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

- Increase 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) 2016 Objectives

- Using extended surface catalysts prepared by atomic layer deposition (ALD), demonstrate initial mass activity in rotating disc electrode (RDE) >2,200 mA/mg Pt (900 mV internal resistance free) (5X DOE membrane electrode assembly [MEA] target).
- Demonstrate a mass activity of 880 mA mgPt–1 at 0.9 V (2 X DOE 2020 target) and less than a 5% loss after durability testing (30,000 cycles, mass activity) in RDE tests with a total transition metal dissolution of less than 1% of initial catalyst mass.

- Demonstrate a mass activity of >440 mA mgPt–1 at 0.9 V (DOE 2020 target) in fuel cell MEA tests (stretch goal) and demonstrate synthesis of Ni nanostructures with Ni (111) surface-faceted, extended surfaces with aspect ratios >50.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Office 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 synthesizes novel extended thin film electrocatalyst structures (ETFECS) and incorporates these catalysts into electrodes with and without carbon blacks for further study. The project has targets outlined in the Multi-Year Research, Development, and Demonstration Plan for both electrocatalysts for transportation applications (Table 3.4.13) and MEAs (Table 3.4.14). The specific targets and status of highest relevance are presented in Table 1.

TABLE 1. Technical Targets for Electrocatalysts for Transportation Applications

Characteristic	Units	2017/2020 Targets	Status
Mass Activity (150,000 Pa H_2/O_2 80°C 100% RH)	A/mg-Pt @ 900 mV	0.44/0.44	0.15
Electro Catalyst Support Stability	% mass activity loss	<10/<10	TBD
Loss in Initial Catalytic Activity	% mass activity loss	<40/<40	TBD

TBD – To be determined; RH – Relative humidity

FY 2016 Accomplishments

- The project has demonstrated the ability to deposit both Pt and Ni by ALD onto extended surface nanostructures.
- Surface areas of 90 m^2/g Pt and specific activities of 8 mA/cm^2 Pt (0.9 V infrared free) have been reached

although not in the same sample, mass activity Pt of 2,400 mA/mg Pt has been demonstrated (in RDE).

- ETFECS materials have been incorporated into MEAs showing greatly improved performance with acid leaching.

- Diagnostic studies including limiting current and impedance have been applied to elucidate performance losses and optimized structures.

✦   ✦   ✦   ✦   ✦

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 RDE 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 have been delayed due to contracting issues, but the University of Delaware has demonstrated Ni nanoflowers and we have begun working with our Ni nanowire supplier to impact upstream processing, as we have found that the properties of the supplied nanowires have varied greatly over time as highlighted in Table 2 below.

TABLE 2. Ni Nanowire Properties

Ni Nanowire Batch Size and Date Received	Fe Content (at%)	Surface Area (m^2/g)	Maximum Pt ECA (m^2/g)
1 g (2014)	0.4	6.1	~90
50 g (2015)	0.8	2.0	~50
100 g (2016)	0.5	1.1	TBD

ECA – Electrochemical surface area

The application of Ni and Pt ALD onto nanostructures as a novel synthesis technique has been the primary focus of our efforts to date. We have demonstrated the ability to deposit both Pt and Ni onto samples using hydrogen chemistry based ALD. Figure 1 shows high resolution microscopy and elemental mapping of Pt and Ni deposited onto Ni nanowires. While ALD was targeted for ability to go to larger batch sizes, improve sample homogeneity, and independently control Pt and Ni deposition, ALD turned out to have greater heterogeneity compared to spontaneous galvanic displacement (SGD). Figure 2 shows the relative deviation between six digestions for Pt composition. This data shows that SGD is much more homogeneous relative to ALD (for both oxygen and hydrogen based ALD routes). Still, we were able to demonstrate exceptionally high site specific activity (is) above 8,000 µA/cm^2 Pt and a mass activity of
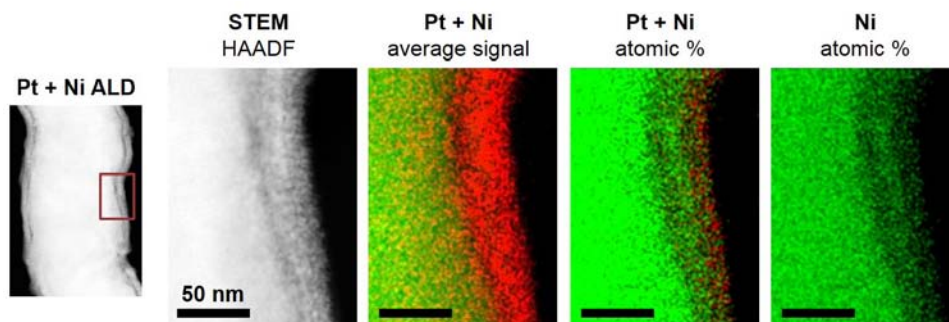
STEM – Scanning transmission electron microscopy; HAADF – High-angle annular dark-field

FIGURE 1. High resolution microscopy and elemental mapping of Ni nanowires following deposition of Pt and Ni by ALD
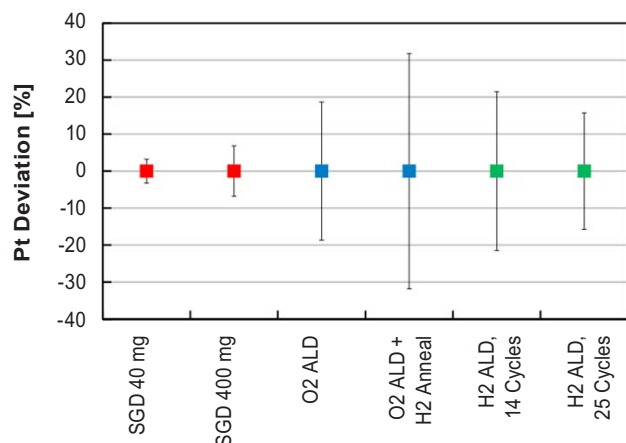
FIGURE 2. Standard deviation of six separate inductively coupled plasma mass spectrometry measurements of Pt composition for various synthesis routes of ETFECS including SGD, oxygen-based (O2) and hydrogen-based (H2) ALD

FIGURE 3. Site specific (i_s) and mass (i_m) activity for ALD synthesized PtNi nanowires as a function of Pt deposition

>2,400 mA/mg Pt (~5 X the DOE 2020 MEA target when characterized by RDE, as shown in Figure 3.)

We have also made significant efforts into incorporating the novel electrocatalysts synthesized within the project and optimizing performance in fuel cells. The high transition metal content of the as synthesized materials creates Ni dissolution concerns that we are investigating through acid pre-leaching. Fuel cell results with current materials are shown in Figure 4 as a function of acid washing. This data shows that Ni contamination is a critical limitation for unwashed MEAs with performance improving significantly with subsequent acid washing steps. We have also begun to perform advanced diagnostics on these MEAs to better understand optimized electrode structures.

Specifically, we have performed impedance measurements that have shown high proton conductivity is maintained in these systems at ionomer contents down to 10 wt%. Our impedance studies suggest that even at these low ionomer contents we still exhibit limitations in limiting current. These results suggest we should be targeting even lower ionomer contents than those investigated to date (10–30 wt%).

CONCLUSIONS AND FUTURE DIRECTIONS

The project has demonstrated the ability to deposit both Pt and Ni by ALD onto extended surface nanostructures. Surface areas of 90 m^2/g Pt and specific activities of 8 mA/cm^2 Pt (0.9 V internal resistance free) have been reached although not in the same sample; mass activity of 2,400 mA/mg Pt has been demonstrated. ETFECS materials have been incorporated into MEAs showing greatly improved performance with acid leaching. Diagnostic studies including limiting current and impedance have been applied
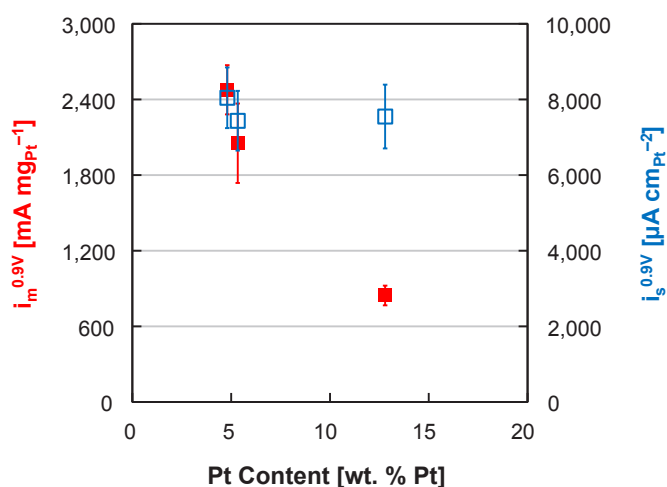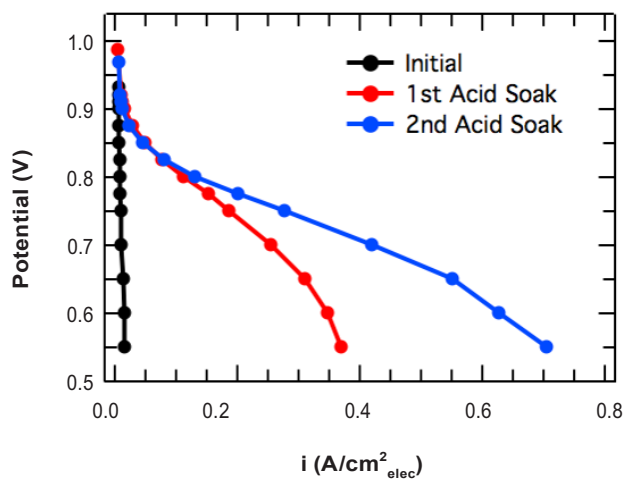

FIGURE 4. Fuel cell polarization curves of PtNiWs as a function of acid washing steps to remove Ni contamination from the MEA

to elucidate performance losses and optimized structures. Future work includes:

- Nanotemplate synthesis:
    - Develop routes to novel Ni nanostructures and demonstrate at useful scale. Focus on clean, well shape controlled nanowires and nanoflowers.
- Electrocatalyst synthesis:
    - ALD-controlled co-deposition of Pt/Ni onto nanotemplates.
    - Post-processing optimization of resultant catalysts (annealing and acid leaching).
    - Characterization and optimization (electrochemical and structural studies).

- Electrode structure and fuel cell studies:

  - Optimization of electrode structure and performance (including electrospinning and spraying and incorporation of different geometry carbons).

  - 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 2016 PUBLICATIONS/PRESENTATIONS

1. Kazuma Shinozaki, Jason W. Zack, Svitlana Pylypenko, Bryan S. Pivovar, and Shyam S. Kocha, "Oxygen Reduction Reaction Measurements on Platinum Electrocatalysts Utilizing Rotating Disk Electrode Technique: II. Influence of Ink Formulation, Catalyst Layer Uniformity and Thickness Fuel Cells, Electrolyzers, and Energy Conversion," J. Electrochem. Soc. 2015 162(12): F1384–F1396. doi:10.1149/2.0551512jes.

2. Shaun M. Alia, Svitlana Pylypenko, K.C. Neyerlin, Shyam S. Kocha, and Bryan S. Pivovar, "Platinum Nickel Nanowires as Methanol Oxidation Electrocatalysts Fuel Cells, Electrolyzers, and Energy Conversion," J. Electrochem. Soc. 2015 162(12): F1299–F1304. doi:10.1149/2.0231512jes.

3. Shinozaki, K.; Zack, J.W.; Richards, R.; Pivovar, B.S.; Kocha, S.S.; "Oxygen Reduction Reaction Measurements on Platinum Electrocatalysts Utilizing Rotating Disk Electrode Technique," J. Electrochem. Soc., 162 (10), F1144–F1158, 2015. DOI: 10.1149/2.1071509jes.

4. Chlistunoff, J. and Pivovar, B., "Effects of Ionomer Morphology on Oxygen Reduction on Pt," J. Electrochem. Soc., 162(8), F890–900, 2015. DOI: 10.1149/2.0661508jes.

5. Shaun M. Alia, Svitlana Pylypenko, K.C. Neyerlin, Shyam S. Kocha, and Bryan S. Pivovar, "Nickel Nanowire Oxidation and Its Effect on Platinum Galvanic Displacement and Methanol Oxidation," ECS Trans. 2014 64(3): 89–95; doi:10.1149/06403.0089ecst.

6. Pivovar, B. (Feb, 2016). "An Overview of Fuel Cell R&D at the National Renewable Energy Lab (NREL)," Michigan State University, February 18, 2016.

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.