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

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Project Start Date: July 20, 2009
Project End Date: Project continuation and direction determined annually by DOE

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) 2014 Objectives

- Demonstrate an initial performance of >0.66 A mg_{Pt}^{-1} @ 900 mV (internal resistance [IR]-free) (50% increase over the DOE 2020 Target), and <30% loss in initial mass activity (25% improvement on DOE 2020 Target).
- Develop membrance electrode assemblies (MEAs) using novel electrocatalysts that show less than 10% mass activity loss in electrocatalyst support stability tests.
- Go/No-Go decision for annealing. No-go if mass activity gain is less than 10% of unannealed samples and durability gain is less than 25% compared to unannealled samples.
- Demonstrate fuel cell performance using novel electrocatalysts of 0.44 A mg_{Pt}^{-1} @ 900 mV (IR-free, DOE 2020 Target).

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)

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 3.4.13) 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 kPa H_2/O_2 80°C 100% relative humidity)	A/mg-Pt @ 900mV	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

FY 2014 Accomplishments

- Go decision for annealing as a method to improve catalyst activity.
- Demonstrated mass activities of ETFECS as high as 2,400 mA mg_{Pt}^{-1} @ 900 mV in rotating disc electrode (RDE) tests.

- Reduced leaching of the Ni template by annealing catalyst in oxygen (<2% following break-in, <2% following durability in RDE half-cells).
- Demonstrated ETFECS with mass activities (RDE) prior to and following durability testing of 1,963 and 1,564 mA mg_{Pt}^{-1}. The initial activity represents a 446% increase over the DOE 2020 target and the final activity was a 20% loss from initial activity (355% increase over the DOE 2020 target).
- Demonstrated fuel cell mass activity using ETFECS 50% higher than that of Pt/C baseline materials.
- Demonstrated greatly improved durability using ETFECS when exposed to carbon corrosion cycling.

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 offers the possibility of higher specific activities, comparable to that of bulk poly-Pt. ETFECS materials formed by direct deposition traditionally exhibit lower electrochemical surface areas (ECAs), and lower mass activities; synthesis by galvanic displacement, however, has in cases allowed for a thrifting of the noble metal layer, and for ECAs comparable to conventional nanoparticle catalysts. Although these materials exceed the 2020 activity target following durability testing (in RDE half-cells), durability are somewhat limited by the high template metal (Ni, Co) content which is more susceptible to leaching. By investigating post-synthesis processing conditions, we expect to: form Pt Ni alloys with improved specific activity (comparable to that observed in the Pt Co system); to minimize leaching during electrochemical testing; and to improve retention of ECA and activity following durability testing.

APPROACH

Our overall approach is towards developing extended surface Pt catalysts with high mass activity and durability, and incorporating these structures into robust, high-efficiency MEAs. This approach has focused on the synthesis of novel ETFECS formed by spontaneous galvanic displacement, specifically with Ni and Co templates. These materials have demonstrated high specific activity and durability, as well as surface areas significantly larger than traditionally found in extended surface Pt catalysts (3M [1], others [2]). In our work, we examine post-synthesis annealing in oxygen to improve catalyst durability and annealing to improve activity, potentially by an alloying effect.

RESULTS

We have completed detailed studies on Co nanowires (NWs) galvanically displaced with Pt, shown in Figure 1. This completed the study initially presented in FY 2013, by examining additional compositions or degrees of partial displacement. Pt-coated Co NWs reached a mass activity of 800 mA mg_{Pt}^{-1} at a Pt composition of 5.5 wt%. These materials, however, produced significantly lower ECAs (30 m^2 g_{Pt}^{-1}) than the Pt-Ni system and the gains in activity are therefore primarily due to the specific activity. This improvement was also correlated to Pt lattice compression, where the specific activity generally increased with an increased degree of alloying (at lower Pt content). Following durability testing (30,000 cycles, 0.6–1.0 V in RDE), these materials exceeded mass activities of 600 mA mg_{Pt}^{-1}. Future work will focus on improving the retention of activity (and ECA) following durability testing by post synthesis processing (as completed in FY 2014 on Pt-Ni NWs).

We have examined annealing of Pt-Ni NWs in oxygen to reduce Ni leaching during electrochemical testing and to improve the retention of activity following durability testing. As shown in Figure 2, annealing in oxygen significantly reduced Ni leaching. At a temperature of 200°C, less than 2% of the Ni was lost into the RDE electrolyte (<4% total including durability testing). At this temperature, the initial activity of the Pt-Ni NWs was slightly reduced but the retention of activity (and ECA) dramatically improved. As shown in Figure 2, the ECA of Pt-Ni NWs (200°C) improved in durability testing (3%); the mass activity increased as well (6%).

Novel, next-generation Pt NWs (NG Pt NWs) were also synthesized in FY 2014. As shown in Figure 3, catalysts were produced with mass activities as high as 2,400 mA mg_{Pt}^{-1}, a 5x improvement over the 2020 DOE target. These novel

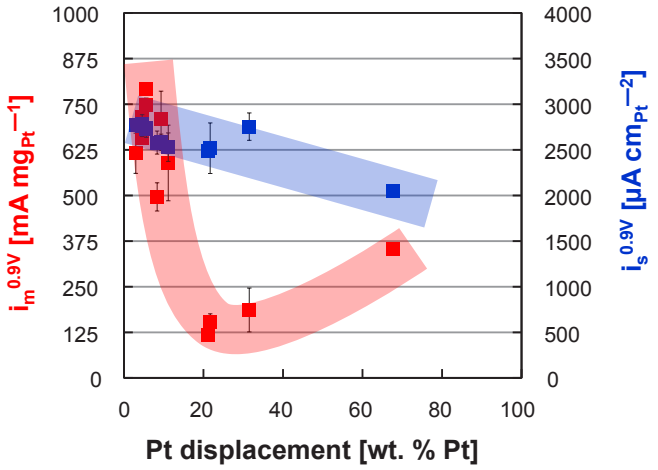

FIGURE 1. Mass and specific activity of Pt-Co NWs as a function of displacement.

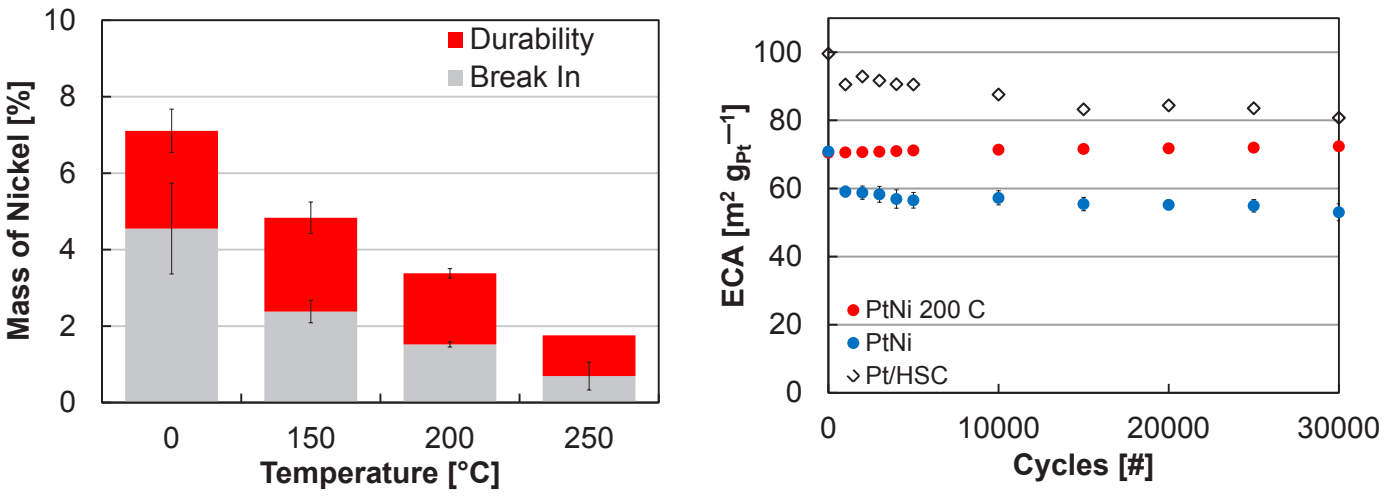

FIGURE 2. Percent loss of Ni (following RDE break-in and durability testing) as a function of annealing temperature in oxygen. ECA of catalysts (Pt Ni NWs annealed and untreated, Pt nanoparticles supported on high surface area carbon, Pt/HSC) as a function of durability cycle.

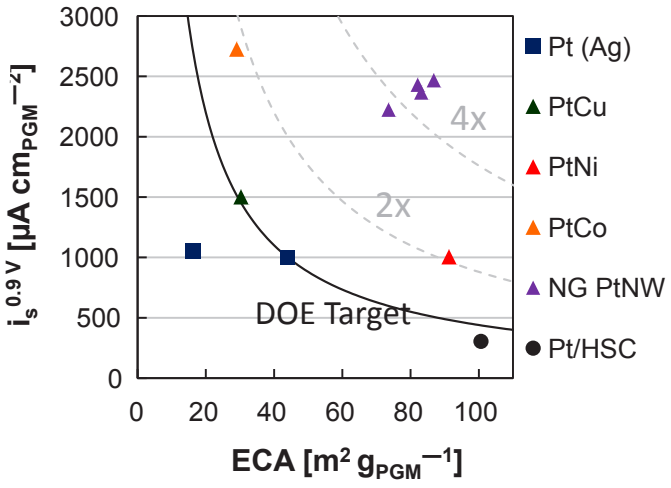

FIGURE 3. ECA and specific activities (i_s) summary of past synthesis routes and currently developed materials (NG Pt NW), lines of constant mass activity shown for DOE 2020 target, and 2 and 4 times the DOE 2020 target.

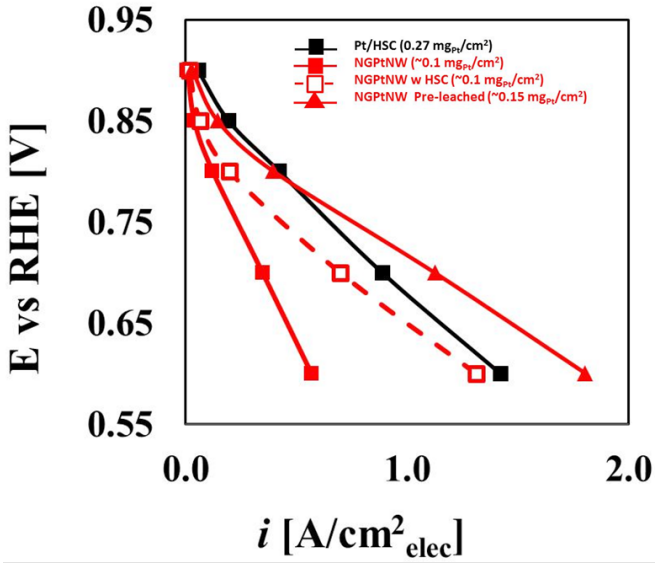

FIGURE 4. Fuel cell polarization curves of Pt NWs compared to Pt/C baseline material.

catalysts also showed the ability to maintain performance following potential cycling. The catalyst shown in Figure 3 with an initial activity of 1,963 mA mg_{Pt}^{-1} (446% increase over the DOE 2020 target in RDE half-cells) demonstrated a final activity of 1,564 mA mg_{Pt}^{-1} (20% loss from initial activity, 355% increase over the DOE 2020 target in RDE half-cells).

We have substantially increased our efforts to demonstrate our novel materials in fuel cell testing. We have scaled up synthesis and explored different fabrication routes. Figure 4 shows polarization curves and loadings for four different fuel cell tests. Pt/C has been included as a baseline comparison. The fuel cell performances presented represent improvements over time in both the catalysts themselves and in our ability to fabricate improved performance MEAs. The NG Pt NW MEA shows increased performance compared to Pt/C, in spite of lower catalyst loading, and all Pt NW samples show significantly improved durability when evaluated by potential cycling in the region of carbon corrosion. The observed Pt NW MEA performances are still far below the observed properties of RDE tests. The difference in performance is most pronounced at high voltage where the Pt NW samples

demonstrate lower specific activities than anticipated relative to lower voltage operation.

CONCLUSIONS AND FUTURE DIRECTIONS

The project has synthesized many novel catalysts using materials, geometries, and approaches not previously demonstrated. We improved upon the activity of Pt Ni NWs reported in FY 2013, reaching mass activities of 2,400 mA mg_{Pt}^{-1}. We have further demonstrated ETFECS catalysts with a high initial mass activity (2,400 mA mg_{Pt}^{-1}) and a high level of activity following durability testing (20% loss). 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 the following.

- Electrocatalyst synthesis:
  - Focus on durability and the role of transition metals.
  - Continued investigation of oxide layer role in passivation of transition metal components.
  - Selective removal of transition metals to limit impact of performance loss.
- Fuel cell studies:
  - Optimization of fuel cell performance (ECA) using ETFECS with a focus on catalyst ink dispersions and composition.
  - Isolation of overpotential losses in MEA electrodes made with ETFECS materials (separation of mass transfer, ohmic, kinetic losses).
  - Durability studies to quantify and reduce impact of performance loss with specific emphasis on transition metal leaching.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Shaun M. Alia, Svitlana Pylypenko, K.C. Neyerlin, David A. Cullen, Shyam S. Kocha, Bryan S. Pivovar, "Platinum-Coated Cobalt Nanowires as Oxygen Reduction Reaction Electrocatalysts" ACS Catalysis 2014, 4, 2680.

2. K.C. Neyerlin, Brian A. Larsen, Svitlana Pylypenko, Shyam S. Kocha, Bryan S. Pivovar "Activity of Pt Extended Network Electrocatalyst Structures Made from Spontaneous Galvanic Displacement" ECS Transactions 2013, 50, 1405.

3. Justin Bult, K.C. Neyerlin, Steven Christensen, Arrelaine Dameron, Shyam S. Kocha, Jason W Zack, Bryan S. Pivovar, Katherine Hurst "Synthesis and Electrochemical Characterization of Carbon Supported Platinum Grown by Template Assisted Gas Phase Deposition," ECS Transactions 2013, 50, 1723.

4. Kazuma Shinozaki, Bryan S Pivovar, Shyam S Kocha "Enhanced Oxygen Reduction Activity on Pt/C for Nafion-free, Thin, Uniform Films in Rotating Disk Electrode Studies," ECS Transactions 2013, 58, 15.

5. Alexander B. Papandrew, Robert W. Atkinson III, Gabriel A. Goenaga, Shyam S. Kocha, Jason W. Zack, Bryan S. Pivovar, Thomas A. Zawodzinski Jr. "Oxygen Reduction Activity of Vapor-Grown Platinum Nanotubes," Journal of the Electrochemical Society 2013, 160, F848.

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9. Shaun M. Alia, Bryan S. Pivovar, Yushan Yan "Platinum Coated Copper Nanowires with High Activity for Hydrogen Oxidation Reaction in Base" Journal of the American Chemical Society 2013, 135, 13473. DOI: 10.1021/ja405598a

10. Shyam S. Kocha, Jason W. Zack, Shaun M. Alia, K.C. Neyerlin, Bryan S. Pivovar, "Influence of Ink Composition on the Electrochemical Properties of Pt/C Electrocatalysts" ECS Transactions 2013, 50, 1475.

11. Shaun M. Alia, Svitlana Pylypenko, K.C. Neyerlin, Brian A. Larsen, Shyam S. Kocha, Bryan S. Pivovar "Platinum Coated Cobalt Nanowires," November 3–8, San Francisco, California, AIChE Annual Meeting 2013, Abstract 729c.

12. Shaun M. Alia, Brian A. Larsen, Svitlana Pylypenko, David A. Cullen, David R. Diercks, K.C. Neyerlin, Shyam S. Kocha, Bryan S. Pivovar "Platinum Coated Nickel Nanowires as Oxygen Reducing Electrocatalysts," October 27 – November 1, San Francisco, California, 224th ECS Meeting 2013, Abstract 1308.

13. Kazuma Shinozaki, Bryan S. Pivovar, Shyam S. Kocha "Influence of Film Morphology on the Oxygen Reduction Reaction Activity in Rotating Disk Electrode Studies," October 27-November 1, San Francisco, California, 224th ECS Meeting 2013, Abstract 1239.

14. Bryan S Pivovar, K.C. Neyerlin, Shaun M Alia, Brian A Larsen, Svitlana Pylypenko, David A Cullen, David R Diercks, Shyam S Kocha "Extended Surface Pt Electrocatalysts: Synthesis and Challenges in Fuel Cell Applications," October 27 – November 1, San Francisco, California, 224th ECS Meeting 2013, Abstract 1245.

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