

## V.D.2 Rationally Designed Catalyst Layers for PEMFC Performance Optimization

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Project End Date: April 30, 2016

- Develop a method to impart proton conductivity to high surface area carbon supports

### 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:

- Durability
- Cost
- Performance

### Technical Targets

The technical targets for this project are listed in Table 1.

**TABLE 1.** Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Metric	Units	DOE 2020 Target	Project Status
ORR mass activity	A/mg <sub>PGM</sub> @ 900 mV <sub>IR-free</sub>	≥0.44	0.57
ORR specific activity	μA/cm <sup>2</sup> <sub>PGM</sub>	720	986
PGM total loading	mg <sub>PGM</sub> /cm <sup>2</sup> <sub>geo</sub>	≤0.125	0.092 (cathode only)
MEA performance	mA/cm <sup>2</sup> @ 800 mV	≥300	298

### FY 2014 Accomplishments

- Standard Pt/C, annealed Pt/C, and d-PtNi/C catalysts and catalyst-coated membranes (CCMs) containing approximately 0.1 mg Pt/cm<sup>2</sup> loading of these cathode catalysts have been fabricated, tested, and characterized.
- Three iterations of the d-PtNi with decreasing Ni content have been synthesized and fabricated into CCMs. Each iteration showed increasing ORR mass activity (0.53 A/mg-Pt to 0.57 A/mg-Pt) and improved H<sub>2</sub>/air CCM performance at >1 A/cm<sup>2</sup>.
- The best ORR mass activity obtained for the d-PtNi/C in a CCM was 0.57 A/mg-Pt, which exceeds the DOE 2020 target.
- Mass transport losses are higher with d-PtNi/C and annealed Pt/C-based cathodes as compared to conventional Pt/C.
- Modeling effort shows that mass transport losses are related to lower surface area enhancement factors (cathode catalyst electrochemically active surface area [ECA]/electrode area) of d-PtNi.

### Overall Objectives

To realize the oxygen reduction reaction (ORR) mass activity benefits of dealloyed cathode electrocatalysts in membrane electrode assemblies (MEAs) and stacks operating at high current densities and on air and at low platinum group metal (PGM) loading (≤0.1 mg<sub>Pt</sub>/cm<sup>2</sup> on the cathode).

### Fiscal Year (FY) 2014 Objectives

- Determine catalyst and cathode layer properties responsible for decline in dealloyed PtNi cathode air performance at >1 A/cm<sup>2</sup>
- Develop a cathode catalyst layer model for dealloyed catalyst

- Annealed Pt/C inks show smaller carbon agglomerates and a more branched and open secondary carbon structure than d-PtNi/C inks. This may impact interaction of ionomer with catalyst surface and consequently mass transport to catalytic sites.
- A functionalized carbon black with promising proton conductivity has been synthesized to address performance of low surface enhancement factor catalysts.



## INTRODUCTION

One of the major cost contributors to polymer electrolyte membrane fuel cell (PEMFC) systems for automotive and stationary power applications is the PGM cathode electrocatalyst [1]. The high cost of the cathode electrocatalyst results from the high loadings of catalyst necessary to overcome the limitations of low ORR activity, low utilization of PGM, and loss of activity with operating time. Alloying platinum with base metals (e.g., cobalt, iron, and nickel) is well known to improve its intrinsic ORR activity [2]. While ORR activities exceeding the DOE 2017 targets ( $>0.44$  A/mg PGM and  $720 \mu\text{A}/\text{cm}^2$  @ 900 mV) have been demonstrated for high-surface-area-carbon-supported Pt alloy and core-shell nanoparticle catalysts in aqueous cell rotating disk electrode tests [3], some as high as  $5.75$  A/mg-Pt [4], the full activities and performance of these promising catalysts have yet to be achieved in MEAs, especially when operating at realistic current densities and on air rather than oxygen.

There are several possible reasons the full potentials of the advanced alloy, de-alloyed, and core-shell materials have not been realized in MEAs operating on air and at current densities  $>1$  A/cm<sup>2</sup>. One may arise from the complex requirements for full utilization of the electrocatalytic sites and for adequate reactant transport in the MEA cathode layer. These requirements are easily met in the fuel cell at low current densities in an oxygen environment where the electrocatalytic reaction rate dominates the voltage losses and demands on transport to the reactive sites are easily filled. Fulfillment of these requirements at high current densities in an MEA cathode relies on optimization of the electrode composition and structure to balance the structure of the proton-conducting phase, the electron-conducting phase, and the distribution and size of pores for reactant/product diffusion. This optimization is a lengthy, trial-and-error process and has taken several years for the traditional Pt-only cathode layers. The goal of this project is to optimize the electrode layer composition, structure, and materials properties of cathodes based on advanced alloy catalysts so their intrinsically high performance for the ORR can be translated into performances at high current densities and on air which exceed simultaneously the DOE performance, durability, and cost targets for PEMFCs for automotive applications.

## APPROACH

The advanced Pt alloy catalyst chosen for this project consists of a range of dealloyed PtNi (d-PtNi) catalysts developed by Johnson Matthey Fuel Cells in the General Motors-led project (FC087). A range of PtNi alloys were chosen with different Pt:Ni ratios in order to investigate the impact of base metal content on mass activity and performance at high current density on air. The key catalyst characteristics and metrics are:

- Catalyst deposited as nanoparticles onto Ketjenblack<sup>®</sup> supports
- Catalyst deposition chemistry is proven and via methods scalable to commercial levels
- Mass activity exceeds DOE 2020 target
- Mass activity loss after 30,000—0.60 to 1.0 V cycles exceeds the DOE kinetic stability target.

This project is following a multi-pronged approach to achieving the goals. The approach to translating these high ORR mass activities to MEA performance at automotive-relevant high current densities is to first determine the property or properties of the electrode/catalyst that limit(s) the high current density/air performance of electrodes based on this catalyst type. The approach and techniques being used to elucidate these properties are:

- In-cell diagnostics of d-PtNi versus high-surface-area Pt (non-annealed Pt) and Pt of comparable ECA (annealed Pt).
- In situ and ex situ characterization: transmission electron microscopy (TEM), cryogenic TEM, dynamic light scattering, ultra-small angle X-ray scattering, and X-ray absorption spectroscopy to:
  - Study the dispersion of d-PtNi/C catalyst aggregates and the perfluorinated sulfonic acid ionomer particles in liquid media and in electrodes and compare them to Pt/C-based inks and electrodes.
  - Study the effects of solvent type and solvent removal processes on the agglomerate structure of the electrodes.
- Modeling to correlate electrode performance under a variety of conditions to electrode structure and morphology.

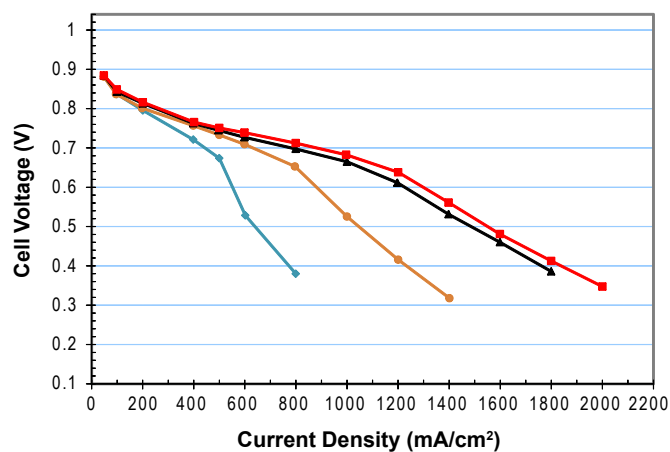
Once the performance-limiting properties are determined, the project approach is to use computational modeling to guide the design of the catalyst layer composition and structure and carbon support functionality to mitigate the performance limitations. Tools which can be used to modify the electrode structure are the use of alternative ink compositions and solvent removal processes to minimize Ni corrosion and result in the optimum agglomerate structure in d-PtNi/C-based electrodes. An

approach being pursued to allow greater flexibility in the design of the electrode structure is the decoupling of the proton-conducting and binder electrode components by imparting proton conductivity to the carbon support through functionalization.

## RESULTS

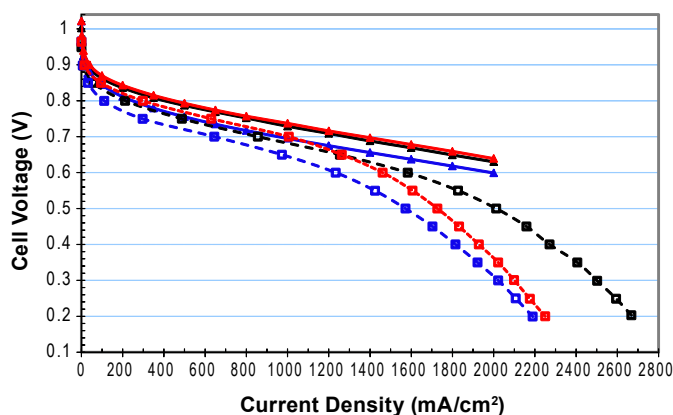
Four iterations of the d-PtNi/C with decreasing Ni content were synthesized and fabricated into CCMs. Each iteration showed improved ORR mass activity (0.53 A/mg-Pt to 0.57 A/mg-Pt) and improved H<sub>2</sub>/air performance at >1 A/cm<sup>2</sup> (Figure 1). The best ORR mass activity obtained for the d-PtNi/C in a CCM was 0.57 A/mg-Pt, which exceeds the DOE 2020 target (0.44 A/mg-Pt).

To determine the electrode property or properties limiting the performance of the d-PtNi/C-based cathode and decouple the effect of catalyst surface area from an effect unique to the base metal-containing catalysts, the standard Pt/C catalyst of 2.0 nm mean Pt particle diameter was annealed to grow the mean particle size to 5.8 nm which is comparable to that of the d-PtNi/C catalysts (5.1 to 5.8 nm). CCMs with cathodes comprised of standard Pt/C, annealed Pt/C, and d-PtNi/C at loadings of 0.1 mg Pt/cm<sup>2</sup> and an ionomer to carbon ratio of 0.8 were fabricated, tested, and characterized under a variety of test conditions and using numerous characterization techniques. The diagnostics included hydrogen pump, hydrogen crossover, ECA by CO stripping, cyclic voltammetry and impedance characterization under nitrogen and air atmospheres. The various test conditions included different oxygen concentrations on the cathode (pure oxygen to 1% oxygen), temperatures (60°C, 70°C, 80°C, and 90°C), back pressures (100, 150, 200, and 250 kPa<sub>abs</sub>), and relative humidities (100,

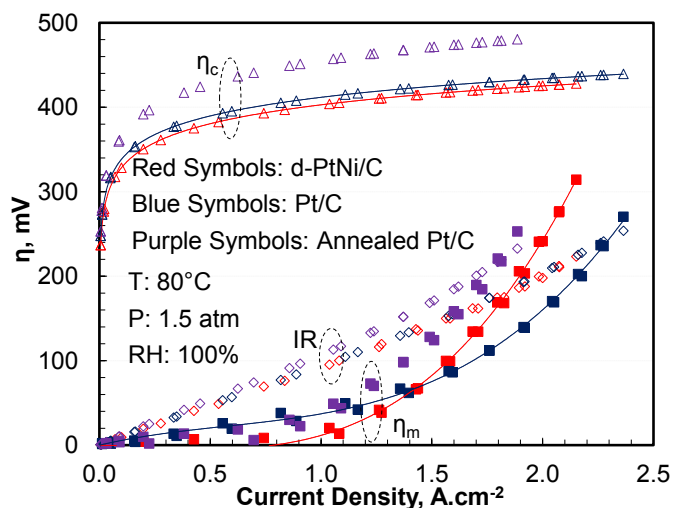


**FIGURE 1.** Hydrogen-air polarization curves at 80°C, 100% relative humidity, and 2 atm for MEAs with subsequent versions of the d-PtNi/C cathode catalyst (blue – first version; red – latest version) at a cathode loading of ~0.09 mgPt/cm<sup>2</sup>.

85, 55, and 30%). The polarization curves for MEAs with d-PtNi/C, standard non-annealed Pt/C, and annealed Pt/C cathode catalysts are shown in Figure 2. Modeling of these data to determine the sources of the observed voltage losses (i.e., purely resistive, kinetic, or mass transport) showed that mass transport losses are higher with d-PtNi/C and annealed Pt/C-based cathodes as compared to standard non-annealed Pt/C, while the kinetic losses are lower for d-PtNi/C and standard non-annealed Pt/C as compared to the annealed Pt/C due to higher area-specific activity and higher ECA, respectively (Figure 3). The modeling effort showed that the mass transport losses, particularly under fully humidified conditions, are related to lower surface area enhancement



**FIGURE 2.** Hydrogen-oxygen (solid lines) and hydrogen-air (dashed lines) polarization curves at 80°C, 100% relative humidity, and 1.5 atm for MEAs with d-PtNi/C, non-annealed Pt/C, and annealed Pt/C cathode catalysts at a cathode loading of ~0.09 mgPt/cm<sup>2</sup>.



**FIGURE 3.** Breakdown of overpotentials for hydrogen-air polarization curves taken at 80°C, 100% relative humidity, and 1.5 atm for MEAs with d-PtNi/C (red), non-annealed Pt/C (blue), and annealed Pt/C (purple) cathode catalysts at a cathode loading of ~0.09 mgPt/cm<sup>2</sup>.

factors (ECA/electrode area) of the d-PtNi/C-based cathodes and indicated a relatively minor role of Ni in the increased mass transport losses.

Catalyst-ionomer inks with ionomer to carbon ratios of 0.8, 1.0, and 1.2 and with varied concentration of solids and ink solvent (water or water-propanol mixtures) were characterized by dynamic light scattering, ultra-small angle X-ray scattering (USAXS), and cryogenic TEM to determine carbon-ionomer aggregate and agglomerate size distributions. As shown in Figure 4, the aqueous annealed Pt/C inks show smaller carbon agglomerates and a more branched and open secondary carbon structure than d-PtNi/C inks of equivalent formulation. It was also found, by USAXS, that the type of solvent in the inks changes the aggregate structure of the d-PtNi/C inks, but not that of the annealed Pt/C inks (Figure 4). This is an effect which can be exploited to improve the transport properties of the d-PtNi/C-based cathodes.

A diazonium coupling reaction was used to functionalize carbon black and catalyzed carbon black with sulfonate groups to impart proton conductivity to decrease the reliance on ionomer for adequate proton conductivity in the cathode layer [5]. Functionalization levels of 15 wt% for the annealed Pt/C catalyst were verified by thermogravimetric analysis. A proton conductivity of 0.05 S/cm was measured ex situ for a catalyst layer comprised of sulfonate-functionalized carbon black and a Teflon® binder.

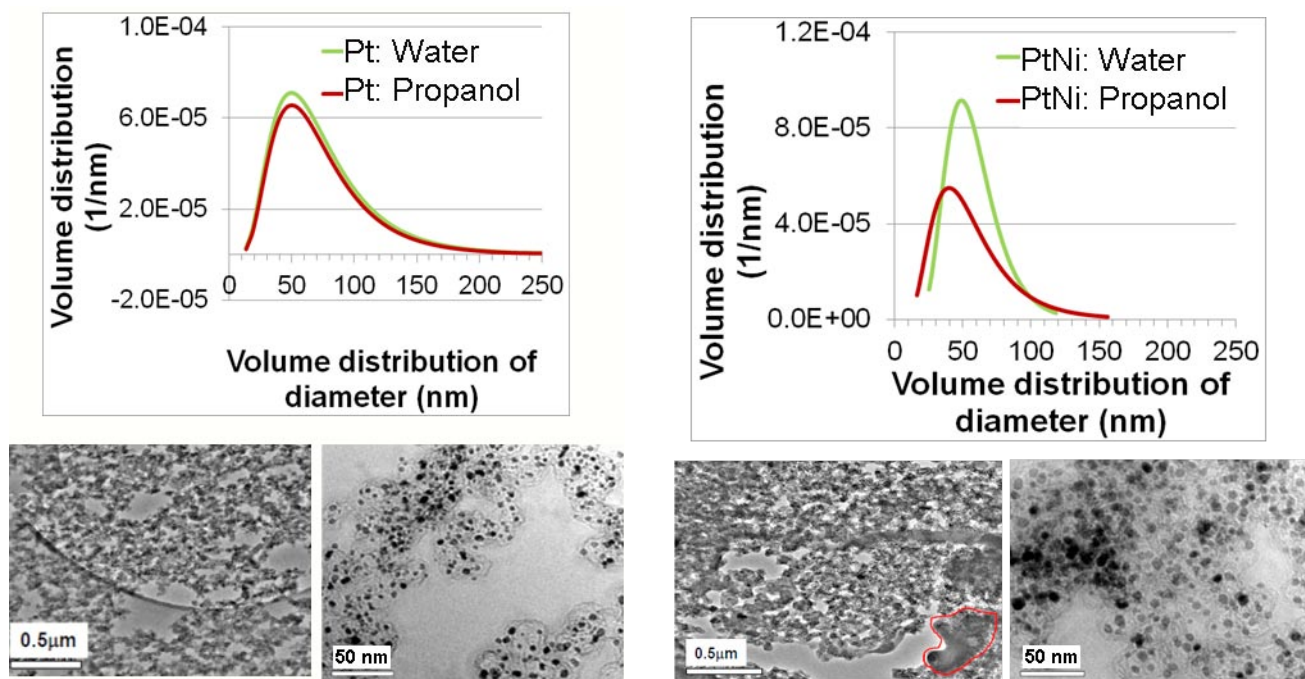
## CONCLUSIONS AND FUTURE DIRECTIONS

### Conclusions

- Mass transport losses are higher with d-PtNi/C and annealed Pt/C-based cathodes as compared to conventional Pt/C.
- Modeling of the cell losses suggest that mass transport losses are related to the lower surface area enhancement factors (ECA/electrode area) of the d-PtNi and annealed Pt/C.
- Annealed Pt/C inks show smaller carbon agglomerates and a more branched and open secondary carbon structure than d-PtNi/C inks. This may impact interaction of ionomer with catalyst surface and consequently mass transport to catalytic sites.
- A functionalized carbon black with promising proton conductivity and low relative humidity performance has been synthesized to address performance of low-SEF catalysts.

### Future Directions

- Determine if Ni leached from d-PtNi/C during electrode fabrication is impacting electrode structure/properties:



**FIGURE 4.** Ultra-small angle X-ray scattering-determined agglomerate distributions of water-ionomer and water-propanol-ionomer catalyst inks and cryogenic transmission electron micrographs of water-ionomer-catalyst inks: annealed Pt/C (left) vs. d-PtNi/C (right).

- Experiments are planned to add Ni<sup>2+</sup> to Pt/C electrode layers
- Improve performance at high current densities for low-SEF electrodes with different ionomer content, equivalent weight ionomer, ink solvent, and/or proton-conducting carbon supports:
  - d-PtNi/C-containing CCMs with new ionomer/carbon ratio have been delivered to UTRC for testing/diagnostics
  - Electrodes using proton-conducting supports are being fabricated by IUPUI
  - The effect of the testing conditions, such as cell pressure and cell temperature, will be examined.
- Complete USAXS, cryo-TEM, TEM analysis of ink and electrodes for input into the model of electrode structure.
- Additional analysis of diagnostic data for annealed Pt/C and d-PtNi/C electrode layers and CCMs:
  - Impedance spectroscopy for breakdown of mass transport overpotentials for GDL, catalyst layer pores, and ionomer.
  - Steady-state oxide coverage measurements, kinetics of oxide formation.
- Determine proton conductivity and electronic conductivity as a function of temperature and relative humidity (ex situ) for electrodes made from the various catalysts and inks.

## FY 2014 PUBLICATIONS/PRESENTATIONS

1. Nancy Kariuki, Deborah Myers, and James Gilbert, “X-ray Scattering and Absorption Studies of Polymer Electrolyte Fuel Cell Cathode Electrocatalysts”, Abstract and Invited Presentation, 248<sup>th</sup> American Chemical Society National Meeting, San Francisco, California, August 10–14, 2014.
2. Deborah Myers, James Gilbert, Nancy Kariuki, Xiaoping Wang, and A. Jeremy Kropf, “Durability of Low-Temperature Fuel Cell Electrocatalysts”, Abstract and Invited Presentation, 225<sup>th</sup> Electrochemical Society Meeting, Orlando, Florida, May 11–16, 2014.
3. Deborah J. Myers, Nancy N. Kariuki, A. Jeremy Kropf, and James A. Gilbert, “In situ X-ray absorption and scattering studies of proton exchange membrane fuel cell electrocatalysts”, Abstract and Invited Presentation, *In Situ Studies of Fuel Cell Materials and Devices Symposium*, 247<sup>th</sup> American Chemical Society National Meeting, Dallas, Texas, March 19, 2014.
4. Deborah Myers, Nancy Kariuki, and Xiaoping Wang, “The Effects of Polymer Electrolyte Fuel Cell Fabrication on Pt and Pt alloy Electrocatalysts”, Abstract and Presentation, 224<sup>th</sup> Electrochemical Society Meeting, San Francisco, California, October 27 – November 1, 2013.
5. Lili Sun, Zhefei Li, Andrew Saab, and Jian Xie, “Improving MEA Kinetic Performance through Removing Nafion Ionomer Binders in a Catalyst Layer”, Abstract and Presentation, 224<sup>th</sup> Electrochemical Society Meeting, San Francisco, California, October 27 – November 1, 2013.

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