

V.A.1 Extended, Continuous Pt Nanostructures in Thick, Dispersed Electrodes

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Project End Date: Sept 30, 2015

- 1,000 mW/cm² at rated power and less than 40% loss in catalytic activity
- Develop membrane electrode assemblies (MEAs) with 100% improvement in initial mass activity when compared to baseline Pt/C catalysts at rated power (5 A/mgPt at 0.75 V infrared [IR] corrected) using novel electrocatalysts
- Demonstrate less than 40% loss of mass activity at rated power (0.75 V IR free) 80°C, 100% relative humidity (RH) after 30,000 potential cycles between 0.6 and 1.0 V at 500 mV/s

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 (MYRDD) 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 MYRDD 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% RH)	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 RDE, following 30,000 cycles between 0.6 V and 1 V

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) 2015 Objectives

- Using pre-leaching on top performing novel electrocatalysts to reduce transition metal dissolution impact on durability, demonstrate a mass activity of 880 mA mg Pt⁻¹ at 0.9 V (2x DOE 2020 target) and less than a 5% loss after durability testing (30,000 cycles, mass activity) in rotating disk electrode (RDE) tests with a total transition metal dissolution of less than 1% of initial catalyst mass (current high performance materials experience dissolution rates up to 7% mass under these conditions)
- Aligned with DOE's 2020 targets

FY 2015 Accomplishments

- The project has demonstrated extended surface catalysts with remarkably high surface area and specific activity that offer the potential to dramatically decrease required Pt loadings through exceptionally high mass activities (>2,500 mA/mg Pt).
- These materials have also demonstrated good durability under select (potential cycling, both RDE and MEA) conditions, including dramatically reduced transition metal dissolution rates.
- The project has advanced the performance of these materials in MEAs and demonstrated the need for further understanding and development in these areas.



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 direct deposition traditionally exhibit lower electrochemical surface areas ([ECAs], and lower mass activities); synthesis by galvanic displacement, however, has in cases allowed for a thrifiting of the noble metal layer, and for ECAs comparable to conventional nanoparticle catalysts. This year we have for the first time demonstrated materials that not only greatly exceed the 2020 mass activity target, but also demonstrate exceptional durability when exposed to acid and potential cycling.

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 surfaces areas significantly larger than traditionally found in extended surface Pt catalysts (3M [1], others [2]). In our most recent work, we have optimized post-synthesis processing parameters including annealing conditions in different environments and acid leaching in order to both improve catalyst performance and durability.

RESULTS

We have completed detailed studies focused on post-processing of PtNi nanowires (NWs) to increase durability while still retaining performance. We have conducted post-processing of PtNi NWs synthesized via galvanic displacement through annealing under reducing and/or oxidizing conditions as well as acid leaching. We have optimized each one of these processes independently and arrived at optimized conditions for all three combined processes. Figure 1a shows the mass and specific activity of PtNi NWs for samples following annealing under oxidizing conditions. These samples had been previously annealed under reducing conditions and acid leached. The peak performance for these samples occurred at 10.7% Pt, >2,500 mA/mg Pt (>5x improvement in mass activity in rotating disc electrode studies, compared to DOE 2020 MEA target). These samples also exhibited exceptionally high

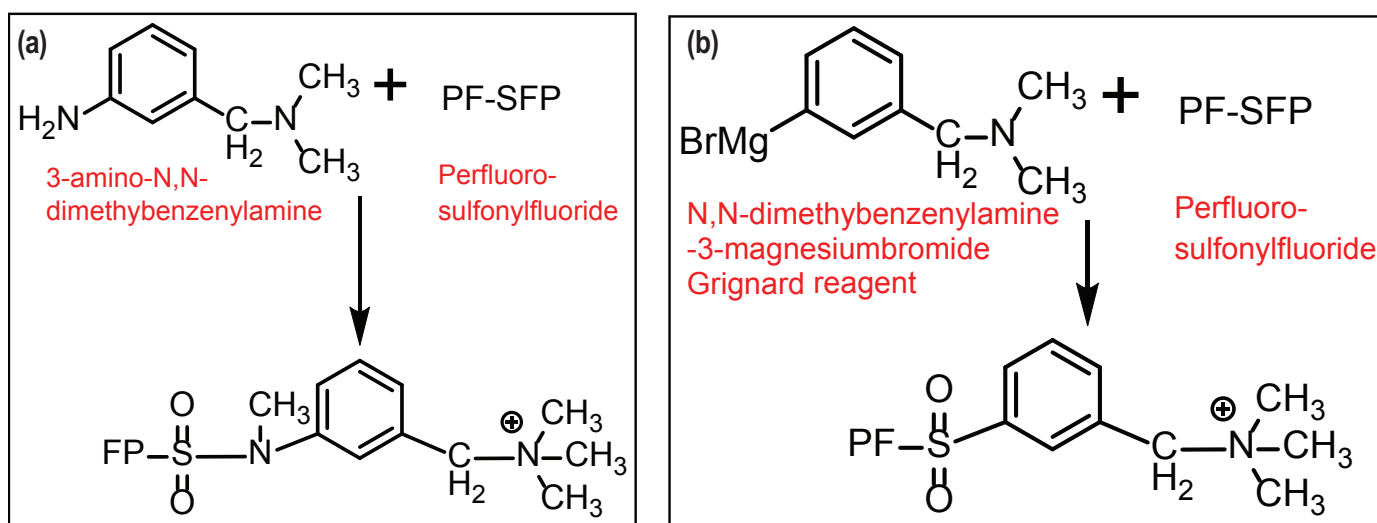


FIGURE 1. (a) Specific and mass activity of PtNWs after annealing under reducing conditions, acid leaching and annealing under oxidizing conditions; (b) Pt and Ni dissolution rates upon exposure to acid and post-potential cycling of samples shown in Figure 1a

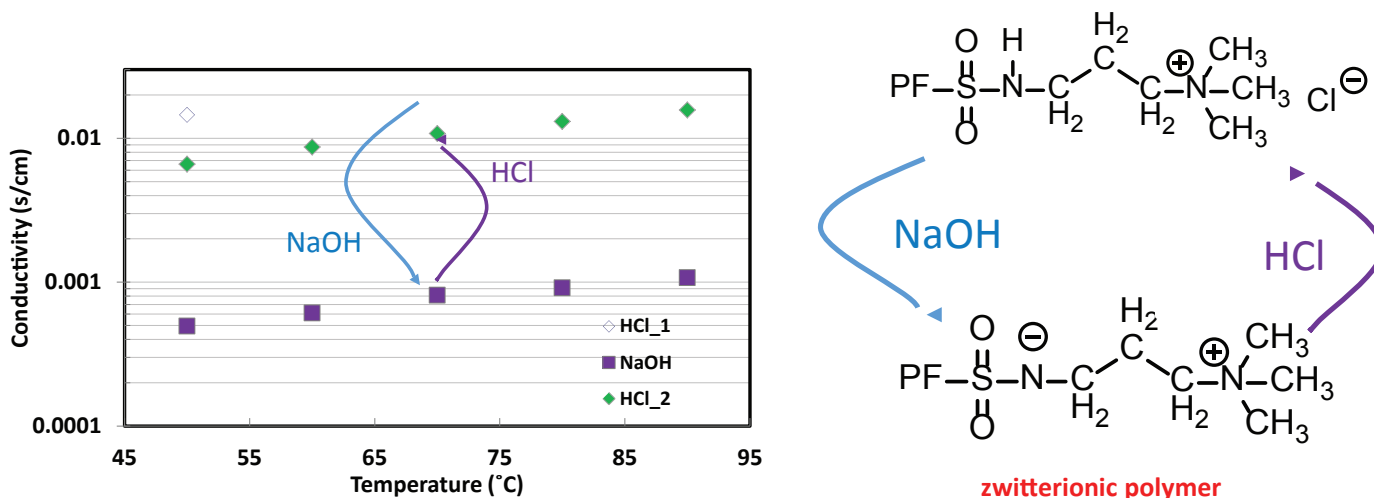


FIGURE 2. Summary of high ECA PtNi NWs before and after potential cycling (30,000 cycles, 0.6 V to 1 V) compared to baseline Pt/C (solid line denotes DOE 2020 MEA target)

durability to Ni dissolution (Figure 1b) following exposure to acid (break-in) and 30,000 potential cycles between 0.6 V and 1.0 V. Through the optimized post-processing conditions we were able to both make highly active samples and highly durable samples, advancing the performance of our materials relative to those reported in FY 2014, particularly in the area of durability/transition metal dissolution. Figure 2 provides a summary of the performance of our top performing catalysts (all with initial electrochemical surface areas >80 m²/g Pt). The arrows in Figure 2 denote performance following potential cycling (30,000 cycles between 0.6 V and 1 V in RDE studies). While earlier samples with high performance showed poor stability, the optimized materials maintained their high performance post-cycling. These results were exceptionally promising, however, our attempts to scale up synthesis batch size resulted in losses in performance (~25%) and batch to batch reproducibility concerns that remain as on-going issues.

In order to address scale up and reproducibility issues, we applied atomic layer deposition (ALD) as a potential route to reproducing the performance of galvanically displaced samples with a potentially more reproducible method, lower cost, and amenable to large scale manufacture. Preliminary results (shown in Figure 3) based on post-synthesis annealing demonstrated that high ECA could be obtained by this route, as samples annealed to 250°C exhibited ECAs ~95 m²/g Pt. Specific activity of these ALD samples has not reached the level of galvanically displaced samples, but remains an area of potential interest.

PtNi NWs were also fabricated into electrodes of MEAs to gauge fuel cell performance and durability. The unique density and dispersion characteristics of PtNi NWs render them difficult to effectively process into high performance MEAs. In previous work we had shown MEA performance

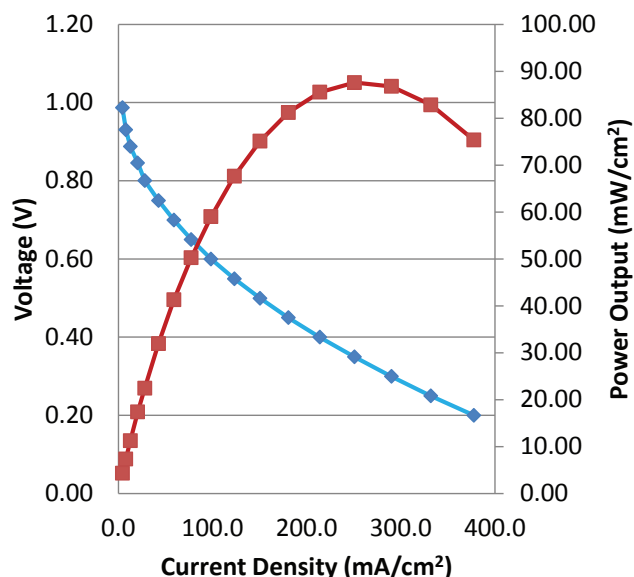


FIGURE 3. Electrochemical properties of PtNiNWs synthesized via atomic layer deposition following annealing in a reducing atmosphere as a function of reducing temperature

improvements through the incorporation of carbon into electrodes or through improved dispersion preparation. For the first time our team applied impedance and limiting current measurements to these systems in order to assess performance losses attributed to mass transport and protonic resistance in the electrode layer. We also demonstrated significantly improved durability of these materials when compared to traditional Pt/C materials when tested in the carbon corrosion region (potential cycling between 1 V and 1.5 V), Figure 4. While both samples showed similar initial performance, the PtNi NW sample showed negligible

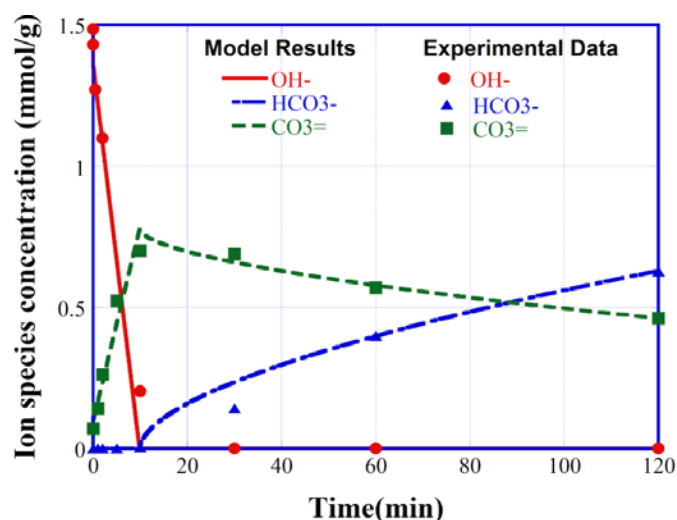


FIGURE 4. Fuel cell polarization curves of PtNWs compared to Pt/C baseline material before and after potential cycling

degradation after being subject to 6,000 potential cycles; in contrast, Pt/C showed significant performance loss after only 1,000 cycles.

CONCLUSIONS AND FUTURE DIRECTIONS

The project has synthesized many novel catalysts using materials, geometries, and approaches not previously demonstrated. We improved upon the durability of Pt Ni nanowires reported in FY 2014, decreasing Ni metal dissolution rates to obtain highly durable, high performing samples. Our efforts going forward will seek to further increase the catalyst activity and optimize MEA performance in order to maintain RDE activity in fuel cell tests by focusing on the following.

- Electrolyte synthesis focus on reproducibility/increased batch size
 - Galvanic displacement to produce materials of target performance in increased quantity
 - Further post-processing studies of ALD synthesized materials, use of rotary ALD system to improve intra- and inter-batch reproducibility
- Electrode structure/fuel cell studies
 - Optimization of electrode structure/fuel cell performance using ETFECS with a focus on catalyst ink dispersions and composition
 - Isolation of overpotential losses in MEA electrodes made with ETFECS materials (deconvolution of mass transfer, ohmic, and kinetic losses)
 - Durability studies to quantify performance loss with a specific emphasis on transition metal leaching

FY 2015 PUBLICATIONS/PRESENTATIONS

1. 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.
2. Jeremy Leong, Abbas Ebnonnasir, Maxwell C. Schulze, Matthew B. Strand, Chilan Ngo, David Maloney, Sarah L. Frisco, Huyen N. Dinh, Bryan Pivovar, George Gilmer, Suneel Kodambaka, Cristian V. Ciobanu, and Ryan M. Richards, "Shape-directional growth of Pt and Pd nanoparticles," *Nanoscale*, 2014.
3. S.M. Alia, Y. Yan, B.S. Pivovar, "Galvanic Displacement as a Route to Highly Active and Durable, Extended Surface Electrocatalysts," *Catalysis Science and Technology*, 2014, 4 (10), 3589–3600.
4. Leong, G.J.; Schulze, M.C.; Strand, M.B.; Maloney, D.; Frisco, S.L.; Dinh, H.N.; Pivovar, B.; Richards, R.M., "Shape-directed Platinum Nanoparticle Synthesis: Nanoscale Design of Novel Catalysts," *Applied Organometallic Chemistry*, 28, 1–17, 2014.
5. Shaun M. Alia, Svitlana Pylypenko, Arrelaine Dameron, K.C. Neyerlin, Shyam S. Kocha, and Bryan S. Pivovar, "Oxidation of Platinum Nickel Nanowires to Improve Durability of Oxygen-Reducing Electrocatalysts," submitted.
6. Pivovar, B. (Aug., 2014). "Fuel Cell and Electrolysis Activities at the National Renewable Energy Lab," Presented at MRES, Northeastern University, August 21, 2014.
7. Pivovar, B. (Nov., 2014). "Fuel Cell R&D focused on Alkaline Membranes and Advanced Catalysis at the National Renewable Energy Lab," Presented at Wuhan University, Wuhan, China, November 12, 2014.
8. Pivovar, B. (Nov., 2014). "Fuel Cell R&D focused on Alkaline Membranes and Advanced Catalysis at the National Renewable Energy Lab," Presented at Dalian Institute of Chemical Physics, Dalian, China, Nov. 13, 2014.
9. Pivovar, B. (March, 2015). "Past, Current, and Future Research in Polymer Electrolyte Fuel Cells," Presented at University of Colorado – Denver, Denver, CO, March 6, 2015.
10. Pivovar, B. (April, 2015). "Past, Current, and Future Research in Polymer Electrolyte Fuel Cells," Presented at University of Wyoming, Laramie, WY, April 2, 2015.
11. Pivovar, B. (April 2014). "Past, Current, and Future Research in Polymer Electrolyte Fuel Cells," Presented at Purdue University, West Lafayette, IN, April 3, 2014.

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.