

## V.A.5 The Science and Engineering of Durable Ultra-Low PGM Catalysts

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Project Start Date: October 2009

Project End Date: October 2014

### Overall 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 of high-activity PGM catalysts to validate advanced concepts

### Fiscal Year (FY) 2013 Objectives

- Incorporation of Pt supported on pyrolyzed polypyrrole (PPy) nanowire catalysts into fuel cells
- Optimization of ceria particle size for high-performance, low free radical generation cathode catalysts

- Accelerated stress testing of fuel cells incorporating ceria-free radical scavengers
- Extensive materials characterization of fuel cell components after accelerated stress testing
- Completion of theoretical modeling of the effect of size and geometry on Pt nanowire catalyst performance
- Completion of theoretical modeling of ceria particle-free radical scavenging mechanism

### 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 2013 Accomplishments

- Achieved preparation of fuel cells with novel nanowire PGM catalyst layers <25 μm thick with <0.1 mg Pt/cm<sup>2</sup> and an electrochemical surface area >70 m<sup>2</sup>/g.
- Optimized Pt-ceria ratios for low free radical generation catalysts with less than 10% difference in fuel cell performance at 0.6 V from non-ceria catalysts.
- Completed high-resolution transmission electron microscopy (HRTEM) imaging of novel PPy nanowire PGM catalysts.
- Completed optimization of fuel cell components using novel nanowire PGM catalysts to demonstrate 5-cm<sup>2</sup> single-cell performance with <<0.1 mg Pt/cm<sup>2</sup> that equal

or exceed conventional membrane electrode assemblies (MEAs) with 0.2 mg Pt/cm<sup>2</sup>.

- Accelerated stress testing of fuel cells incorporating free-radical scavengers commenced with first cycle completed.
- Completed characterization of accelerated stress testing samples.
- Completed the extension of theoretical modeling to larger structures that better approximate the dimensions of experimental nanowire materials.



## INTRODUCTION

Minimizing the quantity of Pt-group metals used in polymer electrolyte membrane fuel cells (PEMFCs) is one of the remaining 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
- Formulating 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 MEA
- 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 underlying 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 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. New methods to reduce the free radical attack on fuel cell components are being studied. We study and test the performance of the catalysts in electrochemical cells, single-cell fuel cells, and fuel cell stacks. The new catalysts are being extensively characterized before and after fuel cell operation.

## RESULTS

During normal operation of PEMFCs, free radicals (OH<sup>•</sup>, OOH<sup>•</sup>, H<sup>•</sup>) are formed which attack the catalyst layer ionomer, catalyst support, and membrane, leading to significant performance loss and eventual membrane failure due to pinhole and/or crack formation [1-2]. In an effort to reduce this commonly observed mode of membrane degradation, the addition of free radical scavengers into the anode catalyst layer, cathode catalyst layer (CCL), and/or the membrane has been investigated. These free radical scavengers are typically salts (such as Mn<sup>2+</sup> or Ce<sup>3+</sup>) or oxides (such as CeO<sub>2</sub>). Through accelerated stress testing (designed to greatly amplify the degradation of the membrane), it has been demonstrated that these additives can greatly increase membrane lifetime by consuming free radicals before they are able to attack the membrane.

While these antioxidants greatly improve membrane lifetime, they have a deleterious impact on performance, particularly when the cathode is degraded. Specifically, the antioxidant cations (released as Ce<sup>3+</sup>/Ce<sup>4+</sup> through dissolution in the case of CeO<sub>x</sub>) will accumulate in the CCL through strong interactions with the sulfonate in the ionomer. These cations then compete with protons for sulfonate sites in the CCL, leading to increased CCL ionic resistance and a subsequent loss in performance. This effect is more evident once the cathode has degraded as the reaction distribution shifts towards the cathode-gas diffusion layer interface. Controlling the rate of CeO<sub>x</sub> dissolution is therefore of great importance, as it may be possible to maintain sufficient cerium oxide for free radical scavenging while minimizing the impact of the dissolved cations on the CCL. Therefore, our work focuses on the impact of CeO<sub>x</sub> crystallite size on dissolution rate. Three different CeO<sub>x</sub> samples (6 nm–30 nm particle size) were synthesized and were characterized using X-ray diffraction and gas sorption measurements.

The chemical stabilities of these CeO<sub>x</sub> samples were investigated in 1 M H<sub>2</sub>SO<sub>4</sub> using ultraviolet-visible spectroscopy to monitor the concentration of Ce<sup>3+</sup>/Ce<sup>4+</sup> cations. The trend in chemical stability was found to be:

CeO<sub>x</sub> 25 nm > CeO<sub>x</sub> 13 nm > commercial 30 nm > CeO<sub>x</sub> 6 nm. Interestingly, two of the LANL materials showed higher stability than the larger particle size commercial control sample.

In situ testing was then performed by incorporating the CeO<sub>x</sub> additives into the anode catalyst layer of an MEA. Accelerated stress testing was then performed on each MEA (1.3 V upper potential limit, 0.6 V lower potential limit for 4,700 cycles) to evaluate the impact of the CeO<sub>x</sub> additives on end-of-life (EOL) performance. Significantly, despite the clear differences in chemical stability found through ex situ testing, no difference in EOL performance was observed among the MEAs prepared using the four different CeO<sub>x</sub> additives. This may suggest that at the loadings used for this study, the CCL becomes saturated with Ce cations even with the most stable 25-nm CeO<sub>x</sub> prepared at 800°C. Finally, the impact of relative humidity (RH) was also investigated. By varying the anode RH between 50 and 100%, it was determined that anode RH has a large impact on EOL performance of the MEAs containing CeO<sub>x</sub>. The effect is believed to be related to the dissolution rate of CeO<sub>x</sub> and the transport of cations in the relatively larger water fluxes.

In order to enhance the catalytic properties of cerium oxides, dopants such as praseodymium and gadolinium have been used to increase the electrical and/or ionic conductivity of cerium oxide. Our recent ex situ experiments show an enhancement of selectivity for free radical elimination upon the substitution doping of ceria. While many groups have reported on the synthesis of these mixed-metal oxides, there is little known about where these dopants are incorporated into the cerium oxide lattice. Our recent work represents the first direct evidence of praseodymium phase separation in mixed cerium-praseodymium oxides. X-ray diffraction and HRTEM were used to verify the presence of a single cubic phase with no amorphous coating. X-ray photoemission spectroscopy showed a strong decrease in surface Ce<sup>+3</sup>, and that increasing the bulk composition of praseodymium results in a shift towards the Pr<sup>+4</sup> oxidation state for surface praseodymium atoms, suggesting the formation of a PrO<sub>2</sub> shell. From HRTEM paired with energy dispersive X-ray spectroscopy, we have determined that the concentration of praseodymium does not increase in proportion with cerium, demonstrating a core shell structure. Regardless of particle size and method of synthesis, praseodymium preferentially incorporates into or onto the surface of a cerium oxide core. Further research will be performed to better understand why these materials show enhanced selectivity for oxygen-free radical destruction.

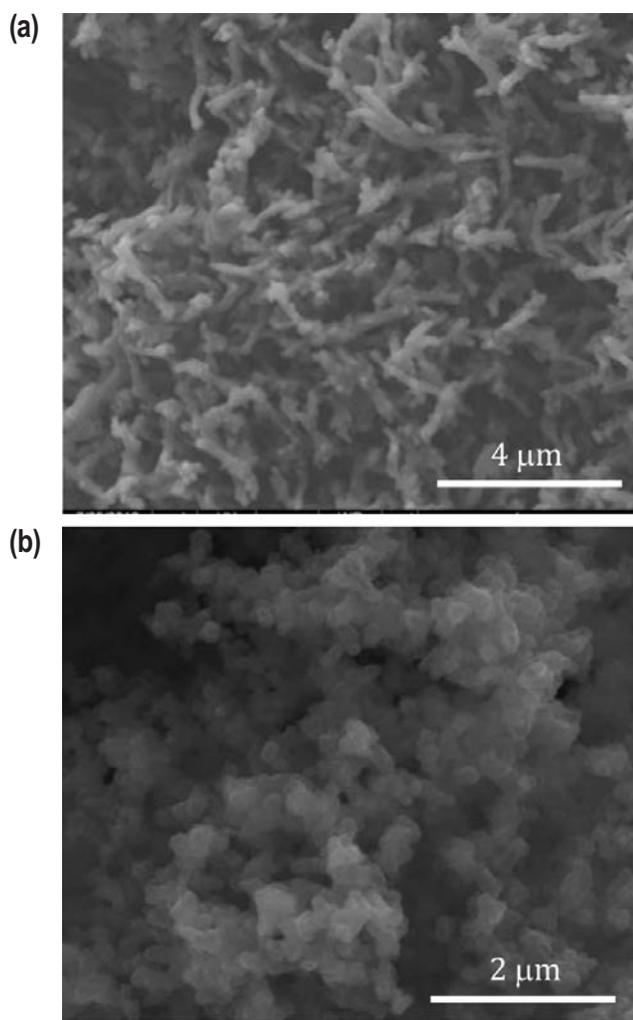
Previously in this project, nanowire catalyst supports were prepared by electropolymerizing pyrrole to PPy onto conductive substrates and even gas diffusion layers. While desirable morphologies were obtained, difficulties were encountered in achieving high Pt catalyst dispersions and utilizations, and the “thin-film” style of electrode easily

flooded. Consequently, the approach was redirected to investigating bulk, chemically polymerized nanowires that are catalyzed and fabricated into MEAs as a powder, thus using conventional processes. The advantages over standard carbon blacks, such as higher porosities and connectivity, are retained as with the electro-polymerized structures.

While going to chemical polymerization conceivably enables the introduction of other nanowire fabrication processes, pyrrole is still preferable over, for example, aniline, because the pyrolysis of the former has a much higher yield and better retention of the original structure than the latter. While it is not as easy to synthesize nanofibers as with aniline, there are a number of “soft” template processes for synthesizing PPy nanofibers. Of the simpler methods explored, one particular process provided high yields, good product uniformity, and a desirable “branched” morphology that serves to maintain open porosity and resist fibers from aligning or bundling. The soft template in this case consists of heparin and methylene blue [3], and a micrograph of nanowires synthesized by a generally similar procedure to the literature is shown in Figure 1a. A benefit of this process is that the ratio of heparin to methylene blue can be used to provide some control over fiber diameter. On the other hand, heparin is too expensive to be practical as a precursor. Coincidentally, heparin was originally used as a template in our earlier electropolymerization efforts, but starch served as a satisfactory replacement. When the heparin was replaced with starch in the methylene blue soft template process, however, PPy globules instead of nanofibers were obtained, as shown in Figure 1b.

The failure of the starch to form nanofibers is likely due to an inability to ionically pair with the two tertiary amine ligands on methylene blue because of the lack of anionic functional groups, whereas heparin has a pair of anionic functional groups per ring. In order to effectively replace heparin with its 2<sup>(-)</sup> groups per saccharide ring, several common carbohydrates with anionic functionality were investigated. These were pectin (<1<sup>(-)</sup>/ring), sodium alginate (1<sup>(-)</sup>/ring) and the ι (iota) and λ (lambda) carrageenans (1 and 1.5<sup>(-)</sup>/ring, respectively). Since purified carbohydrates can be quite expensive, very low-cost food grade supplies were tested. Interestingly, only the alginate failed to form nanofibers, while even the pectin, with lower functionality due to partially methoxylated carboxylate groups, provided nanofibers. However, the linked globules formed with the alginate indicated some inclination to form fibers. Not surprisingly, the best results were obtained with the highest functionality saccharide, the λ-carrageenan, which became the basis for further efforts.

Transmission electron micrographs of PPy synthesized using a methylene blue plus λ-carrageenan template are shown in Figure 2. The fibers in this sample are approximately 60 nm in diameter with no discernable structure or interface between the template and PPy

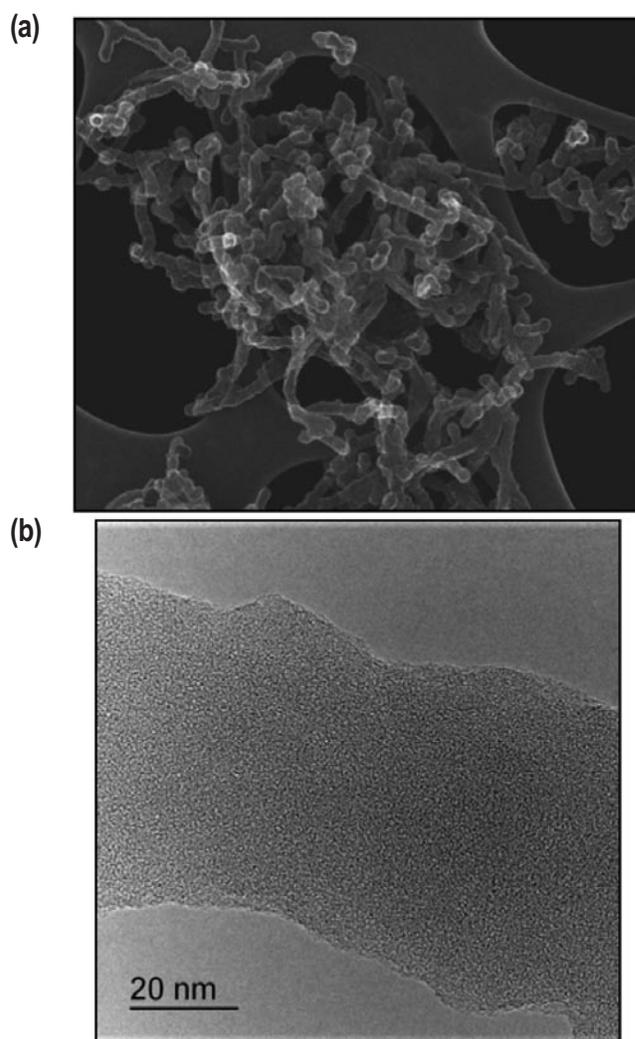


**FIGURE 1.** Scanning electron micrographs of PPy structures formed using templates of methylene blue combined with a) heparin and b) starch.

components. Further, the fibers are clearly solid (as preferred), unlike the tubes that are often obtained. To a large extent, the components are intermingled, as evidenced by the change in solution color that occurs as the methylene blue is taken up during the polymerization process.

Pyrolysis at 1,000°C for 1 h in nitrogen or argon retains the general morphological features of the precursor, but a highly graphitic, yet convoluted, structure evolves, as seen in Figure 3a. After a pyrolysis heat treatment, about 10% (atomic) of the graphitic material remains as nitrogen. Despite the relatively modest pyrolysis temperature and the high nitrogen content, the nanowires are highly graphitic as measured by X-ray and electron beam diffraction.

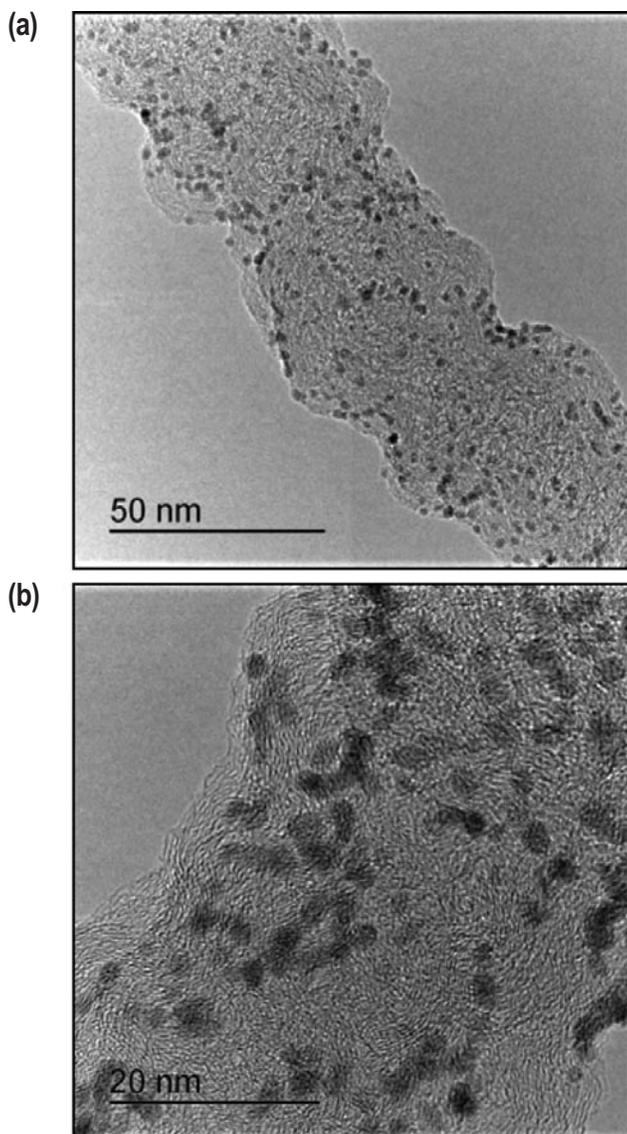
The highly convoluted surface of the nanowires, evident in the Figure 3 micrographs, as well as the high nitrogen content, might be expected to provide a high density of nucleation and anchor sites for Pt catalyzation.



**FIGURE 2.** Micrographs of a) PPy nanowires (supported on a microgrid) and b) an individual PPy nanowire.

Indeed, platinization by the polyol process provided highly dispersed Pt despite a relatively high catalyst surface loading (13.5 wt% Pt on a 70 m<sup>2</sup>/g support). The Pt crystallites are about 2 nm by X-ray diffraction peak broadening, and the particles average about 2.2 nm by transmission electron microscope analysis and provide an electrochemical surface area of 91 m<sup>2</sup>/g Pt (loading determined by X-ray fluorescence spectroscopy). As can be seen in Figure 3, many of the Pt particles are oriented in strings, primarily along interfaces between graphitic features.

Because of the unusual nature of the porous nanowire powders, some difficulties were encountered in formulating inks for fabricating MEAs, but the polarization and resistance curves for one with a very low 0.03 mg Pt/cm<sup>2</sup>/electrode loading that provided good fuel cell performance and behavior are shown in Figure 4. Operation of the cell for 250 h under various operating conditions resulted in no loss of performance except for the hysteresis observed, reflecting



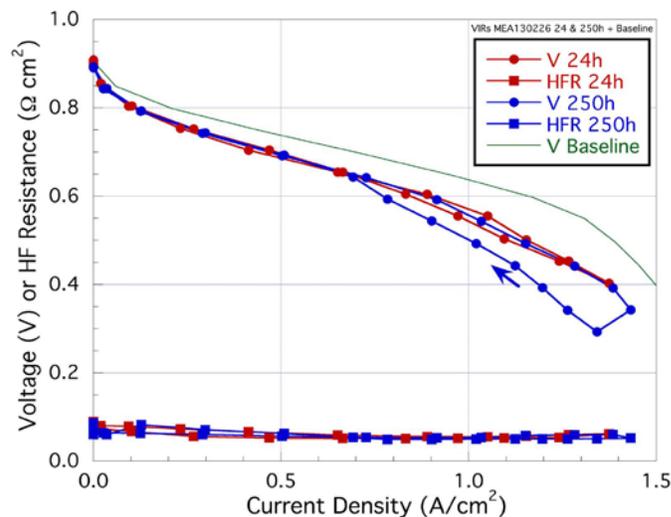
**FIGURE 3.** Transmission electron micrographs of pyrolyzed and platinized PPy nanowires at a) lower and b) higher magnifications.

a bit of flooding at high-current density operation. Carbon corrosion of the nanowires was not visually evident, but while the 250 h test does not constitute a very long-term carbon durability test, it is at least promising that the nitrogen-rich and convoluted nanowire surface is not unusually susceptible to corrosion.

## FUTURE DIRECTIONS

### Modeling

- Density functional theory modeling of nanotubes/wires:
  - Complete computations on larger Pt tubes/wires



**FIGURE 4.** Polarization and resistance curves of a 0.03 mg Pt/cm<sup>2</sup>/electrode fuel cell operating at 30 psig and 80°C after 24 and 250 h of operation. Compared to a “baseline” cell (green) fabricated in a similar manner with identical membrane and gas diffusion layers but with 0.19 mg Pt/cm<sup>2</sup>/electrode of 20 wt% Pt-C catalyst.

- Catalyst layer microstructural calculations:
  - Transient simulations
  - Incorporate water transport
  - Investigate nanowire supports

### Ceria Free Radical Scavenger Additives

- Free radical and peroxide decomposition studies of doped cerias
- Fuel cell lifetime testing with differing ceria particle sizes, dopants
- Accelerated stress test studies of prime candidates

### Pyrolyzed PPy Nanowire Supports

- Synthesize finer nanowires
- Characterize PPy nanowire functionality and durability
  - Tailor pyrolyzed nanowire composition
- Catalyst layer composition and processing optimization
- Comprehensive fuel cell and accelerated stress test testing
  - Synthesize large Pt-PPy batches

## FY 2013 PUBLICATIONS

1. Sansiñena, J.-M.; Wilson, M.S.; Garzon, F.H., Conductive Nanostructured Materials for Supported Metal Catalysts. *ECS Transactions* **2013**, *50* (2), 1693-1699.

2. Matanovic, I.; Kent, P.R.C.; Garzon, F.H.; Henson, N.J., Theoretical Study of the Structure, Stability and Oxygen Reduction Activity of Ultrathin Platinum Nanowires. *ECS Transactions* **2013**, *50* (2), 1385-1395.
3. Matanovic, I.; Kent, P.R.C.; Garzon, F.H.; Henson, N.J., Density Functional Study of the Structure, Stability and Oxygen Reduction Activity of Ultrathin Platinum Nanowires. *Journal of the Electrochemical Society* **2013**, *160* (6), F548-F553.
4. Matanovic, I.; Kent, P.R.C.; Garzon, F.H.; Henson, N.J., Density functional theory study of oxygen reduction activity on ultrathin platinum nanotubes. *Journal Of Physical Chemistry C* **2012**, *116* (31), 16499-16510.
5. Alia, S.M.; Jensen, K.; Contreras, C.; Garzon, F.; Pivovar, B.; Yan, Y., Platinum Coated Copper Nanowires and Platinum Nanotubes as Oxygen Reduction Electrocatalysts. *ACS Catalysis* **2013**, *3* (3), 358-362.
6. Ogumi, Z.; Matsuoka, H.; Garzon, F.; Kim, H.; Wan, L.-J.; Tamao, K.; Nakamura, M., Electrochemistry 80th Anniversary Special Issue. *Electrochemistry* **2013**, *81* (3), 140-197.

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5. 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.

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1. L. Gubler, S. Dockheer, W. Koppenol, *J. Electrochem. Soc.*, 2011, **158** (7), B755-B769.
2. L. Gubler, W. Koppenol, *J. Electrochem. Soc.*, 2012, **159** (2), B211-B218.
3. Wei, M., T. Dai, and Y. Lu, *Synthetic Metals*, 2010. **160**(9–10): p. 849-854.