

V.E.7 Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes

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Objectives

- Produce novel catalysts based on extended Pt surfaces with increased activity and durability.
- Further increase mass activity of extended surface catalysts.
- Effectively incorporate extended Pt catalysts into more traditional dispersed electrodes for improved mass transport/water management.
- Demonstrate and validate models for catalysts and electrodes based on extended surfaces.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability (of catalysts and membrane electrode assemblies)
- (B) Cost (of catalysts and membrane electrode assemblies)
- (C) Performance (of catalysts and membrane electrode assemblies)
- (D) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

This project is synthesizing novel extended surface Pt catalysts and will be incorporating these catalysts into thick, dispersed electrodes. The project has targets outlined in the Multi-Year Research, Development and Demonstration Plan for both electrocatalysts for transportation applications (Table 3.4.12) and membrane electrode assemblies (MEAs) (Table 3.4.13). A summary of these targets is presented in Table 1.

TABLE 1. Technical Targets for Electrocatalysts for Transportation Applications and MEAs

| Characteristic | Units | 2010/2015 Targets |
|---|---------------------------------------|-------------------|
| PGM Total Content | g/kW rated in stack | 0.3/0.2 |
| PGM Total Loading | mg PGM/cm ² electrode area | 0.3/0.2 |
| PGM Cost | \$/kW @ \$15/g | 8/6 |
| Electrochemical Area Loss | % | <40%/<40% |
| Mass Activity (150 kPa H ₂ /O ₂ 80°C 100% RH) | A/mg-Pt @ 900mV | 0.44/0.44 |
| Specific Activity (150 kPa H ₂ /O ₂ 80°C 100% RH) | μA/cm ² -Pt @ 900 mV | 720/720 |
| Durability with Cycling ≤80°C | Hours | 5,000/5,000 |
| Unassisted Start from Low Temperature | °C | -40°C/-40°C |
| Thermal Cyclability in Presence of Condensed Water | | Yes/Yes |

PGM = platinum group metal; RH = relative humidity

Accomplishments

- Synthesized novel extended surface Pt catalysts using Cu nanowires and spontaneous galvanic

displacement (SGD). These materials advance our team's earlier work in the area of Ag and Se nanowires as templates [1]. Cu-based systems offer potential advantages as Pt-Cu alloys have been found to yield materials with greatly enhanced specific activity [2]. Preliminary results have shown significantly enhanced specific activity of these structures compared to traditional Pt catalysts.

- Demonstrated for the first time continuous, conformal coating of Pt on carbon nanotubes (CNTs). CNTs offer the potential of high conductivity and low corrosion compared to other support materials. Demonstrated control of Pt layer thickness by deposition time.
- Investigated vertically aligned CNTs growth and Pt deposition by several techniques. Optimized growth parameters to allow a wide range of tube lengths and packing densities providing tunable substrates for deposition.



Introduction

Pt remains a primary limitation for the widespread commercialization of fuel cell vehicles. To date, approaches looking to replace Pt with a non-PGM have met with limited success. “Thrifting” of Pt (i.e., ultra-low Pt loadings) seems to be the most likely (near-term) option for meeting cost, performance and durability targets. Typical Pt catalysts for fuel cell applications are small nanoparticles (such as cubooctahedron) that have high surface areas, and therefore significant fractions of Pt atoms are surface accessible. This makes sense as one would want as many Pt atoms on the surface as possible. However, catalytic activity and durability of extended surfaces can outweigh the surface area advantages of smaller particles, particularly if these advantages can be maintained at thin wall thickness, as highlighted by the promising work done on nanostructured thin film catalysts based on Pt or Pt alloys at 3M [3] and Pt and Pt alloy nanotubes UC Riverside [1]. The synthesis of catalysts with high mass activity and the effective implementation of these catalysts in high-performance, durable and robust MEAs will help enable fuel cell commercialization on a significant scale.

Approach

Our approach involves synthesizing novel catalyst particles using either a nanostructured support material such as CNTs, metal oxide nanoparticles, or perylene red nanowhiskers; or a sacrificial metal template. Pt is deposited on these materials either through vapor deposition (including sputtering and atomic layer deposition [ALD]) or solution deposition (including galvanic displacement). Our goal is to produce

nanostructures with thin, continuous films of Pt as similar structures have shown high catalytic activity and durability. The materials synthesized are characterized by several techniques with a strong focus on microscopy and electrochemistry. To date, extended surface catalysts have not been demonstrated in traditional, thick catalyst layers that include Nafion[®] and have been shown to exhibit good tolerance to a wide range of operating conditions including cold-start. The novel catalysts produced in this project will be implemented in thick, dispersed electrodes to investigate the production of high-performance, robust electrodes from these materials. Modeling will be used in support of our catalyst synthesis studies and our electrode studies, extending established models involving wetting of Pt on supports, simulating electrode architecture, and evaluating criteria that impact electrode performance.

Results

We have investigated a number of substrates for their potential application as supports for extended surface Pt hosts. Our results with CNTs have focused on two approaches: CNT mats, where mats are drop cast onto substrates prior to Pt deposition; and vertically aligned CNTs. Based on the high surface tension of Pt and the tendency of numerous Pt/CNT catalysts reported to form isolated particles, we expected difficulty in getting CNTs to conformally coat with Pt. Our early studies resulted in the first reported continuously coated CNTs. These materials, an example of which is shown in Figure 1, obtained from Pt-sputtered CNT mats, demonstrated the potential of CNTs as hosts for continuous thin films of Pt and resulted in an early project milestone being accomplished. Through systematic studies of deposition time we were able to obtain target Pt thickness of ~2 nm, such as that estimated from Figure 1 from comparisons of coated regions of CNTs to uncoated regions highlighted by the measurements within Figure 1.

Vertically aligned CNTs were investigated as they resulted in an increased materials yield on a geometric area basis compared to the drop cast CNT mats. As part of this project vertically aligned CNTs were for the first time synthesized at NREL. In the area of vertically aligned CNT synthesis, we performed tests to investigate reproducibility of our methods both from sample to sample and within a sample. These studies focused on Fe-catalyst deposition for vertically aligned carbon nanotubes (VACNTs) and involved sputtering, ALD, and electrochemical deposition. We also modified synthesis conditions to include water assisted deposition. We now have a wider materials set for study and a better appreciation for the variables controlling VACNT formation. We also isolated that it is largely reproducibility of the Fe-based catalyst used for VACNT growth that is the principal step leading to

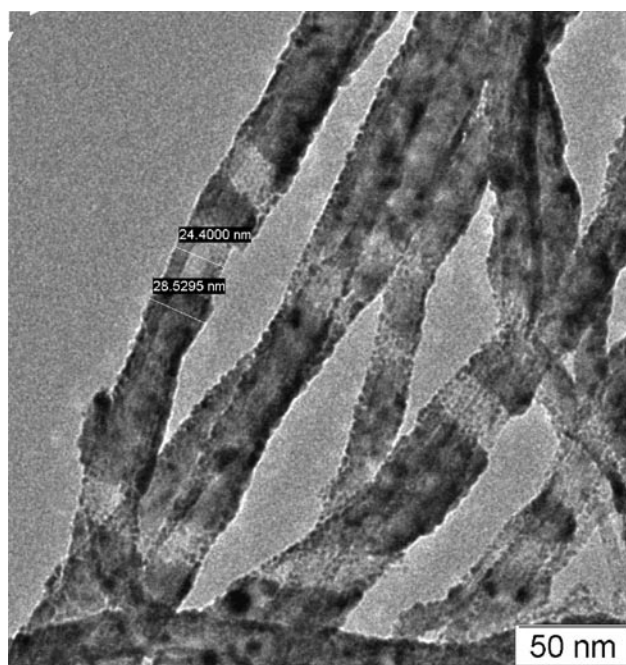


FIGURE 1. Transmission Electron Microscopy of Multiwalled Drop Cast CNT Mats with Pt Sputter Deposited

reproducibility issues between samples. The use of ALD allows for better reproducibility than what was obtained using other techniques. Figure 2 and Table 2 summarize the impact of temperature on the growth conditions presented and give examples of the different VACNTs that we have synthesized and how by controlling specific parameters (in this case temperature) we produce materials with specific properties.

In the area of Pt deposition, our studies have shown that VACNTs have very heterogeneous coatings of

TABLE 2. Effect of Synthesis Temperature on the Length and Width of VACNTs

| Synthesis Temperature (°C) | Approx. Width (nm) | Approx. Length (μm) |
|----------------------------|--------------------|---------------------|
| 700 | 30 | 3-5 |
| 725 | 20 | 21 |
| 750 | 15 | 50 |
| 775 | 15 | 115 |
| 800 | 12 | 87 |

Pt regardless of deposition technique, although ALD provides slightly better uniformity than sputtering in most cases. Because ALD is a step-by-step process that offers the potential for very thin, conformal coatings we had hoped for much more uniform coatings using ALD. Of particular issue is the slow nucleation process of Pt on CNTs, as reflected in Figure 3a, which shows the Pt composition at the bottom, middle and top of 20 micron VACNTs. Pt deposition on the surface takes over 100 cycles before significant nucleation takes place. The resultant particles either tend to have exceptionally thick coatings or discrete particles using the approaches we have investigated and are strongly dependent on their location along the CNTs. In order to investigate the nucleation process we have performed a number of pretreatments to the CNTs including oxygen plasma, Ar plasma, and trimethylaluminum (TMA). Of these three pretreatments, only the TMA pretreatment showed an enhancement in nucleation rate. Even with this increased nucleation, the sample still showed a strong dependence on position Figure 3b. With further increases in nucleation rate it is possible that ALD will yield the target structures we are striving for, so continued effort will be placed on investigation of nucleation rates using ALD.

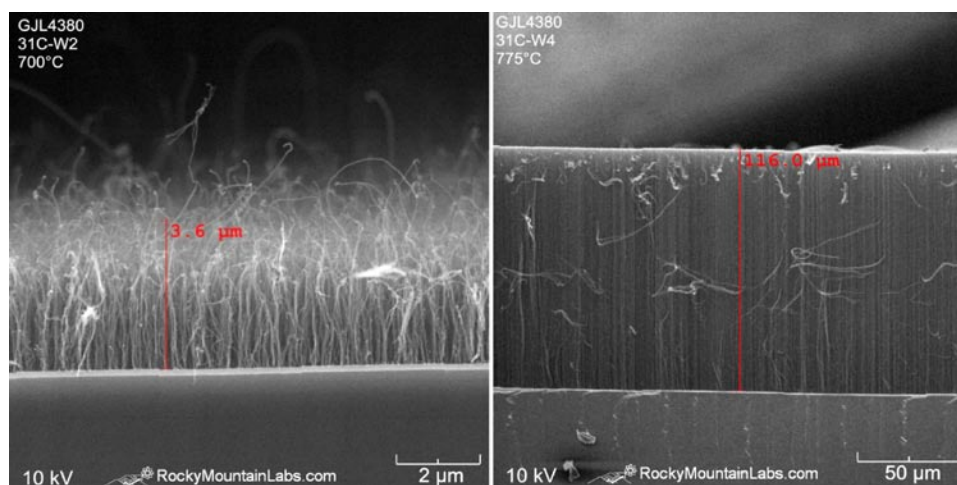


FIGURE 2. (left): VACNT Synthesized at 700°C; (right): VACNT synthesized at 775°C

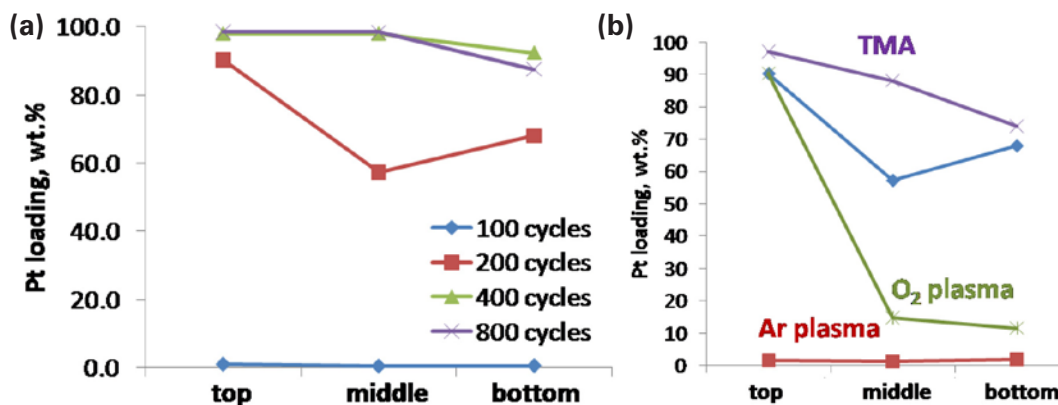


FIGURE 3. a (left): Pt Loading on ~20 Micron High VACNTs as a Function Number of Pt ALD Cycles; b (right): Effect of Pretreatment on Pt Coating after 200 Pt ALD Cycles

In the area of metal template synthesis and SGD, we have focused on Cu nanowires followed by subsequent displacement by Pt. There are only a few reports of Cu nanowire synthesis in the literature and the reported procedures have taken many hours with limited yields. We have developed a microwave-assisted wet chemical approach that takes only 15 minutes and greatly increases our yield of materials, examples of the materials generated are shown in Figure 4. These nanowires add to the Ag and Se nanowires that have already been demonstrated as templates for spontaneous galvanic displacement by our project subcontractor UC Riverside [1]. Cu offers potential advantages over Ag and Se because it has been shown to lead to improved activity when used in alloys with Pt [2]. We have examined a limited materials set after galvanic displacement and have found improvements in specific activity when compared to traditional materials (~6x improvement). Our studies in this area are in the

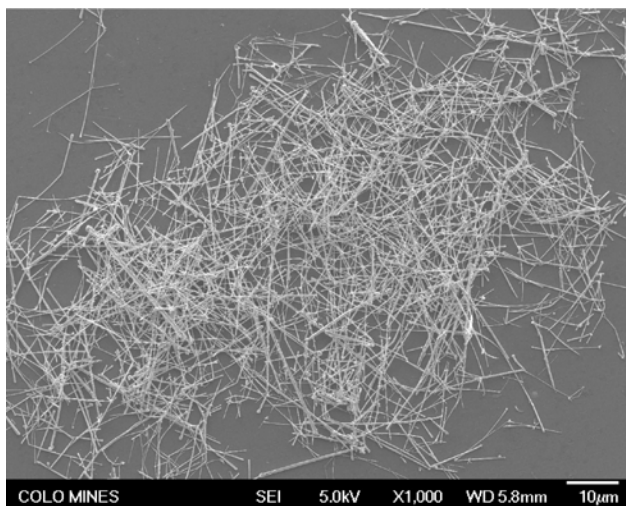


FIGURE 4. Scanning Electron Microscopy of Cu Nanowires

preliminary stages and will continue with a focus on mass activity and durability.

Conclusions and Future Directions

We have demonstrated for the first time conformal Pt coatings on CNTs, and Pt nanostructures from Cu nanowires. We have performed controlled growth of CNTs. We have investigated Pt ALD, sputtering, SGD and other solution based routes as Pt deposition techniques. Future work, broken down by topical area, includes:

- Templates/Cores
 - Further advancement of Cu-based nano-templates.
 - Development of short, less dense VACNTs that are analogous to the 3M nano-structured thin-film whiskers.
 - Investigation of metal oxide supports.
- Pt Deposition
 - Continued investigation of sputtering onto CNT mats in order to increase heterogeneity and yield.
 - ALD studies investigating the effect of adhesion layers and processing conditions on Pt nucleation and growth.
 - Optimization of SGD displacement process, resultant structures/composition, and electrochemical performance and durability.
- Electrode Studies
 - Electrochemical screening (specific and mass activity) of novel catalysts.
 - Incorporation of highest performing catalysts into electrode studies.
 - MEA fabrication and fuel cell testing of novel catalysts.

- Modeling
 - Advancement of models and correlation of experimental data with models involving Pt wetting on surfaces, electrode structure and performance.

FY 2010 Publications/Presentations

1. Arrelaine Dameron, Svitlana Pylypenko, Justin Bult, Christopher Bochert, Jeremy Leong, Sarah Frisco, Chaiwat Engtrakul, Ryan O'Hayre, Lin Simpson, Huyen Dinh and Bryan Pivovar, "Surface Functionalization for Pt Atomic Layer Deposition in Carbon Nanotube Arrays", June 20–23, 2010, ALD 2010, Seoul, South Korea.
2. KC Neyerlin, Tim Olson, Brian Larsen, Justin Bult, Arrelaine Dameron, Svitlana Pylypenko, Jeremy Leong, Huyen Dinh, Chai Engtrakul, Lin Simpson, Shyam Kocha, Bryan Pivovar, "Innovative Catalyst Layer Structures Based on Extended Pt Surfaces", 217th Meeting of the Electrochemical Society, Vancouver, CA, April 26, 2010.

3. B. Pivovar, "Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes", FreedomCAR Fuel Cell Tech Team, March 10, 2010, Southfield, MI.
4. B. Pivovar, "Advanced Catalysis, Electrode Studies and the Pt-Ionomer Interface", November 3, 2009, 3M, Woodbury, MN.

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1. Z. Chen, W. Li, M. Waje, Y. S. Yan, *Angew. Chem. Int. Ed.* 2007, 46:4060-4063.
2. R. Srivastava, P. Mani, N. Hahn, P. Strasser, *Angew. Chem. Int. Ed.* 46 (2007), 8988.
3. http://www.hydrogen.energy.gov/pdfs/review08/fc_1_debe.pdf.