

V.D.3 Rationally Designed Catalyst Layers for PEMFC Performance Optimization

Deborah J. Myers (Primary Contact),
Nancy N. Kariuki, Rajesh Ahluwalia,
Xiaohua Wang, Jui-Kun Peng, and C. Firat Cetinbas
Argonne National Laboratory
9700 S. Cass Avenue
Lemont, IL 60439
Phone: (630) 252-4261
Email: dmyers@anl.gov

DOE Manager: Nancy L. Garland
Phone: (202) 586-5673
Email: Nancy.Garland@ee.doe.gov

Subcontractors:

- Jonathan Sharman, Alex Martinez, Dash Fongalland, Brian Theobald, L. Smith, D. Ozkaya, M. Gutierrez, and Graham Hards, Johnson Matthey Fuel Cells, Sonning Common, United Kingdom
- Zhiwei Yang and Michael Perry, United Technologies Research Center, East Hartford, CT
- Paulo Ferreira, Kang Yu, Somaye Rasouli, Andres Godoy, and Daniel Groom, University of Texas at Austin, Austin, TX
- Jian Xie, Le Xin, Zhefei Li, Yadong Liu, Yuan Zhou, and Fan Yang, Indiana University Purdue University Indianapolis, Indianapolis, IN

Project Start Date: May 1, 2013
Project End Date: April 30, 2016

Overall Objectives

- Realize the oxygen reduction reaction (ORR) mass activity benefits of advanced Pt-based cathode electrocatalysts in membrane electrode assemblies (MEAs) and stacks operating at high current densities and on air and at low precious group metal (PGM) loading (≤ 0.1 mgPt/cm² on cathode).
- Determine the source(s) of performance limitations of de-alloyed PtNi (d-PtNi)-containing MEAs at high current densities ($>1,000$ mA/cm²) when operating on air.
- Design and develop an electrode layer composition and/or structure, based on in-cell diagnostics, advanced characterization, and performance modeling to exceed the technical targets for MEAs for transportation applications.

Fiscal Year (FY) 2016 Objectives

- Determine effect of the equivalent weight (EW) of the ionomer in the cathode catalyst layer (CCL) on cell performance and performance durability.
- Diagnose source of performance loss with Ni²⁺ contamination in CCL utilizing X-ray scattering, water uptake measurements, and doping Ni²⁺ into Pt-based CCLs.
- Diagnose source(s) of activity losses of d-PtNi with functionalized support.
- Calculate porosities and diffusivities of Pt/C and d-PtNi/C electrodes utilizing X-ray tomography and transmission electron microscopy images, image analysis, and image reconstructions.
- Achieve a hydrogen-air current density of 1,250 mA/cm² at 0.675 V, under differential cell conditions (high stoichiometries), using cells with 0.125 mg-Pt/cm² fabricated using the best compositions and preparation procedures developed throughout the project.
- Determine the durability of cells with d-PtNi cathode catalysts and total cell Pt loadings of <0.125 mg-Pt/cm² using DOE-recommended protocols and alternative protocols. Performance and durability goals are 6.5 kW/g-Pt at peak power and $<10\%$ drop in power after application of the U.S. DRIVE Fuel Cell Tech Team Cell (FCTT) component accelerated stress tests (ASTs).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cell section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan.

- (C) Performance
- (B) Cost
- (A) Durability

Technical Targets

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

FY 2016 Accomplishments

- Achieved a hydrogen-air current density of 1,259 mA/cm² at 0.675 V with cathode loading of 0.112 mg-Pt/cm² and under differential conditions. Achieved 1,060 mA/cm² at 0.675 V with a total cell

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

Metric/Units	DOE 2020 Target	Project Status with High Anode Loading	Project Status with Low Anode Loading
Mass activity ($A/mg_{PGM} @ 0.9mV_{IR-free}$)	≥ 0.44	0.59	0.6
Specific activity ($\mu A/cm^2_{PGM} @ 0.9 mV_{IR-free}$)	≥ 720	1,151	1,015
PGM total loading ($mg-PGM/cm^2_{geo}$)	≤ 0.125	0.112 cath.	0.1159 cath. 0.018 anode
MEA performance ($mA/cm^2_{geo} @ 800 mV$) FCTT Pol Curve	≥ 300	347 n/d	371 200
MEA performance ($mW/cm^2_{geo} @ 675 mV$) FCTT Pol Curve	$\geq 1,000$	878 n/d	850 672
MEA performance ($mW/cm^2_{geo} @ 600 mV$) FCTT Pol Curve	$\geq 1,000$	999 n/d	1,025 750

n/d – not determined

loading of 0.1107 mg-Pt/cm² when using a modified FCTT protocol with higher cell operating temperature, allowing cell to meet Q/ΔT targets. (Achieved 890 mA/cm² at 0.675V using standard FCTT protocol).

- MEA with d-PtNi/C cathode at a loading of 0.1159 mg-Pt/cm² and a Pt/C anode at a loading of 0.018 mg-Pt/cm² achieved 7.7 kW/g-Pt at peak power under differential conditions and 6.2 kW/g-Pt under standard DOE FCTT-recommended polarization curve protocol.
- Achieved a 7% loss in peak power after 30,000 triangle cycles (0.6–0.925 V, 50 mV/s) and 22% loss in peak power after 30,000 trapezoid cycles (0.6–0.95 V, 700 mV/s, 6 s/cycle).



INTRODUCTION

One of the major contributors to the cost of 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 mass activities exceeding the DOE 2020 targets ($>0.44 A/mg$ PGM and $720 \mu A/cm^2$ at 900 mV) have been demonstrated for numerous Pt alloy and core-shell nanoparticle catalysts [3], the full high current density performance of CCLs based on low loadings of these promising catalysts has yet to be achieved in MEAs. There are several possible reasons the full potentials of these advanced catalysts have not been realized in MEAs, such as inadequate transport of protons and oxygen to the catalytic sites arising from less than optimum spatial distribution of

ionomer, catalyst, and pores. The goal of this project is to optimize the composition, structure, and materials properties of cathodes based on an advanced cathode catalyst to translate the catalyst's intrinsically high ORR mass activity into high performance at peak power. The advanced catalyst chosen for this project is dealloyed PtNi (d-PtNi) developed by Johnson Matthey Fuel Cells within a DOE-supported General Motors project [3].

APPROACH

The overall approach of the project is to:

- Determine the properties of advanced alloy-based catalysts and/or cathode catalyst layers that limit the high current density/air performance using:
 - *In-cell* diagnostics of d-PtNi/C versus high surface area Pt/C and Pt/C of comparable electrochemically active surface area.
 - A suite of in situ and ex situ techniques, such as transmission electron microscopy, cryogenic transmission electron microscopy, dynamic light scattering, ultra-small angle X-ray scattering, X-ray absorption spectroscopy, X-ray tomography, and porosimetry.
- Design the catalyst layer composition and structure and support functionality to mitigate the performance limitations, guided by computational modeling, by:
 - Studying the dispersion of d-PtNi/C catalyst aggregates and the ionomer particles in liquid media and in electrodes and compare them to Pt/C-based inks and electrodes.
 - Developing an ink composition and/or ink processing (e.g., solvent removal process) that result in optimum agglomerate structure in d-PtNi/C-based electrodes.

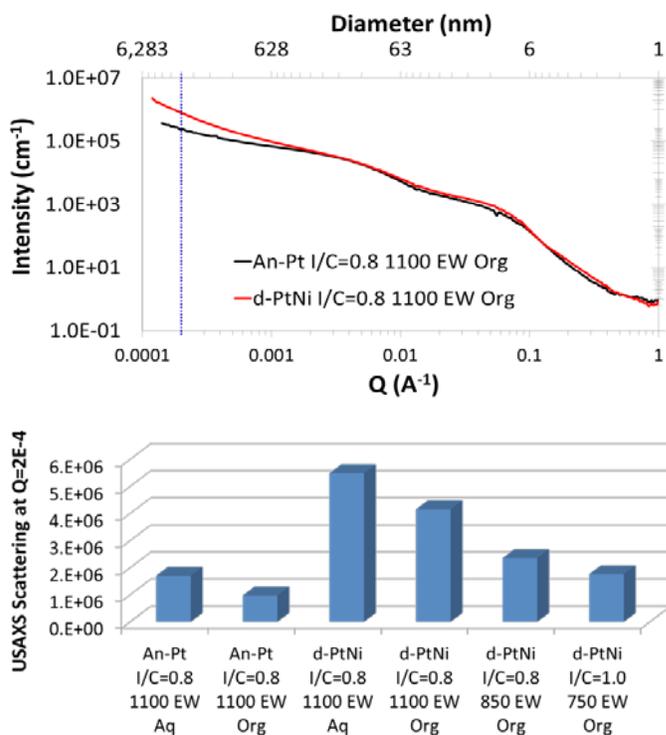
- Developing the catalyst support surface functionality to increase the performance of the catalyst and cathode – to decouple proton conductivity from ionomer content.

The d-PtNi catalysts were synthesized by Johnson Matthey Fuel Cells using a catalyst precursor comprised of 5.4 nm mean diameter PtNi₃ alloy particles deposited on Ketjen black carbon, via a commercially-scalable method, followed by annealing to drive alloy formation. The resulting catalyst precursor is dealloyed via an acid treatment step to leach Ni to form a catalyst with an approximate composition of Pt₃Ni₂ and a Pt loading on the carbon support of approximately 30 wt%. As shown in Table 1, the ORR mass activity of this catalyst in an MEA far exceeds the DOE 2020 target.

RESULTS

The effects of ionomer EW on the agglomerate structure in catalyst-ionomer-solvent inks, agglomerate structure in electrodes, and CCL performance and performance durability under a variety of oxygen partial pressures and relative humidities (RHs) were determined for the d-PtNi/C catalyst and, for comparison, for a Pt/C catalyst with a particle size distribution comparable to that of the d-PtNi/C (An-Pt/C). The following summarizes the results of these characterization and performance studies.

- Lower EW ionomer in inks:
 - In general causes greater break-up of agglomerate structure than the standard 1100 EW ionomer, effect is dependent on I/C (Figure 1)
 - Best overall cell performance under high and low RHs observed for lowest EW ionomer and intermediate I/C (1.0) (Figure 2)
- Functionalization of carbon support with –SO₃H groups improves low RH performance, but decreases catalyst mass activity.
 - Lower mass activity due to adsorption of sulfur species on Pt surface and to loss of both Pt and Ni from catalyst during functionalization
- Performance Status (cells with ~0.1 mg-Pt/cm² anode loading):
 - Differential conditions, organic ink, I/C = 0.8, acid-washed CCM: 1,300 mA/cm² at 0.675 V
- Performance Status (cells with ~0.025 mg-Pt/cm² anode loading):
 - Differential conditions, organic ink, I/C = 1.0, 850 EW, acid-washed CCM: 1,259 mA/cm² at 0.675 V



USAXS – Ultra-small angle X-ray scattering

FIGURE 1. (Top) Ultra-small angle X-ray scattering curves of d-PtNi/C and An-Pt/C electrode layers. Vertical line shows the scattering angle for ~3 μm diameter agglomerates. The scattering intensity at this angle is plotted in the (Bottom). (Bottom) Effect of catalyst type, catalyst ink solvent, and ionomer EW on the prevalence of large agglomerates (>3 μm equivalent diameter) in the electrode structures.

- FCTT polarization curve:
 - 1,060 mA/cm² at 0.675 V with a total cell loading of 0.1107 mg-Pt/cm² at 90°C
 - 890 mA/cm² at 0.675 V under standard FCTT conditions (80°C)
- Durability status after 30,000 AST cycles (cells with ~0.025 mg-Pt/cm² anode loading) (Figure 3)
 - Mass activity loss: 34%; electrochemical surface area (ECA) loss: 49%, (0.6–1.0 V, 50 mV/s, triangle, limited diagnostics)
 - Mass activity loss: 26%; ECA loss: 26%; Voltage decrease at 1.5 A/cm²: 33 mV (0.6–0.925 V, 50 mV/s, triangle, limited diagnostics)
 - Mass activity loss: 46%; ECA loss: 51%; Voltage decrease at 1.5 A/cm²: 121 mV (0.6–0.95 V, 700 mV/s trapezoid, extensive diagnostics)

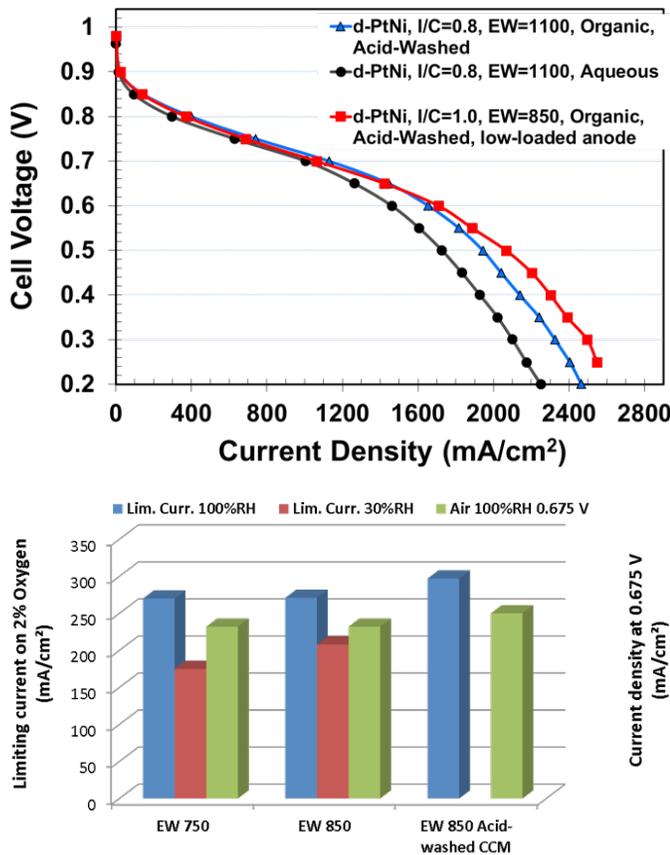


FIGURE 2. (Top) Hydrogen-air polarization curves with 0.1 mg-Pt/cm² d-PtNi/C cathode and either 0.1 mg-Pt/cm² or <0.02 mg-Pt/cm² Pt/C anode, 80°C, 150 kPa (abs.), high and fixed flow for differential conditions (3 slpm air). (Bottom) Limiting current on 2% oxygen at 80°C at 100% RH and 30% RH and current density on air at 0.675 V. Conditions: 150 kPa, 80°C, perfluorosulfonic acid ionomer to carbon ratio (I/C) = 1.0 in cathode, organic solvent used in cathode catalyst ink.

CONCLUSIONS AND FUTURE DIRECTIONS

Issues with the d-PtNi/C catalyst-based electrodes are drop-off in performance at >1,000 mA/cm² (i.e., not maintaining mass activity benefit relative to high-surface area Pt/C) under high and intermediate humidity conditions and a severe drop-off at low RHs. The sources of these issues and potential solutions to the issues are:

- Mass transport to low loadings of large particles.
 - Can be mitigated with smaller particles that are >~4 nm to insure stability against dissolution-related ECA loss.
- Sensitivity to low humidity conditions is unique to d-PtNi/C and can be partially mitigated with increased ionomer content, organic solvents, and lower EW ionomer which improve dispersion of d-PtNi/C particles, and can be greatly improved with acid treatment of CCM.

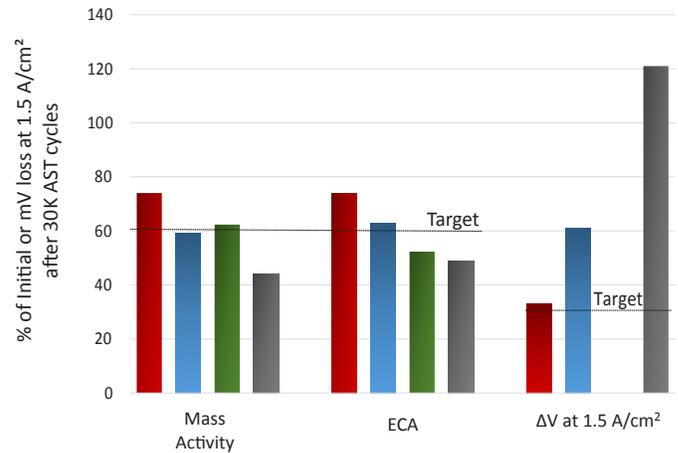


FIGURE 3. Durability results for MEAs with -0.1 mg-Pt/cm² d-PtNi/C cathode catalyst and -0.02 mg-Pt/cm² Pt/C anode. Organic solvent and 850 EW ionomer with I/C = 1.0 used in cathode catalyst ink. CCMs were acid-washed after fabrication. Red: 0.6–0.925 V triangle, 50 mV/s; limited intra-cycle diagnostics Blue: 0.6–0.925 V triangle, 50 mV/s; extensive intra-cycle diagnostics Green: 0.6–1.0 V triangle, 50 mV/s; limited intra-cycle diagnostics Grey: 0.6–0.95 trapezoid, 700 mV/s; extensive intra-cycle diagnostics

- Results indicate that Ni²⁺ in ionomer, leached during ink and CCM fabrication is altering the structure of the ionomer, which alters the agglomerate structure of cathode catalyst layer, decreasing mass transport, especially at low RH.
 - More aggressive leaching of Ni²⁺ prior to ink synthesis and CCM fabrication can improve d-PtNi/C cathode performance, especially under dry conditions.
- Leaching of Ni from particles continues during ASTs, especially when upper potential of the AST is 1.0 V
 - Mitigate through control of highest voltage encountered by cathode.
 - Continue development of catalyst particles with more uniform morphology, intra-particle composition distribution, more uniform Pt shell.
- d-PtNi/C shows higher ECA, mass activity, and high current density performance loss than An-Pt/C when subjected to catalyst ASTs.
- Acid-washing d-PtNi/C-containing CCMs does not adversely affect ECA and mass activity decay with AST cycling and decreases low and high current density performance decay.
- The decay rates with AST cycling were comparable for d-PtNi/C-containing electrodes containing either 850 or 1100 EW ionomer.

- Intra-AST-cycling diagnostics, such as CO stripping for ECA measurement, dramatically increases ECA, mass activity, and high and low current density performance loss of the d-PtNi/C-based CCL (Figure 3).
- New trapezoid AST causes more degradation of ECA, mass activity, and air performance than DOE 0.6–1.0 V, 50 mV/s triangle AST and General Motors-suggested 0.6–0.925 V triangle AST (Figure 3).
- d-PtNi/C can meet ECA and mass activity durability targets and approaches high current density performance loss durability target (30 mV) when limiting upper potential of triangle AST to 0.925 V (Figure 3).

FY 2016 PUBLICATIONS/PRESENTATIONS

1. N.N. Kariuki, D.J. Myers, D. Fongalland, A. Martinez, and J. Sharman, “Microstructure Analysis of Polymer Electrolyte Membrane Fuel Cell Catalyst-Ionomer Inks and Cathode Catalyst Layers by Ultra Small Angle X-ray Scattering,” 229th Electrochemical Society Meeting, San Diego, CA, May 29–June 2, 2016.
2. Le Xin, Fan Yang, Zhe-Fei Li, Somaye Rasouli, Paulo J. Ferreira, Cheng-Jun Sun, Yu-Zi Liu, and Jian Xie, “Understanding of Pt nanoparticle anchoring on graphene supports through surface functionalization,” *ACS Catalysis*, 2016, 6 (4), 2642–2653.
3. S. Rasouli, Z. Yang, M. Gummalla, S.C. Ball, D. Myers, and P.J. Ferreira, “Surface Area Loss Mechanisms of Pt₃Co Nanocatalysts in PEM Fuel Cells: A Parametric Study” (submitted).
4. James A. Gilbert, A. Jeremy Kropf, Nancy N. Kariuki, Stacy DeCrane, Xiaoping Wang, Somaye Rasouli, Kang Yu, Paulo J. Ferreira, Dane Morgan, Deborah J. Myers, “In-Operando Anomalous Small-Angle X-Ray Scattering Investigation of Pt₃Co Catalyst Degradation in Aqueous and Fuel Cell Environments,” *Journal of The Electrochemical Society*, 162, 2015, F1487–F1497.
5. Mallika Gummalla, Sarah C. Ball, David A. Condit, Somaye Rasouli, Kang Yu, Paulo J. Ferreira, Deborah J. Myers, Zhiwei Yang, “Effect of Particle Size and Operating Conditions on Pt₃Co PEMFC Cathode Catalyst Durability,” *Catalysts*, 5, 2015, 926–948.
6. Zhe-Fei Li, Le Xin, Fan Yang, Yadong Liu, Yuzi Liu, Hangyu Zhang, Lia Stanciu, and Jian Xie, “Hierarchical Polybenzimidazole-grafted Graphene/Carbon Hybrids as Supports for Pt Nanoparticle Catalysts with Excellent PEMFC Performance,” *NanoEnergy*, 16, 2015, 281.
7. Paulo Ferreira, “NanoSpain 2016,” Logrono, Spain, March 2016.
8. Paulo Ferreira, “Nano Monterrey 2015,” Monterrey, Mexico, October 22–23, 2015.
9. Paulo Ferreira, “Seeing small: Enabling new discoveries in energy materials through advanced transmission electron microscopy,” AGH University of Science and Technology, Krakow, Poland, December 2015.
10. Somaye Rasouli, Best Poster Award, 15th Frontiers of Electron Microscopy in Materials Science, (FEMMS), 2015.

REFERENCES

1. Brian D. James, “Fuel Cell Vehicle and Bus Cost Analysis,” 2015 DOE Hydrogen and Fuel Cells Program Review, Arlington, VA, June 8–12, 2015.
2. H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, “Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs.” *Appl. Catal B-Environ.*, 2005, 56 (1-2), 9–35.
3. A. Kongkanand, “High-Activity Dealloyed Catalysts,” 2014 DOE Hydrogen and Fuel Cells Program Review, Washington, D.C., June 16–20, 2014.