

V.C.2 Rationally Designed Catalyst Layers for PEMFC Performance Optimization

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Project Start Date: May 1, 2013

Project End Date: April 30, 2016

Overall Objectives

- To realize the oxygen reduction reaction (ORR) mass activity benefits of advanced platinum-based 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 mgPt/cm² on cathode)
- To determine the source(s) of performance limitations of de-alloyed PtNi-containing membrane-electrode assemblies at high current densities (>1 A/cm²) when operating on air
- To 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

- To develop the catalyst support morphology, surface functionality, and/or catalyst ink composition to optimize the performance of the cathode, guided by modeling

Fiscal Year (FY) 2015 Objectives

- Synthesize d-PtNi catalyst with functionalized proton-conducting carbon support and determine performance of this functionalized catalyst/support in MEAs
- Fabricate and test MEAs with alternative cathode catalyst layer ionomer to carbon ratio, with alternative solvent in catalyst-ionomer inks, and with post-MEA-fabrication treatment toward the goal of improving the high current density air performance
- Improve high current density air performance of an MEA containing the dealloyed PtNi-based cathode catalyst by ≥ 115 mA/cm² at 0.675 V/cell to achieve ≥ 850 mW/cm² at rated power, toward the DOE 2020 target of 1,000 mW/cm² at rated power

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:

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

Technical Targets

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

FY 2015 Accomplishments

- Determined effect of increased ionomer content on An-Pt/C and d-PtNi/C catalyst layer structure and performance
- Determined effect of organic versus aqueous solvent in inks on An-Pt/C and d-PtNi/C performance
- Determined agglomerate structure of An-Pt/C and d-PtNi/C inks and dry inks/electrode layers
- Determined extent of Ni lost from d-PtNi catalyst during ink preparation, MEA fabrication, and testing and impact of Ni²⁺ in ionomer on cathode resistance and ionomer oxygen permeability

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

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Project Status (50 cm ² cell, differential conditions)
Mass activity	A/mg _{PGM} @ 0.9 mV _{IR-free}	≥0.44	0.57
Specific activity	μA/cm ² _{PGM} @ 0.9 mV _{IR-free}	≥720	986
PGM total loading	mg-PGM/cm ² _{geo}	≤0.125	0.092, cathode
MEA performance	mA/cm ² _{geo} @ 800 mV	≥300	347
MEA performance	mW/cm ² _{geo} @ 675 mV	≥1000	827

- Increased hydrogen/air current density by 90 mA/cm² to 1,225 mA/cm² and power density by 89 W/cm² to 827 mW/cm² at 0.675 V of a d-PtNi-containing MEA through a combination of increase of ionomer content in the cathode catalyst layer (CCL) and acid-washing of the catalyst-coated membrane (CCM)



INTRODUCTION CCL

One of the major cost contributors to a polymer electrolyte membrane fuel cell (PEMFC) is the 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 2020 targets (>0.44 A/mg PGM and 720 μA/cm² @ 900 mV) have been demonstrated for high surface area carbon supported platinum alloy and core-shell nanoparticle catalysts in aqueous cell rotating disk electrode (RDE) tests and in MEAs [3], some as high as 5.75 A/mg-Pt in RDE tests [4], the full performance of cathode catalyst layers based on these promising catalysts has yet to be achieved in MEAs, especially at the low cathode platinum loadings necessary to achieve the DOE MEA PGM loading target (≤0.125 mg-Pt/cm²) and when operating at realistic current densities on air rather than oxygen. There are several possible reasons the full potentials of these advanced catalysts have not been realized in MEAs operating on air and at current densities >1 A/cm² arising from the complex requirements for full utilization of the electrocatalytic sites and for adequate reactant transport in the MEA cathode layer. 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 platinum-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 that exceed simultaneously the DOE performance, durability, and cost targets for PEMFCs for automotive applications.

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 versus high surface area platinum and platinum of comparable electrochemically active surface area (ECSA).
 - A suite of in situ and ex situ techniques, such as transmission electron microscopy (TEM), cryogenic TEM, dynamic light scattering, ultra-small angle X-ray scattering (USAXS), X-ray absorption spectroscopy, and porosimetry.
- Design the catalyst layer composition and structure and support functionality to mitigate the performance limitations, guided by computational modeling.
 - Study 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
 - Develop an ink composition and/or ink processing (e.g., solvent removal process) that result in optimum agglomerate structure in d-PtNi/C-based electrode
 - Develop the catalyst support surface functionality to increase the performance of the catalyst and cathode to decouple proton conductivity from ionomer content

The catalyst selected for this project is high surface area carbon supported dealloyed PtNi nanoparticles (d-PtNi), which was developed by Johnson Matthey Fuel Cells within the General Motors-led project [5]. The catalyst precursor is 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 with 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 exceeds the DOE 2020 target [5], the kinetic stability of this catalyst can exceed the DOE 2020 target.

RESULTS

The effects of ionomer to carbon ratio and organic versus aqueous solvents in the ionomer-catalyst inks on agglomerate structure in inks, agglomerate structure in electrodes, and cathode catalyst layer performance under a variety of oxygen partial pressures and relative humidities 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:

Increased ionomer content (I/C ratio) in the catalyst-ionomer inks:

- Enhances the MEA performance under dry and wet conditions, except for d-PtNi/C at 100% relative humidity (RH) where it increased mass transport on air (Figure 1).
- Increases breakup of carbon agglomerates, increasing fraction of small agglomerates (70–100 nm) as determined by dynamic light scattering of dilute inks and USAXS of the as-prepared ionomer-carbon inks (Figure 2).
- Decreases catalyst layer pore volume fraction and permeability, as determined by porosimetry.

Organic solvent vs. aqueous solvent in catalyst-ionomer inks:

- Increases breakup of carbon agglomerates, increasing fraction of small agglomerates (70–100 nm) (Figure 2).
- Increases porosity and permeability of resulting catalyst layer.
- Increases amount of ionomer not associated with catalyst/carbon and decreases size of ionomer rods.
- Decreases amount and effect of Ni²⁺ in the “free” ionomer (Figure 3).

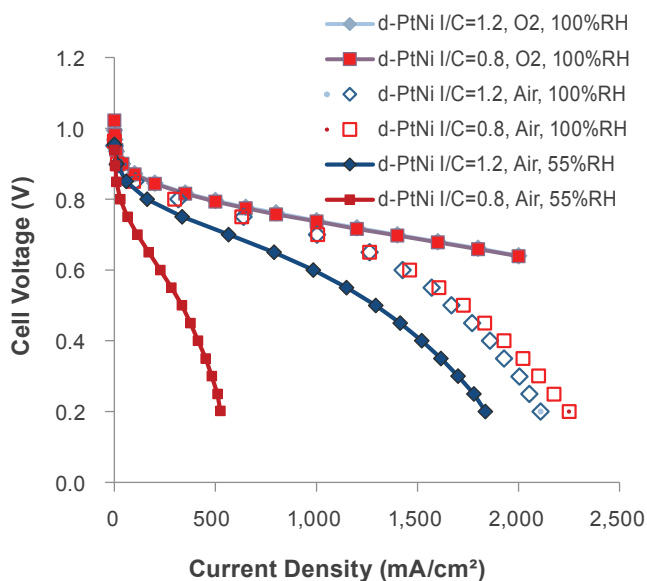
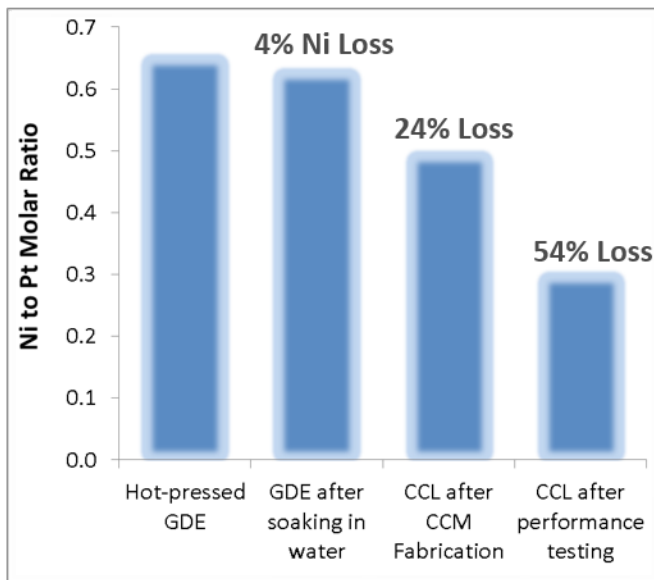
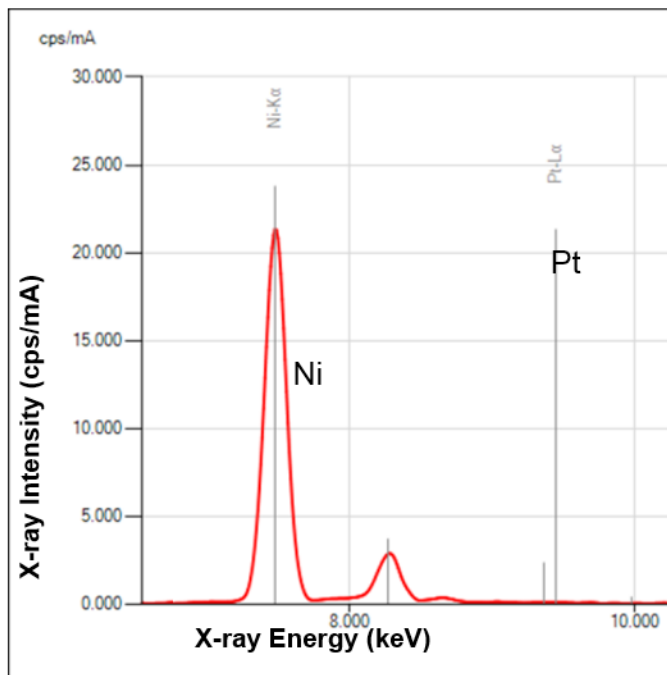


FIGURE 1. Hydrogen-oxygen and hydrogen-air polarization curves for MEAs with ~ 0.1 mg-Pt/cm² loading of d-PtNi/C with I/C ratios in the CCL of 0.8 or 1.2. Cell conditions: 80°C, 150 kPa (abs.), high and fixed flow for differential conditions (3 slpm O₂ or air).

- Primarily enhances cathode performance at high and low RH. Extent of effect is pO₂ dependent.

d-PtNi/C vs. An-Pt/C:

- Inks have larger agglomerates and less agglomerate breakup.
- Inks have more “free” ionomer not associated with catalyst/carbon, for I/C of 0.8.
- “Free” ionomer in inks has rod-like structure in solvent and diameter of rods is larger for free ionomer in d-PtNi/C inks than in An-Pt/C inks.
- Reactant transport to d-PtNi/C at 100% RH is linked to low absolute catalyst ECSA (same as for An-Pt/C). At low RH additional mass transport losses are observed that are unique to d-PtNi/C.
- Ni²⁺ is leached from d-PtNi into ionomer during ink preparation and MEA fabrication (Figure 2).
- Ni²⁺ in ionomer decreases oxygen permeability and decreases catalyst layer ionic conductivity, as determined by RDE-ORR diffusion-limited current measurements and by in-cell electrochemical impedance spectroscopy measurements.
- Acid-washing CCM improves mass transport in d-PtNi/C catalyst layer, improving hydrogen–air performance at 0.675 V by 90 mA/cm² to 1,225 mA/cm² and greatly improving low RH performance (Figure 4).



GDE: Gas Diffusion Electrode
 CCL: Cathode Catalyst Layer
 CCM: Catalyst Coated Membrane

FIGURE 2. (Top) XRF of dried supernatant from d-PtNi/C-ionomer-solvent organic ink showing that Ni²⁺ has leached into the ionomer-solvent. The ratio of the Ni to S XRF peak areas was 16 for the aqueous ink and 2.7 for the organic ink showing that the organic ink leaches less Ni²⁺ from the d-PtNi/C catalyst. (Bottom) XRF of d-PtNi/C electrode layers at various stages of MEA fabrication and testing illustrating that Ni is removed from the cathode at all stages.

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions

- Issues with the d-PtNi/C-containing catalyst are drop-off in performance at >1 A/cm² (i.e., not maintaining mass

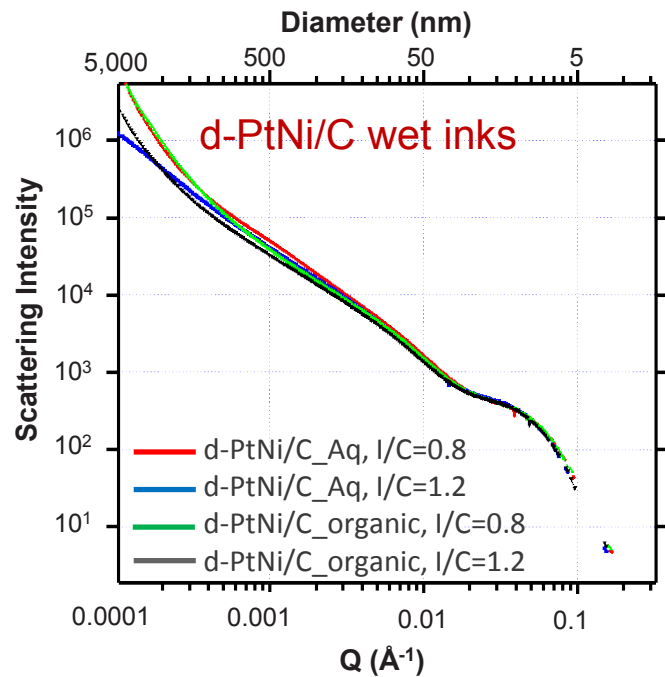


FIGURE 3. USAXS curves of as prepared d-PtNi/C inks made with aqueous or organic solvents and with I/C ratios of 0.8 or 1.2, illustrating that increased ionomer content and use of organic solvent versus aqueous solvent decreases the sizes of agglomerates in the inks.

activity benefit relative to high-surface-area Pt/C) under high and intermediate humidity conditions and a severe drop-off at low RHs, due to:

- Mass transport to low loadings of large particles.
 - Can be mitigated with smaller particles that are greater than approximately 4 nm to ensure stability against dissolution-related ECSA loss
- Sensitivity to low humidity conditions unique to d-PtNi/C (i.e., not observed with comparably-sized Pt/C).
 - Can be partially mitigated with increased ionomer content and organic solvents that improve dispersion of d-PtNi/C particles, and can be greatly improved with acid treatment of CCM
- Results thus far indicate that Ni²⁺ in the ionomer, leached during ink and CCM fabrication, is altering the agglomerate structure of the CCL and also altering the oxygen permeability of the ionomer phase, 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.

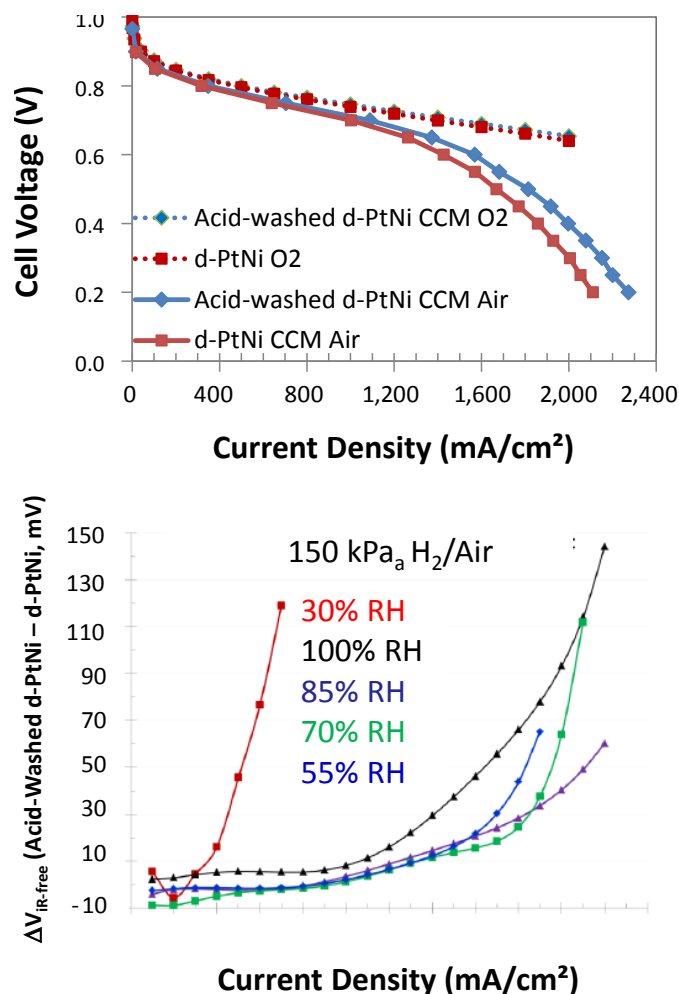


FIGURE 4. Hydrogen-oxygen and hydrogen-air polarization curves (top, 150 kPa_a, 100% RH) and the difference between the polarization curves (bottom, air, RH dependence) of as-fabricated and acid-treated MEAs with ~ 0.1 mg-Pt/cm² loading of d-PtNi/C, I/C ratio of 1.2, and using an aqueous ink to fabricate the CCL.

- Functionalization of carbon support with $-\text{SO}_3\text{H}$ groups improves low RH performance, but decreases catalyst mass activity.

Future Directions

- Conduct acid-treatment and performance testing of a CCM containing a d-PtNi-based cathode made with organic solvent to achieve ≥ 850 mW/cm² at 0.675 V
- Perform USAXS tomography for spatial distribution of agglomerates in catalyst layers, coupled with TEM for ionomer imaging
- Perform nano x-ray tomography for spatial distribution of pore and agglomerates in catalyst layers

- Continue analysis of electrochemical impedance spectroscopy data for proton conductivity of all electrode layer compositions and electrode loss breakdown
- Take solid state cell measurements of permeability of oxygen through ionomer and impact of Ni²⁺ on permeability/solubility
- Complete transport model of electrode layer using imaging results
- Determine causes of loss of mass activity of d-PtNi/C upon functionalization of carbon and develop solutions to mitigate activity loss
- Fabricate and test of CCMs and stack using ink compositions and catalyst and CCM treatments that result in the best overall hydrogen-air performance as a function of RH (40 to 100% RH)

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3. Li, Zhe-Fei; Zhang, Hangyu; Yang, Fan; Stanciu, Lia; Xie, Jian, "Pt Catalysts Supported on Polybenzimidazole-Grafted Graphene for PEMFCs," Abstract 1210, 226th Electrochemical Society Meeting, October 5–9, 2014.
4. Myers, Deborah; Kariuki, Nancy; Hammons, Joshua; Ahluwalia, Rajesh; Xiaohua; Peng, Jui-Kun; Fongalland, Dharshini, "Dealloyed Pt-Ni Polymer Electrolyte Fuel Cell Cathodes: Effects of Catalyst-Ionomer Ink Composition on Structure and Performance," Abstract 1555, 227th Electrochemical Society Meeting, May 24–28, 2015.
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7. Wang, Xiaohua; Peng, Jui-kun; Ahluwalia, Rajesh; Myers, Debbie; and Yang, Zhiwei, "Mass Transfer Overpotentials in Dispersed Pt/C and De-alloyed PtNi/C Polymer Electrolyte Fuel Cell Cathodes," Abstract 1666, 227th Electrochemical Society Meeting, May 24–28, 2015.
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