

## V.D.7 The Science and Engineering of Durable Ultralow PGM Catalysts

Fernando H. Garzon (Primary Contact),  
Jose-Maria Sansiñena, Mahlon Wilson,  
Jerzy Chlistunoff, Ivana Matanovic, Neil Henson  
and Eric L. Brosha

Los Alamos National Laboratory  
MPA-11, MS. D429  
Los Alamos, NM 87545  
Phone: (505) 667-6643  
E-mail: garzon@lanl.gov

### DOE Manager

HQ: Nancy Garland  
Phone: (202) 586-5673  
E-mail: Nancy.Garland@ee.doe.gov

### Subcontractors:

- Yushan Yan, University of California, Riverside, Riverside, CA
- Abhaya Datye and Elena Beriba-Vera, University of New Mexico, Albuquerque, NM
- Siyu Ye and David Harvey, Ballard Fuel Cells, Burnaby, BC, Canada

Project Start Date: October 2009

Project End Date: October 2014

### Fiscal Year (FY) 2011 Objectives

- Development of durable, high mass activity platinum group metal (PGM) cathode catalysts enabling lower cost fuel cells.
- Elucidation of the fundamental relationships between PGM catalyst shape, particle size and activity to help design better catalysts.
- Optimization of the cathode electrode layer to maximize the performance of PGM catalysts improving fuel cell performance and lowering cost.
- Understanding the performance degradation mechanisms of high mass activity cathode catalysts to provide insights to better catalyst design.
- Development and testing of fuel cells using ultra-low loading high activity PGM catalysts – validation of advanced concepts.

### Technical Barriers

- PGM catalysts are difficult to synthesize in configurations other than quasi-spherical particles.
- PGM area specific activity may decrease with decreasing particle size.
- Durability may decrease with greater PGM surface area to volume ratios.

### Technical Targets

The technical targets for catalyst loading are indicated in Table 1. These targets were formulated with the assumption that fuel cell durability and impurity tolerance would not be impacted by the decreased Pt loadings used in the fuel cells.

**TABLE 1.** Technical Targets: Electrocatalysts for Transportation Applications (Extracted from Table 3.4.12. Technical Plan. April 27, 2007)

Characteristic	Units	2005 Status		Stack Targets	
		Cell	Stack	2010	2015
PGM total content (both electrodes)	g/kW (rated)	0.6	1.1	0.3	0.2
PGM total loading	mg PGM/cm <sup>2</sup> electrode area	0.45	0.8	0.3	0.2

### FY 2011 Accomplishments

- Synthesis, structural, (high resolution transmission electron microscopy [HRTEM] and X-ray diffraction [XRD]) and electrochemical characterization of Pt Pd nanoplates completed.
- Synthesis structural, (HRTEM and XRD) and electrochemical characterization of Pt/ceria/carbons catalysts completed and published.
- Synthesis structural, (HRTEM and XRD) and electrochemical characterization of Pt polypyrrole nanowires completed and published.
- Thermal characterization of Pt/ceria/C catalysts completed and published.
- Theoretical model of Pt-Ni nanoparticles developed and published.
- Theoretical modeling of Pt nanotubes completed.
- Microstructural model of the catalyst electrode layer validated against experimental work.
- Pt nucleation growth study on carbon completed and published.



### Introduction

Minimizing the quantity of Pt group metals used in polymer electrolyte membrane fuel cells (PEMFCs) is one of the remaining grand challenges for fuel cell commercialization. Tremendous progress has been achieved over the last two decades in decreasing the Pt loading required for efficient fuel cell performance. Unfortunately, the fluctuations in the price of Pt represent a substantial barrier to the economics of widespread fuel cell use.

Durability and impurity tolerance are also challenges that are tightly coupled to fuel cell Pt electrode loading. Traditional approaches to decreasing the amount of Pt required for good performance include:

- Increasing mass activity by decreasing Pt particle size by supporting on carbon.
- Alloy formulation Pt-Co, Pt-Cr alloys to improve mass activity.
- Increasing Pt utilization by optimization of electronic and ionic contact of the Pt particles.
- Improving conductivity of the electronic and ionic conducting constituents of the membrane electrode assembly.
- Improving reactant to and product mass transport away from the electroactive sites.

Recent novel approaches include the nanoengineering of core shell catalysts and Pt particles of unusual geometries such as nanowires/whiskers.

The success of the aforementioned approaches has been great; however further advances using such approaches have been hampered by a lack of underlining scientific understanding of the catalyst activity, particle growth mechanisms, and optimization strategies for designing composite electrodes.

## Approach

Our approach to new PGM catalyst design is multi-tiered. We are designing new low platinum loading catalysts on novel support materials to improve fuel cell performance. Novel PGM shapes; nanoparticles, nanotubes and nanowires are being synthesized in a variety of sizes. We are using contemporary theoretical modeling and advanced computational methods to understand and engineer the new catalysts. We are also modeling and designing appropriate catalyst architectures to maximize the performance of our novel catalysts. Catalyst-support interactions and their effects on durability and mass activity are also investigated. We study and test the performance of the catalysts in electrochemical cells, single cell fuel cells and fuel cell stacks. The new catalysts are extensively characterized before and after fuel cell operation.

## Results

We have improved our theoretical understanding of the Pt-Ni alloy catalyst system, a very promising catalyst system recently demonstrated to meet the DOE technical targets for catalyst activity for oxygen reduction. The structure, reactivity and stability of three different Pt-Ni alloys, PtNi, Pt<sub>3</sub>Ni and PtNi<sub>3</sub> were studied using periodic density functional theory (DFT) calculations. The influence of the alloying component concentration on the catalytic activity of the platinum surface was studied by calculating equilibrium adsorption potentials for oxygen reduction reaction (ORR)

intermediates and by constructing free energy diagrams in the ORR dissociative mechanism network. In addition, the stability of these materials in aqueous environments was investigated in the terms of relative electrochemical dissolution shifts and by determining the most stable state of the surface as a function of pH and potential as represented in Pourbaix diagrams. The (111) surface of all three studied Pt-Ni alloys show improved oxygen reduction activity over Pt(111). The ORR overpotential was calculated to decrease as Pt (0.55 V) > Pt<sub>3</sub>Ni (0.24 V) > PtNi<sub>3</sub> (0.19 V) > PtNi (0.15 V). Thus, it can be expected that the catalytic activity towards ORR will increase in the order Pt < Pt<sub>3</sub>Ni < PtNi<sub>3</sub> < PtNi. Around 50% alloying with Ni induced the biggest change in activity. Shifts in the electrochemical dissolution potentials of the studied Pt-Ni alloys relative to platinum were estimated to be -0.27 V for PtNi<sub>3</sub>, +0.13 V for Pt<sub>3</sub>Ni and +0.30 for PtNi. Thus, among all studied materials PtNi is predicted to be the least susceptible to corrosion at similar pH and cell potentials.

The formation of Pt catalysts on active oxide supports may also improve activity and fuel cell durability. Highly crystalline ceria nanoparticles in porous carbon matrices were formed by the simple pyrolysis of cerium-loaded ion-exchange resins. The resulting cerium/carbon composite structures maintain the original bead or powder form of the precursor resins (Figure 1), with an increase in specific surface area. Incorporating Gd or Pr dopants with Ce in the resins provided uniform dispersions and equally small ceria crystallites upon pyrolysis, typically 1–2 nm (Figure 2). Highly active particles were obtained, as demonstrated by air light-off of the ceria/carbon composites as low as 200°C. The combination of the high pyrolysis temperature (1,000°C) and the controlled dispersion and stable environment provided by the ion-exchange resin precursors are key to provide highly crystalline and extremely small ceria particles

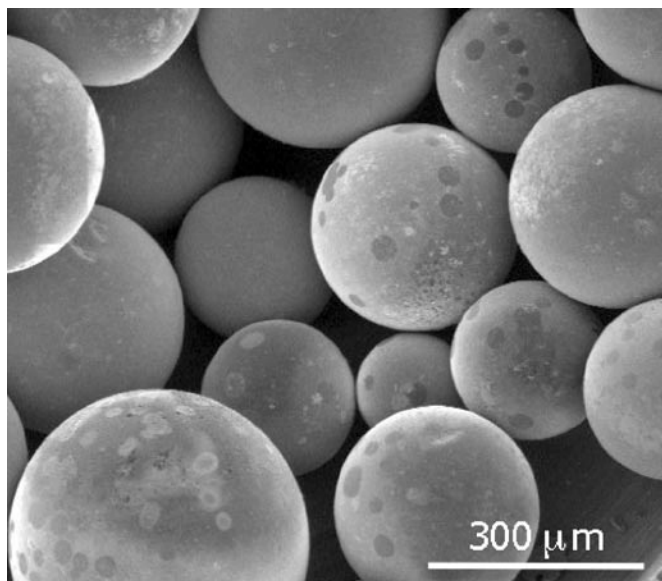
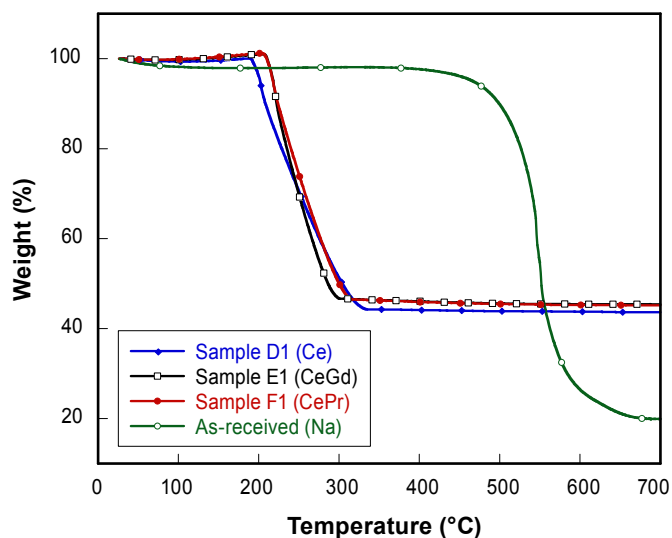


FIGURE 1. Scanning Electron Micrograph of Pyrolyzed IRC748 Beads

in a conductive carbon matrix. Various types of cation-exchange resins are considered and the best results are obtained with highly cross-linked or styrene-divinyl benzene matrices and cation chelating or weak acid functionalities.

One of the outstanding challenges in the wider deployment of PEMFCs is improving the utilization of Pt. While decreasing particle size improves accessibility of the Pt, it also destabilizes the Pt particles and leads to dissolution/re-precipitation and rapid grain growth. A parameter that is as yet poorly characterized is the number of nucleation sites on the carbon support. Increased nucleation site density could provide a valuable approach to improve Pt utilization. We have characterized the nucleation density by determining the number of particles per  $m^2$  using HRTEM and energy dispersive X-ray spectroscopy (EDS). Ranges of metal loadings were explored to investigate their effect on the number of Pt particles on three types of carbon supports. It was concluded that the number of nucleation sites is relatively constant over the Vulcan family of carbon supports, see Table 2. However, activated carbons such as Norit SX-1G show much higher nucleation density.



**FIGURE 2.** Air thermal gravimetric analysis of pyrolyzed IRC748 resins loaded with Ce (D1), Gd-doped Ce (E1), Pr-doped Ce (F1), and as-received Na form.

**TABLE 2.** Pt number density on Vulcan carbon derived from HRTEM analysis and EDS.

Catalyst	Pt wt%	Number of Pt particles/ $m^2$
Aqueous Impregnation Pt/Vulcan XC72	3.7	$1.20E+17$
E-TEK 10 wt% Pt/Vulcan XC72R	11.3	$1.04E+17$
Cabot 20 wt% Pt/Vulcan XC72	29.8	$1.01E+17$

## Conclusions and Future Directions

- Pt/Ceria/catalyst research and development:
  - Improve Pt dispersion and scale up synthesis for fuel cell testing.
  - Calculate optimal MEA geometries.
  - Ionomer incorporation into catalyst layers and MEA optimization.
  - Fuel cell performance and durability testing.
- Pt/Pd nanoplatelet research and development:
  - Decrease nanoplate size by surfactant modification.
  - Scale up synthesis for fuel cell testing.
  - Incorporation into catalyst layers and MEA optimization.
  - Fuel cell performance and durability testing.
- Development of models and theory:
  - DFT model extension to nanoplates and nanowires.
  - Sintering model extension to include dissolution and reprecipitation.
  - Microstructural model application to novel catalysts fuel cell validation.

## FY 2011 Publications

- Sansinena, J.-M.; Nelson, M.; Wilson, M.S.; Garzon, F.H., Electrochemical Synthesis of Oxygen Reduction Catalysts Based on Pt Coated Polypyrrole Nanowires Using Starch as Template Molecule. ECS Transactions 2011, 33 (27), 13-19.
- Berliba-Vera, E.K.; Delariva, A.T.; Atanassov, P.; Datye, A.K.; Garzon, F.H., Nucleation of Platinum on Carbon Blacks. ECS Transactions 2010, 33 (1), 73-82.
- Wu, G.; Nelson, M.A.; Mack, N.H.; Ma, S.; Sekhar, P.; Garzon, F.H.; Zelenay, P., Titanium dioxide-supported non-precious metal oxygen reduction electrocatalyst. Chemical Communications 2010, 46 (40), 7489-7491.
- Wilson, M.A.; Garzon, F.H., Synthesis of sub-2nm ceria crystallites in carbon matrixes by simple pyrolysis of ion-exchange resins, accepted for publication, Chemistry of Materials 2011.
- Matanovic, I.; Henson, N.J.; Garzon; F.H. Theoretical Study of Electrochemical Processes on Pt-Ni Alloys, accepted for publication, Journal of Physical Chemistry C. 2011.

## FY 2011 Presentations

- Sansinena, J.-M.; Nelson, M.; Wilson, M.S.; Garzon, F., Electrochemical Synthesis of Oxygen Reduction Catalysts Based on Pt Coated Polypyrrole Nanowires Using Starch as Template Molecule. ECS Meeting Abstracts 2010, 1002 (6), 356-356.
- Matanovic, I.; Garzon, F.; Henson, N., Theoretical Study of Electrochemical Processes on Novel Platinum Group Metal Catalysts. ECS Meeting Abstracts 2011, 1101 (41), 1894-1894.

3. Berliba-Vera, E.K.; Delariva, A.; Atanassov, P.; Datye, A.; Garzon, F., Nucleation of Platinum on Carbon Blacks. ECS Meeting Abstracts 2010, 1002 (10), 640-640.