

V.D.4 Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes

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Project End Date: 2013

Technical Barriers

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

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

Technical Targets

This project synthesizes novel extended thin film electrocatalyst structures (ETFECs) and incorporates these catalysts into electrodes with and without carbon for further study. 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). The specific targets and status of highest relevance are presented in Table 1.

TABLE 1. Technical Targets for Electrocatalysts for Transportation Applications

Characteristic	Units	2010/2015 Targets	Status
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	0.33
Specific Activity (150 kPa H ₂ /O ₂ 80°C 100% RH)	μA/cm ² -Pt @ 900 mV	720/720	800-1,300

RH – relative humidity

Fiscal Year (FY) 2011 Objectives

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

FY 2011 Accomplishments

- Synthesized novel ETFECs that routinely surpass DOE 2015 target for specific activity.
- Demonstrated ETFECs with ECA as high as 40 m²/g_{Pt} and mass activities of 330 mA/mg_{Pt} far beyond the surface area of most extended surface catalysts with a mass activity approaching the 2015 DOE target.
- Demonstrated significantly improved durability of ETFECs towards potential cycling in rotating disc electrode (RDE) studies for both the Pt dissolution (0.6-1.0 V) and carbon corrosion region (1.0-1.6 V).

- Incorporated carbon into electrode structures that contain ETFECS while maintaining durability and activity.
- Demonstrated high specific activities of ETFECS in fuel cells.



Introduction

Pt remains a primary limitation for the widespread commercialization of polymer electrolyte fuel cells. To date, approaches looking to replace Pt with a non-platinum-group metal 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. Clearly, having as many Pt atoms on the surface as possible is advantageous. 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 [1] and Pt and Pt alloy nanotubes at UC Riverside [2]. 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 ETFECS using either a nanostructured support material such as carbon nanotubes (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 because 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 are being implemented in thick, dispersed electrodes to investigate the production of high performance, robust electrodes from these materials. Modeling is being 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

In the past year, we added a number of additional substrates to our studies probing supports as extended surface Pt hosts. Included on our list of substrate nanomaterials to date are: carbon nanotubes, inorganic oxides, metals, and perylene red whiskers. Examples of novel templates synthesized this past year are shown in Figure 1.

In the area of Pt deposition, we focused on sputtering, ALD, and spontaneous galvanic displacement (SGD). Sputtering remains an area of interest, as we and 3M [1] have shown it to be a viable technique for depositing thin, continuous Pt layers. We have focused on deposition onto mats and short (>2 μm) vertically aligned CNTs. Transmission electron microscopy close-ups of Pt sputtered CNT mats show a transition between discrete particles and continuous Pt coating. These micrographs suggest that continuous coatings can be obtained at thicknesses of ~2 nm. Unfortunately, our ability to generate these

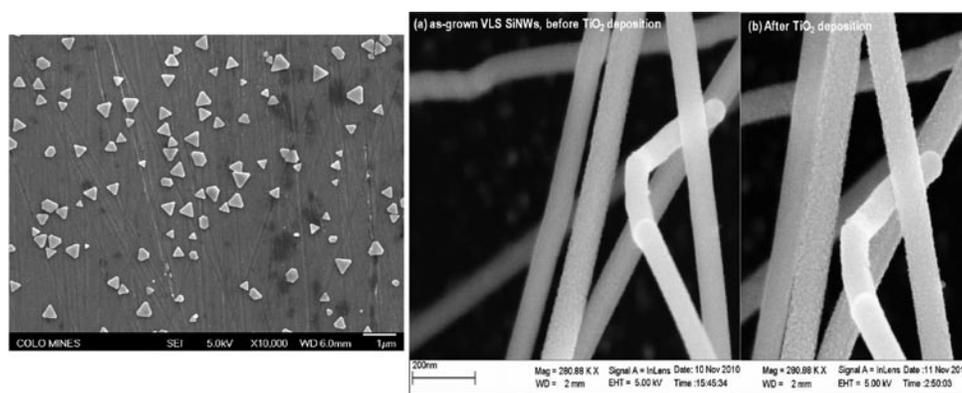


FIGURE 1. Ag nanoplatelets synthesized by solvothermal process (left); SiNWs synthesized by vapor-liquid-solid process (center); after TiO₂ deposition by ALD (right).

materials consistently and in higher yields has been poor. We have continued to investigate ALD for its ability to produce thin continuous Pt films. The most promising results have focused on using TiO_2 as a bonding layer. We found that a minimum thickness of TiO_2 followed by thermal treatment (annealing) results in the conversion of amorphous TiO_2 to anatase. The anatase form showed the fastest and most consistent Pt nucleation rates and is now being explored at ultra-thin (>5 nm) coating thicknesses and on nanostructured substrates. In the area of SGD we used Ag and Cu nanowires and Ag nanoplates as templates for Pt displacement and performed studies that have also included Pd or Au.

Our electrochemical characterization and electrode studies made significant strides in the past year. We established agreement with literature and demonstrated a high degree of reproducibility. We quantified the increases in specific activity from our novel materials and showed reasonably high surface areas (up to $40 \text{ m}^2/\text{g Pt}$) in ETFECS. While a few studies with CNTs were performed, our primary focus of electrochemical characterization was on materials synthesized by SGD, because we obtained higher yields and higher performance with these materials. A select portion of our data is highlighted in Figure 2. The three different colors/symbols represent a systematic series of novel materials based on SGD of either Cu or Ag nanowires investigating features including: reactant delivery rate, stoichiometry, temperature, reaction solvent, and post-processing. While we commonly surpass the DOE 2015 target for specific activity ($720 \mu\text{A}/\text{cm}^2 \text{ Pt}$), highlighted in Figure 3, we have not yet achieved the 2015 target for mass activity. Although extended surface catalysts have typically

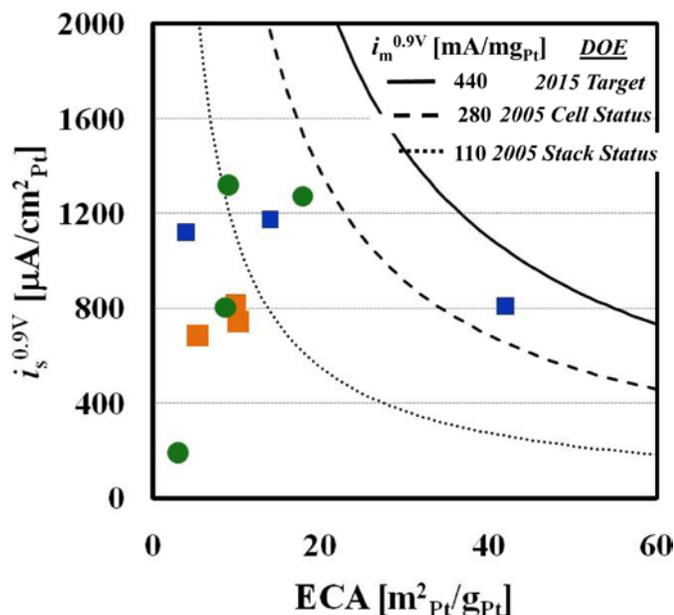


FIGURE 2. Specific activity vs. ECA for SGD ETFECS at NREL. Lines of constant mass activity shown as well.

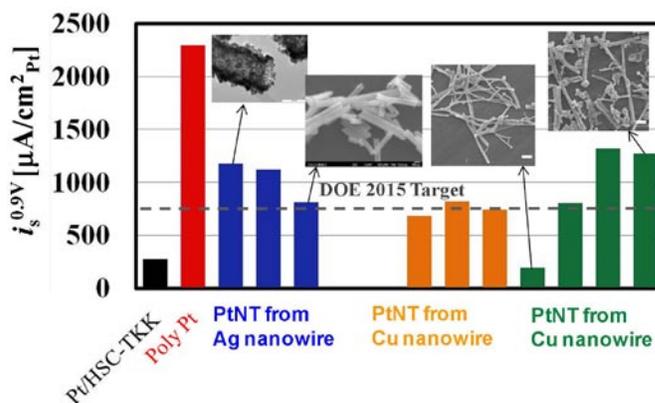


FIGURE 3. Specific activity of ETFECS compared to traditional Pt/C and polycrystalline Pt disc.

been limited to ECAs around $10 \text{ m}^2/\text{g Pt}$ we demonstrated ETFECS with ECA up to $\sim 40 \text{ m}^2/\text{g Pt}$. This high ECA material resulted in a novel catalyst with mass activity of $330 \mu\text{A}/\text{g Pt}$, approaching the $440 \mu\text{A}/\text{g Pt}$ DOE 2015 target. Continued investigations will seek to further increase both specific activity and ECA.

Beyond the improvements in electrochemical properties determined for the SGD ETFECS already highlighted, we also explored the impact of carbon incorporation on the electrochemical performance of these materials, tested the materials in fuel cells, and investigated the durability of these materials. All of these studies showed the promise of extended surfaces as novel fuel cell catalysts. Highlights from our studies are shown in Figure 4. The specific and mass activities of our ETFECS have essentially no impact on the observed specific and mass activity. Normalized ECAs show that traditional catalysts, as expected, show much poorer durability with potential cycling. Similar results were observed in the Pt dissolution region (0.6-1.0 V) in similar potential cycling studies.

Conclusions and Future Direction

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

Templates/Cores:

- Metal oxide substrate development.

Pt Deposition:

- SGD process further optimization focusing on post-processing parameters.
- ALD studies investigating Pt growth on carbon and with reduced thickness/decreased nucleation cycles.

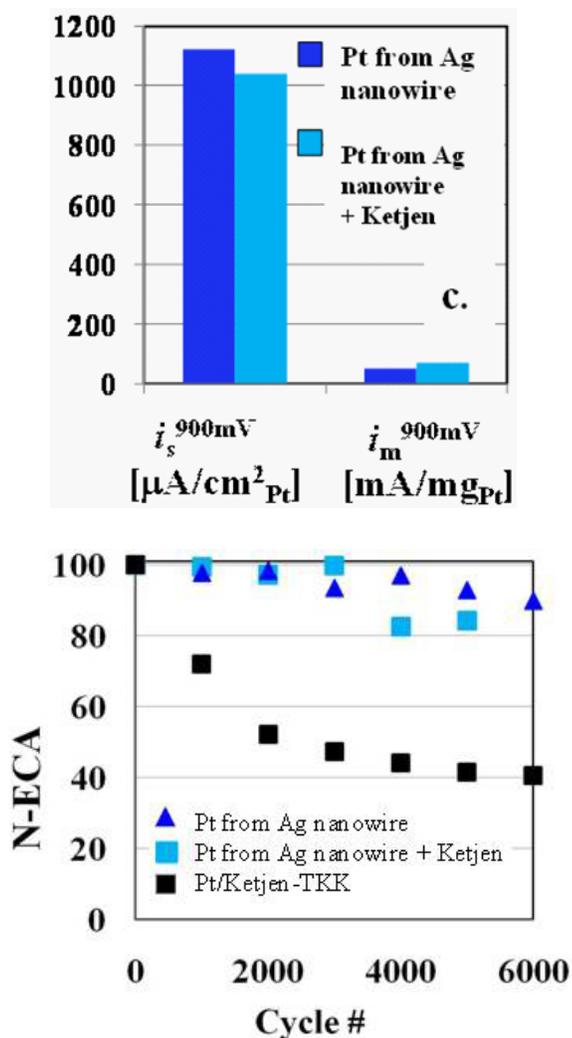


FIGURE 4. Specific and mass activities of ETFECS with and without carbon (top), stability to potential cycling from 1.0-1.6 V (carbon corrosion region), (bottom).

Electrode Studies:

- Electrochemical (RDE) durability screening of ETFECS as a function of initial ECA.
- Incorporation of highest performing catalyst ($330 \text{ mA}/\text{mg}_{\text{Pt}}$) into electrode studies.
- Expanded MEA fabrication and fuel cell testing of ETFECS.

Modeling:

- Advancement of models to electrode structures incorporating model ETFECS – PtNT of 150 nm diameter, 2 micron length.
- Expansion of porous electrode models to ETFECS incorporated electrodes.

FY 2011 Publications/Presentations

1. J. Bult, A. Dameron, S. Pylypenko, C. Engtrakul, C. Bochert, L. Chen, J. Leong, S. Frisco, L. Simpson, H.N. Dinh, B. Pivovar, "Atomic Layer Deposition of Platinum onto Functionalized Aligned MWNT Arrays for Fuel Cell Electrode Application," *ECS Trans.* 33 (1), 89 (2010).
2. Shyam Kocha, KC Neyerlin, Tim Olson, Bryan Pivovar, "Electrochemical Characterization and Implementation of Extended Surface Pt Catalysts in PEMFCs" 218th ECS Meeting, Las Vegas, NV, Oct. 2010.
3. Brian A Larsen, Svitlana Pylypenko, Tim S. Olson, KC Neyerlin, Bryan S. Pivovar, "Synthesis of Pt-Cu Nanowires by Spontaneous Galvanic Displacement as Novel Catalyst Materials" 218th ECS Meeting, Las Vegas, NV, Oct. 2010.
4. Tim S. Olson, KC Neyerlin, Brian A. Larson, Svitlana Pylypenko, Shyam Kocha, Bryan Pivovar, "Pt-Cu Nanowires for Fuel Cell Catalyst Applications" 218th ECS Meeting, Las Vegas, NV, Oct. 2010.
5. Justin Bult, Arrelaine Dameron, Svitlana Pylypenko, Christopher Bochert, Chaiwat Engtrakul, Limeng Chen, Jeremy Leong, Sarah Frisco, Ryan O'Hayre, Lin Simpson, Huyen Dinh and Bryan Pivovar, "Atomic Layer Deposition of Platinum onto Functionalized Aligned MWNT Arrays for Fuel Cell Application" 218th ECS Meeting, Las Vegas, NV, Oct. 2010.
6. B. Pivovar, "Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes", FreedomCAR Fuel Cell Tech Team, March 16, 2011, Southfield, MI.
7. B. Pivovar, "Extended Surface Catalysts", June 2, 2011, LANL, Los Alamos, NM.
8. B. Pivovar, "Extended Surface Catalysts", June 13, 2011, GM, Honeoye Falls, NY.
9. Shyam S. Kocha, K.C. Neyerlin and Bryan Pivovar, "Electrocatalyst Durability in Automotive PEMFCs", PBFC-5, August 2011, Chicago, IL.
10. S. Alia, Y. Zhang, Q. Xu, K. Jensen, C. Contreras and Y. Yan, "Gold Stabilized Platinum and Palladium Nanotubes" AIChE Annual Meeting, Salt Lake City, UT, Nov. 2010.
11. S. Alia, Y. Zhang, Q. Xu, K. Jensen, C. Contreras and Y. Yan, "Copper Templated Platinum Nanotubes as Oxygen Reducing Electrocatalysts" AIChE Annual Meeting, Salt Lake City, UT, Nov. 2010.
12. S. Alia, Y. Zhang, Q. Xu, K. Jensen, C. Contreras and Y. Yan, "Platinum Thin-Coated Palladium Nanotubes for the Oxygen Reduction Reaction" AIChE Annual Meeting, Salt Lake City, UT, Nov. 2010.
13. S.M. Alia, G. Zhang, D. Kisailus, D. Li, S. Gu, K. Jensen, Y. Yan, *Adv. Funct. Mat.* 2010, 20:3742-3746.

References

1. http://www.hydrogen.energy.gov/pdfs/review08/fc_1_debe.pdf.
2. Z. Chen, W. Li, M. Waje, Y. S. Yan, *Angew. Chem. Int. Ed.* 2007, 46:4060-4063.