Rationally Designed Catalyst Layers for PEMFC Performance Optimization

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Project ID# FC106

Project Overview

Timeline

- Project Start Date: April, 2013*
- Project End Date: March, 2016
- Percentage complete: 33%

* Not reviewed at 2013 AMR

Budget

- FY13 DOE Funding: $843K
- Planned FY14 DOE Funding: $1,345K
- Total DOE Project Value: $3,480K
- Cost Share Percentage: 20%

Barriers

Barrier	2020 Target
A. Electrode Performance	>300 mA/cm² at 800 mV >1000 mW/cm² at rated power
B. Cost	$5-9/$kW_e$ catalyst, <$30 kW_e system, <0.125 mg_{PGM}/cm^2
C. Durability	<40% loss of initial catalytic mass activity at 900 mV on O_2; <30 mV loss at 0.8 A/cm²

Partners and Project Lead

- **Johnson Matthey Fuel Cells**
  - Jonathan Sharman, Alex Martinez, Dash Fongalland, Stephen Thorpe, Brian Theobald, L. Smith, D. Ozkaya, M. Gutierrez, Eleanor Dann, Graham Hards, and Willie Hall
- **United Technologies Research Center**
  - Mike Perry and Zhiwei Yang
- **University of Texas at Austin**
  - Paulo Ferreira, Kang Yu, Somaye Rasouli, and Andres Godoy
- **Indiana University Purdue University Indianapolis**
  - Jian Xie, Chuankun Jia, Zhefei Li, Yun Zhou, and Fan Yang
- **Project lead: Argonne National Laboratory**
  - Debbie Myers, Nancy Kariuki, Rajesh Ahluwalia, Xiaohua Wang, and Jui-Kun Peng
  - Project management, characterization of structure of catalysts, inks, and electrodes using X-ray techniques; modeling and development of optimum catalyst layer structure, ink formulations, agglomerate size analysis; conductivity and electrochemical analysis of electrode layers

Relevance

- **Project Objective**
  - To realize the ORR mass activity benefits of advanced Pt-based cathode electrocatalysts in MEAs and stacks operating at **high current densities** and on **air** and at **low PGM loading (≤0.1 mg_{Pt}/cm^2 on cathode)**
- **Current Year's Objective**
  - Determine catalyst and cathode layer properties responsible for decline in advanced Pt-based cathode air performance at >1 A/cm^2
  - Develop a cathode catalyst layer model for advanced Pt-based catalyst
  - Develop a method to impart proton conductivity to high surface area carbon supports
- **Impact**

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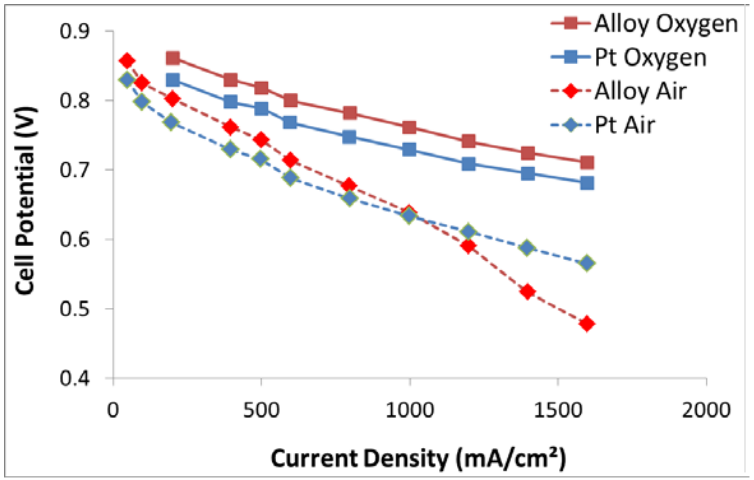


Example of lack of performance benefit of a Pt alloy over Pt when operating at > 1000 mA/cm^2 on air (cathode loading 0.2 mg Pt/cm^2, 80°C, 50/50 kPa gauge)

Metric	Units	DOE 2020 Target	Project Status
Mass activity	A/mg_{PGM}@ $900mV_{iR\text{-}free}$	≥0.44	0.57
Specific activity	$\mu A/cm^2_{PGM}$	720	986
PGM total loading	mg_{PGM}/cm^2_{geo}	≤0.125	0.092 (cathode)
MEA performance	mA/cm^2 @ 800 mV	≥300	298

Approach

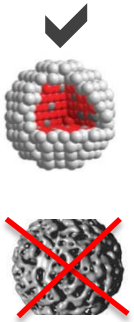
- Determine property of electrode/catalyst that limits the high current density/air performance of electrodes based on advanced Pt-based cathode catalyst
  - The advanced Pt-based catalyst is **dealloyed PtNi (d-PtNi)** developed by Johnson Matthey in the General Motors-led DOE-FCTO project (FC087). The key catalyst characteristics and metrics are:
    - Catalyst deposited as nanoparticles onto Ketjen Black 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 1.0V cycles can exceed the DOE kinetic stability target

- Use information from characterization efforts to determine the performance-limiting property of the current d-PtNi electrode (used in FC087)
  - *In-cell* diagnostics of d-PtNi versus high surface area Pt and Pt of comparable electrochemically-active surface area
  - Using a suite of *in situ* and *ex situ* techniques: TEM, cryogenic TEM, dynamic light scattering, ultra-small angle X-ray scattering, X-ray absorption spectroscopy

- 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 solvent removal process that minimize Ni corrosion and 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

Catalyst variants and metrics

- High temperature annealing is needed to drive complete alloying of Pt and Ni in $PtNi_3$ precursor, which increases particle size
- Annealing is followed by **chemical** dealloying (see FC087 for details) which dissolves Ni, not Pt
- Goal is to avoid nano-porosity by using mild de-alloying conditions and by limiting particle size

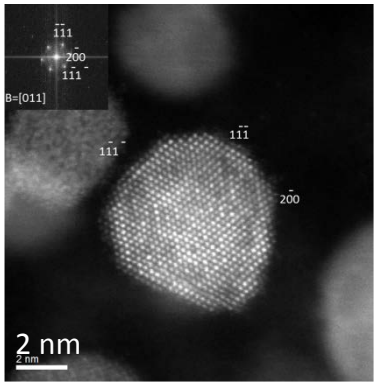


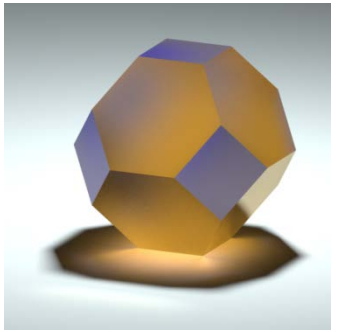
Catalyst Code	Catalyst Type/ Annealing Conditions	Wt% Pt	Wt% Ni	Metal area by *ex situ* CO ads. (m^2/g-Pt)	Particle Size by TEM (nm)
Catalyst A (13/21)	Pt/C Not annealed	28.3	-	92	2.0±0.1
Catalyst B (13/176)	Pt/C High T	29.7	-	37	5.8±0.3
Catalyst C (12/409)	PtNi (45:55) High T	22.4	8.24	52	5.8±0.2
Catalyst D (13/228)	PtNi (50:50) High T	31.1	7.01	38	5.6±2.2
Catalyst E (13/239)	PtNi (59:41) High T	30.6	6.50	47	6.5±3.0
Catalyst F (13/300)	PtNi (57:43) High T	29.1	6.68	50	5.1±1.0

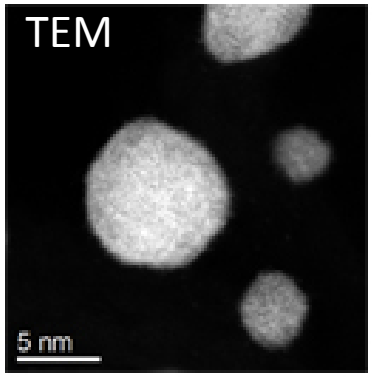
Structure and distribution of Pt and Ni in d-PtNi

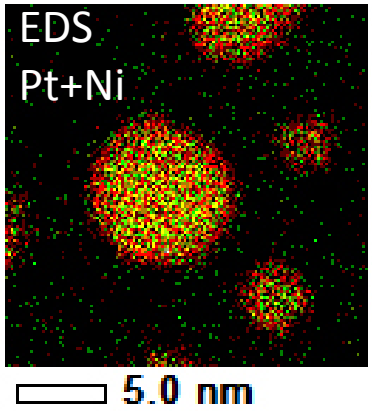
JM 12/409 d-PtNi Catalyst Powder

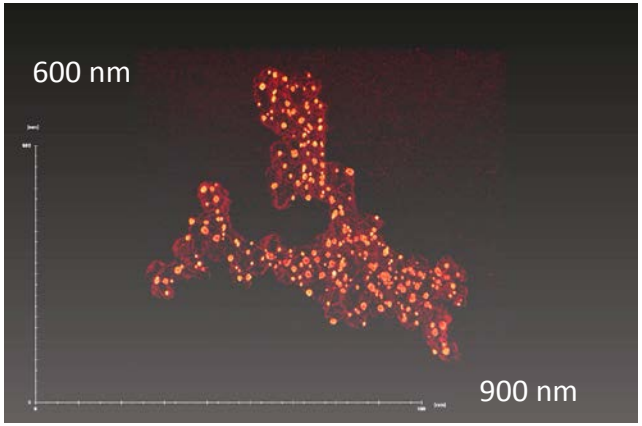
- d-PtNi particles are primarily solid solutions with a truncated octahedron shape
- A minority of particles are ordered alloys
- All particles have a Pt-rich outer shell
- Particles are well-dispersed on carbon support

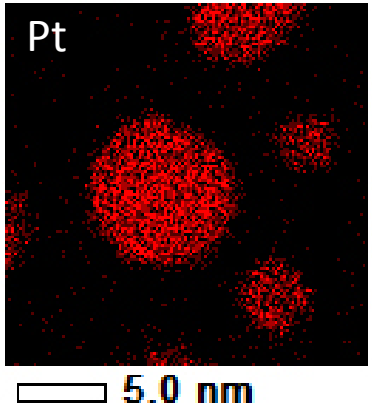


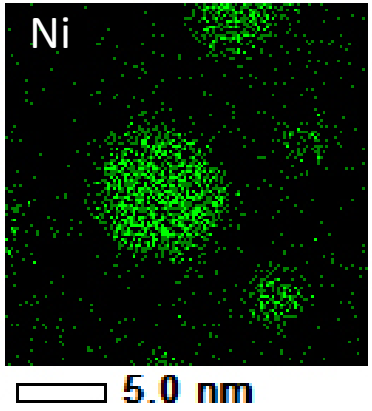


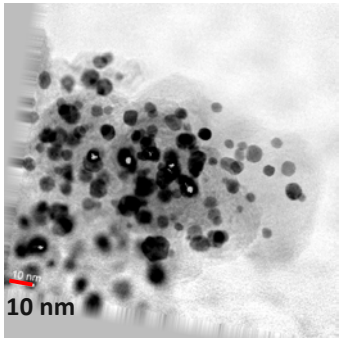






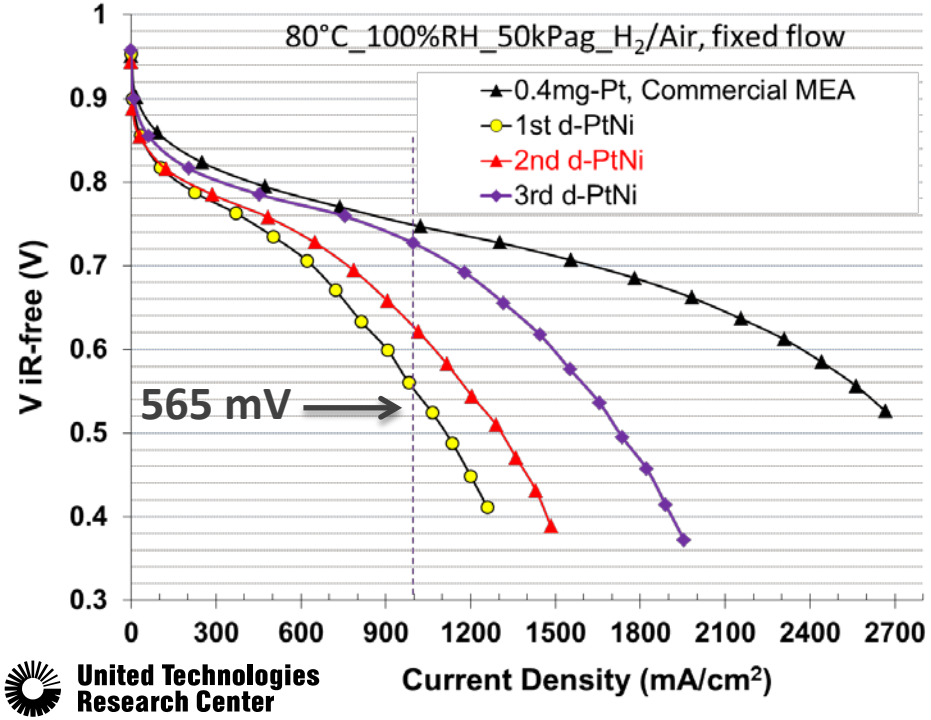




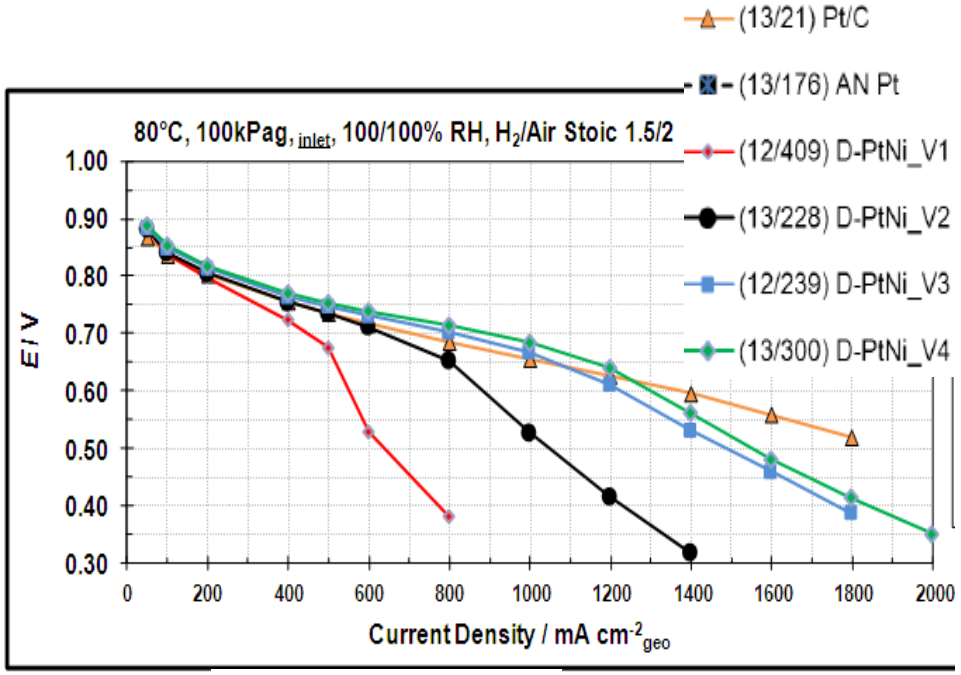


Progress: Improvements in H_2/Air fuel cell performance of d-PtNi catalysts

12/409 d-PtNi catalyst 0.1 mg-Pt/cm² cathode loading



- Results of 1st PtNi ccm using 12/409 d-PtNi cathode catalyst were used to set the project milestones
- Improvements in performance of CCMs with 12/409 d-PtNi catalyst were obtained with variation of cell compression.



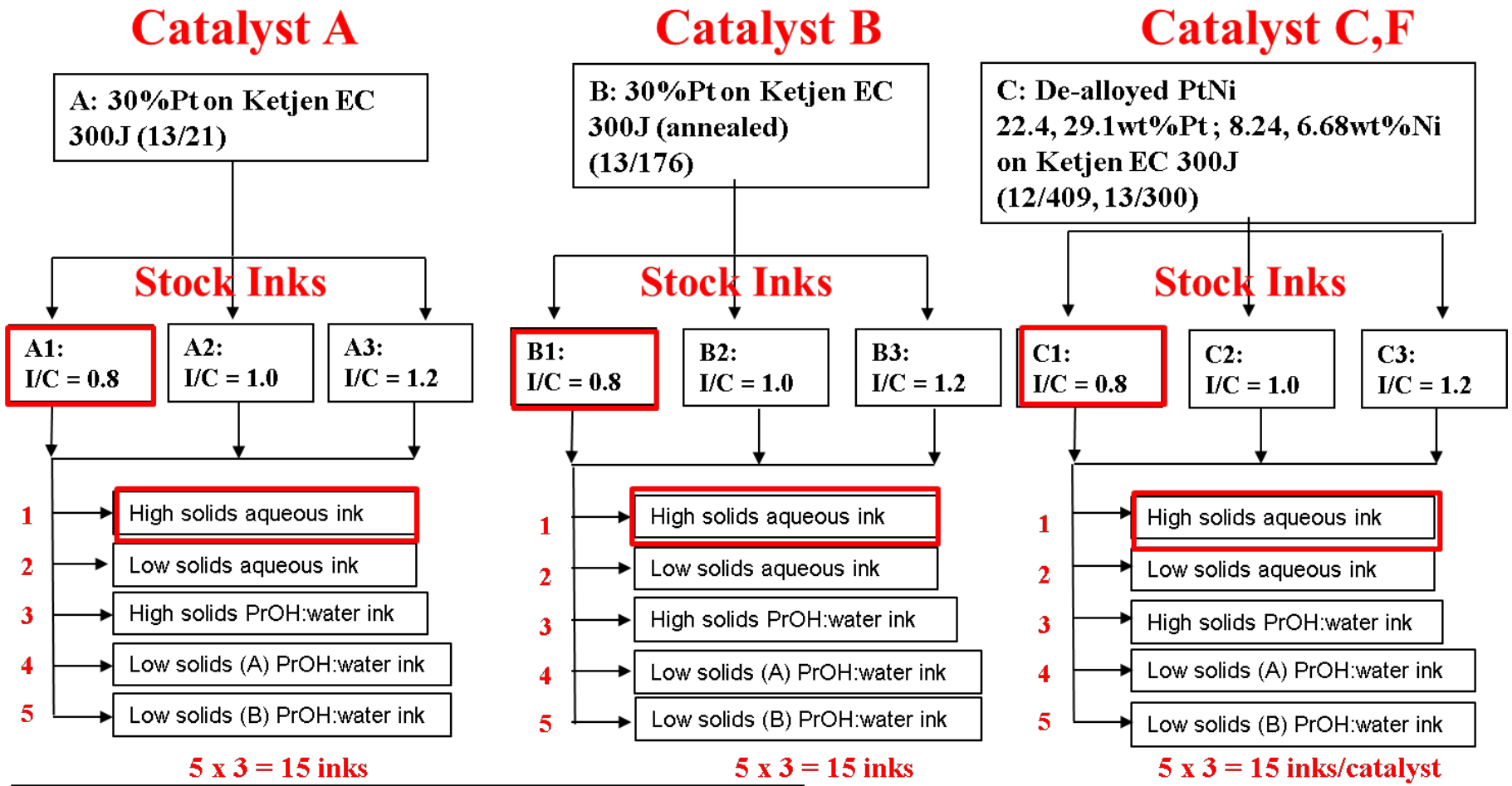
- The air performance of the d-PtNi cathode has been improved with each new version
- The latest versions of d-PtNi outperform high surface area Pt (13/21 Pt/C) at <1.2 A/cm²

FY'14 Milestones and Go/No-Go

Date	Milestone	Status
12/31/13	Improve the high current density air performance of the advanced alloy catalyst by 15% (increase iR-free cell voltage at 1 A/cm² by 20 mV to **585 mV)**	**Exceeded.** An iR-free voltage of 740 mV at 1 A/cm² on air was achieved in Dec., 2013.
3/31/14	Improve performance by 30% (increase iR-free cell voltage at 1 A/cm² by 40 mV to **606 mV**)	**Exceeded.**
6/30/14	Improve performance by 40% (increase iR-free cell voltage at 1 A/cm² by 54 mV to **619 mV**)	**Exceeded.**
9/30/14 Go/No-Go	Improve performance by 50% (increase iR-free cell voltage at 1 A/cm² by 67 mV to **632 mV**)	**Exceeded.**

- Milestones were established based on 1st d-PtNi cell performance shown on previous slide
- Improvements in cell performance were the result of cell compression optimization and improved catalyst formulation
- **Milestones and Go/No-Go are being revised to reflect the latest performance in d-PtNi-based CCMs**

Description of catalyst inks studied: baseline Pt, annealed Pt, and d-PtNi



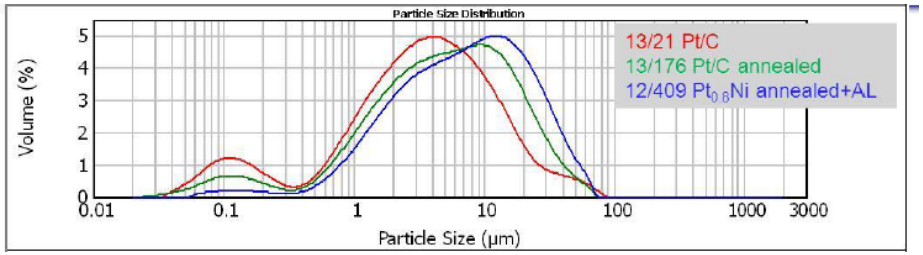
Parameters being studied:

- Ni content in d-PtNi
- Ionomer to carbon ratio
- Solids content
- Solvent type

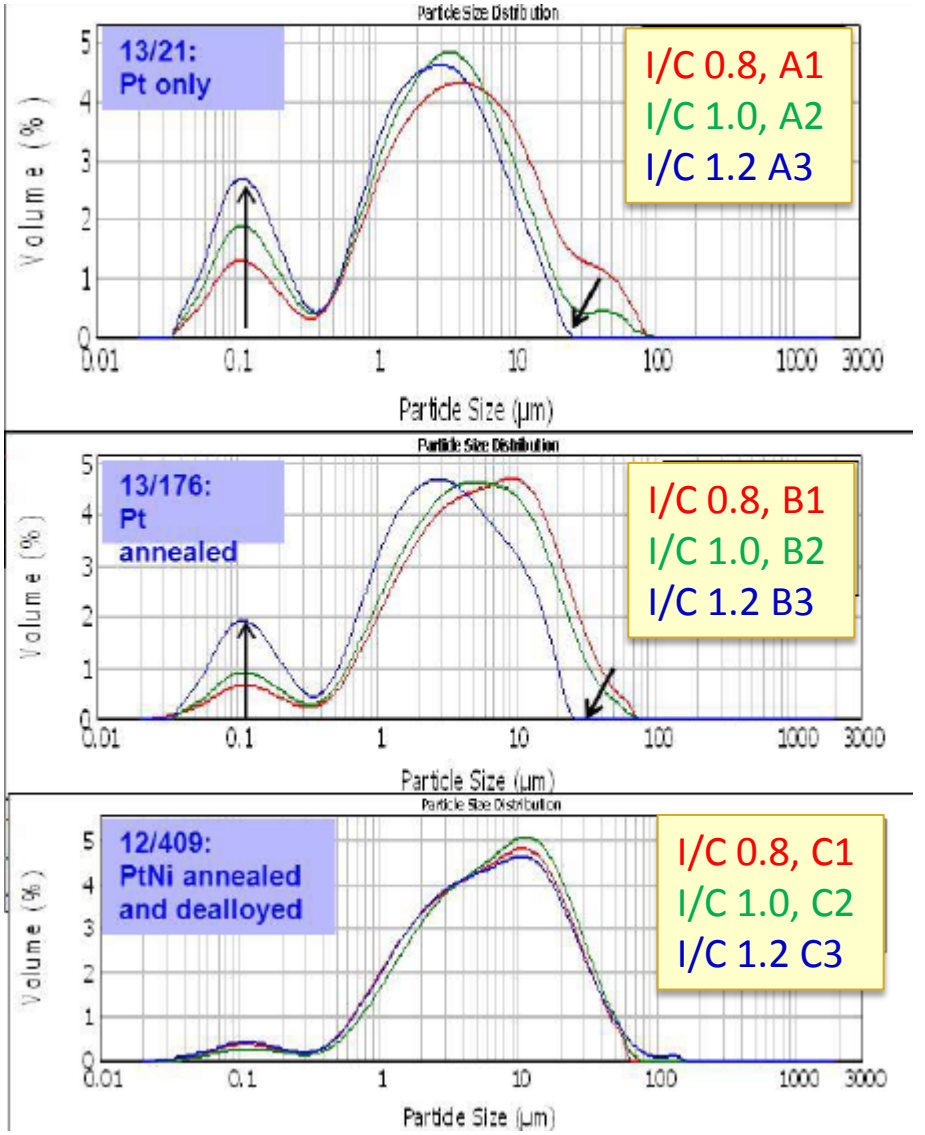
I/C = ionomer to carbon weight ratio

= inks used for cathodes of baseline ccms

Light scattering of catalyst inks for C agglomerate size



- Standard high solid, I/C = 0.8 catalyst inks (used for CCMs) diluted for light scattering
- Carbon agglomerate size: Pt/C<<annealed Pt/C<d-PtNi/C
- Agglomerate size dependence on ionomer content (I/C = 0.8, 1.0, 1.2):
  - Pt/C: agglomerate size decreases with increasing ionomer content
  - Annealed Pt/C: agglomerate size decreases with ionomer content, but less than for Pt/C
  - d-PtNi/C: very little dependence of agglomerate size on ionomer content
- d-PtNi/C shows less interaction with ionomer than Pt/C or annealed Pt/C



Ultra-small angle X-ray scattering and cryogenic electron microscopy of catalyst inks: d-PtNi/C vs. annealed Pt/C

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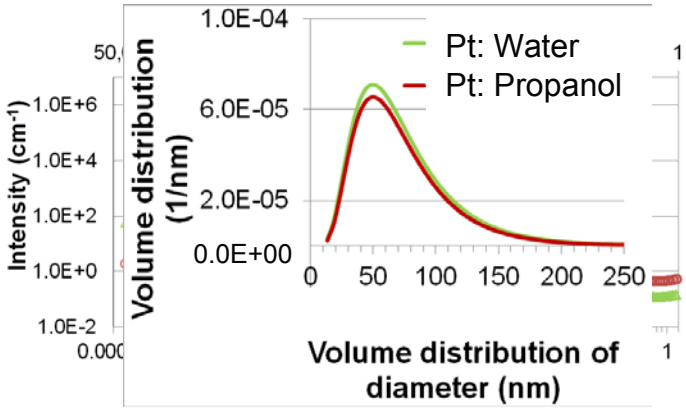
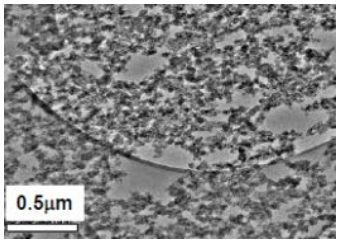
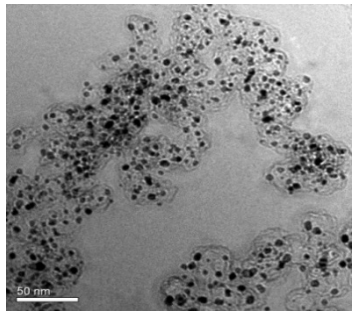
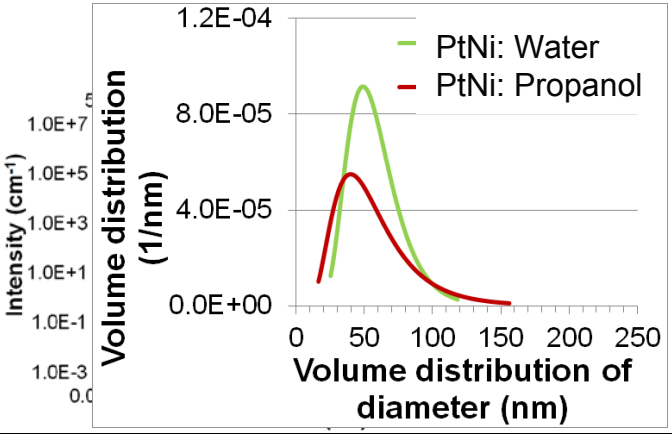
Pt
Similar microstructure in aqueous and propanol-based inks

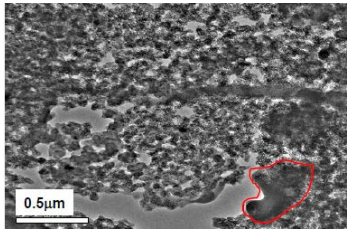


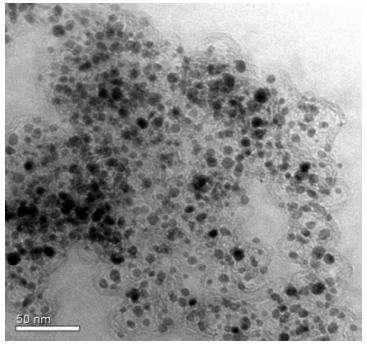




d-PtNi (13/300)
Higher volume distribution of aggregates in aqueous versus propanol-based inks



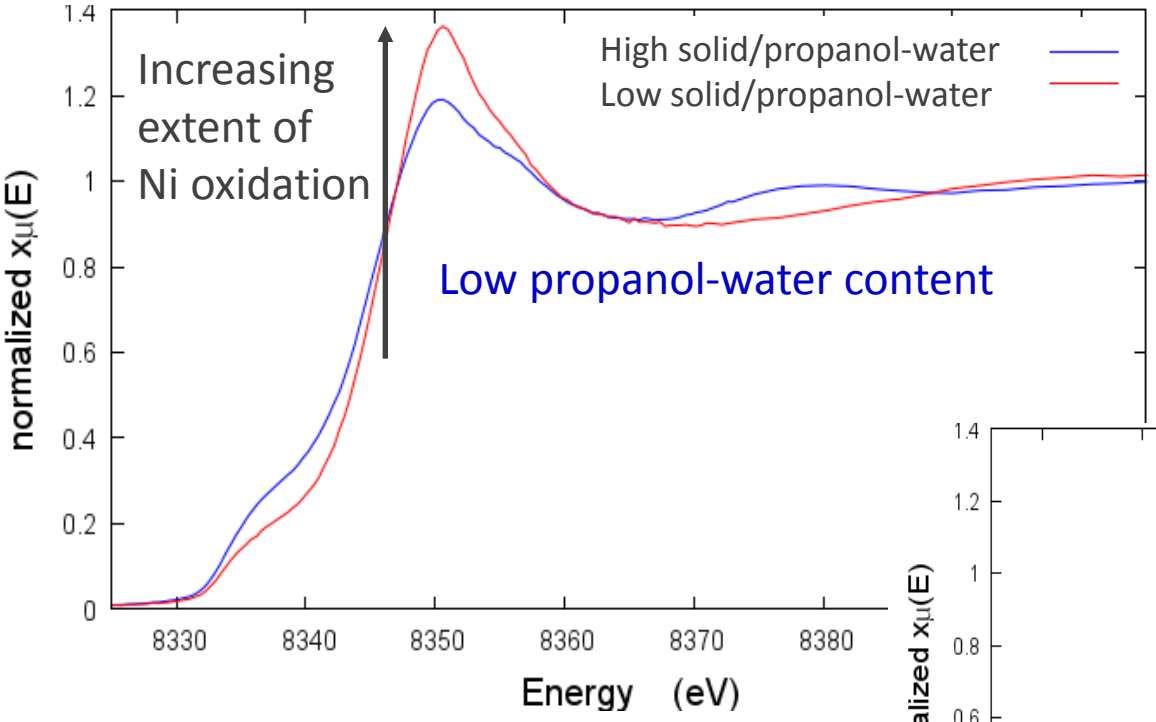




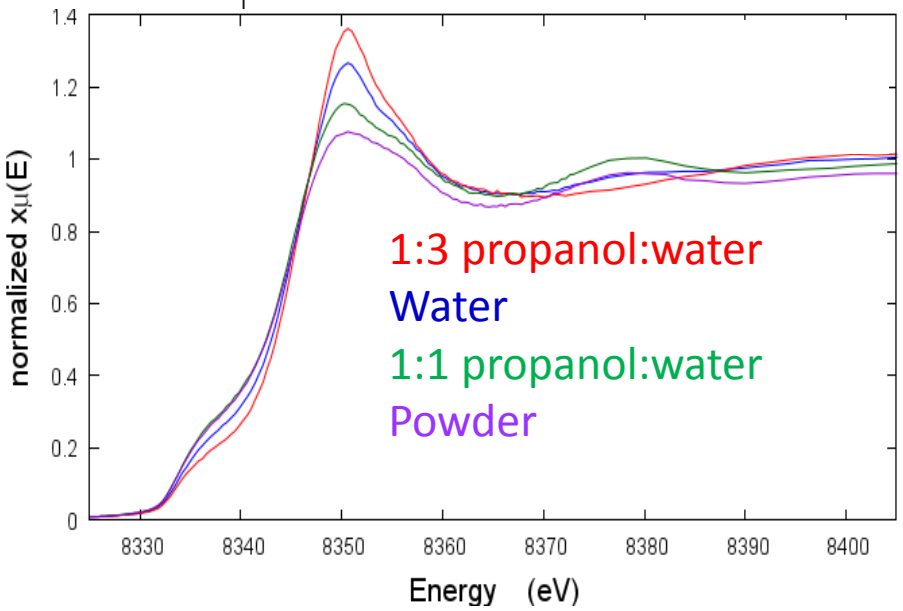
- There are differences in the catalyst/carbon agglomerate structure of Pt and d-PtNi inks which may affect transport within the PEMFC cathodes
- The solvent in the inks changes the agglomerate structure and can be used to improve the transport properties of the cathodes

Effect of ink composition on Ni oxidation in d-PtNi/C: *in situ* X-ray absorption spectroscopy

High propanol-water content



- Though PtNi has been extensively dealloyed and annealed, dispersing catalyst in Nafion®, water, and propanol attacks and oxidizes the nickel
- A solvent-ionomer combination has been found which is less aggressive toward Ni than those shown



Results from the 12/409 (higher Ni content) d-PtNi catalyst shown.

The trends with solids content and solvent type were the same for the newer and lower Ni content 13/300 d-PtNi catalyst

Nickel is leached out of d-PtNi during fuel cell testing

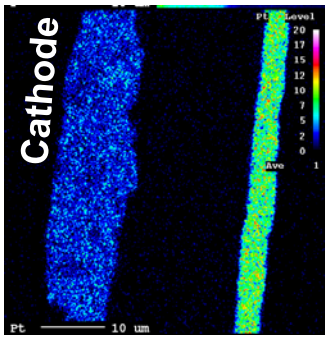
Electron probe microanalysis of d-PtNi CCMs

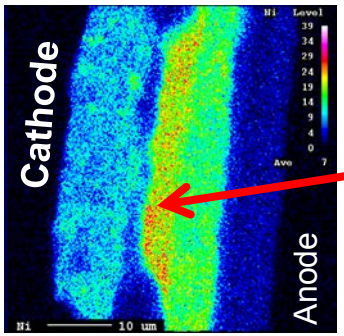
Results for higher Ni content d-PtNi: similar to 12/409 d-PtNi

Platinum signal

Nickel signal

d-PtNi Tested only for activity

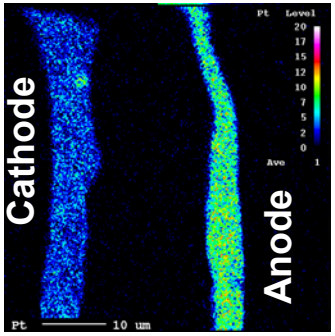


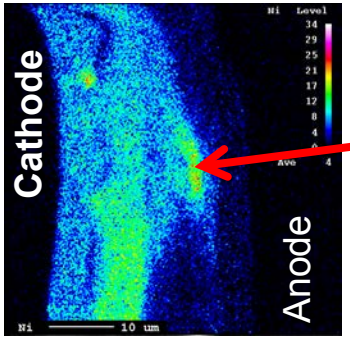


After testing for Mass Activity only

Nickel at the Cathode/membrane interface

d-PtNi Tested only for activity and stability (10K durability cycles)





After 10,000 cycles

Nickel at the Anode/membrane interface

- Significant presence of Nickel at the cathode/membrane interface
- After 10,000 cycles there is some evidence of Ni at the membrane/anode interface

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Performance Model

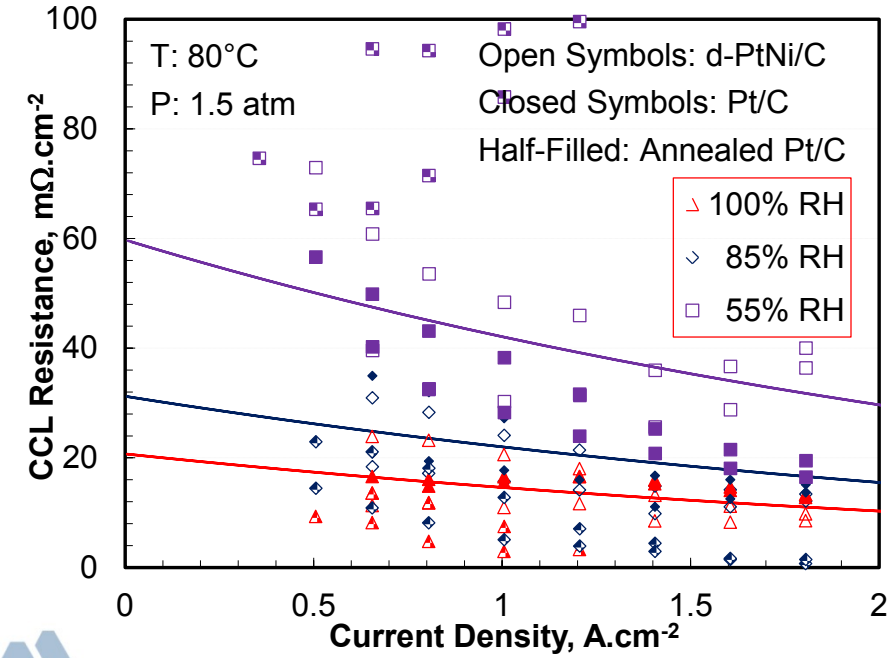
$$E = E_N - iR_\Omega - (iR_\Omega^c + \eta_c^c + \eta_m^c) - (iR_\Omega^a + \eta_c^a + \eta_m^a)$$

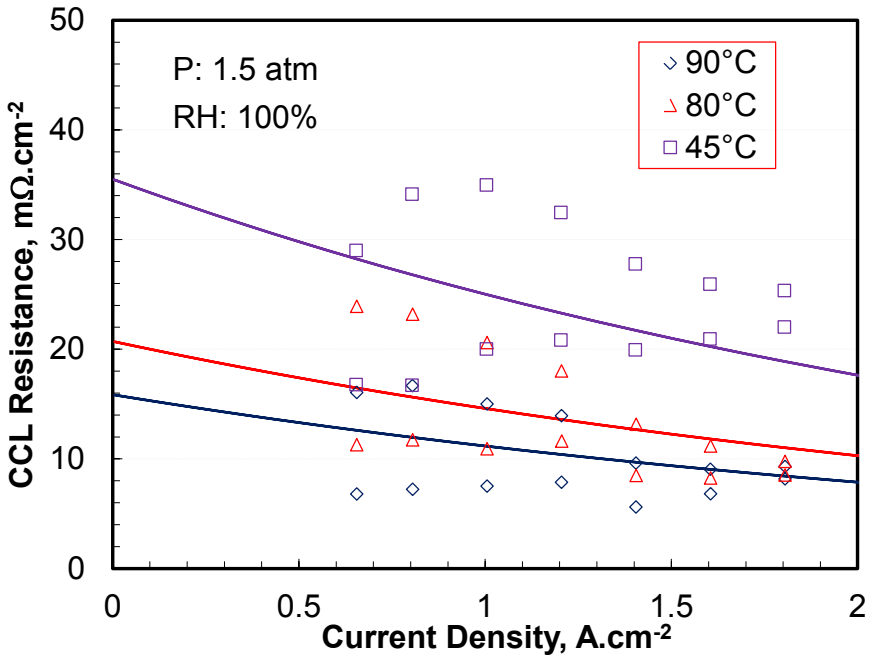
- R_Ω: High frequency resistance as measured by the current interrupt method. It includes membrane and contact resistances.
- η_c^c: ORR kinetic overpotential as determined from a kinetic model formulated using H_2/O_2 polarization data. It includes any kinetic effects due to limited O_2 solubility in ionomer.
- R_Ω^c: Cathode catalyst layer (CCL) resistance estimated from H_2/O_2 polarization data and ORR kinetic model
- η_m^c: Cathode mass transfer overpotential. It includes transport resistances due to O_2 diffusion in gas diffusion layer (GDL), CCL pores and ionomer film surrounding the catalyst particles.
- All anode overpotentials neglected
- Multi node finite-difference model for co-current and counter-current anode and cathode streams

Empirical Correlation for CCL Resistance

Potential drop (iR_{Ω}^{c}) in electrode estimated as difference in VIR measured in H_2/O_2 and VIR calculated using the ORR kinetic parameters

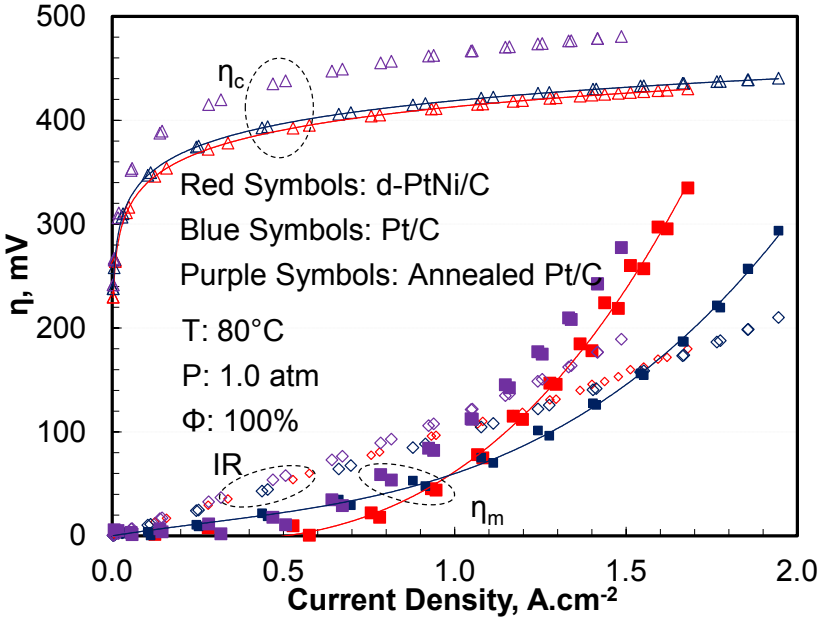
- R_{Ω}^{c} correlated with T, RH and current density
- Large uncertainty, inadequate differentiation between R_{Ω}^{c} of d-PtNi/C, annealed Pt/C and non-annealed Pt/C electrodes
- Separate impedance measurements needed for more accurate characterization of R_{Ω}^{c}

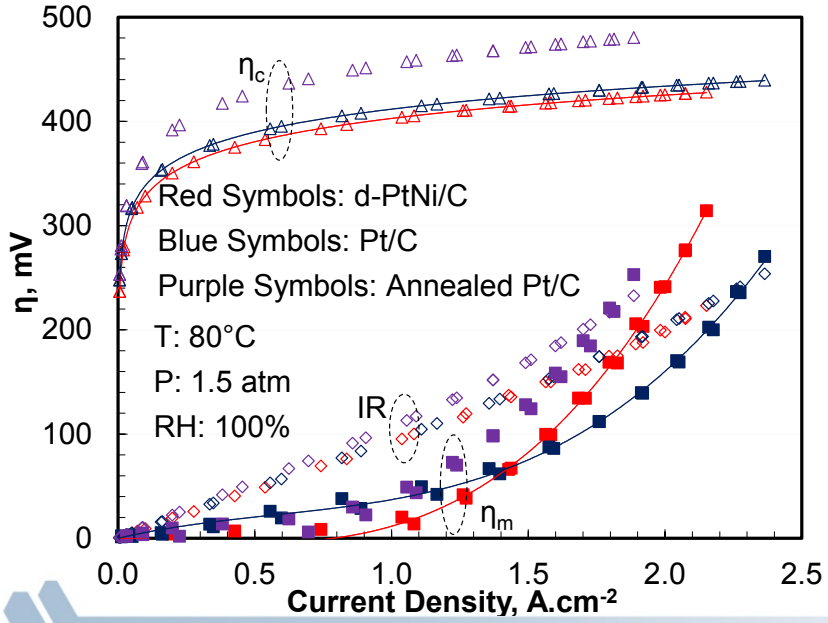


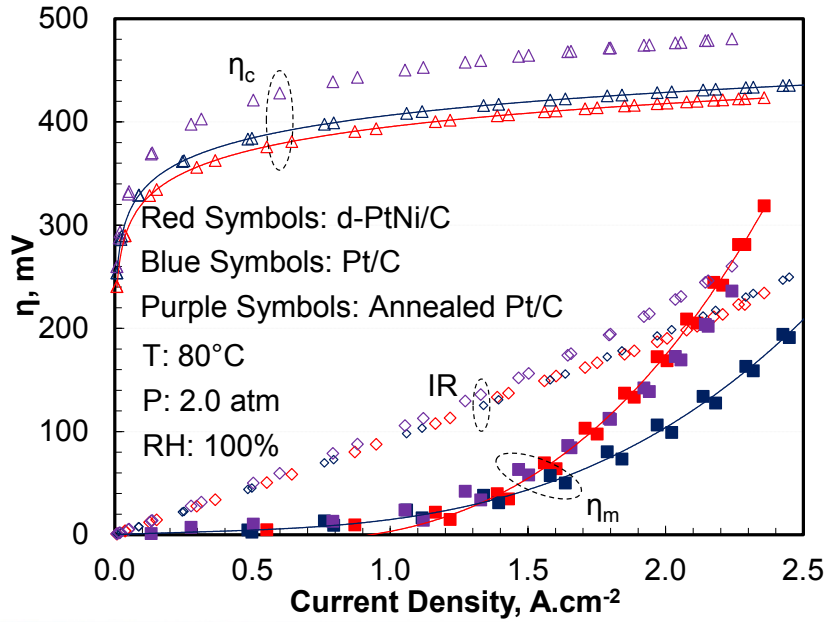


H_2/Air Cell Performance: Breakdown of Overpotentials

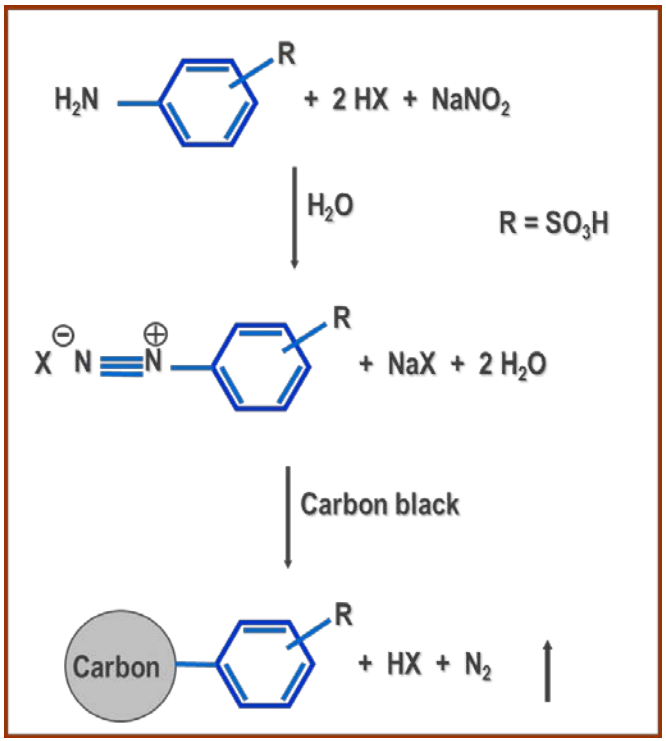
- Loss in performance of d-PtNi/C (relative to non-annealed Pt/C) at high current densities is due to higher mass transfer overpotentials
- Mass transfer overpotentials are related to surface enhancement factor (SEF, ECA/electrode area) and, therefore, are higher if Pt loading is reduced or particle size is increased
- Mass transfer overpotentials do not correlate with mass activity
- Effect of Ni contamination (compare with annealed Pt/C) on η_m appears to be small at beginning of life







Diazonium functionalization of carbon supports

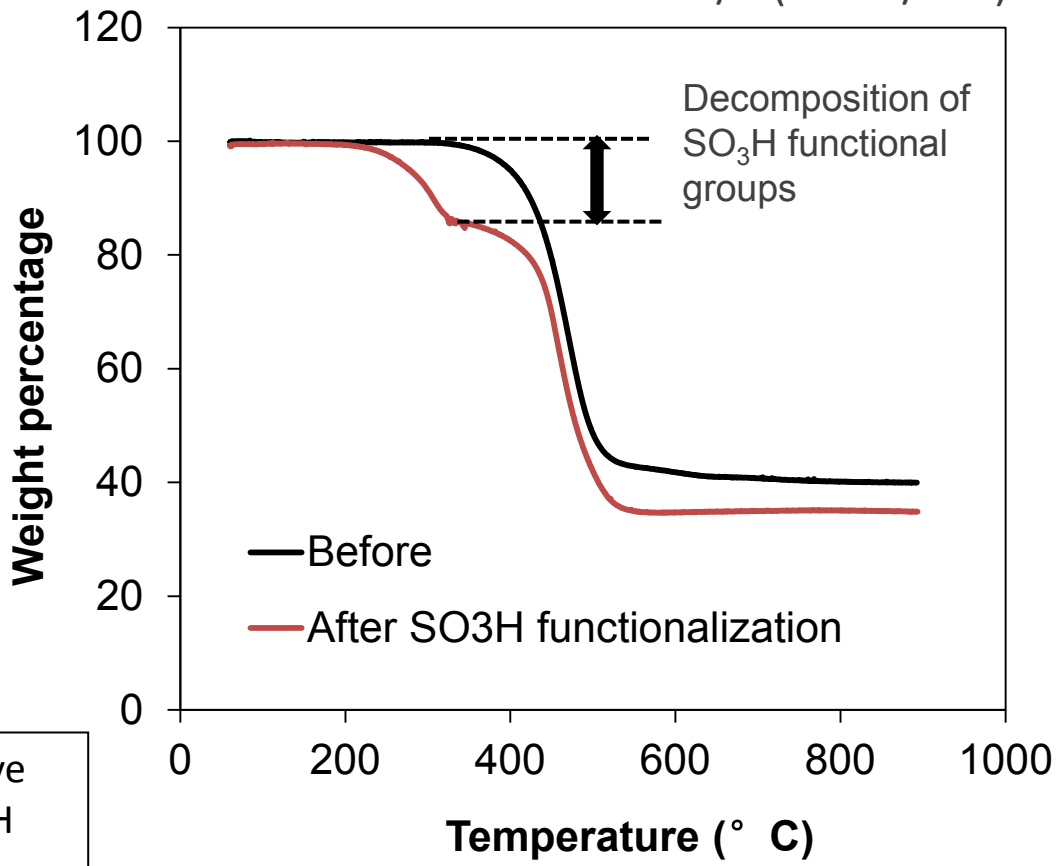


100% surface coverage: 6 µmol/m^2

US Patent 5,554,739; Electrochimica Acta 94 (2013) 172– 181

- Ketjen C, Pt/Ketjen, and d-PtNi/Ketjen have been successfully functionalized with SO_3H groups
- Proton conductivity of ~0.05 S/cm has been observed with Teflon® instead of PFSA binder

Thermogravimetric analysis of functionalized annealed Pt/C (JM 13/176)



BET Surface area after functionalization: 146 m^2/g
Proton conductivity at 80°C (PTFE binder): 0.05 S/cm

Summary of progress

- Standard Pt/C, annealed Pt/C, and d-PtNi/C catalysts and CCMs containing approximately 0.1 mg Pt/cm² 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 (0.53A/g-Pt to 0.57A/g-Pt) and improved H_2/Air CCM performance at >1A/cm².
- The best ORR mass activity obtained for the d-PtNi/C in a CCM was 0.57A/g-Pt (UTRC data), 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 (ECA/electrode area) of d-PtNi
- 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 SEF catalysts.

Remaining Challenges and Barriers: Next steps

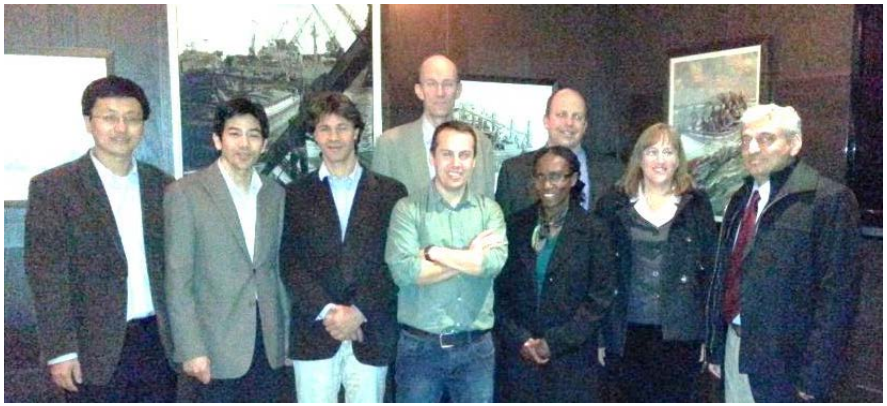
- Determine if Ni leached from d-PtNi/C during electrode fabrication is impacting electrode structure/properties
  - Experiments planned to add Ni^{2+} to Pt/C inks and electrode layers
- Improve performance at high current densities for low SEF electrodes with different ionomer content, equivalent weight ionomer, ink solvent, or proton-conducting carbon supports
  - d-PtNi cathode CCMs with new ionomer/carbon ratio have been delivered to UTRC for testing/diagnostics
  - Electrodes using proton-conducting supports are being fabricated by IUPUI
- Complete USAXS, cryo-TEM, TEM analysis of ink and electrodes for input into Monte Carlo 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, 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

Collaborations and acknowledgment

- Project team (subs) within DOE H_2 Program
  - Johnson Matthey Fuel Cells
    - Provide state of the art catalysts, inks, and CCMs for characterization efforts; fabricate CCMs using new ink compositions, materials, and techniques; scale-up the CCMs for large cells and short stacks
  - United Technologies Research Center
    - Integrate JMFC CCMs with state-of-the art cell fixture and fabrication procedure; test and perform diagnostics on cells; fabricate and test a short stack based on these CCMs
  - University of Texas at Austin
    - Pre- and post-test electron microscopy characterization of catalysts, electrodes, and CCMs
  - Indiana University Purdue University Indianapolis
    - Functionalize carbon blacks; develop ink compositions; perform cryogenic transmission electron microscopy analysis of catalyst/ionomer inks; develop ink solvent removal processes; perform porosimetry measurements on the catalyst layer; test small-scale CCMs

- General Motors
  - In-kind contributor, project advisor

- Strategic Analysis, Inc.
  - In-kind contributor, cost analysis



Thanks!

DOE, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office
  - Nancy Garland (Technology Development Manager)

Backup Slides

Description of Modeling of d-PtNi/C Electrodes and Membrane-Electrode Assemblies

1. Structural simulations of electrodes derived from microscopic and X-ray scattering characterization
2. Performance of fuel cells with d-PtNi/C membrane-electrode assemblies

2.1 Kinetics of oxygen reduction reaction on d-PtNi/C catalyst

2.2 Characterization of mass transfer overpotentials

- Helox measurements
- Limiting current density measurements
- Electrochemical impedance studies

2.3 PtO_x equilibrium coverage and kinetics of PtO_x formation and reduction

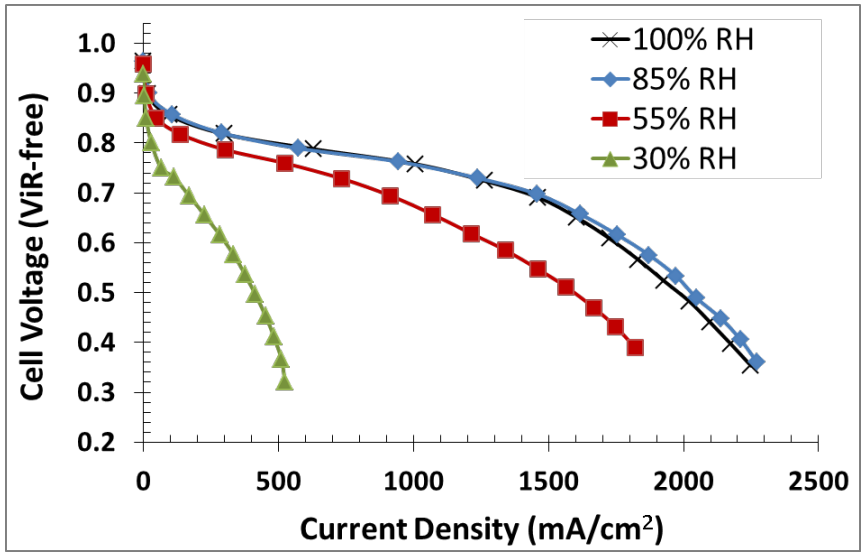
- H_2/N_2 impedance study
- Cyclic voltammetry study

Description of UTRC testing/diagnostics of Pt and d-PtNi MEAs

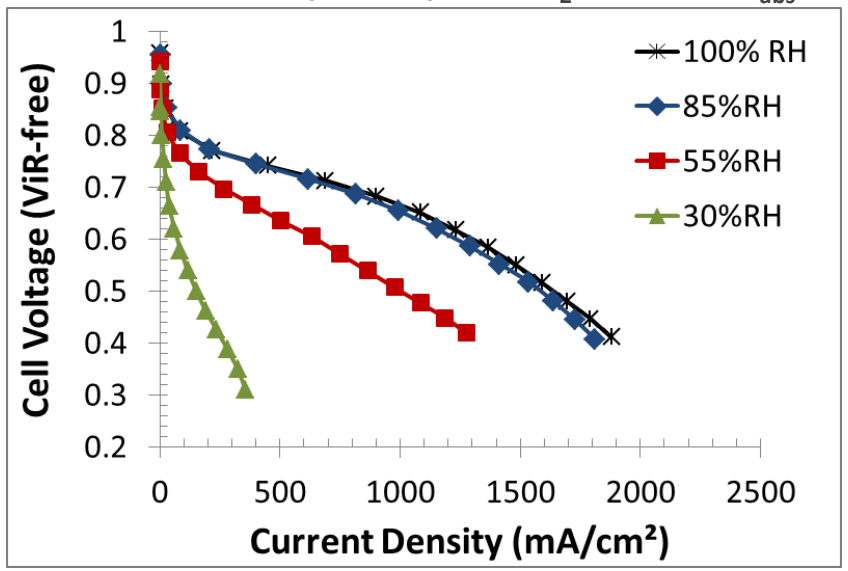
- **Beginning-of-Life (BOL) performance of MEAs (all ~ 0.1 mg/cm^2-Pt loading, except where noted):**
  - d-PtNi/C
  - Annealed Pt/C (baseline)
  - As-prepared Pt/C
- **Cell Builds:**
  - Solid bipolar plates with triple serpentine flow channels
  - Co-flow of hydrogen and oxidant flows
  - Active area = 12.25-cm^2
- **Testing protocol:**
  - Wet-up to reach cells' peak performance
  - BOL diagnostics, including:
    - H_2-pump, H_2-crossover, and ECA by CO stripping
    - Cyclic voltammetry and impedance characterization under nitrogen and air atmosphere
  - BOL performances under various conditions, including:
    - O_2 concentrations (pure O_2 - 1%)
    - Temperatures (60°C, 70°C, and 80°C)
    - Back pressures (100, 150kPa, and 200 kPa abs)
    - RHs (100%RH, 85%RH, 55%RH, and 30%RH)

Effect of RH on Air performance of d-PtNi/C, Annealed Pt/C, and non-Annealed Pt/C CCMs

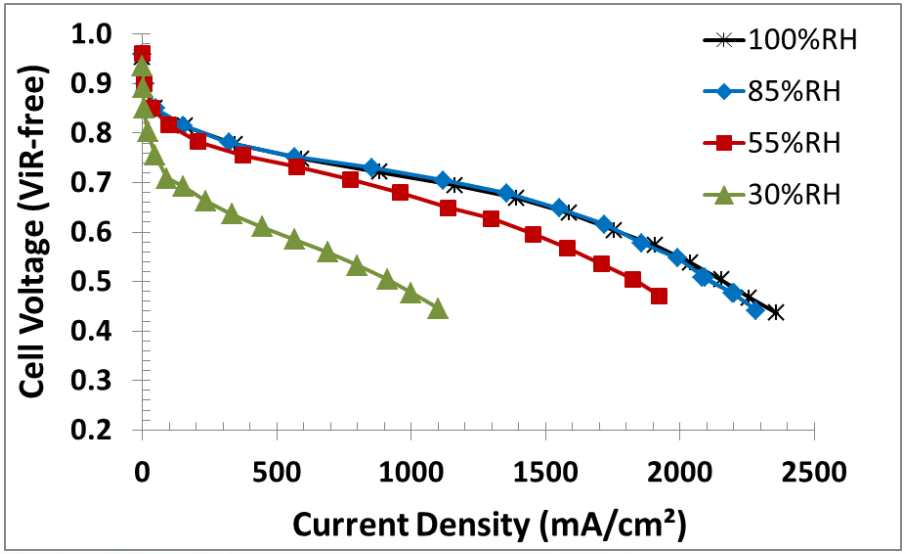
d-PtNi/C (13/300) 80°C: H_2/Air, 150kPa$_{abs}$



Annealed Pt/C (13/176) 80°C: H_2/Air, 150kPa$_{abs}$



Non-Annealed Pt/C (13/21) 80°C: H_2/Air, 150kPa$_{abs}$

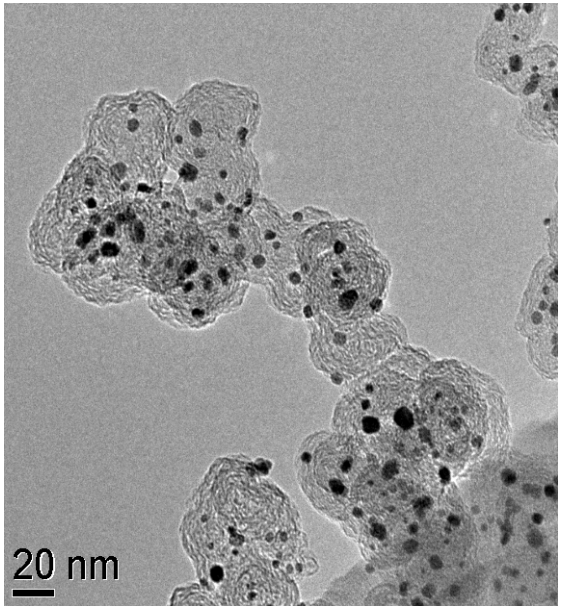


- Low SEF cathodes (d-PtNi and Annealed Pt/C) have more significant performance loss at low RH than high SEF cathodes

Comparison of annealed Pt/C and d-PtNi/C cathodes

Electrodes

Annealed Pt/C

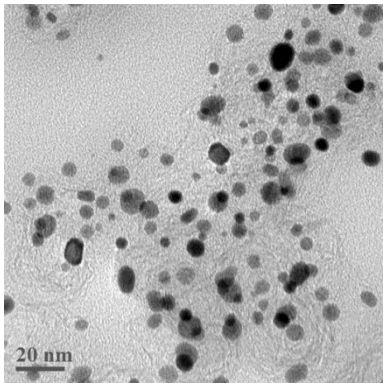


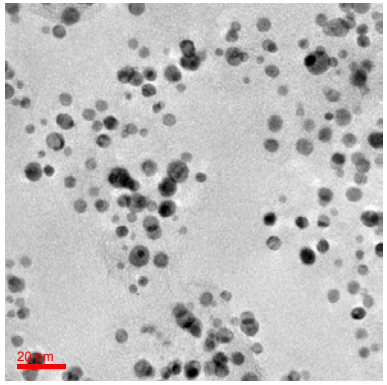
Powder

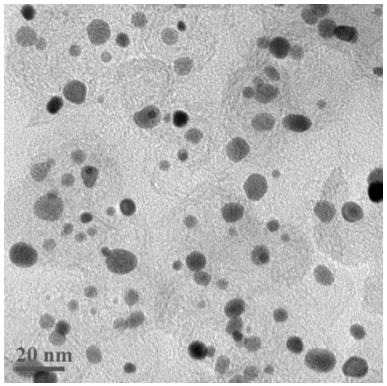
Region A
Near
membrane

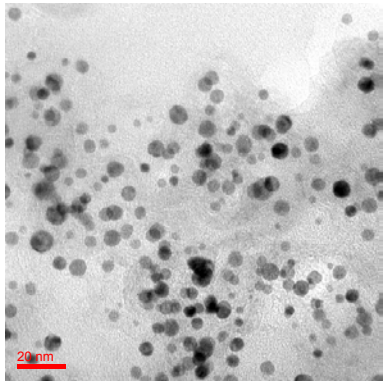
Region B
Middle of
electrode

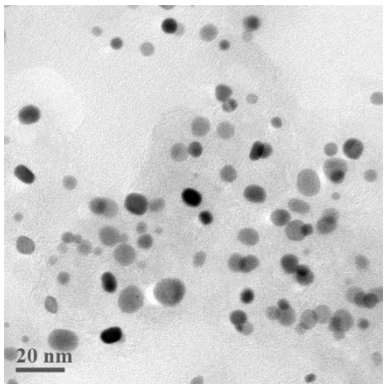
Region C
Near GDL

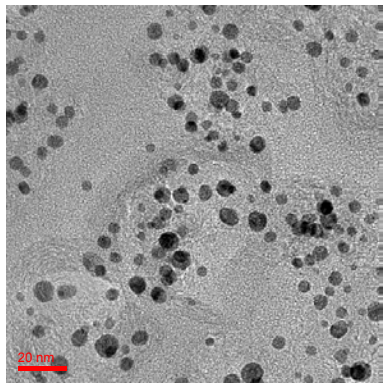




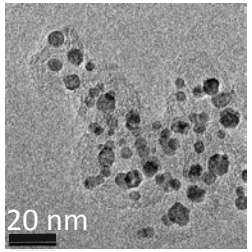








12/409
d-PtNi/C



Powder