Extended Surface Electrocatalyst Development

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Subcontractors:
- Colorado School of Mines, Golden, CO
- University of Colorado, Boulder, CO
- ALD Nanosolutions, Broomfield, CO

Project Start Date: December 10, 2015
Project End Date: March 30, 2019

Overall Objectives

- Increasing mass activity and durability of platinum (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 2018 Objectives

- 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 the Fuel Cell Technologies Office's membrane electrode assembly (MEA) durability targets.
- Demonstrate atomic layer deposition (ALD) batch synthesis at >10 g per batch scale.
- Synthesis of >5 g of ALD-deposited Pt nanowires (PtNWs) of acceptable quality (>500 mA/mg Pt) for MEA testing.
- Quantify the non-Fickian oxygen transport resistance of at least three unique electrodes containing platinum-nickel nanowire (PtNiNW) electrocatalysts, a key metric for achieving high performance at low loading.
- In alignment with the DOE 2020 target for rated power (1,000 mW/cm^2), demonstrate 600 mW/cm^2 at rated power (cathode 3x improvement for electrodes based on PtNiNWs).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

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

[1] https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

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% relative humidity)	A/mg-Pt @ 900 mV	0.44	>0.5
Electrocatalyst support stability	% mass activity loss	<40	41
Loss in initial catalytic activity	% mass activity loss	<40	66

FY 2018 Accomplishments

- Demonstrated the ability to produce large quantities of PtNiNWs using ALD with reasonable performance.
- Repeatedly demonstrated MEA performance, in excess of DOE 2020 targets, with PtNiNWs through inter- and intra-batch testing.
- Exceeded the DOE 2020 durability target for support stability (5,000 cycles, 1–1.5 V)
- Developed Pt-Ni co-deposition technique onto cobalt (Co) nanowires for improved control of alloying and composition following acid leaching.
- Improved high-current-density performance with carbon integration and optimization in the catalyst layer.

INTRODUCTION

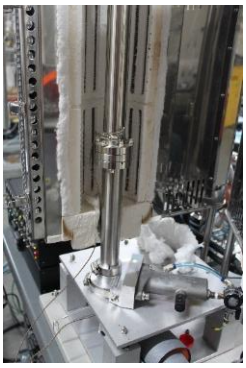
Conventional nanoparticle Pt/C electrocatalysts (2–5 nm) used in automotive fuel cells appear to have plateaued in terms of electrochemical area and catalytic activity. ETFECS offers the possibility of higher specific activities—comparable to that of bulk polycrystalline Pt. The ETFECS materials formed 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) [1]. We are focusing on Pt and Ni ALD to address these limitations from galvanic displacement. The materials are then explored for optimum electrode structures through cell diagnostics that isolate and target mitigation strategies for loss mechanisms.

APPROACH

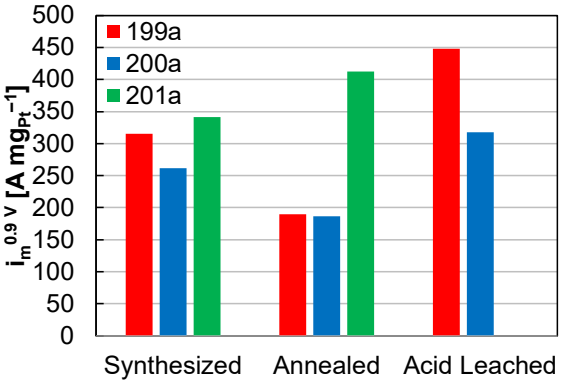
Our overall approach is towards developing extended surface Pt catalysts synthesized by ALD with high mass activity and durability, and incorporating these structures into robust, high-efficiency MEAs. This approach focuses on the synthesis of novel ETFECS formed by ALD, specifically with the co-deposition of Pt and Ni. We are targeting high surface areas, as this has been a specific challenge for extended surface Pt catalysts (3M [2], others [3]). Our multitiered 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 ALD synthesis of ETFECS materials, we have taken two approaches: (1) Pt deposition onto Ni nanowires—improving batch consistency and increasing batch size while maintaining high levels of activity; and (2) Pt and Ni co-deposition onto Co nanowires to improve control of lattice integration and composition. Within Pt ALD, oxygen concentration in the packed bed reactor was found to significantly impact the performance of resulting materials. At too high of a concentration, synthesized materials oxidized and hardened into aggregates. Lower oxygen concentrations resulted in improved consistency in material composition and oxygen reduction activity. The University of Colorado Boulder synthesized catalysts at 0.5 g and 2 g batch sizes to supply the National Renewable Energy Laboratory (NREL) with material for MEA testing. For larger quantities, ALD Nanosolutions used a research fluidized bed reactor to produce 5 g batches, although further scaling could be used to produce 3 mt per day (Figure 1). Testing of the 5 g batches has shown target composition and reasonable performances when screened with rotating disk electrode tests. Microscopy of the 5 g batches further demonstrates that these materials are similar in structure to the smaller ALD batches or materials previously formed by galvanic displacement.



10-200 g
Research FBR



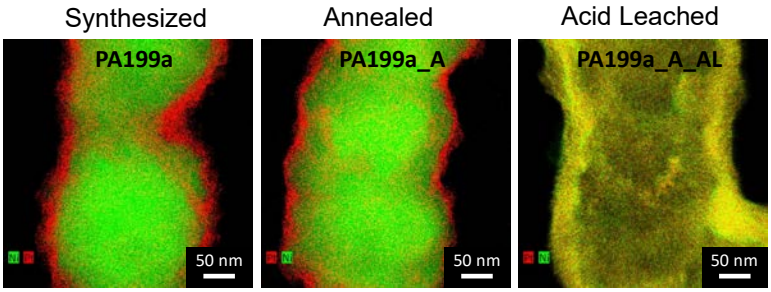


Figure 1. The 5-g batch synthesis of PtNiNWs. Mass activities in rotating disk electrode tests, as-synthesized and following hydrogen annealing and acid leaching steps. Microscopy of PtNiNWs, as-synthesized and following hydrogen annealing and acid leaching steps.

Additionally, the University of Colorado Boulder has used ALD to co-deposit Pt and Ni onto Co nanowires (Figure 2). By using co-deposition, we intend to better control Pt- and Ni-lattice integration and isolate the Pt-Ni alloy from the nanowire core to produce more active materials while maintaining high Pt composition. Through synthesis, Pt/Ni deposition cycles and temperatures were varied, where it was found that Pt and Ni deposit to different extents and at different rates. Current efforts are aimed at increasing the amount of Ni deposition so that acid leaching does not remove most of the Ni, and that the Co core is not contributing during alloying/annealing.

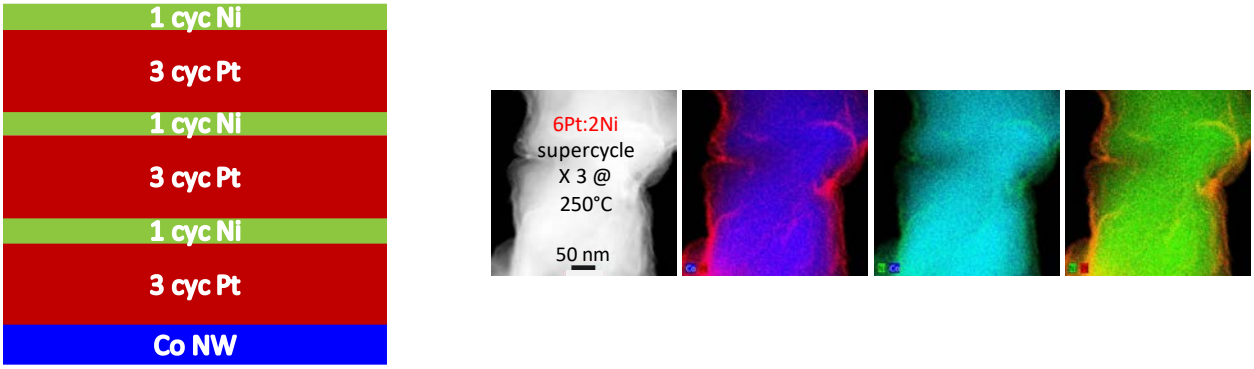


Figure 2. Schematic of Pt-Ni co-deposition onto cobalt nanowires. Microscopy and energy dispersive X-ray spectroscopy of the resulting nanowires, shown with Pt (red), Ni (green), and Co (blue).

MEA testing has been completed at NREL on a number of Pt-Ni materials. Testing of PtNiNWs formed by ALD-oxygen chemistry has shown performances in excess of the DOE 2020 target. Reducing the oxygen concentration during ALD synthesis was found to be a significant contributor, and MEA trends matched those observed from rotating disk electrode tests. Subsequent MEAs from the same batch and from different PtNiNW batches were evaluated and produced performances consistently in excess of this target (Figure 3). Additionally, the ETFECS materials surpassed the DOE target for support durability.

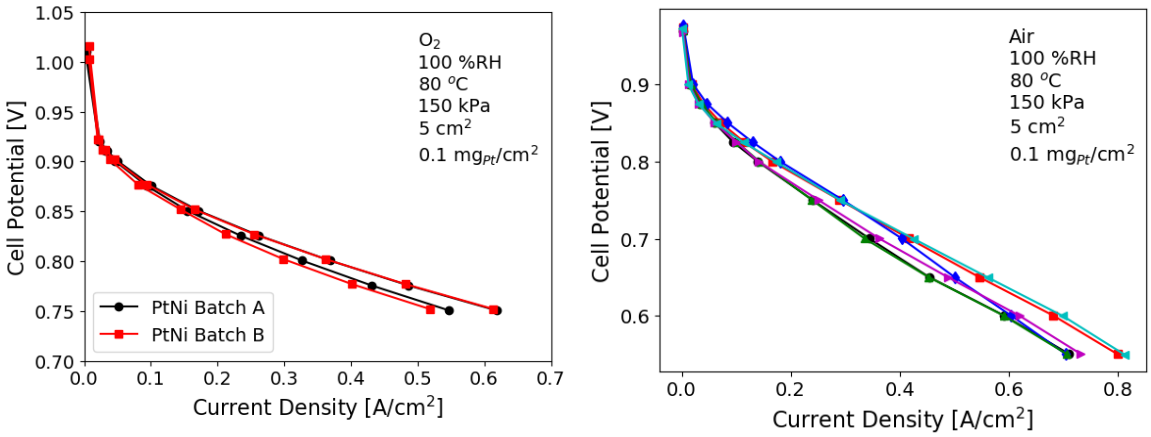


Figure 3. MEA testing of PtNiNWs to evaluate intra- and inter-batch consistency.

The MEA diagnostics and optimization were completed to evaluate and improve ETFECS performance at high current density. Studies of the non-Fickian oxygen transport resistance showed that ETFECS materials were more similar to Pt supported on Vulcan as opposed to Pt (or Pt-Co) supported on high-surface-area carbon. Analysis of local oxygen transport resistance, however, showed high resistances overall. Although the local mass transport resistance may not limit ETFECS materials, the electrode structure may be limiting, and microscopy after MEA operation showed morphological loss within the catalyst layer. Carbon was incorporated into the catalyst layer using different carbon types and at different carbon-to-catalyst ratios. The addition of Ketjenblack to the PtNiNWs was found to result in the greatest improvement at high current density (Figure 4). Although performance in the kinetic region remained relatively unchanged, a Pt-Ni to carbon ratio of 2:1 resulted in a 30% improvement at 0.6 V. Microscopy also has been used to study catalyst layer morphology and ionomer integration.

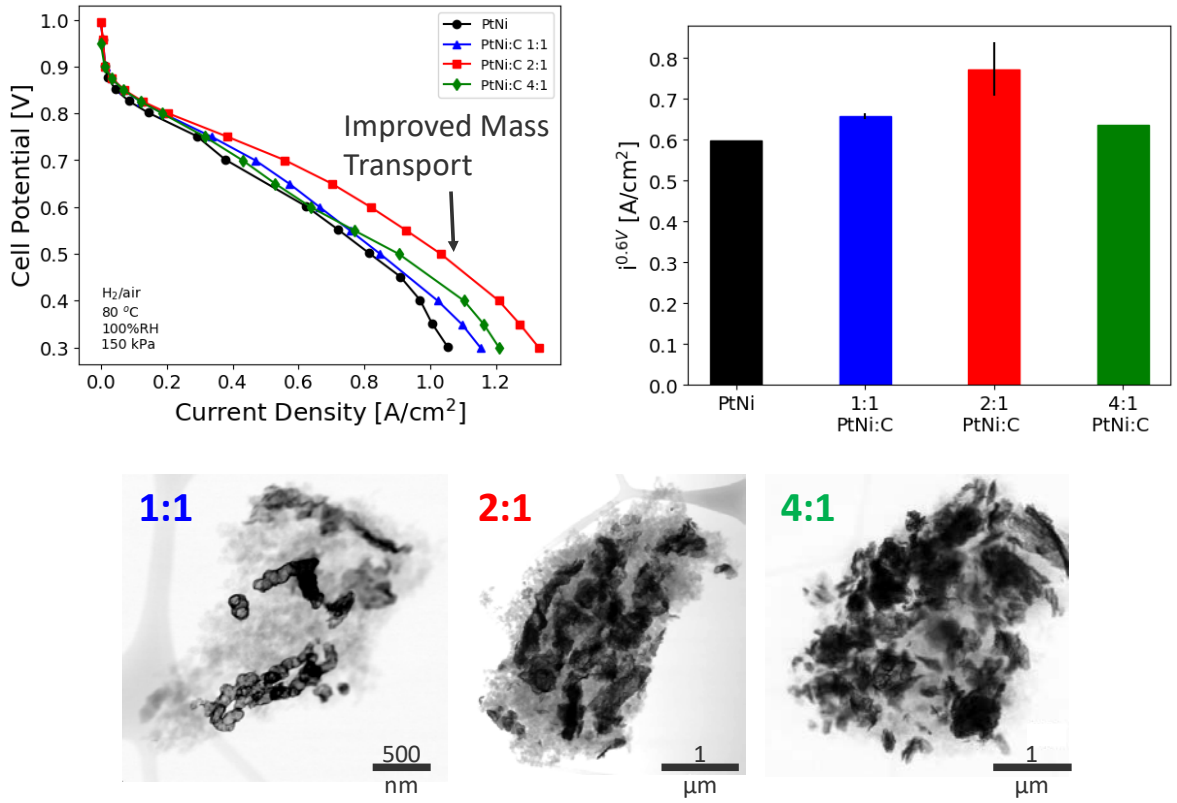


Figure 4. Polarization curves, current densities at 0.6 V, and microscopy of Pt-Ni catalyst layers with carbon (Ketjenblack) incorporated at a Pt-Ni to carbon ratio of 1:1 (blue), 2:1 (red), and 4:1 (green).

CONCLUSIONS AND UPCOMING ACTIVITIES

The project has demonstrated the ability to achieve high-performance MEAs with ALD-synthesized PtNiNWs. ALD synthesis has further demonstrated reproducibility and materials produced at a reasonable scale. Performance and durability have been significantly improved with annealing and pre-leaching. MEAs with ETFECS materials have demonstrated mass activities beyond the DOE 2020 performance target and with durability greater than the support stability target. Future work includes the following.

- 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 2018 PUBLICATIONS/PRESENTATIONS

1. S.M. Alia, C. Ngo, S. Shulda, M.-A. Ha, A.A. Dameron, J. Nelson Weker, K.C. Neyerlin, S.S. Kocha, S. Pylypenko, B.S. Pivovar, "Exceptional Oxygen Reduction Reaction Activity and Durability of Platinum-Nickel Nanowires Through Synthesis and Post-Treatment Optimization," *ACS Omega* 2, no. 4 (2017): 1408–1418. doi: 10.1021/acsomega.7b00054.
2. S.A. Mauger, K.C. Neyerlin, S.M. Alia, C. Ngo, S.K. Babu, K.E. Hurst, S. Pylypenkno, S. Lister, B.S. Pivovar, "Fuel Cell Performance Implications of Membrane Electrode Assembly Fabrication with Platinum-Nickel Nanowire Catalysts," *J. Electrochem. Soc.* 165, no. 3 (2018): F238–F245. doi:10.1149/2.1061803jes.
3. C. Ngo, M.J. Dzara, S. Shulda, S. Pylypenko, "Spectroscopy and Microscopy for Characterization of Fuel Cell Catalysts," Chapter 15, *Electrocatalysts for Low Temperature Fuel Cells: Fundamentals and Recent Trends* (Wiley, 2017): 443.
4. S. Pylypenko, "Characterization of Electrocatalytic Materials: Challenges and Novel Approaches," New Mexico Chapter AVS symposium, Albuquerque, NM, May 16, 2017.
5. S. Pylypenko, "Challenges and Novel Approaches in Multiscale Characterization of Active Materials," Forschungszentrum Juelich, Germany, July 12, 2017.
6. S.M. Shulda, J.N. Weker, C. Ngo, S.A. Mauger, S.M. Alia, K.C. Neyerlin, B.S. Pivovar, S. Pylypenko, "Chemical and Structural Investigation of Pt-Ni Extended Surface Catalyst Electrodes," 232nd ECS Meeting, National Harbor, MD, October 4, 2017.
7. S.M. Alia, K.C. Neyerlin, K. Hurst, J.W. Zack, S.A. Mauger, W.W. McNeary, A. Weimer, W. Medlin, S.M. Shulda, C. Ngo, S. Pylypenko, B.S. Pivovar, "Development and Implementation of Catalysts and Membrane Electrode Assemblies Based on Extended Thin Film Electrocatalysts," 232nd ECS Meeting, National Harbor, MD, October 4, 2017.
8. S. Pylypenko, "Multi-scale characterization of nanowire-based electrocatalysts," Rocky Mountain ACS regional meeting, Loveland, CO, October 25–28, 2017.
9. W. McNeary, K. Hurst, S.M. Alia, S.A. Mauger, K.C. Neyerlin, C. Ngo, J.W. Medlin, A.W. Weimer, S. Pylypenko, K.J. Buechler, B.S. Pivovar, "Atomic Layer Deposition for Extended Surface Electrocatalyst Development," 2017 AIChE Annual Meeting, Minneapolis, MN, November 2, 2017.
10. W. McNeary, K. Hurst, S.M. Alia, S.A. Mauger, K.C. Neyerlin, C. Ngo, J.W. Medlin, A.W. Weimer, S. Pylypenko, K.J. Buechler, B.S. Pivovar, "Extended Thin Film Electrocatalyst Structures Via Pt Atomic Layer Deposition," 2017 AIChE Annual Meeting, Minneapolis, MN, November 2, 2017.
11. S. Zaccarine, C. Ngo, S. Shulda, S. Pylypenko, S. Mauger, S. Alia, K.C. Neyerlin, B. Pivovar, S. Pylypenko, "Characterization of extended surface catalysts for optimization of performance in polymer electrolyte membrane fuel cells," GRADS, CSM, April 2018.

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