

V.E.10 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

Collaborators

- 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, British Columbia

DOE Technology Development Manager:
Nancy Garland

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

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

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 ultra-low loading high-activity PGM catalysts – validation of advanced concepts.

Technical Barriers

This project addresses the following technical barriers from Section 3.4 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability: PGM catalysts durability goals have not been achieved for transportation and stationary systems.
- (B) Cost: The amount of expensive PGM catalyst currently required in fuel cell stacks does not meet cost targets for transportation and stationary systems.
- (C) Performance: The performance of PGM catalysts at required loadings to meet cost targets does not meet the current 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.

Technical Targets

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 ² electrode area	0.45	0.8	0.3	0.2

Accomplishments

- New nanowires supports for low PGM catalysts developed.
- Polypyrrole nanowire supports developed using electrosynthesis.
- Ultra-low loading Pt layers successfully deposited by radio frequency magnetron sputtering.
- Pt dispersion onto differing supports studied by scanning electron microscopy (SEM) and X-ray diffraction.
- Theoretical density functional theory modeling commenced.
- Single-cell fuel cell testing of new low-PGM catalysts commenced.



Introduction

Minimizing the quantity of Pt group metals used in proton exchange membrane fuel cells 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. Prior work at Los Alamos has led to a twenty-fold reduction in the amount of Pt required for good fuel cell performance at acceptable power densities. 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 may be reaching a number of limitations. In the case of decreasing particle size, a peak in mass activity is observed around 2.5 nm Pt particle size due to a steady decrease in the area specific catalytic activity for oxygen reduction when the quasi-spherical particle size decreases below threshold bulk values in the ~10 nm range. The mass activity continues to improve due to an inverse linear relationship between particle surface area and particle volume (mass). The decrease in area specific activity overwhelms the increase in surface area for a given mass for Pt particles sizes between 2 and 3 nm. Durability also suffers as the difference in positive free energy between the nanoparticle and a bulk crystal also increases with decreasing particle size. The energetic destabilization of the Pt particles with decreasing size makes them more susceptible to oxidation, dissolution/re-precipitation and grain growth via Oswald ripening processes. Long-term fuel cell durability testing, cyclic voltammetry and thermodynamic measurements confirm this behavior.

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

Activation of Pyrograf and Bulk Chemical Deposition of Polypyrrole with Light and Heavy Deposits

Low-cost Pyrograf III carbon nanofibers (Applied Sciences Inc.) were “activated” with concentrated nitric acid to impart surface functionality. The hydrophilic surface moieties provided relatively stable aqueous suspensions and purportedly improved the adhesion and uniformity of polypyrrole depositions. For bulk chemical depositions of polypyrrole, appropriate amounts of pyrrole were added to roughly 2 mg/cm³ aqueous Pyrograf suspensions and stirred briskly. After at least 10 minutes, ammonium persulfate was then added to catalyze the polymerization. The suspensions quickly flocculated to a degree commensurate with the pyrrole addition. The PPy-coated nanofiber products were filter rinsed with deionized water.

Activated Pyrograf with Ti and Pt Depositions

To form thin and uniform carbon nanofiber films, dilute aqueous suspensions of activated Pyrograf were filter cast onto hydrophilic microporous filter membranes (Millipore HVLP). The hydrophilic nature of the filter was crucial for achieving an equal flow throughout and hence an even amount of material accumulation. After thorough drying, the thin film coated filters were loaded into a multi-target sputtering system (Model 2400, High Tech Services, Inc.) equipped with 15 cm titanium and platinum targets. The Ti target was first sputter cleaned for 15 min with 300 W radio frequency power under 8 mTorr of argon and then the filter samples were sputter coated with the Ti for 12 min at 50 W. The Ti-coated samples were removed from the sputtering chamber for analysis and to allow air-induced formation of oxides to avoid possible alloying with the subsequent Pt deposition. Later, the samples were reintroduced into the sputtering system. After sputter cleaning for 10 min at 300 W radio frequency power, Pt was deposited on the samples for 3 min at 50 W in

8 mTorr argon for a target deposition of 0.05 mg Pt/cm². Subsequent analyses with X-ray fluorescence (XRF) were used to verify platinum loadings. The Pt-catalyzed Ti-coated Pyrograf films were applied to vacuum-table-dried Nafion[®] NRE212 membranes by hot-pressing the nanofiber coated filters under high-pressure (15 MPa) at 130°C for 3 min. Despite the pressure, the full depth of the film did not always transfer. In this example, XRF indicated that a nanofiber layer corresponding to 0.042 of the original 0.05 mg Pt/cm² adhered to the membrane. The 5 cm² active area fuel cell was completed with the use of an ELAT[®] SSE 2.22 carbon cloth gas diffusion layer (GDL) backing the nanofiber cathode and a Nafion[®]-impregnated Pt catalyzed carbon cloth ELAT[®] electrode on the anode side (ELAT[®] materials originally supplied by E-Tek). The cloths and catalyzed membrane were assembled loose, cell compression was relied upon to provide the necessary interfacial continuity.

Activated Multi-Walled Carbon Nanotubes (MWCNTs) and Pt Deposition

MWCNTS (Nanostructured and Amorphous Materials Inc.) were activated in a similar manner as the Pyrograf, although the MWCNTS were not as easily suspended. Well-dispersed aqueous suspensions could only be obtained using high dilutions and the direct insertion of a high-power ultrasonic horn (Branson Sonifier 450) into the mixture to break up agglomerates. When filter cast, these suspensions provided highly uniform thin films. Platinum deposition, catalyzed membrane preparation and the remaining fuel cell components were similar to the above Pt/Ti/Pyrograf cell, except that an even higher pressure (20 MPa) was used to obtain a similar transfer effectiveness corresponding to a loading of 0.044 mg Pt/cm².

Fibron Carbon Supports and Pt Deposition

An aqueous nanofiber polypyrrole dispersion (PPC-10-1-01 from Fibron Technologies, Inc.) was further diluted and filter cast as above to form a uniform thin film. Pt was sputter deposited for loadings of 0.05 mg Pt/cm². Even though the catalyzed nanofiber polypyrrole Fibron film was hot-pressed to the membrane at the higher pressure (20 MPa), only 0.035 equivalents of the 0.05 mg Pt/cm² Fibron film transferred to the membrane. The remaining fuel cell aspects of this particular Fibron-based cell were the same as above. An improved fuel cell environment for the nanofiber catalyst layer and a simpler cell fabrication process was achieved by eliminating the problematic step of hot-pressing the nanofiber film to the membrane. This was accomplished by directly filter casting the nanofiber suspension onto the GDL. Since the surface of a carbon cloth GDL varies substantially in topography and porosity around the weaves, much

more uniform microporous layer-coated carbon paper GDL materials were used instead. In the filter casting process, the Nafion[®]-coated GDL was first soaked with methanol to promote wetting of the full structure before the aqueous suspension was introduced. An SGL 30 DC carbon paper gas diffusion layer was first coated with 0.18 mg Nafion[®]/cm². A dilute suspension of Fibron nanofiber polypyrrole was filter cast onto the GDL. After drying, the nanofiber-coated GDL was sputter coated with 0.05 mg Pt/cm². For the remaining fuel cell components, SGL 30 DC was painted with a 2:1 Pt/C:Nafion[®] ink with a 0.05 mg Pt/cm² loading to serve as the anode and Nafion[®] NRE 212 was used for the membrane. The fuel cell was assembled with loose components. In this configuration, the cathode interfaces superficially consisted of Nafion[®] membrane/Pt-coated polypyrrole/Nafion[®] recast/GDL microporous layer. After compression, significant intermingling of these layers probably occurred.

Fuel Cell Testing

The 5 cm² fuel cells were tested at 80°C with hydrogen/air pressures of 30/30 psig (285/285 kPa) and reactant humidifiers operating at 80°C. High air-flow stoichiometries (up to 4 x stoichiometry at 1 A/cm²) and/or sub-saturated air humidification conditions were required to obtain stable operation of the flooding-prone cathode nanofiber structures. Elevated cell resistances in the polarization curves occurred due to the relatively dry operating conditions and the corresponding improvements in performance and high-frequency resistance on the return (upward) voltage scan. Due to the precarious balance between excessively dry and flooding, performance of these nanofiber-based fuel cells are much more sensitive to operating conditions than conventional electrodes. High charge transfer resistances were also observed due to the lack of ionomer penetration into the nano-composite electrodes.

Electrochemical Synthesis of Polypyrrole Nanowires

Our alternative support material studies include the development of low Pt loading catalysts on polypyrrole nanowires [1-4]. Using electrochemical synthesis methods, we were able to grow polypyrrole nanowires on a carbon paper GDL using template molecules such as heparin and starch. With this new approach we can achieve a high surface area structure that may lead to a higher oxygen reduction reaction catalytic activity with lower Pt loadings.

Electrochemical synthesis was carried out in an aqueous solution containing 0.2 M pyrrole, 0.40 wt% heparin sodium salt and 0.07 M LiClO₄ by applying potential square waves between 0.300 V (2 s) and 0.850 V (8 s) for 1,200 s at room temperature. Potentials

measured vs. Ag/AgCl (3.5 M KCl) reference electrode. Without the use of templating agents, a low surface area dendritic structure results (Figure 1).

In order to increase the surface area in the polypyrrole film, we first used heparin as a template molecule during the polypyrrole electropolymerization process on a glassy-carbon electrode while applying cyclic multipotential steps. As shown in Figure 2, the presence of heparin results in polypyrrole/heparin nanowires with a much higher surface area than the polypyrrole dendrite structure. After the use of heparin as a template molecule proved to be effective for the formation of a nanowire



FIGURE 1. Typical dendrite structure of a polypyrrole film electrochemically deposited onto a glassy carbon electrode in absence of any template molecules.

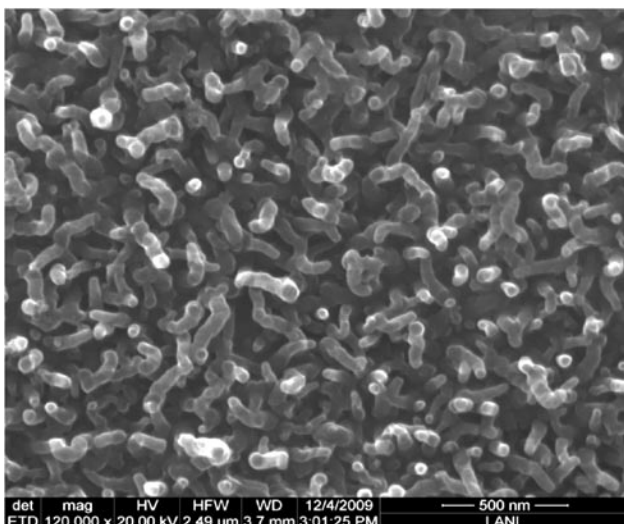


FIGURE 2. Electropolymerization of polypyrrole/heparin nanowires on glassy-carbon using heparin as template molecule.

structure, we obtained a similar result on a carbon paper GDL, so it could be used as a new high surface area gas diffusion electrode (GDE) in a fuel cell configuration. By studying different variables such as pyrrole/heparin ratio and deposition time, the electropolymerization process was optimized so we one can control the diameter and length of the nanowires as desired.

While heparin worked very well as a proof of concept template molecule we immediately searched for a low-cost replacement since heparin is an expensive prescription drug used as a blood thinner. As a result of our search for an alternative template molecule, we found that starch is a very good candidate as is shown in Figure 3. Additionally, starch has the advantage of being inexpensive, easy to find and environmentally benign. Moreover, as in the case of heparin, we found that the tuning of different variables such as pyrrole/starch ratio and deposition time allows controlling the diameter and length of the nanowires.

We are currently investigating Pt deposition by RF magnetron sputtering and by electrochemical deposition. After the optimization of the electrochemical synthesis of the Pt coated polypyrrole/starch nanowires is completed, fuel cell test studies will be carried out in order to obtain performance and stability data for the new GDE. Additionally, the structure will be also prepared on a glassy carbon disk electrode and rotating ring disk electrode studies will be performed to determine the catalytic activity of the Pt coated polypyrrole/starch nanowires.

Conclusions and Future Directions

- Pt catalysts can be deposited uniformly on a variety of nanowire supports using radio frequency magnetron sputtering.

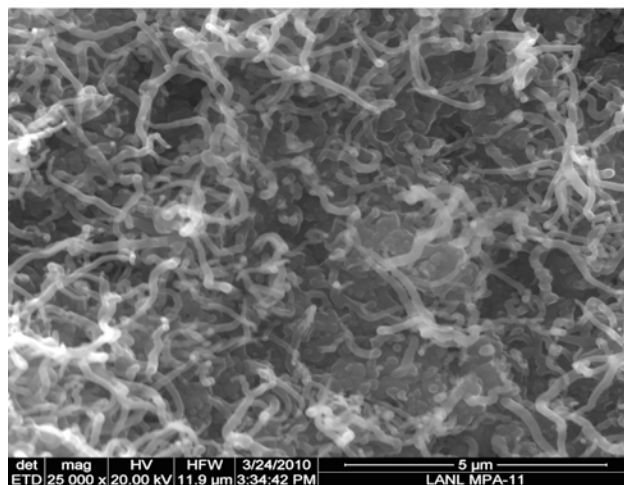


FIGURE 3. SEM picture of polypyrrole/starch nanowires electrochemically synthesized on a carbon paper GDL using starch as template molecule.

- New oriented polypyrrole nanowire catalyst supports were developed for fuel cell cathode use.
- Novel supported Pt catalysts require optimization of the electrode layer.
- Oxygen reduction activity as a function of loading will be probed by rotating disk electrode electrochemical methods.
- Support stability will be studied using cyclic voltammetry and post testing materials characterization.
- Mechanism of the nucleation and growth of PGM on the supports will also be studied.

References

1. H. Zhao, L. Li, Jun Yang, Y. Zhang, *Journal of Power Sources*, 184, 375–380 (2008)
2. R. Dersch, M. Steinhart, U. Boudriot, A. Greiner, J.H. Wendorff, *Polym. Adv. Technol.*, 16, 276–282 (2005).
3. T. Ochi, *Biochem. Biophysic. Res. Commun.*, 11, 67–70 (2004).
4. G.G. Wallace, P.C. Innis, *J. Nanosci. Nanotechnol.*, 2, 441–451 (2002).