V.E.2 Highly Dispersed Alloy Catalyst for Durability

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• Texas A&M University, College Station, TX
• Brookhaven National Laboratory, Upton, NY

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Objectives

- Develop structurally and compositionally advanced supported alloy catalyst system with loading ≤ 0.3 mg platinum group metal (PGM)/cm^2.
- 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 Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

TABLE 1. DOE 2010 Technical Targets for Electrocatalysts and the Current Status of this Project

Characteristic	Units	Project Status as of 06/01/2009	DOE 2010 Target
PGM Total Content	g/kW	0.84	0.3
PGM Total Loading	mg/cm^2	0.64[‡]	0.3
Cost	$/kW at 47.67/g	~38[†]	5
Mass Activity	A/mg$_{PGM}$ at 900 mV 9iR-Free)	0.28	0.44
Specific Activity	μA/cm^2 at 900 mV 9iR-Free	550	720
Cyclic Durability At T $\leq$ 80°C At T $\geq$ 80°C	h h	TBD TBD	5,000 2,000
ECA Loss	%, percent	30*	<40

[‡] Anode/Cathode loading – 0.4/0.24 mg$_{PGM}$/cm^2.
[†] Based on 5 year average PGM price $ 47.67/g (Pt = $1166.22/Troy Oz; Ir = $316.58/troy oz); costs not projected to high volume production.
* Durability data measured after 30,000 cycles under UTC Power defined accelerated test protocol.
ECA - electrochemical surface area
iR - internal resistance
TBD - to be determined

Accomplishments

- 30% Pt$_4$IrCo$_3$ and 30% Pt$_2$IrCr were down-selected as the dispersed alloy catalyst systems to be scaled-up for single cell demonstration. Mass activities of ~0.3 A/mg$_{PGM}$ were reproduced in both rotating disk electrode (RDE) and subscale membrane electrode assembly (MEA) testing (3x the activity of standard pure Pt catalyst).
- Dissolution trends of metal atoms other than Pt in Pt-based alloys were evaluated.
- Electronic structure and segregation properties of Pt$_3$Cr, Pt$_2$IrCr, and Pt$_2$IrCo alloys were investigated using quantitative models to determine the most stable surface distributions.
- Surface segregation trends and stability of the surface atoms against dissolution for various shell compositions were evaluated as a function of the shell thickness for Pt monolayer (ML) catalysts on Pd$_3$Co and Ir cores.

- Catalyst mass activities that surpass the DOE 2010 target for dispersed catalysts ($\geq$0.7 A/mg$_{PGM}$) were demonstrated in RDE testing.
- A Pt ML on Pd$_3$Co/C core-shell catalyst was scaled up from 300 mg to a 5 g batch.
- MEA catalyst layer optimization is in progress.

✧   ✧   ✧   ✧   ✧

Introduction

It is well known that, in order for the proton exchange membrane fuel cell technology to become commercially viable, the production 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 a conventional but high performance highly dispersed Pt alloy catalyst on a carbon support. The second system utilizes a novel "Pt ML core-shell" approach capable of achieving very high Pt mass activities [1-3]. Under this latter concept, the main objective is 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 develop scalable fabrication methods.

Approach

To achieve the objectives on this project, UTC Power (UTCP) has teamed with Brookhaven National Laboratory (BNL), Texas A&M University (TAMU) and Johnson Matthey Fuel Cells (JMFC). Figure 1 shows a schematic of the research focus and the role of all partners. BNL's role comes with over 40 years of experience of Dr. Adzic in the field of fundamental electrocatalysis and spectroscopy. Their role on the project focuses on the development of Pt ML "core-shell" system 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. This is achieved by using advanced spectroscopic techniques such as extended X-ray absorption fine structure (EXAFS) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) combined with electron energy loss spectroscopy (EELS). Dr. Balbuena's group at 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, (ii) novel synthesis methodologies to scale-up Pt ML core-shell catalysts and (iii) MEA optimization and fabrication.
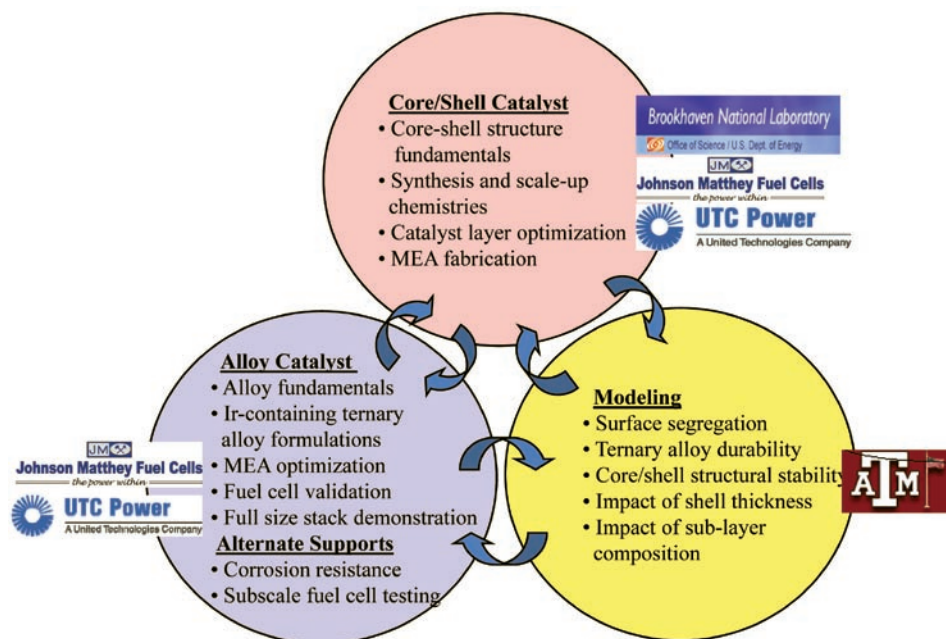

FIGURE 1. Schematic representation of the UTC Power catalyst project approach and partners. (The arrows represent the relationship between the different tasks and partners.)

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 modeling support for MEA optimization, fuel cell testing on single-cell level and fabrication and test of a 20-cell short stack for verification.

Results

Molecular Modeling

The main topic that was studied this year was calculation of adsorption energies of atomic oxygen on segregated Pt-skin and non-segregated Pt_3M and Pt_2IrM (M= Cr, Fe, Co, and Ni) alloy surfaces. The results indicate that in non-segregated Pt_3M alloy surfaces, the adsorption energies of 0.25 ML atomic oxygen follows the trend $Pt < Pt_3Ni < Pt_3Co < Pt_3Fe$ which is exactly opposite of the trend observed in segregated Pt_3M surfaces. To investigate the origin of the differences between the two types of surfaces, d-band center and d-band filling were calculated along with their main geometric parameters. Table 2 illustrates that the shift of the d-band center for Pt_3M and Pt-skin is very similar, and so is filling of the d-band center. This indicates that electronically, the Pt atoms on skin surfaces differ little from those on the non-segregated alloy surface. It was found that in non-segregated surfaces, electronic effects dominate because the 3-d metals are oxophilic. In contrast, the Pt segregated surfaces are affected by both electronic and geometric effects. In addition, the electronic structure of segregated and non-segregated Pt_3M and PtIrM alloys (M= Cr, Fe, Co, and Ni) were also correlated to adsorption strength and surface stability against dissolution. Examination of the segregation trends of the Pt_2IrCr alloy reveals that the ordered alloy surface is electrochemically more stable than Pt-skin surfaces against Pt dissolution. The

most favorable Pt skin surface has a composition of $PtIrCr_2$ in the subsurface. However, the d-band center of the non-segregated surface was found to be -2.3 eV, almost the same as that of the segregated Pt-skin surface (-2.31 eV), denoting similarity of these two electronic configurations.

In the core-shell catalyst concept, the stability and segregation trends of Pt ML on various core materials such as Pd-containing metal cores, IrCo alloyed cores, and different compositions of Ir_xCo_y cores were investigated as a function of several parameters including (a) composition of the Pd in the second layer, (b) the adsorption site for atomic oxygen and (c) the Pt-shell thickness. It is observed that the 1-layer shells offer slightly enhanced resistance for the Pt atoms to dissolve from the surface relative to 2-layer shells, as revealed by the positive potential shift relative to those in a pure Pt (111) surface both under vacuum and in 0.25 ML oxygen. The relative stability decreases for the 2-layer shell, though Pt atoms are still more stable than in pure Pt (111). Based on the above results it was observed that the Pd core enhances the stability of the atoms in the 1-layer shell and the benefit of the Pd core is reduced when the shell thickness increased.

Dispersed Pt Alloy Catalyst

Many factors such as structure, particle dispersion, particle size, type of carbon support used etc, influence the electro-catalytic activity of Pt and Pt alloy nanoparticles. Previously, within this project it was established that a 30 wt% Pt in Pt_2IrCo exhibited an activity almost two times higher than 20 and 40 weight percent samples [4]. In the past year, a significant amount of effort was focused towards development and optimization of the composition of PtIrM (M= Co, Cr, Ni, Fe etc.,) alloy catalysts to further improve electro-catalytic activity and enable lower PGM loading. This involved synthesis, physical characterization (using inductively coupled plasma, transmission electron microscopy and X-ray diffraction), electrochemical characterization in a liquid electrolyte using RDE and verification in an MEA. These catalysts were also subjected to potential cycling. The potential cycling was interrupted at various intervals during the experiment to measure the electrochemical surface area (ECA) and oxygen reduction reaction activity.

Figures 2a and 2b show the ECA and PGM mass activity vs. potential stability during cycling test, respectively, obtained from RDE testing for 30% Pt_4IrCo_3 (DOE 48), 30% Pt_2IrCr (DOE 52) and 30% Pt_6IrCo_7 (DOE 59-1) ternary alloys compared to a commercial TKK 46.4% Pt catalyst. It should be noted that Pt_6IrCo_7 was synthesized in an effort specifically to reduce the total PGM content in the catalyst nanoparticles. The change in ECA with number of potential cycles (Figure 2a) shows that the 30% Pt_4IrCo_3
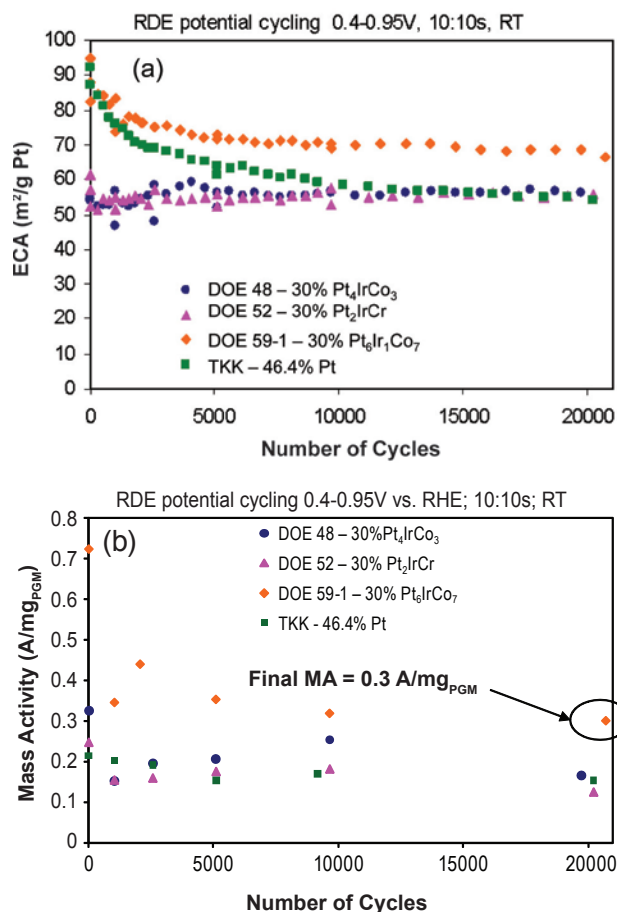
TABLE 2. Calculated Geometric and Electronic Properties of Pt (111) and Pt_3M (111) Surfaces[a]

	interlayer distance (Å)			
	d_{12}	d_{23}	$\varepsilon_d - \varepsilon_F$ (eV)	f (%)
Pt (111)	2.323	2.283	− 2.40	90.1
Pt_3Fe (111)	2.231	2.263	− 3.11	89.8
Pt_3Fe – Pt skin	2.303	2.235	− 3.06	89.3
Pt_3Co (111)	2.221	2.257	− 3.02	89.5
Pt_3Co – Pt skin	2.241	2.169	− 2.98	89.3
Pt_3Ni (111)	2.236	2.277	− 2.51	89.6
Pt_3Ni – Pt skin	2.238	2.219	− 2.46	89.3

[a] d_{12} and d_{23} refer to the distance between the first and second layers and between the second and the third layers, respectively; ε_d - ε_F refers to the d-band center of the surface Pt atoms referenced to the Fermi level; and f is the filling of the d-band of the surface Pt atoms.

FIGURE 2. (a) ECA decay and (b) PGM mass activity decay, as a function of number of potential cycles on various PtIrM (M = Co and Cr) ternary alloy catalysts obtained from RDE testing in 0.1 M HClO$_4$ at room temperature between 0.4 (10 sec) and 0.95 (10 sec) V vs RDE.

FIGURE 3. iR corrected fuel cell polarization curves in O$_2$/H$_2$ at 80°C; 100% relative humidity; 150 kPa, for the PtIrM ternary alloys compared to a state-of-art Pt/C MEA before and after 10s – 10s square wave potential subjected between 0.4 – 0.95 V for 30,000 cycles.

and 30% Pt$_2$IrCr ternary alloy compositions are more resistant to loss of electrochemical area compared to the commercial Pt/C. Preliminary results on the 30% Pt$_6$IrCo$_7$ alloy catalyst shows a high initial mass activity (~0.72 A/mg of PGM) and ECA (~91 m^2/g$_{Pt}$). This exceeded previously reported mass activities for state-of-the-art cathode catalysts by approximately 3.5x. The durability of this electrocatalyst under accelerated potential cycling test was 0.3 A/mg$_{PGM}$ after 20,000 cycles. This is approaching the DOE 2010 initial mass activity targets for catalysts.

Figure 3 shows the internal resistance (iR) corrected fuel cell performance curves in H$_2$/O$_2$ for the 30% Pt$_4$Ir$_{.5}$Co$_{1.53}$ (DOE 48) and 30% Pt$_2$IrCr (DOE 52) compared to a standard Gore 57 Pt/C (G57) before and after 30,000 potential cycles. At the beginning of life, the Pt/C shows higher performance compared to the PtIrM ternary alloy catalysts. It should be noted that initial Pt loading in commercial MEA is about two times that of the alloy MEAs used in this project. After 30,000 cycles, the end of life performance (EOL) for the Gore
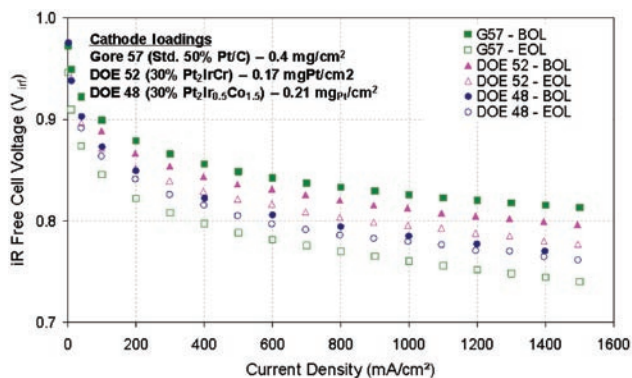
57 Pt/C catalyst is lower than the alloy catalysts in spite of unfavorable loading in alloy MEA. This trend closely follows the results obtained from potential cycling in RDE as shown in Figures 2a and 2b. The benefit of the Ir containing ternary alloy catalysts are evident from the mass activity and ECA under potential cycling shown in Figures 4a and 4b, respectively. The initial mass activity obtained for the 30%Pt$_2$IrCr (DOE 52) alloy catalyst is ~0.39 A/mg$_{Pt}$ (0.28 A/mg$_{PGM}$) and EOL activity is 0.22 A/mg$_{Pt}$ (0.16 A/mg$_{PGM}$). After 30,000 cycles, the mass activity of Gore standard Pt/C is less than 0.1 A/mg$_{Pt}$, a loss of more than 50% whereas the PtIrM ternary alloy catalysts show much lower loss in mass activity (~30%).

Core-Shell Pt Catalysts

The primary focus of core-shell development was (a) to synthesize Pt ML catalysts on Pd$_3$Co and Ir cores using scalable chemistries without compromising the intrinsic activity of the catalyst as demonstrated by BNL and (b) to characterize the structure of the core-shell catalysts. For this purpose, a large batch (30 g) of Pd$_3$Co and Ir cores were synthesized at JMFC. Subsequently, a large 5 g batch Pt ML core-shell catalyst was synthesized successfully by JMFC via a chemical method. A 300 mg batch of Pt ML core-shell catalyst was also prepared by BNL using the galvanic displacement of underpotentially deposited (UPD) Cu ML. High mass activities of >1 A/mg Pt are observed for a Pt ML on a carbon supported Pd$_3$Co nanoparticle on a glassy carbon tip under RDE test conditions. However, correcting for the PGM in the core, the activity normalized to total PGM content is lower than the catalysts prepared via the electrochemical UPD method. Figure 5 shows the mass activity based on PGM loading for three Pt$_{ML}$/Pd$_3$Co core-shell catalysts (i) prepared via Cu UPD on an RDE tip (red) (ii) 300 mg batch prepared using Cu UPD
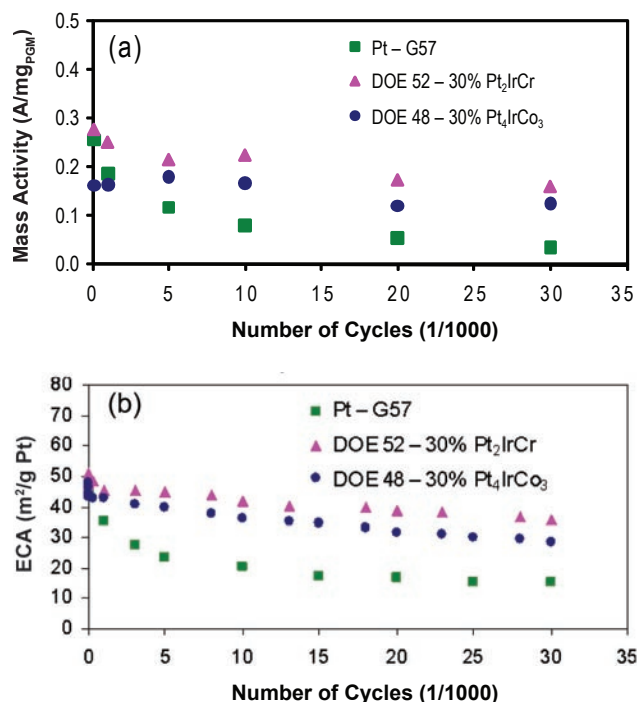
FIGURE 4. (a) PGM mass activity decay and (b) ECA decay, as a function of number of potential cycles on two PtIrM (M = Co and Cr) ternary alloy catalysts obtained in MEA testing.
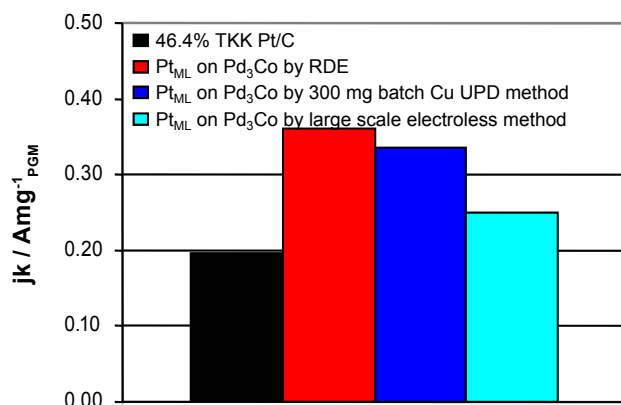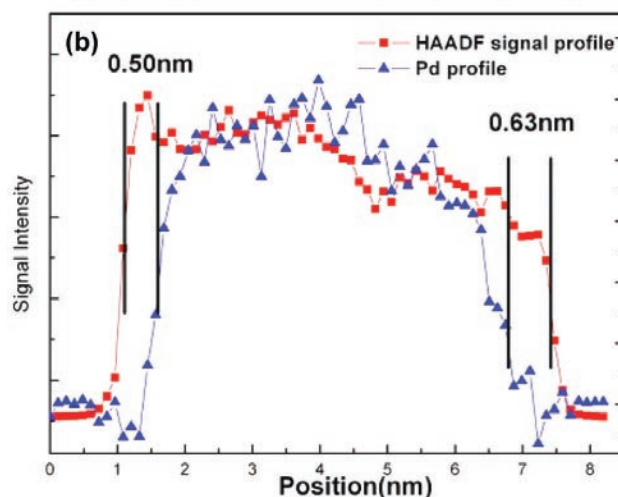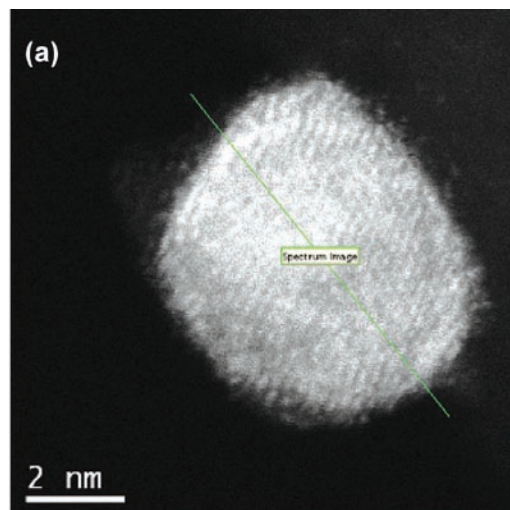

FIGURE 6. (a) High resolution STEM images of a PtML/Pd$_3$Co/C particle synthesized using Cu UPD method and (b) the corresponding cross-sectional compositional line profiles of HADDF-STEM (information of particle size) and Pd M-edge EELS signal (information of Pd distribution along the line) from image (a). The core-shell structure as well as the shell thickness can be directly derived from the difference between HADDF signal and EELS Pd signal.

FIGURE 5. PGM mass activity vs. RHE for a commercial Pt/C catalysts and a Pt ML on Pd$_3$Co/C catalysts synthesized via different methods obtained from RDE testing in 0.1 M HClO$_4$ at 1,600 rpm, and 10 mV/s. The same batch of Pd$_3$Co/C was used for all Pt ML core-shell catalysts.

(dark blue) and (iii) large scale (5 g) batch prepared via chemical methods (light blue) compared to a commercial TKK 50 wt% Pt/C (black). The Pt$_{ML}$/Pd$_3$Co/C prepared via Cu UPD intermediate show mass activities ~1.5 times higher than the standard Pt/C. However, the large-scale Pt core-shell catalyst synthesized via chemical method shows little enhancement on a total PGM basis.

In situ EXAFS studies show that the surface oxidation on Pt$_{ML}$/Pd$_3$Co prepared by electroless

method is very similar to that of Pt/C. A STEM study indicates that the as-prepared Pt$_{ML}$/Pd$_3$Co sample has a broad size distribution, from 3-10 nm. HAADF-STEM profile combined with Pd EELS signal for individual nanoparticles within the catalyst structure provides compelling evidence for the presence of Pt shells around the Pd containing cores as shown in Figure 6 with thickness varying from 0.4-1 nm. Figure 6 shows a representative STEM image obtained for a ~7 nm Pt$_{ML}$/Pd$_3$Co/C nanoparticle synthesized using Cu UPD methods and the corresponding HAADF-STEM–EELS profile showing a 0.5-0.6 nm thick Pt shell on a Pd containing core of ~5.5 nm. Similar structural properties are observed for Pt coatings applied to the same Pd$_3$Co core using the scalable synthesis route.

However, after 6,500 potential cycles between 0.7–1.1 V, these samples show a small particle growth and a similar size distribution compared to the as-prepared catalyst. The particle size change does not account for the total electrochemical surface area loss of the catalysts during cycling. This was found to be consistent with STEM observations which indicate a lower particle density and an uneven shell thickness for the post-cycling test in comparison to the as-prepared sample. Root cause analysis to understand discrepancies observed in core-shell materials synthesized using electrochemical and electroless routes is in progress.

Conclusions and Future Directions

Mass activities of almost 0.3 A/mg_{PGM} in both RDE and subscale MEA testing have been reproduced and verified for a 30% Pt_4IrCo_3 and 30% Pt_2IrCr that have been down-selected as the dispersed alloy catalyst systems to be scaled-up for fuel cell demonstration. A 30% Pt_6IrCo_7 alloy shows a high initial mass activity (~0.72 A/mg_{PGM} RDE) and superior durability capable of meeting the 2010 DOE targets. Pt ML catalyst prepared using scalable chemistries and characterized by a range of techniques show strong evidence for a core-shell structure. A key challenge for the core-shell catalysts is their poor durability towards potential cycling due to non-uniform Pt layer on the core structures. Development of various scalable methods specifically geared towards achieving uniform Pt coatings is an ongoing activity in the project.

Future Directions

- Scale-up and optimization of dispersed alloy catalyst systems in MEAs is in progress aiming to approach high mass activity and more importantly, durability towards potential cycling.

- The fundamental benefit of Ir in PtIrM ternary alloys for durability is being investigated based on their structure and electronic properties.

- Experimental verification of the modeling data for core-shell catalysts based on their stability and activity coupled with results from single-crystal work to be conducted by BNL is expected to close the gap between theoretical surfaces and real catalysts.

- In the case of the core-shell catalysts, preventing dissolution of the core material from the bulk phase of nanoparticles is a major challenge that is being addressed. Our modeling effort continues to drive the search for stable non-PGM cores for core-shell catalyst systems.

FY 2009 Publications/Presentations

1. Y. Ma, and P.B. Balbuena, "Surface segregation in bimetallic Pt_3M (M = Fe, Co, Ni) alloys with adsorbed oxygen", *Surf. Sci.*, **603**, 349 (2009).

2. R. Callejas-Tovar and P.B. Balbuena, "Oxygen adsorption and surface segregation in (211) surfaces of Pt (shell)/M (core) and Pt_3M (M=Co, Ir) alloys", *Surf. Sci.*, **602**, 3531 (2008).

3. Y. Ma and P.B. Balbuena, "Surface properties and dissolution trends of Pt_3M alloys in the presence of adsorbates", *J. Phys. Chem. C.*, **112**, 14520 (2008).

4. T.T. Aindow, W. Bi, E.L. Izzo, S. Motupally, V.S. Murthi and C. Perez-Acosta, "Structure-activity-durability relationship of Pt and Pt based alloy electrocatalysts", presented at the 215th meeting of the Electrochem. Soc., 2009, San Francisco, CA.

References

1. J. Zhang, M.B. Vukmirovic, K. Sasaki, F. Uribe and R.R. Adzic, *J. Serb. Chem. Soc.*, **70**, 513 (2005).

2. M.B. Vukmirovic, J. Zhang, K. Sasaki, A.U. Nilekar, F. Uribe, M. Mavrikakis and R.R. Adzic, *Electrochim. Acta*, **52**, 2257 (2007).

3. M. Shao, K. Sasaki, N.S. Marinkovic, L. Zhang and R.R. Adzic, *Electrochem. Comm.*, **9** 2848, (2007).

4. S. Motupally, DOE Merit Review Presentation, June 10, 2008, Washington, D.C.