zero backpressure. Although the beginning of life performance for the Pt and Pt-alloy supported on C4 low surface area carbon shows lower performance than that of the Pt/C, its performance after the 1.2 V potential hold tests show considerable differences. After the fuel cell corrosion test of a total of 17 potential holds of 24 h each (408 h total) at 1.2 V, the 30% Pt/C4 and 20% Pt<sub>2</sub>IrCr/C4 showed 59 mV and 92 mV loss, respectively, at 1.5 A/cm<sup>2</sup> under H<sub>2</sub>/O<sub>2</sub>. While the alloy on C4 did not meet the 2010 DOE target of less than 30 mV iR-free O<sub>2</sub> performance loss at 1.5 A/cm<sup>2</sup> after 400 h, the voltage loss after 360 h (15 potential holds of 24 h each) at 1.2 V for the alloy catalyst was only 40 mV. The durability of the 20%Pt<sub>2</sub>IrCr/C4 under the accelerated potential cycling protocol is currently under investigation.



**FIGURE 4.** (a) Fuel cell performance curves at beginning of life for a 20% Pt<sub>2</sub>IrCr/C4 compared to a standard 0.4 mg<sub>Pt</sub>/cm<sup>2</sup> Gore 57 Pt/C MEA obtained from WTP subscale fuel cell (25 cm<sup>2</sup>) testing at 80°C, 100% RH under H<sub>2</sub>/air at zero backpressure and (b) H<sub>2</sub>/O<sub>2</sub> performance at 0.1, 1 and 1.5 A/cm<sup>2</sup> after 1.2 V potential holds in H<sub>2</sub>/N<sub>2</sub> at 80°C, 100% RH in subscale WTP cells for (0.2 mg<sub>Pt</sub>/cm<sup>2</sup> loading) 30% Pt/C4 and 20% Pt<sub>2</sub>IrCr/C4 compared to a 30% Pt/C MEA.

## Conclusions and Future Directions

The effects of MEA compositions were studied for the scaled-up 30% Pt<sub>2</sub>IrCr/C in full-size WTP fuel cells. A short stack containing the Pt-alloy was built and its durability under an accelerated vehicle drive cycle protocol is currently under investigation. Key barriers to overcome for the incorporation of the 30% Pt<sub>2</sub>IrCr in an MEA such as low catalyst utilization in electrodes and the transition metal stability under operating conditions still remain open. A No-Go decision was made for core-shell catalysts due to their poor durability in an MEA under operating fuel cell conditions. The scaled up synthesis of a 20% Pt<sub>2</sub>IrCr/C4, the down-selected catalyst on stable carbon, preliminary MEA optimization and corrosion durability testing is complete. However, their performance at high current operations is still poor and is being further investigated.

## Future Directions

Our future objective is to demonstrate (i) the durability of the 30% Pt<sub>2</sub>IrCr/C in a short stack and (ii) the high current density performance of the 20% Pt<sub>2</sub>IrCr/C4 alloy catalyst in a subscale and full-size WTP fuel cell at the conditions relevant for automotive applications. Some of the tasks undertaken to achieve these goals are listed below.

- Continued operation of the 30% Pt<sub>2</sub>IrCr/C in a 20-cell short stack under an accelerated vehicle drive cycle protocol.
- Optimization of dispersed alloy catalyst systems on C4 in MEAs is in progress, aiming to approach high current density performance in an operating fuel cell. The higher mass transport losses and poor water management issues are being resolved by tailoring the electrode structure for performance in a WTP fuel cell.
- In the case of the core-shell catalysts, preventing dissolution of the core material from the bulk phase of

nanoparticles remains a major challenge for this class of catalysts, and hence all activities under this task have been terminated and will not be investigated for the rest of the project.

### FY 2011 Publications/Presentations

1. Gong, K.; Chen, W.; Sasaki, K.; Su, D.; Vukmirovic, M.B.; Zhou, W.; Izzo, E.L.; Perez-Acosta, C.; Hirunsit, P.; Balbuena, P.B.; Adzic, R. R. "Platinum Monolayer Electrocatalysts: Improving the Activity for the Oxygen Reduction Reaction with Palladium Interlayer on IrCo Alloy Core", *J. Electroanal. Chem.* **(2010)**, 649, 232.
2. Sarah Ball, "Activity and Stability of Core-shell Electrocatalysts" 2010 Gordon Research Conference in Fuel cells.
3. W. Bi, E. Izzo, V. Murthi, C. Perez-Acosta, J. Lisitano, and L. Protsailo, "Durability of Low Temperature Hydrogen PEM Fuel Cells with Pt and Pt Alloy ORR Catalysts" 218<sup>th</sup> ECS Meeting - Las Vegas, NV, **(2010)**.

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4. V.S. Murthi, DOE Hydrogen Program Annual Progress Report (2010).
5. V.S. Murthi, DOE Hydrogen Program Annual Progress Report (2009).