

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

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Project Start Date: October, 2009
Project End Date: October, 2014

Fiscal Year (FY) 2012 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—provide insights to better catalyst design.
- Development and testing of fuel cells using ultralow 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.

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

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 ² electrode area	0.45	0.8	0.3	0.2

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

FY 2012 Accomplishments

- New Pt/carbon-ceria catalysts were developed and characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), cyclic and rotating disc electrode (RDE) voltammetry, and thermogravimetry and they exhibit enhanced oxygen reduction reaction (ORR) activity over Pt-C.
- New Pt-Y and Pt-Sc alloy catalysts were developed and characterized by transmission electron microscopy (TEM) and cyclic and RDE voltammetry which show greater ORR activity than Pt-C.
- Pt on pyrolyzed polypyrrole synthesized and characterized by TEM and cyclic and RDE voltammetry exhibits high activity for ORR and good stability.
- New theoretical models developed for Pt nanotubes and new predictions made for the stability of these active catalysts.
- X-ray absorption spectroscopy experiments on a variety of carbons and using different Pt solution precursors revealed the mechanism of Pt catalyst nucleation and growth.
- The chemical reduction of Pt IV to Pt II by the carbon was shown to be an essential step in the formation of Pt nanoparticles.



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 stability and reactivity of Pt nanotubes and nanowires. We used density functional theory to study the difference

in the structure, stability and catalytic reactivity between ultrathin, 0.5-1.0 nm diameter, platinum nanotubes and nanowires. Inserting an inner chain of platinum atoms in the corresponding nanotubes formed model nanowires. In this way more stable, non-hollow structures were formed. The difference in the electronic structure of platinum nanotubes and nanowires was examined by inspecting the density of surface states and band structure. Furthermore, reactivity towards the oxygen reduction reaction of platinum nanowires was addressed by studying the change in the chemisorption energies of oxygen and hydroxyl groups, induced by inserting the inner chain of platinum atoms into the hollow nanotubes. Ultrathin platinum nanotubes and nanowires both have very different chemical reactivity than bulk platinum. We found that adsorption energies of oxygen and hydroxyl in general decrease as the diameter of the nanotube or a nanowire increases. However, the reactivity towards oxygen and hydroxyl varies considerably with the chirality and structure of the nanotube.

All the studied platinum nanotubes and nanowires with diameters less than approximate 1 nm bind oxygen and hydroxyl stronger than bulk surface and dissolve at very low cell potentials. The best candidates for fuel cell applications were found among single-wall nanotubes with approximately 1-nm diameter and $n=m$ chiralities. However, these tubes still have lower dissolution properties than the bulk platinum by up to 100 meV. Both double-wall nanotubes and nanowires with approximately 1-nm diameter have shown to have favorable interaction with oxygen but bind hydroxyl too strongly which would lead to the poisoning of the catalytic surface with hydroxyl during the ORR cycles.

Optimizing the reactivity of platinum nanotubes and nanowires for fuel cell applications might be challenging due to the complexity of factors that govern their reactivity and due to the inadequacies of simple descriptors, like d -band theory, to predict their reactivity; however, we believe it is still plausible. Future studies would require the evaluation of more chiralities than we have studied in order to find multi-wall nanotubes and nanowires that have smaller affinity for hydroxyl and dissolutions properties superior to those of bulk. However, we believe that this work presents an important first step towards that goal.

We are developing new conductive nanostructured materials based on pyrolyzed polypyrrole (PPy) nanowires that can be used as conductive support for metal catalysts. With this new approach we seek to produce a high surface area metal catalyst that can be easily incorporated into the fuel cell assembly and lead to a higher ORR catalytic activity by enhancing both electronic conductivity and transport properties. Figure 1 shows the typical structure of the Pt coated PPy/starch nanowires electrochemically deposited on the glassy carbon disk electrode. PPy/starch preserved structural integrity during pyrolysis and nanowires were uniformly deposited on the electrode with a narrow

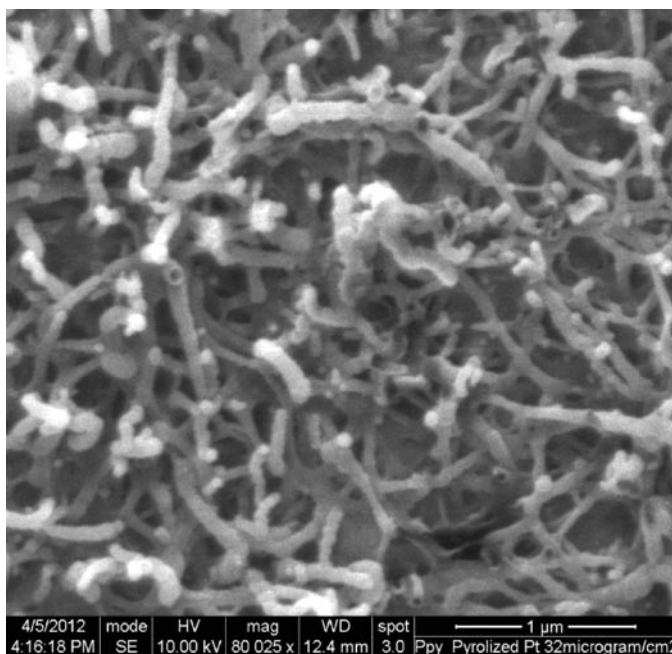


FIGURE 1. Electron micrograph of pyrolyzed polypyrrole nanowires

diameter distribution, which is directly dependent on the polymerization time. Moreover, we proved it was possible to deposit the PPy/starch nanowires on a carbon paper gas diffusion layer, which can be easily incorporated into the MEA structure as a gas diffusion electrode once coated with platinum. The new materials provided very good rotating ring disc electrode results as supports for low Pt load metal catalysts when compared with 46% Pt/C TKK catalyst, which was used as a reference. They demonstrate great potential to increase ORR catalytic activity by enhancing both electronic conductivity and transport properties. The specific surface area for the pyrolyzed PPy/starch nanowires coated with impregnated Pt ($83 \text{ m}^2 \text{ g}^{-1}$) was higher than the one obtained for 46% Pt/C TKK ($72 \text{ m}^2 \text{ g}^{-1}$), while the catalyst based on pyrolyzed PPy/starch nanowires coated with sputtered Pt was much lower ($29 \text{ m}^2 \text{ g}^{-1}$). The higher Pt surface area obtained using the Pt impregnation compared with the sputtering method suggests a smaller Pt particle size. This is consistent with the lower surface activity observed since smaller particles are intrinsically less active than bulk-like larger particles. However, the higher surface area of the impregnated Pt overcomes the deficiency and the apparent (mass) activity becomes comparable with the one obtained for the 46% Pt/C TKK used as a reference. Ultimately, PPy-Pt nanowires based catalysts may facilitate the preparation a fuel cell membrane electrode assembly by incorporating them as part of a GDE when PPy is directly electrodeposited onto a gas diffusion layer.

New alloy formulations may also improve Pt mass activity. In 2011-2012 we synthesized nanoparticles of platinum-scandium and platinum-yttrium using novel

organometallic precursors and synthesis conditions. These methods yielded alloys in the 4-7 nm particle size range as measured by transmission electron microscopy. The nanomaterials show significant improvement in oxygen reduction behavior over commercial catalysts as measured by rotating disk electrode techniques. Figure 2 shows the relative mass activities and area specific activities of these new catalysts compared to conventional nanocrystalline Pt-C and Pt-Pd alloys. The specific activity approaches that of bulk platinum, behavior not observed in nanocatalysts.

The formation of Pt catalysts on active oxide supports may also improve activity and fuel cell durability. Ceria has been shown to effectively eliminate destructive oxygen free radicals. The activity of the ceria is predominately due to the presence of Ce(III) in the oxide lattice. The Ce (III)/Ce(IV) ratio increases with decreasing particle size yet active surface area increases. Highly crystalline ceria nanoparticles were previously formed in porous carbon matrices by the simple pyrolysis of cerium loaded ion-exchange resins. Incorporating Gd or Pr dopants with Ce in the resins provided uniform dispersions and equally small ceria crystallites upon pyrolysis, typically 1–2 nm. Highly active particles were obtained, as demonstrated by fast peroxide decomposition rates. The combination of the high pyrolysis temperature ($1,000^\circ\text{C}$) 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 in a conductive carbon matrix. We have incorporated mixtures of Pt-C and ceria nanoparticles to decrease free radical attack on the fuel cell components and are currently testing them in fuel cells as illustrated by HRTEM in Figure 3.

One of the outstanding challenges in the wider deployment of PEMFCs is improving the utilization of Pt in

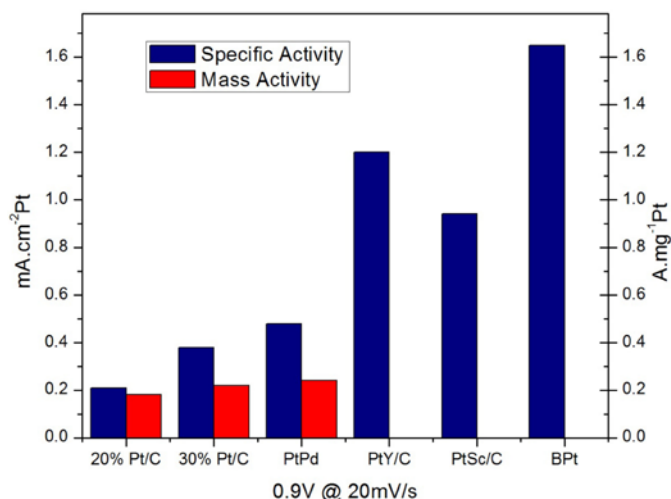


FIGURE 2. Mass activity and area specific activity of various Pt catalysts, Pt alloys and bulk Pt

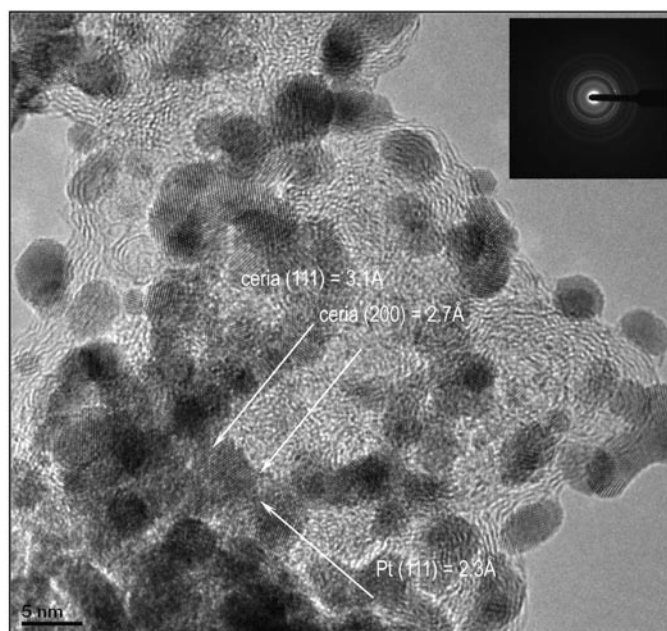


FIGURE 3. TEM and electron diffraction pattern of Pt-C/Ceria composite catalyst

carbon supported Pt nanocatalysts. 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 designed and performed X-ray absorption spectroscopy (XAS) experiments at Argonne National Laboratory that directly studied the formation of the Pt particles from an ionic solution precursor. The XAS experiments are powerful probes of the valence of the species and X-ray absorption fine structure region probes the local near neighbor environment of the nanoclusters of Pt as they nucleate and grow. We observed that the reduction of Pt (IV) chloride precursors to Pt (II) by the carbon surface governed the nucleation and growth of the Pt nanoparticles illustrated in Figure 4. Both types of carbon, high surface area Norit (red) and Vulcan XC-72 (green) show the rapid formation of Pt (II) as indicated by the figure; Pt metal (purple) and Pt(IV) chloride (blue) are plotted for comparison. The reduction site density varied with the types of carbon high surface area activated carbons having the most followed by partially graphitic carbon. No nucleation was observed on vitreous (glassy carbons).

Conclusions and Future Directions

- Pt/Ceria/C catalyst research:
 - Pt-C/Ceria catalyst optimization—improve Pt dispersion
 - Pt/Ceria/catalyst neutron scattering

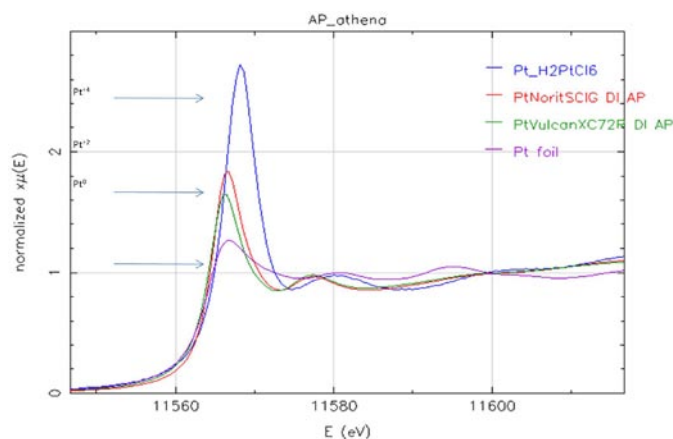


FIGURE 4. XAS spectrum of Pt after exposure to Norit (red) or Vulcan (green) carbon surfaces. Pt foil (blue) and Pt(IV)Chloroplatinic acid (blue) shown for reference

- Scale up for fuel cell testing
- Incorporation into catalyst layers and MEA optimization
- Fuel cell performance and durability testing
- Pt/Polypyrrole catalyst research:
 - Large batch synthesis and fuel cell testing
 - Calculate and synthesize optimal MEA geometries
- Pt/Y,Sc nanoplate research:
 - Decrease nanocrystal size
 - TEM and XRD characterization
 - Scale up for fuel cell testing
 - Incorporation into catalyst layers and MEA optimization
 - Fuel cell performance and durability testing
- Development of models and theory:
 - Density functional theory model extension to catalyst coated nanotube and nanowires
 - Microstructural model application to novel catalysts
 - Model validation

FY 2012 Publications

1. Matanovic, I.; Garzon, F.H.; Kent, P.R.; Henson, N.J., Density Functional Theory Study of Oxygen Reduction Activity on Ultrathin Platinum Nanotubes, submitted to *Journal of Physical Chemistry C*.
2. Matanovic, I.; Garzon, F.H.; Kent, P.R.; Henson, N.J., Theoretical Study of the Structure, Stability and Oxygen Reduction Activity of Ultrathin Platinum Nanotubes. Accepted for publication *ECS Transactions* 2012.
3. Sansinena, J.-M.; Wilson, M.S.; Garzon, F.H., Conductive Nanostructured Materials for Supported Metal Catalysts. Accepted for publication *ECS Transactions* 2012.

4. 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.
5. Wilson, M.S.; Delariva, A.; Garzon, F.H., Synthesis of sub-2 nm ceria crystallites in carbon matrixes by simple pyrolysis of ion-exchange resins. *Journal of Materials Chemistry* **2011**, 21 (20), 7418-7424.
6. Matanovic, I.; Henson, N.J.; Garzon; F.H. Theoretical Study of Electrochemical Processes on Pt-Ni Alloys, *Journal of Physical Chemistry C*. 2011, (2011) Vol.115, iss.21, p.10640-10650.

FY 2012 Presentations

1. Matanovic, I.; Garzon, F.H.; Kent, P.R.; Henson, N.J., Theoretical Study of the Structure, Stability and Oxygen Reduction Activity of Ultrathin Platinum Nanotubes. *ECS Meeting Abstracts 2012, 1202* (13), 1563-1563.
2. Sansinena, J.-M.; Wilson, M.S.; Garzon, F.H., Conductive Nanostructured Materials for Supported Metal Catalysts. *ECS Meeting Abstracts 2012, 1202* (13), 1688-1688.
3. 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.