V.A.6 Extended Surface Electrocatalyst Development

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Project Start Date: December 10, 2015
Project End Date: September 30, 2018

Overall Objectives

- Increasing mass activity and durability of Pt-based electrocatalysts through the synthesis and implementation of high surface area extended surface electrocatalysts.
- Optimize fuel cell performance of extended surface electrocatalysts.
- Demonstrate DOE 2020 target performance and durability in fuel cell tests.

Fiscal Year (FY) 2017 Objectives

- Determine (using experimental measurements and developed models) and report overpotential losses associated with unique features of extended surface electrodes include protonic and electronic resistances of electrodes, and mass transfer losses including $R_{O2,local}$.
- Quantify and report increase in catalytic performance (both specific activity and mass activity at 0.9 V iR corrected) for shape and surface controlled nanostructures relative to standard Ni nanowires (NWs).
- Demonstrate a mass activity of >440 mA/mgPt at 0.9 V (DOE 2020 target) in fuel cell tests while also meeting at least one of Fuel Cell Technologies Office's membrane electrode assembly (MEA) durability targets.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) Durability (of catalysts and MEAs)

(B) Cost (of catalysts and MEAs)

(C) Performance (of catalysts and MEAs)

– 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 for further study. The project has targets outlined in the Multi-Year Research, Development, and Demonstration Plan for both electrocatalysts for transportation applications (Table 3.4.7) and MEAs (Table 3.4.5). The specific targets and status of highest relevance are presented in Table 1.

TABLE 1. Technical Targets for Electrocatalysts for Transportation Applications

Characteristic	Units	2020 Target	Status
Mass Activity (150 kPa H_2/O_2 80°C 100% RH)	A/mg-Pt @ 900 mV	0.44	>0.5
Electro catalyst support stability	% mass activity loss	<40	41
Loss in initial catalytic activity	% mass activity loss	<40	66

RH – relative humidity

FY 2017 Accomplishments

- The project has demonstrated the ability to achieve high performance of atomic layer deposition (ALD) synthesized PtNi NWs in reasonable scale and reproducibility.
- Performance and durability have been significantly improved with annealing and pre-leaching of as-synthesized PtNi NWs.
- Limiting current measurements show very low $R_{O2,local}$ for ETFECS MEAs.

- MEAs with pre-leached ETFECS (spontaneous galvanic displacement [SGD] and ALD) demonstrate mass activity Pt ~240 mA/mgPt with low ionomer content.

INTRODUCTION

Conventional nanoparticle Pt/C electrocatalysts (2–5 nm) used in automotive fuel cells appear to have plateaued in terms of electrochemical area and catalytic activity. ETFECS offer the possibility of higher specific activities, comparable to that of bulk poly-Pt. ETFECS materials formed by galvanic displacement have shown promising performance and durability in rotating disk electrode tests, but have shown limitations in compositional control, reproducibility and batch size (scale-up). We are focusing on Pt and Ni ALD in order to address the limitations found with galvanic displacement. The materials are then explored for optimum electrode structures through cell diagnostics that isolate and target mitigation strategies for loss mechanisms.

APPROACH

Our overall approach is towards developing extended surface Pt catalysts synthesized by ALD with high mass activity and durability, and incorporating these structures into robust, high efficiency MEAs. This approach focuses on the synthesis of novel ETFECS formed by ALD, specifically with the co-deposition of Ni and Pt. We are targeting high surface areas as this has been a specific challenge for extended surface Pt catalysts (3M [1], others [2]). Our multi-tiered approach involves the synthesis of novel template nanostructures, the synthesis and characterization of ALD-synthesized ETFECS, and the optimization of these materials in fuel cells.

RESULTS

In the area of novel template nanostructure development we made a no-go decision on the University of Delaware efforts that were focused on the synthesis of facet controlled extended surface Ni nanoparticles. This effort has been refocused to the area of MEA fabrication and fuel cell testing. In the area of nano-templates, we have worked with a commercial supplier of Ni NWs to determine the materials that offer the best performance once platinized and processed. This has allowed us to focus on larger scale Ni NW batches (100 g) and increase the material availability and performance of novel PtNi NWs.

Our efforts in the area of Pt deposition by ALD have allowed us to routinely generate high performance materials at the 0.5 g scale. We identified oxidation as a key concern and optimized our reaction conditions to work at lower oxygen partial pressure allowing for improved processing characteristics and higher performance. We have also scaled up reaction batch size to 2 g. Initial results suggest we have succeeded in reaching target Pt compositions and that this approach is scalable to much higher batch sizes. Post-processing results have shown significant increases in activity after H_2 annealing, as shown in Figure 1. This increase in performance is attributed to improved alloying of the Pt phase and a shift in the Pt lattice X-ray diffraction spectra. Acid leaching has also been a major focus of our post-processing studies, and we have demonstrated the ability to achieve active catalysts with most of the metallic Ni content removed by acid leaching, see Figure 2, without sacrificing electrochemical surface area. This has allowed for significantly more MEA testing of PtNi NWs.

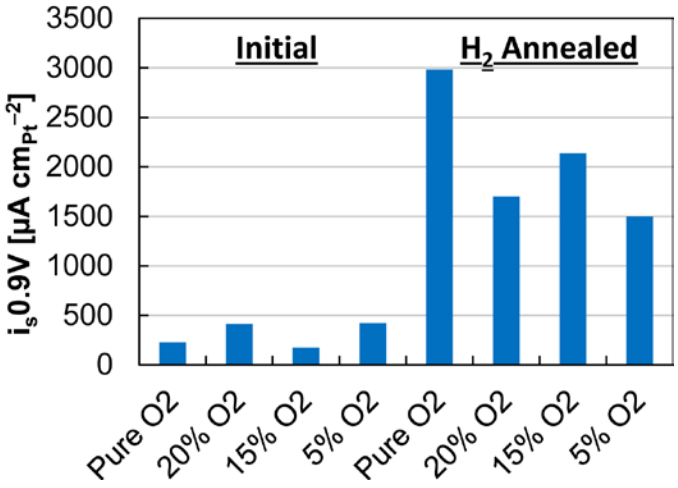

FIGURE 1. Specific activity of PtNi NWs as a function of oxygen partial pressure before and after hydrogen annealing

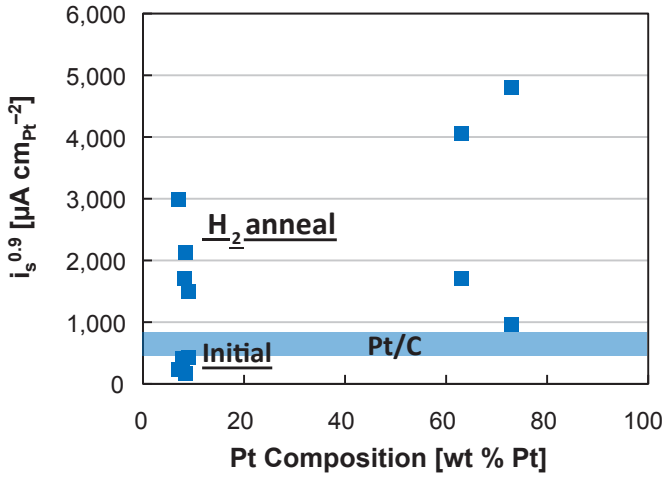

FIGURE 2. Specific activity of PtNi NWs as a function of processing condition: as-synthesized, H_2 annealed, and acid leached

MEA tests of PtNi NWs have been conducted on a number of samples. Scanning electron microscopy cross-section and top down views of the pre-leached PtNi NWs are shown in Figure 3. These catalyst layers are thin, ~1 µ, show short, hollow tubes as the predominant structure within the catalyst layer. Figure 4 shows that we were able to match the fuel cell performance of PtNi NWs synthesized by SGD with PtNi NWs synthesized by ALD. Both of these MEAs were synthesized with pre-leached nanowires and reached mass activity of 280 mA/mg_{Pt} at 0.9 V. We have performed optimization and diagnostic studies on these systems that includes AC impedance and diffusion-limited current measurements. From these and related experiments we have found the highest performance at traditionally low ionomer content (~10 % relative to leached PtNi NW weight). We have found through impedance that low RH performance of these electrodes starts to exhibit alternate behavior to traditional Pt/carbon electrodes. And from limiting current measurements, we have found that local transport resistance of these electrodes is less than that of traditional Pt/carbon electrodes.

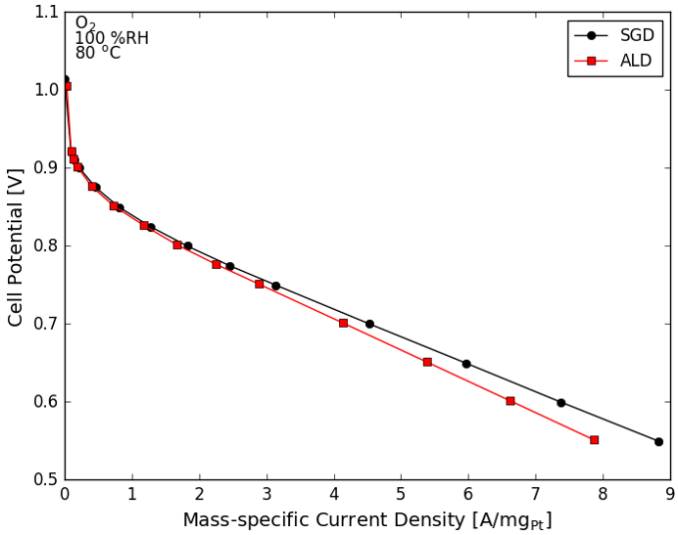

FIGURE 4. Fuel cell polarization curves of PtNi NWs of preleached samples comparing SGD and ALD synthesized materials

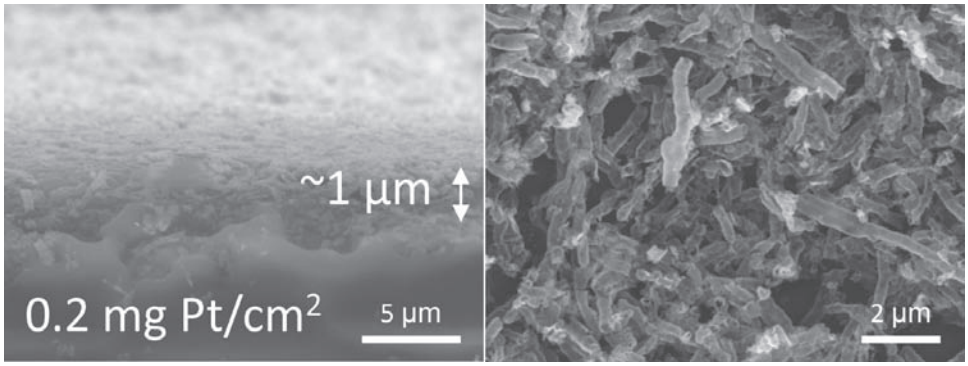

FIGURE 3. Scanning electron microscopy cross-section (left) and top-down (right) micrographs of PtNiNW electrodes using acid leached samples

CONCLUSIONS AND UPCOMING ACTIVITIES

The project has demonstrated the ability to achieve high performance of ALD synthesized PtNi NWs in reasonable scale and reproducibility. Performance and durability have been significantly improved with annealing and pre-leaching. MEAs with pre-leached ETFECS (SGD and ALD) demonstrate mass activity Pt ~240 mA/mgPt with low ionomer content. Limiting current measurements show very low $R_{O2,local}$ for ETFECS MEAs. Future work includes:

- Nano-template synthesis:
  - Validation of targeted performance from commercial supplier.
- Electrocatalysts:
  - ALD scale-up to 10 g batch size. Further increase of electrochemical surface area and specific activity. Co-deposition of Pt and Ni/Co.
  - Post-processing optimization of resultant catalysts (annealing and acid leaching).
  - Characterization and optimization (electrochemical and structural studies).
- Fuel cell testing:
  - Optimization of electrode structure/performance using ALD materials.
  - Isolation and minimization of overpotential losses in MEA electrodes (separation of mass transfer, ohmic, and kinetic losses).
  - Durability studies to quantify and minimize performance losses.

FY 2017 PUBLICATIONS/PRESENTATIONS

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2. Kazuma Shinozaki, Yu Morimoto, Bryan S. Pivovar, and Shyam S. Kocha, "Suppression of oxygen reduction reaction activity on Pt-based electrocatalysts from ionomer incorporation," Journal of Power Sources 325 (2016): 745–751.

3. Shaun Alia, Svitlana Pylypenko, Arrelaine Dameron, K.C. Neyerlin, Shyam Kocha, and Bryan Pivovar, "Oxidation of Platinum Nickel Nanowires to Improve Durability of Oxygen-Reducing Electrocatalysts," J. Electrochem. Soc. 2016 163(3): F296–F301. doi:10.1149/2.0081605jes.

4. Scott A. Mauger, Shaun M. Alia, Siddharth Komini-Babu, Shyam S. Kocha, Chilan Ngo, Katherine E. Hurst, Svitlana Pylypenko, Shawn Litster, Bryan S. Pivovar, and K.C. Neyerlin, "Platinum-Nickel Nanowire Extended Surface Catalysts in PEMFC: Challenges and Lessons Learned," PRiME 2016/230th ECS Meeting, October 4, 2016, Honolulu, HI.

5. William W. McNeary, Katherine M. Hurst, Shaun M. Alia, James W. Medlin, Alan W. Weimer, Karen J. Buechler, and Bryan S. Pivovar, "Atomic Layer Deposition for Extended Surface Electrocatalyst Development," North American Catalysis Society Meeting, Denver, CO, June 4–9, 2017.

6. B. Pivovar, "Development and Implementation of Catalysts and Membrane Electrode Assemblies based on Extended Thin Film Electrocatalysts," CARISMA, Newcastle, UK, April 12, 2017.

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2. Z. Chen, W. Li, M. Waje, Y.S. Yan, *Angew. Chem. Int. Ed.* 2007, 46:4060–4063.