

V.A.2 Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes

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Project Start Date: July 20, 2009

Project End Date: September 30, 2014

Overall Objectives

- Increasing mass activity and durability of Pt-based electrocatalysts through the 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) 2013 Objectives

- Produce novel extended thin-film electrocatalyst structures (ETFECS) with increased activity and durability, moving towards meeting all 2020 DOE catalyst targets.
- Further increase electrochemically available surface area (ECA) and mass activity of extended surface catalysts.
- Down-select and incorporate ETFECS into membrane electrode assemblies (MEAs) for fuel cell testing of performance and durability.
- Demonstrate <40% mass activity loss in initial catalytic activity (DOE 2020 target).
- Go/No-Go decision for catalyst synthesis. No-Go all catalyst synthesis routes that have not demonstrated mass activities above 0.44 A/mg Pt @ 900 mV (internal resistance-free).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.5) 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)

Technical Targets

This project synthesizes novel 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 3.4.13) and MEAs (Table 3.4.14). The specific targets and status of highest relevance are presented in Table 1.

FY 2013 Accomplishments

- Go decision for electrocatalysts synthesized by galvanic displacement; atomic layer deposition, chemical vapor deposition and sputtering were decided to be No-Go.
- Developed Pt nanotube catalysts by galvanic displacement based on Ni and Co nanowire templates.
- Demonstrated mass activities of ETFECS as high as 900 mA/mg-Pt @ 900 mV in RDE tests.

TABLE 1. Technical Targets for Electrocatalysts for Transportation Applications

Characteristic	Units	2017/2020 Targets	Status
Mass Activity (150 kPa H ₂ /O ₂ , 80°C, 100% relative humidity)	A/mg-Pt @ 900 mV	0.44/0.44	0.45
Electro catalyst support stability	% mass activity loss	<10/<10	<10*
Loss in initial catalytic activity	% mass activity loss	<40/<40	<10*

*measured in rotating disk electrode (RDE), following 30,000 cycles between 0.6 and 1 V.

- Demonstrated surface areas as high as 90 m²/g.
- Demonstrated specific activities as high as 3.0 mA/cm² Pt @ 900 mV.
- Demonstrated high durability of ETFECS in potential cycling between 0.6 and 1 V for 30,000 cycles, including ability to maintain mass activity in MEAs for select non-alloyed ETFECS.
- Demonstrated mass activity of ETFECS as high as 150 mA/mg-Pt @ 900 mV in fuel cell tests.



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 typically exhibit lower ECAs and consequently lower mass activities. By investigating a number of alternative synthesis techniques, we expect to raise the ECA to deliver the benefits of both a high specific and mass activity. An additional benefit of ETFECS is that larger Pt structures are less susceptible to oxidation and dissolution thus leading to a highly active, durable and low-cost electrocatalyst system.

APPROACH

Our overall approach towards developing extended-surface Pt catalysts for their high mass activity and durability, and incorporating these structures into robust, high-efficiency MEAs has focused on two areas. (1) Synthesis of novel ETFECS: Pt nanoparticles with continuity over tens of nanometers or more have demonstrated enhanced specific activity and exceptional durability (3M [1], others [2]). In our work we examine vapor deposition including sputtering, chemical vapor deposition and atomic layer deposition as well as wet chemistry methods that include spontaneous

galvanic displacement (SGD). We have focused on increased Pt mass activity. Low-Pt ECAs, typically around 10 m²/gPt, have resulted in limited mass activity in the past and further gains in specific activity (due to alloying effects) are possible. (2) Electrode studies involving ETFECS: effective incorporation of extended-Pt catalysts into high-performance electrodes remains a challenge due to the unique structure and properties of these materials. We have incorporated ETFECS into electrodes for fuel cell and RDE testing and evaluated their performance and durability.

RESULTS

In the area of Pt deposition, we have continued our focus on chemical vapor deposition, atomic layer deposition, and SGD. A summary highlighting our highest performing results to date is shown in Figure 1. Based on this figure, we have only met the DOE mass activity target using SGD and we have down-selected our catalyst synthesis efforts to focus only on SGD materials synthesized from Ni and Co (May 2013). While Ag and Cu have met the DOE target, we included these materials in the No-Go category due to anode contamination concerns and the higher performances of the Ni and Co systems.

We have performed detailed studies on the galvanic displacement of both Ni and Co displaced Pt nanowires. The impact that Pt displacement level had on performance of both of these systems is highlighted in Figure 2. Figure 2 shows that Pt-Ni nanowires (NWs) have reached mass activities up to 900 mA/mg Pt and Pt-Co NWs have reached 800 mA/mg Pt, values significantly higher than the DOE 2020 mass activity target (440 mA/mg Pt). These two systems both exhibit the highest mass activity at low Pt displacement percentages, but achieve their high mass activities in different ways. The Ni system shows exceptionally high ECA, reaching a value as high as 90 m²/g Pt at low displacement percentages. This high ECA is similar to Pt-C nanoparticle catalyst and significantly higher than other

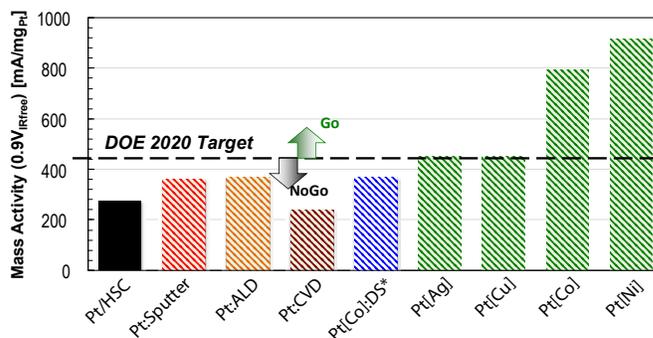


FIGURE 1. Summary of Highest Mass Activity Performance by Synthesis Technique

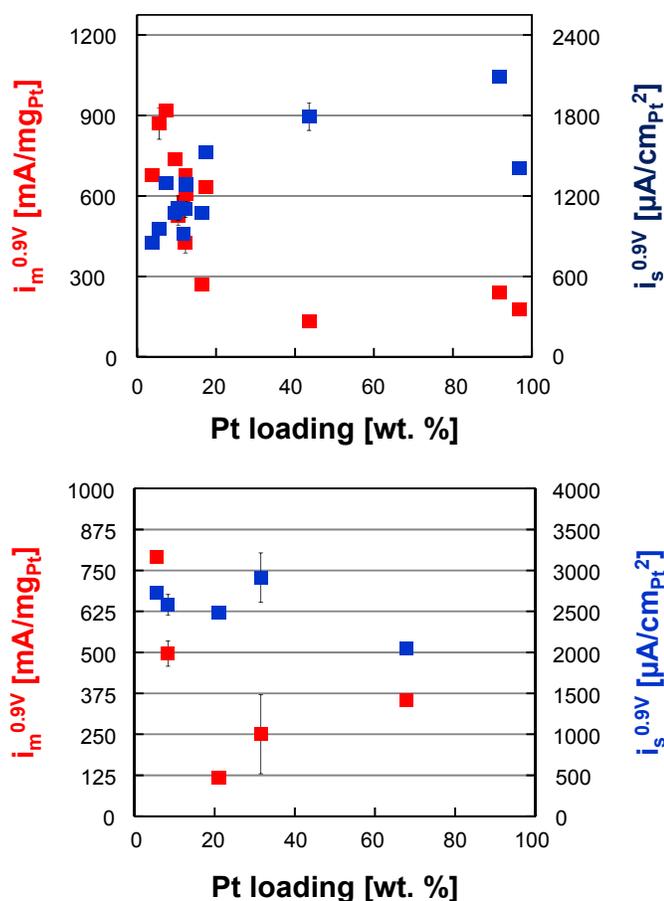


FIGURE 2. Mass and Specific Activity of Pt-Ni NWs and Pt-Co NWs as a Function of Displacement

extended surface electrocatalysts demonstrated to date. The Co system achieves its high activity through gains in specific activity rather than in surface area. The ECA of this system has been limited to $\sim 30 \text{ m}^2/\text{g Pt}$, but has specific activities significantly higher than the Ni-based system. Future work will focus on increasing the specific activity of the Ni system and the surface area of the Co system.

The durability of these systems has also been investigated in RDE tests. Both the Pt-Ni NWs and the Pt-Co NWs have shown the ability to maintain the DOE 2020 mass activity target following 30,000 potential cycles. The two systems show strong differences in their compositions pre- and post- electrochemical testing. The Pt-Ni NWs have shown consistent composition as a function of test conditions where exposure to acid and 30,000 potential cycles have resulted in roughly invariant Pt:Ni compositions of 17:83. Pt-Co NWs, on the other hand, have shown extreme changes in composition on exposure to acid, with a starting material with a Pt:Co composition of 75:25 transforming into a Pt:Co material with 95:5 composition due to leaching out of the Co core of the material. These dramatic differences in behavior between Ni and Co were unexpected and give hope

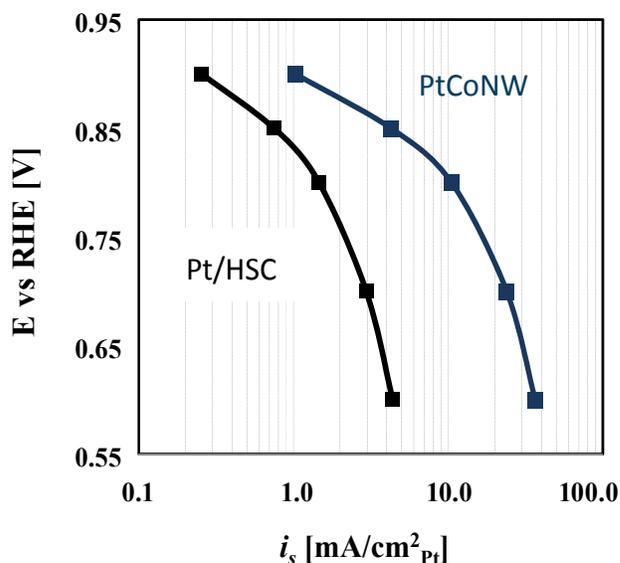


FIGURE 3. Fuel Cell Performance of Pt-Co NWs

that specific features of these systems can be leveraged into producing target materials and properties.

We have significantly increased our efforts in MEA fabrication and fuel cell testing of ETFECS materials. Figure 3 shows our top fuel cell performance to date using an ETFECS catalyst, Pt-Co NWs. Figure 3 is plotted on a surface area normalized basis and shows the significant increase in specific activity of the ETFECS sample compared to traditional Pt-C. These Pt-Co NWs exhibited surface areas in the MEA approaching those of RDE tests and had well defined Pt voltammograms. The specific activity in fuel cell was about half of that of RDE, and the resulting fuel cell mass activity was competitive with Pt/high surface carbon baseline.

Our fuel cell testing efforts with Pt-Ni NWs showed a high specific activity at high current after acid washing. These studies point to a number of concerns for this system that we still need to address, including: Ni dissolution (not apparent in RDE), lack of Pt features in initial cyclic voltammetry; decreased surface areas (relative to RDE); and low-Pt loading during tests (Ni as a magnetic element impacted MEA fabrication and limited our tests to low loading levels).

Fabrication methods investigated to date include direct spraying, decal spray with transfer, filtering with transfer, and direct painting. Beyond fabrications methods we have also focused on issues involving ink formulation, including: difficulties involving support-less electrocatalysts that behave differently than traditional Pt/C catalysts and Pt blacks; the catalyst dispersions (inks) created and MEA fabrication process is significantly more complicated. Preliminary investigations suggest, solvent choices can aid in improving dispersions.

CONCLUSIONS AND FUTURE DIRECTIONS

The project has synthesized many novel catalysts using materials, geometries, and approaches not previously demonstrated. We have down-selected a catalyst synthesis route to focus on galvanic displacement of Co and Ni samples due to the high mass activities achieved (up to 900 mA/g Pt). We have demonstrated exceptionally high surface areas of ETFECS, up to 90 m²/g Pt. We have tested ETFECS in fuel cells and have achieved mass activities as high as 150 mA/g Pt. Our efforts going forward will seek to further increase catalyst activity and optimize MEA performance in order to maintain RDE activity in fuel cell tests by focusing on:

- Electrocatalyst synthesis:
 - Focus on galvanic displacement (NREL, University of Delaware), all other synthesis routes were determined to be No-Go within project. Focus on Pt-Ni, Pt-Co.
 - Pt-Ni: Focus on oxide passivating layer, effects of annealing and attempting to further increase specific activity.
 - Pt-Co: Focus on increasing surface area, leaching of excess Co.
 - Advanced characterization of materials (Colorado School of Mines, ORNL).
- Fuel cell studies:
 - Improve catalyst performance in MEAs with a focus on MEA fabrication using down-selected electrocatalysts.
 - Explore factors impacting observed ECAs, activity, and durability.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Principal Investigator, Bryan Pivovar, was presented the 2012 Charles Tobias Young Investigator Award (Electrochemical Society) at the Fall 2012 Electrochemical Society Meeting, October 2012, Honolulu, HI.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Alexander B. Papandrew, Rob W. Atkinson, Gabriel A. Goenaga, Shyam S. Kocha, Jason W Zack, Bryan S. Pivovar, and Thomas A. Zawodzinski, "Oxygen Reduction Activity of Vapor-Grown Platinum Nanotubes," *J ECS*, 160(8), F848-F852, (2013).
2. Shaun M. Alia, Kurt O. Jensen, Christian Contreras, Fernando Garzon, Bryan Pivovar, and Yushan Yan, "Platinum-Coated Copper Nanowires and Platinum Nanotubes as Oxygen Reduction Electrocatalysts," *ACS Catal.*, 2013, 3, 358-362.

3. K.C. Neyerlin, Brian A. Larsen, Svitlana Pylypenko, Shyam S. Kocha, and Bryan S. Pivovar, "Activity of Pt Extended Network Electrocatalyst Structures Made from Spontaneous Galvanic Displacement," *ECS Trans.* 2013 50(2): 1405-1413.
4. Alexander B. Papandrew, Rob W. Atkinson, Gabriel A. Goenaga, David L. Wilson, Shyam S. Kocha, K.C. Neyerlin, Jason W Zack, Bryan S. Pivovar, and Thomas A. Zawodzinski, "Oxygen Reduction Activity of Vapor-Grown Platinum Nanotubes," *ECS Trans.* 2013 50(2): 1397-1403.
5. Justin Bult, K.C. Neyerlin, Steven Christensen, Arrelaine Dameron, Shyam S. Kocha, Jason W Zack, Bryan S. Pivovar, and Katherine Hurst, "Synthesis and Electrochemical Characterization of Carbon Supported Platinum Grown by Template Assisted Gas Phase Deposition," *ECS Trans.* 2013 50(2): 1723-1727.
6. Brian A. Larsen, K.C. Neyerlin, Justin Bult, Christopher Bochert, Jeffrey L. Blackburn, Shyam Kocha, Bryan Pivovar, "Platinum nanoplates as novel oxygen reduction reaction electrocatalysts" *Journal of The Electrochemical Society*, 159 (10) F1-F5 (2012).
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9. Shyam S. Kocha, Jason Zack, K.C. Neyerlin, and Bryan S. Pivovar "Influence of Nafion on the Electrochemical Activity of Pt-based Electrocatalysts," October 7–12, Honolulu, Hawaii, PRiME 2012, Abstract 1269.
10. Kelly A. Perry, Brian Larsen, K.C. Neyerlin, Bryan S. Pivovar, and Karren L. More, "Elemental and Morphological Analysis of Novel Pt Catalysts Synthesized by Galvanic Displacement," October 7–12, Honolulu, Hawaii, PRiME 2012, Abstract 1273.
11. Shaun M Alia, Brian A Larsen, Svitlana Pylypenko, David A Cullen, David R Diercks, K.C. Neyerlin, Shyam S Kocha, and Bryan S Pivovar "Platinum Coated Nickel Nanowires As Oxygen Reducing Electrocatalysts," October 7–12, Honolulu, Hawaii, PRiME 2012, Abstract 1308.
12. K.C. Neyerlin, Brian Larsen, Shyam S. Kocha, and Bryan S. Pivovar "Electrochemical Performance of Pt Extended Network Catalysts from Spontaneous Galvanic Displacement in MEAs," October 7-12, Honolulu, Hawaii, PRiME 2012, Abstract 1377
13. Justin Bult, K.C. Neyerlin, Steven Christensen, Arrelaine Dameron, Bryan S. Pivovar, and Katherine Hurst "Controlled Pt Coverage for Extended Thin Film Catalyst ORR Studies via Templated Gas Phase Synthesis," October 7–12, Honolulu, Hawaii, PRiME 2012, Abstract 1426.
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15. K.C. Neyerlin, Brian Larsen, Shyam S. Kocha, and Bryan S. Pivovar “Activity and Durability of Pt Extended Network Electrocatalyst Structures Made from Spontaneous Galvanic Displacement,” October 7–12, Honolulu, Hawaii, PRiME 2012, Abstract 1565.

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