Rationally Designed Catalyst Layers for PEMFC Performance Optimization

Debbie Myers and Nancy Kariuki
Rajesh Ahluwalia, Xiaohua Wang, and Jui-Kun Peng

Argonne National Laboratory

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Project ID# FC106

Project Overview

Timeline

- Project Start Date: April, 2013
- Project End Date: March, 2016
- Percentage complete: 67%

Budget

- FY14 DOE Funding: $1,345K
- Planned FY15 DOE Funding: $985K
- 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$_{PGM}$/cm²**
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, Brian Theobald, L. Smith, D. Ozkaya, M. Gutierrez, 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, Le Xin, Zhefei Li, Yadong Liu, Yuan Zhou and Fan Yang

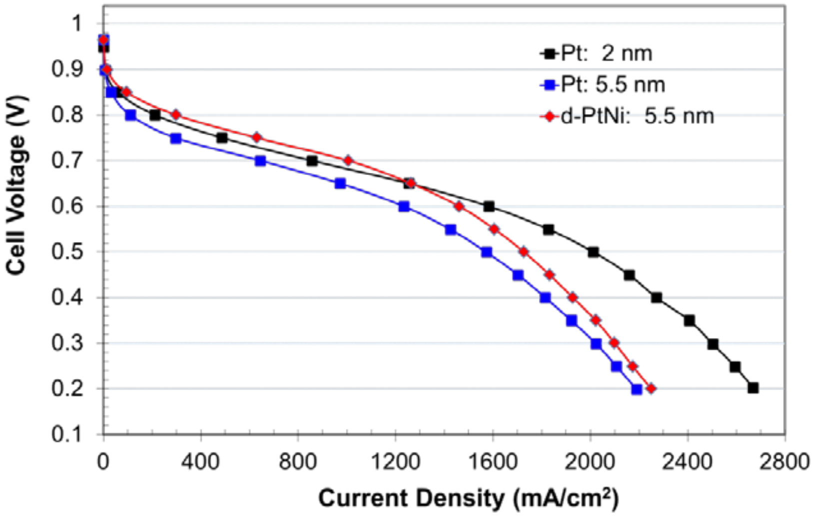
- **Project lead: Argonne National Laboratory**
  - Debbie Myers, Nancy Kariuki, Rajesh Ahluwalia, Xiaohua Wang, and Jui-Kun Peng
  - Project management, characterization of structure of catalysts, inks, and electrodes using X-ray techniques; modeling and development of optimum catalyst layer structure, 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)**

United Technologies Research Center

Johnson Matthey Fuel Cells



80°C, 100% RH, 1.5 atm Air

- **Impact on DOE Targets**

Green – met; Yellow – TBD or in-progress

Metric	Units	DOE 2020 Target	Project Status FY'14 AMR*	Project Status FY'15 AMR*
Mass activity	A/mg_{PGM}@0.9m$V_{iR\text{-}free}$	≥0.44	0.57	0.57
Specific activity	$\mu A/cm^2_{PGM}$@0.9m$V_{iR\text{-}free}$	≥720	986	986
PGM total loading	mg-PGM/cm^2_{geo}	≤0.125	0.092, cathode	0.092, cathode
MEA performance	mA/cm^2_{geo} @ 800 mV	≥300	298	347
MEA performance	mW/cm^2_{geo} @ 675 mV	≥1000	592	827

***The results shown here and in the remainder of the presentation were acquired under test conditions designed for diagnostic and modeling purposes (e.g., differential high flow conditions rather than integral, low stoichiometry conditions)**

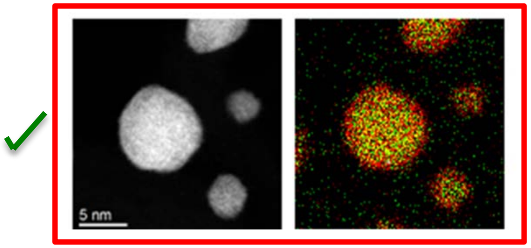
Approach

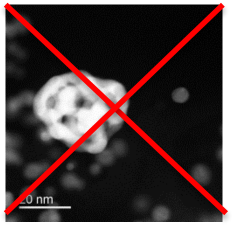
- Determine property of electrode/catalyst that limits the high current density/air performance of electrodes based on advanced Pt-based cathode catalyst
  - The advanced Pt-based catalyst is **dealloyed PtNi (d-PtNi)** developed by Johnson Matthey **(within General Motors-led FC-087 Catalyst Project).** 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 (see FC-087)**
- Use information from characterization efforts to determine the performance-limiting property of the current d-PtNi electrode
  - *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, 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

Catalyst variants and metrics

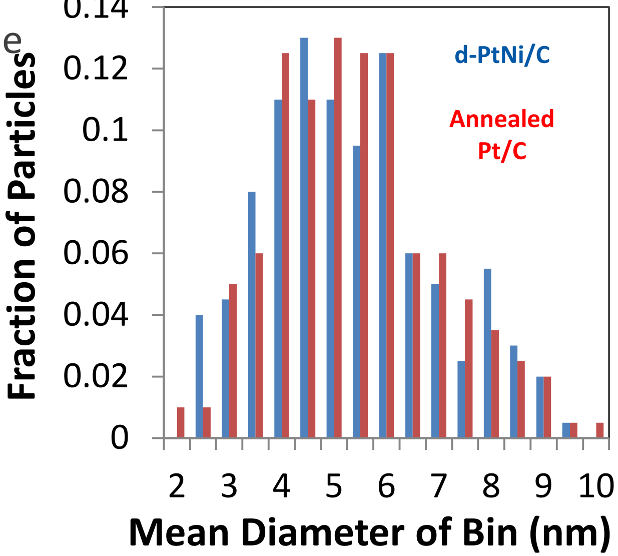
- High temperature annealing is needed to drive complete alloying of Pt and Ni in $PtNi_3$ precursor, which increases particle size
- Initial $PtNi_3$ surface area prior to annealing is ~100 m^2/g
- Annealing is followed by chemical dealloying which dissolves Ni, not Pt
- Goal is to avoid nano-porosity by using mild de-alloying conditions and by limiting particle size
- Low surface area Pt/C (An-Pt/C) with similar particle size distribution to dealloyed PtNi (d-PtNi/C) was prepared to resolve effects of particle size/surface area and catalyst type

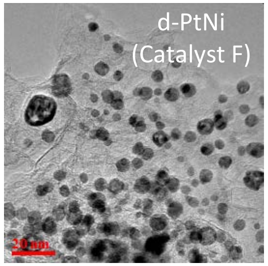
Catalyst Code	**Catalyst Type/ Annealing Conditions**	**Wt% Pt**	**Wt % Ni**	**Metal area by *ex situ* CO ads. (m^2/g-Pt)**	**Particle Size by TEM (nm)**
Pt/C	Pt/C Not annealed	28.3	-	92	2.0±0.1
An-Pt/C	Pt/C High T	29.7	-	37	5.42±1.78
d-PtNi/C	PtNi (57:43) High T	29.1	6.68	50	5.40±1.58





Red-Pt
Green-Ni





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Current Year's Activities

- Improvements in performance, coupled with diagnostics
  - Effect of ionomer content on d-PtNi and annealed Pt/C MEA performance (Perfluorosulfonic acid ionomer to carbon (I/C) ratios of 0.8 and 1.2)
  - Effect of organic solvent in ink on d-PtNi and annealed Pt/C MEA performance
  - Impact of acid-washing of MEA on d-PtNi cathode catalyst layer performance
  - Functionalization of carbon support with proton-conducting groups for An-Pt/C and d-PtNi/C catalysts

- Diagnostics to determine sources of performance limitations for d-PtNi/C cathode catalyst layers and to determine impact of Ni^{2+} in electrode layer
  - Polarization curves as a function of temperature, relative humidity, pO_2, and stoichiometry; limiting current measurements
    - Modeling of polarization curves to extract sources of cell voltage losses
  - Electrochemical impedance spectroscopy and equivalent circuit analysis of cell resistances
  - Effect of doping Ni^{2+} into annealed Pt/C cathode catalyst layer on cell performance
  - Rotating-ring disk experiments to determine impact of Ni^{2+} on ionomer permeability
  - Analysis of Ni^{2+} content in inks and electrode layers using energy dispersive X-ray spectroscopy/electron microprobe and X-ray fluorescence spectroscopy
  - Light scattering of diluted inks to determine carbon agglomerate structure
  - Ultra-small angle X-ray scattering (USAXS) to determine agglomerate structure of Pt/C, An-Pt/C, and d-PtNi/C inks and inks during solvent removal, and of decals, electrodes, and supernatant from inks

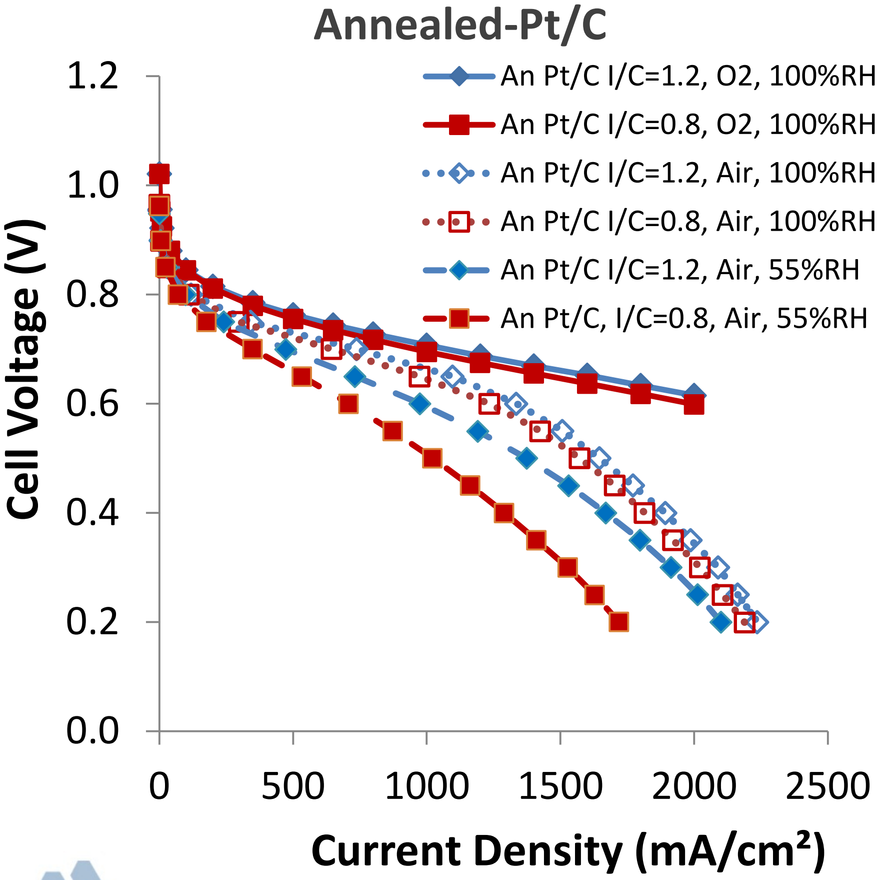
FY'14 Go/No-Go and FY'15 Milestones

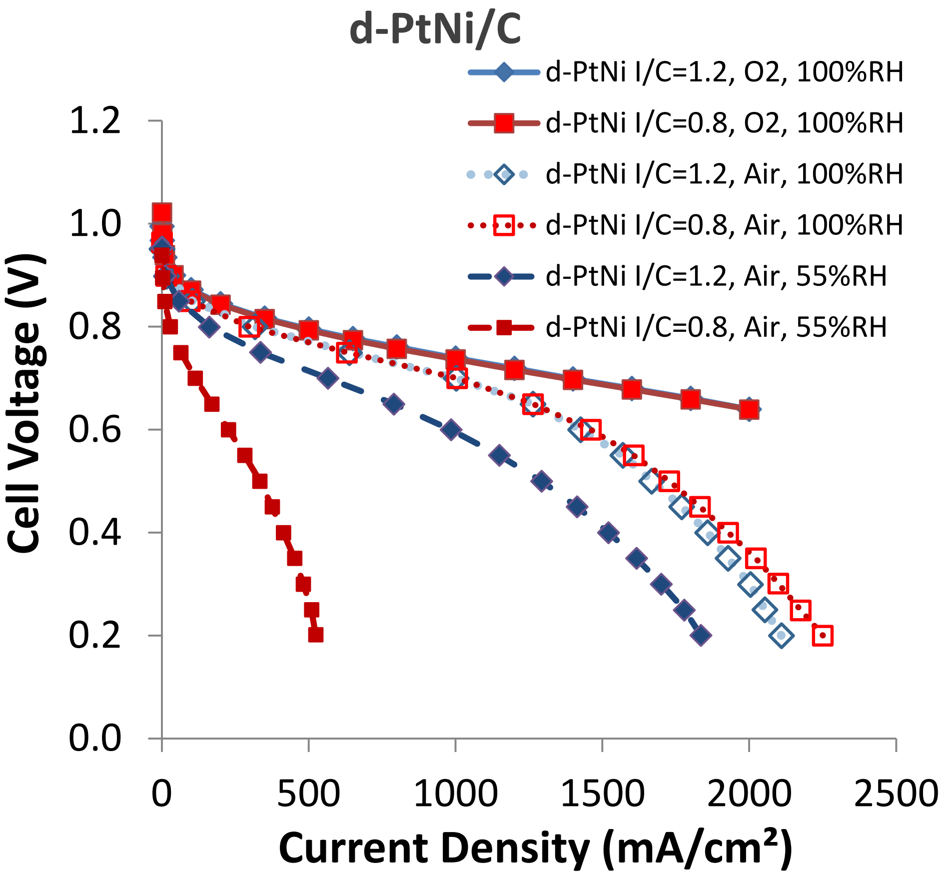
Improve performance by 50% (increase iR-free cell voltage at 1 A/cm² by 67 mV to 632 mV)	9/30/14 Go/No-Go Status: Exceeded – Go. Status of performance as of 9/30/14 was 740 mV at 1 A/cm² on H_2/air
Fabricate and test ccm's containing the annealed Pt/C and dealloyed PtNi/C catalysts with an alternative ionomer to carbon ratio, alternative equivalent weight ionomer, and/or alternative solvent	12/31/2014. Status: Completed. Pt/C and d-PtNi/C CCMs with I/C = 1.2 were fabricated and tested; Pt/C and d-PtNi/C CCM's with I/C=0.8 and organic solvent were fabricated and tested
Fabricate and test three CCMs with dealloyed PtNi cathode catalyst supported on a functionalized proton-conducting carbon support and test their performance on hydrogen-air and hydrogen-oxygen	3/31/2015. Status: Completed. 5 grams each of functionalized d-PtNi/C and annealed Pt/C were synthesized. 5 cm² active area MEAs were fabricated and tested at IUPUI. 50 cm² active area MEAs were fabricated by JM and tested at UTRC.
Complete cathode catalyst layer performance model, using electrode structures obtained from TEM and X-ray scattering data	6/30/2015 Status: on-going
Improve high current density air performance of a membrane-electrode assembly containing the dealloyed PtNi-based cathode catalyst by ≥115 mA/cm² at 0.675 V/cell in order to achieve ≥850 mW/cm² at rated power, toward the DOE 2020 target of 1,000 mW/cm² at rated power.	9/30/2015 Status: Achieved an increase of 90 mA/cm² to 1225 mA/cm² at 0.675 V (827 mW/cm²) through a combination of increase of ionomer content and acid-washing

Accomplishments: Determined Effect of increased ionomer content on An-Pt/C and d-PtNi/C catalyst layer performance

- **Higher ionomer to carbon ratio (1.2 vs. 0.8):**
  - Enhanced the performance of both the Annealed-Pt/C and d-PtNi/C cathodes under dry conditions
  - Enhanced the performance of the An-Pt/C cathode under all relative humidity and pO_2 conditions
  - Decreased the performance of the d-PtNi/C cathode in the mass transport region on air at 100% RH

80°C, 150 kPa (abs.), high and fixed flow for differential conditions (3 SLPM O_2 or air)



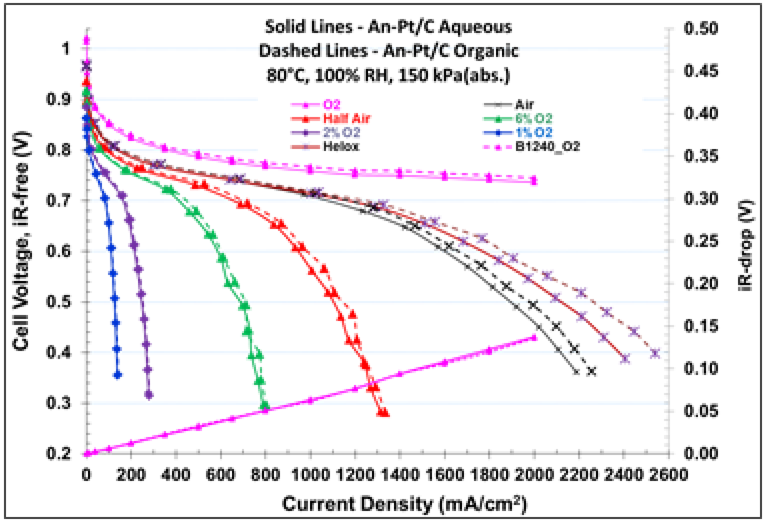


Accomplishments: Determined effect of organic versus aqueous solvent in inks on An-Pt/C and d-PtNi/C performance

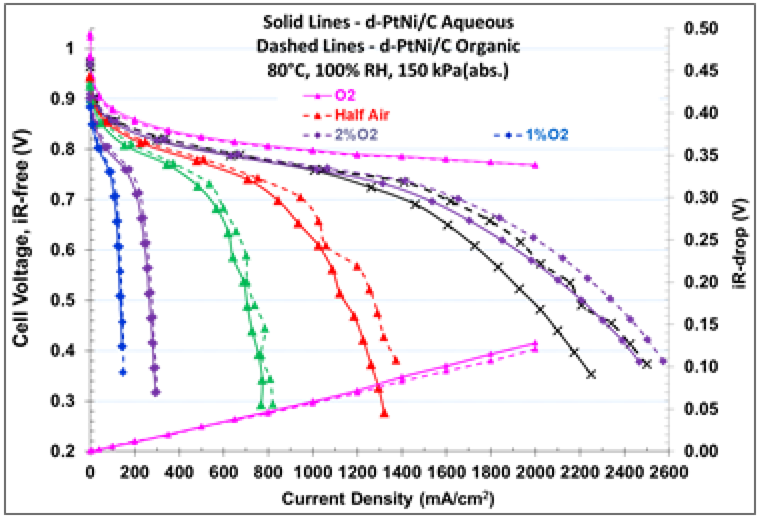
Organic: 0.104 mg-Pt/cm^2 Aqueous:0.090 mg-Pt/cm^2

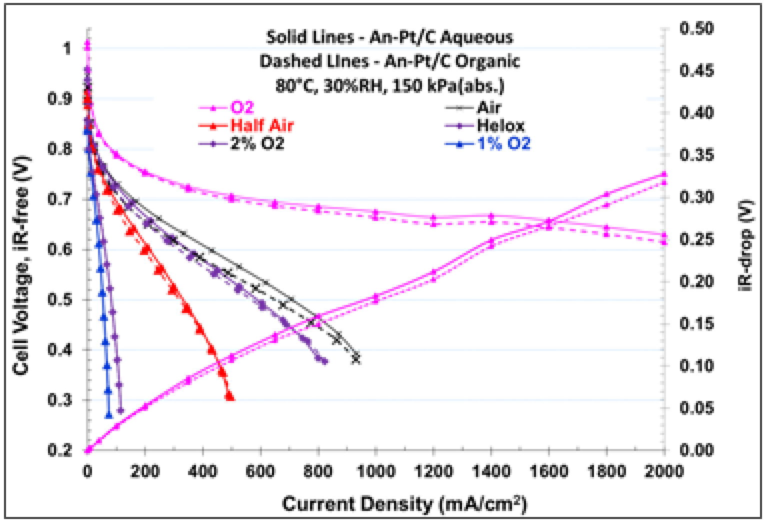
I/C=0.8

Organic: 0.115 mg-Pt/cm^2 Aqueous:0.0949 mg-Pt/cm^2

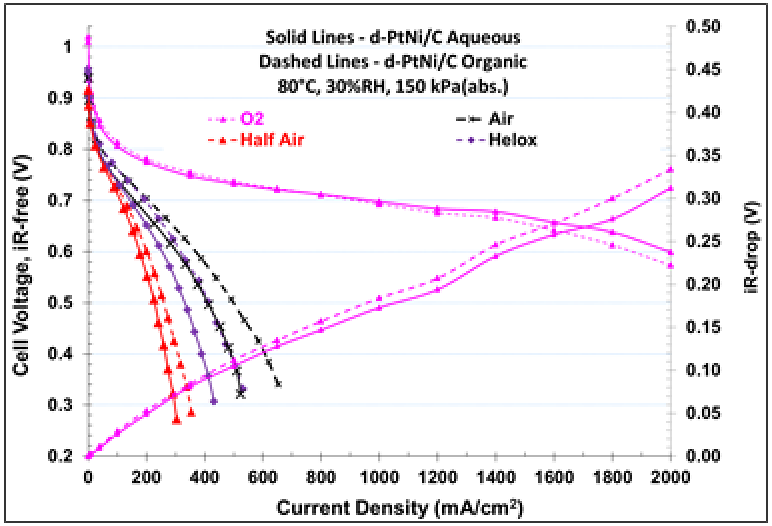


100%RH





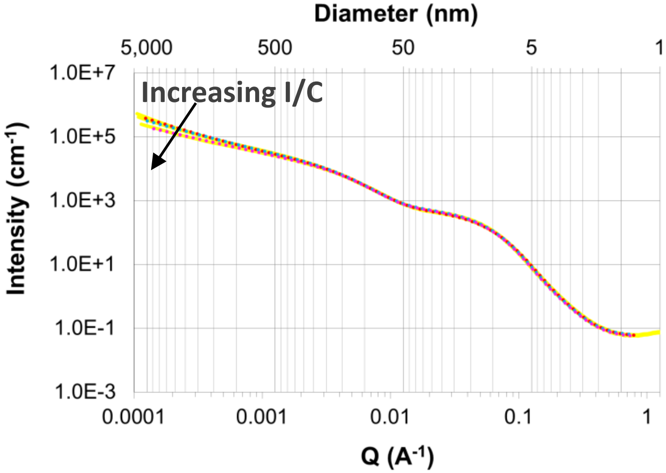
30%RH



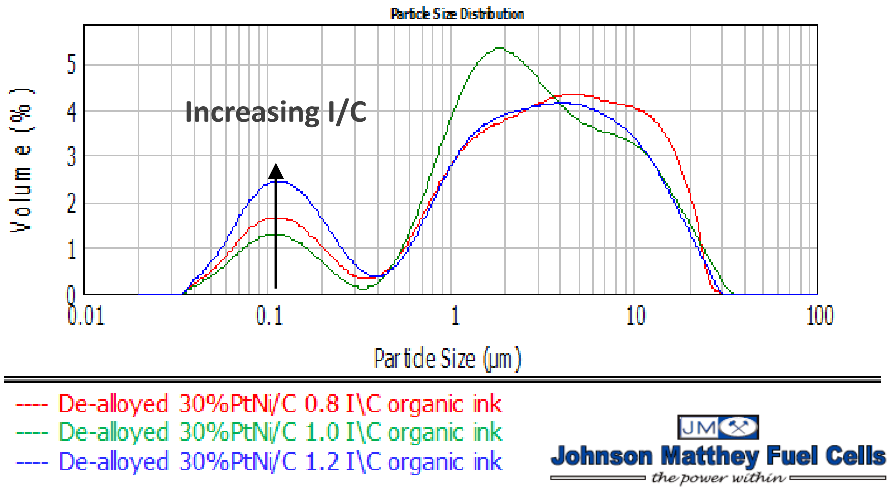
- Organic ink *primarily* enhanced the performance of the An-Pt/C and d-PtNi/C cathode at high and low RH – extent of effect is pO$_2$ dependent. Note: results representative of 1-D conditions, not of behavior under realistic stoichiometry.

Accomplishments: Impact of ionomer content on An-Pt/C and d-PtNi/C inks and electrodes

USAXS of An-Pt/C aqueous ink, I/C=0.8, 1.0, 1.2



Light scattering of d-PtNi/C organic ink; I/C=0.8, 1.0, 1.2

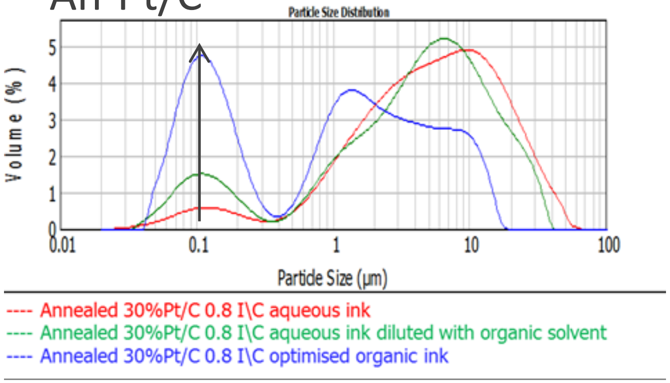


I/C	Agglomerate Mean Size (nm)
0.8	80.5
1.0	77.3
1.2	74.3

- Increasing the ionomer to carbon ratio from 0.8 to 1.2 in general resulted in:
  - More particle breakup in dilute inks (increased volume distribution at 100 nm in light scattering)
  - More particle breakup in concentrated inks (decreased intensity in >500 nm range in USAXS)
  - A 12% reduction in catalyst layer pore volume fraction for d-PtNi/C cathode
  - A 37% reduction in catalyst layer permeability for d-PtNi/C cathode

Accomplishments: Impact of solvent type on An-Pt/C and d-PtNi/C inks and electrodes

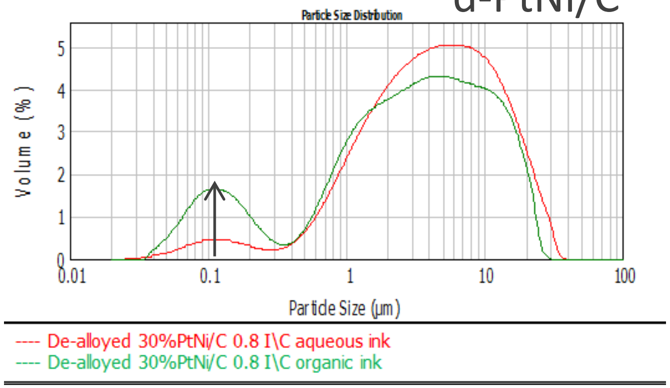
An-Pt/C



I/C = 0.8

Light scattering of dilute inks

d-PtNi/C



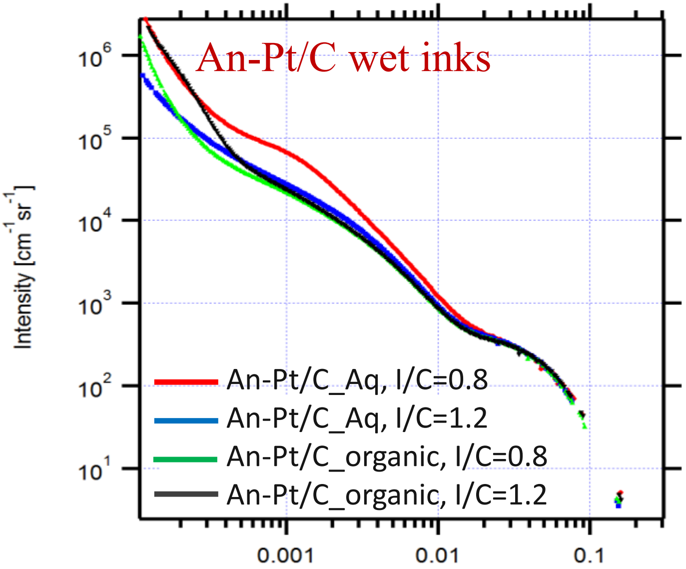
- An-Pt/C aqueous vs. organic solvent in ink:
  - The optimized organic ink gave increased particle breakup compared to the aqueous and un-optimized organic inks

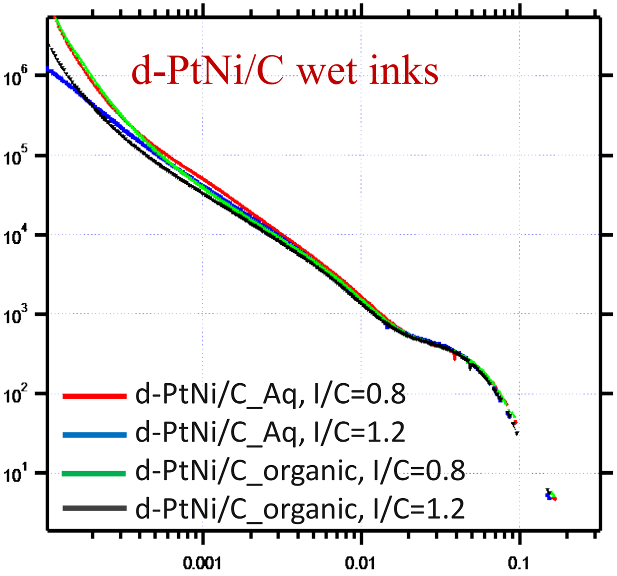
- d-PtNi/C organic vs. aqueous solvent in ink:
  - The organic ink showed more particle breakup compared to the aqueous ink
- Catalyst layers made from the organic ink showed:
  - A 6% increase in pore volume fraction
  - An 18% increase in permeability

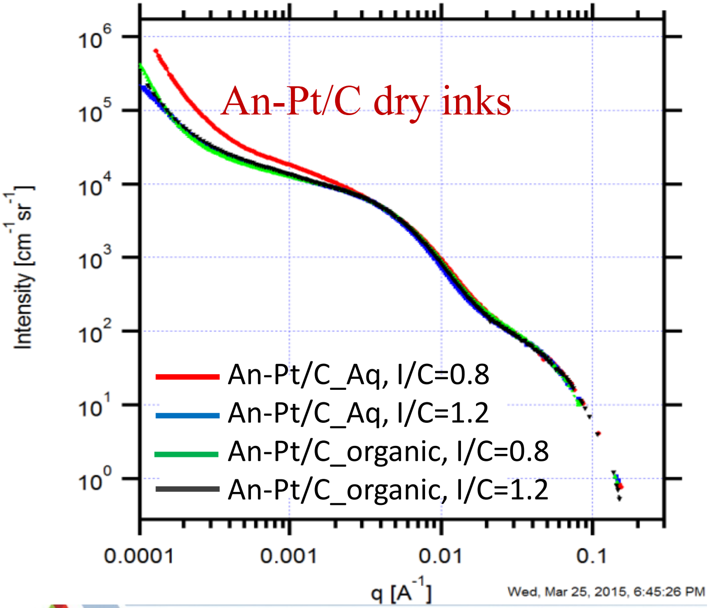
- **For the same ionomer loading and solvent mix, the An-Pt/C catalyst ink showed significantly more particle breakup than the d-PtNi/C material.**
- **Unlike the particle breakup associated with increasing I/C, increased particle breakup associated with organic solvent increased permeability.**

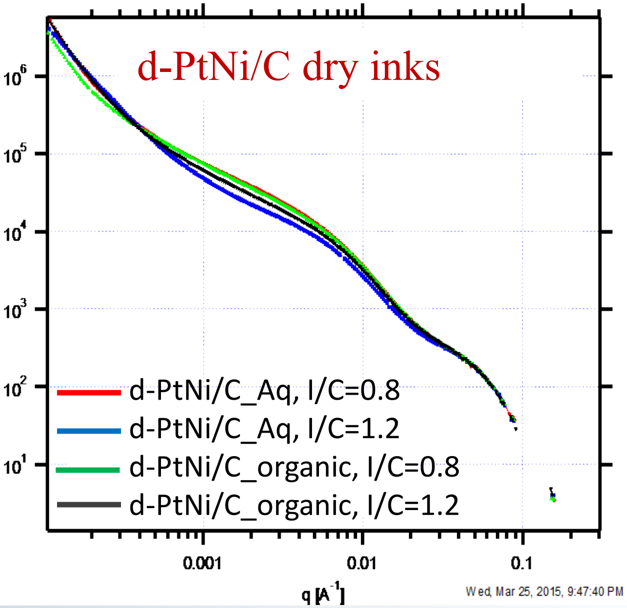
Accomplishments: Agglomerate structure of An-Pt/C and d-PtNi/C Inks and Dry Inks

High solids Inks





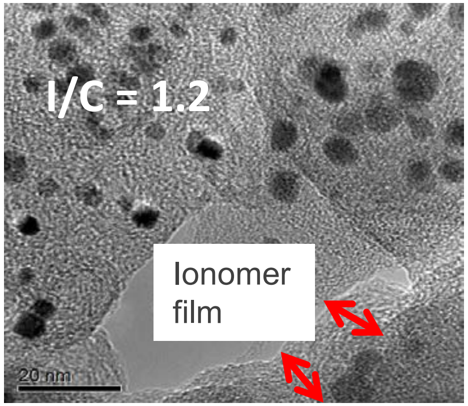




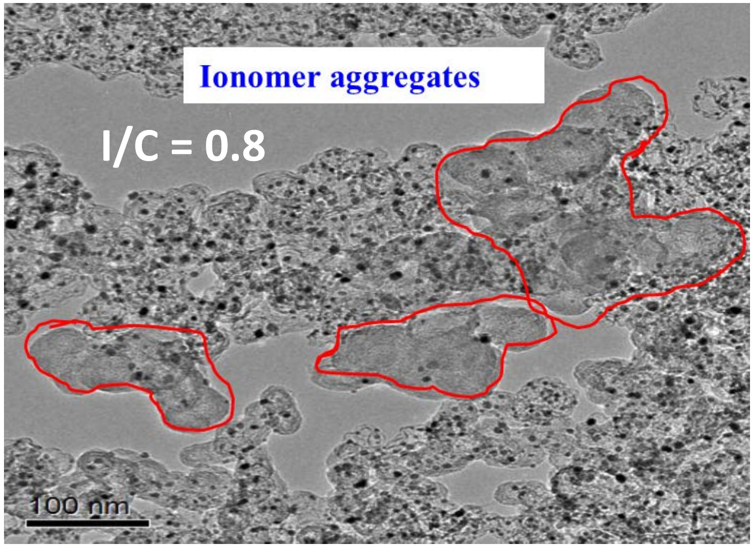
- Pt and d-PtNi inks are influenced by solvent type and ionomer content: low I/C and water inks have large agglomerates, high I/C and/or organic solvent show smaller agglomerates
- Weak scattering of the d-PtNi ink in the low q “agglomerate”: denser particle packing – Ni^{2+} in ionomer aiding “cross-linking” (denser structure shown in 2014 AMR, slide 11)
- An-Pt/C layers from organic solvent have similar agglomerate structure; low I/C aqueous ink has a larger secondary agglomerate structure
- d-PtNi/C dry inks show smaller agglomerate size for high I/C and organic solvent
- d-PtNi/C dry inks have a less uniform agglomerate structure than An-Pt/C dry inks

Accomplishments: TEM/SEM characterization of inks and catalyst layers

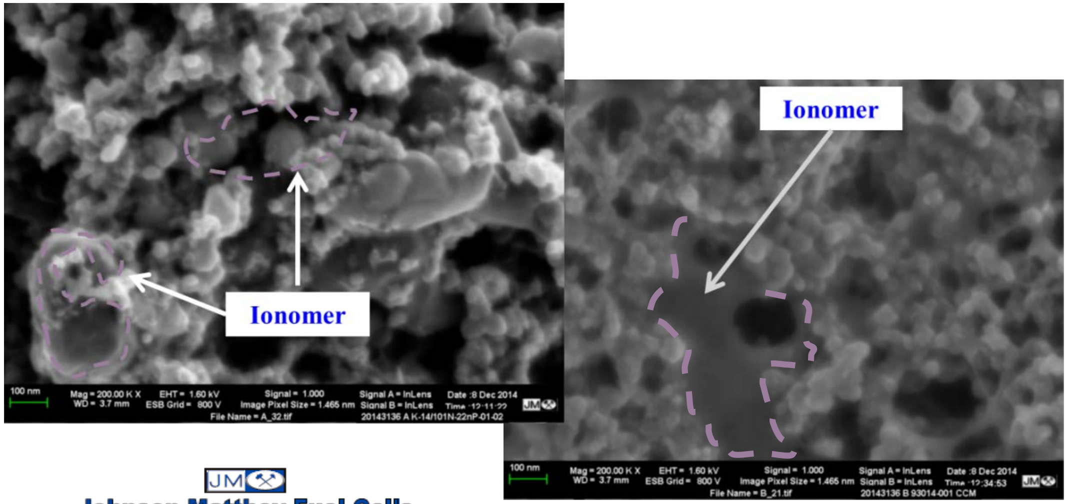
Cryogenic TEM of
An-Pt/C Aqueous Inks



- A thicker ionomer film on the catalyst was observed at high ionomer loading (I/C=1.2 vs 0.8).
- In addition to ionomer coating the catalyst/carbon, large agglomerates of ionomer were observed.
- The catalyst layer with I/C = 1.2 had reduced porosity, possibly caused by a combination of thicker ionomer loading on support and increased particle breakup causing denser particle packing.



HR-SEM characterization of d-PtNi/C catalyst layer made from organic ink with I/C=0.8



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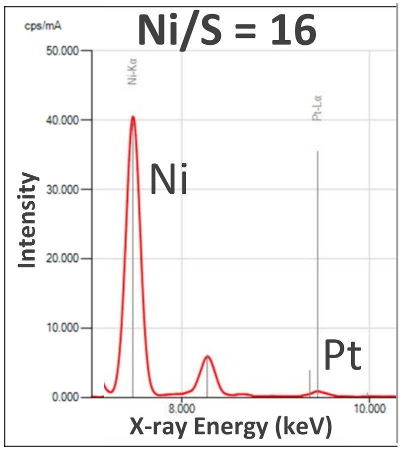
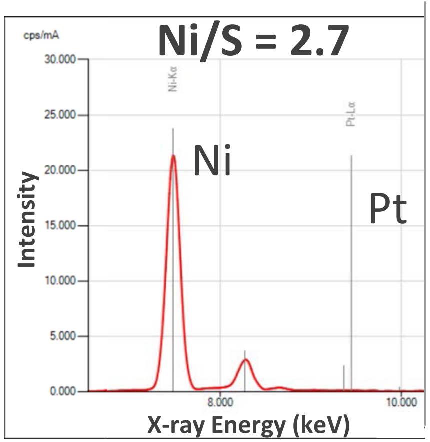
Accomplishments: Determined extent of Ni lost from d-PtNi catalyst during ink preparation, MEA fabrication, and testing

Centrifuged ionomer/solvent from d-PtNi high solids aqueous ink. Supernatant contains **2% Ionomer.**

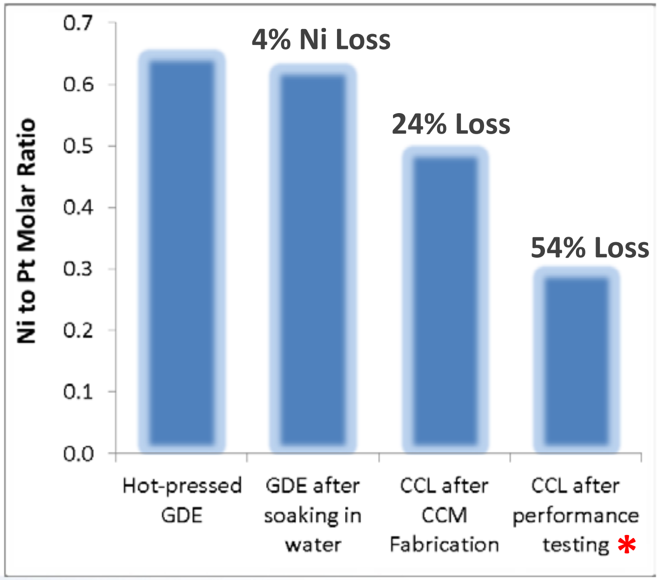


X-ray fluorescence (XRF) of dried supernatant from catalyst-ionomer-solvent inks

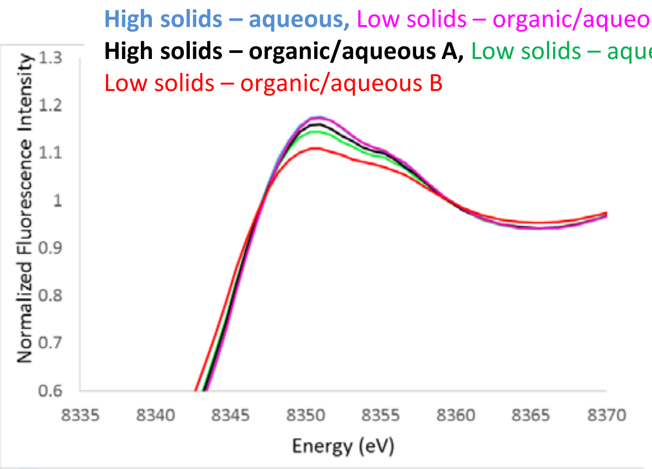
Centrifuged ionomer/solvent from d-PtNi high solids organic ink. Supernatant contains **5% Ionomer.**



XRF of GDEs and CCLs at various stages of preparation and testing. High solids aqueous ink with I/C = 0.8 used to make GDE and CCLs



Ni K-edge XANES

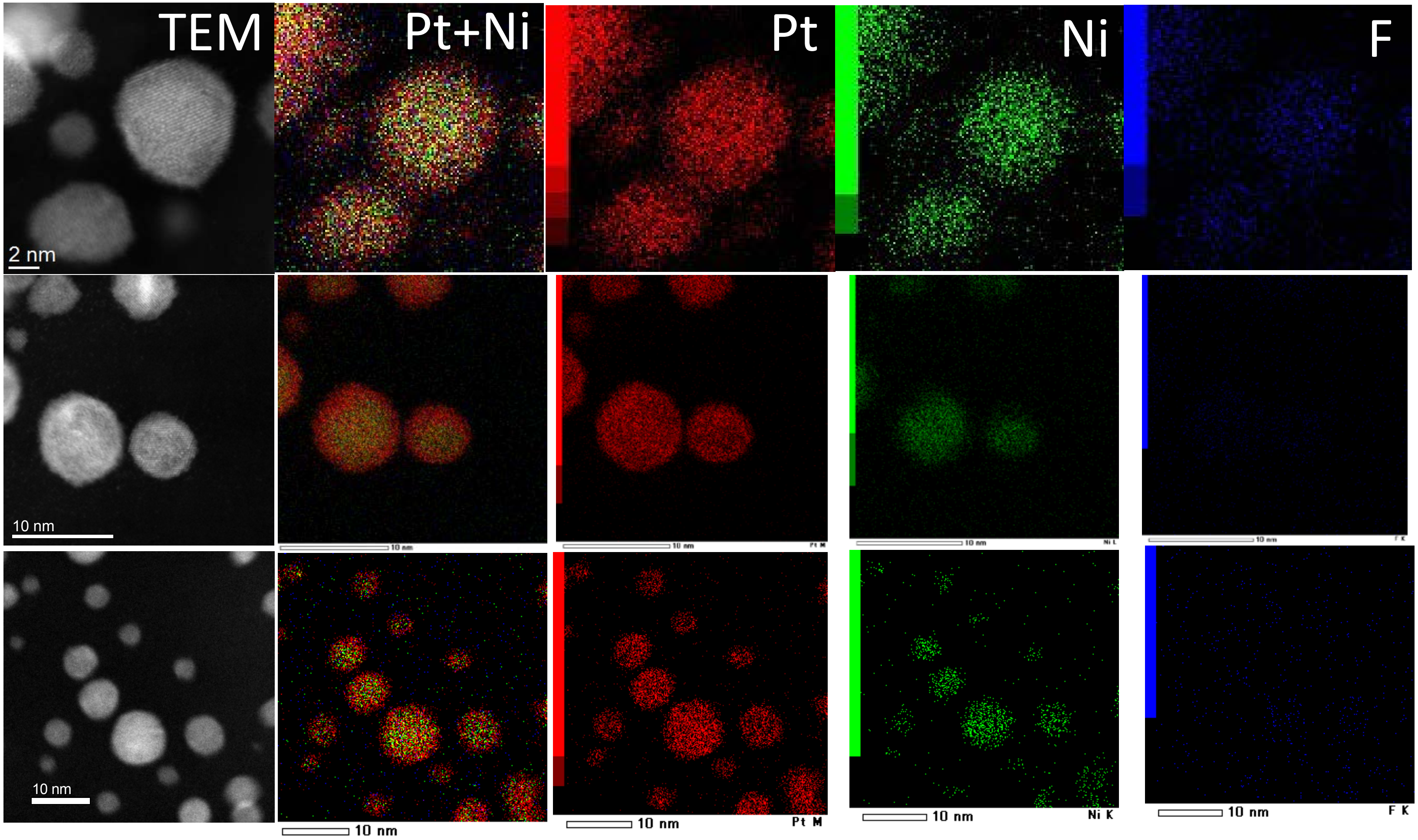


GM FC087 2014 AMR presentation (slide 9): approx. 63% of Ni lost after voltage cycling

GDE: Gas-diffusion electrode
CCL: Cathode catalyst layer
CCM: Catalyst-coated membrane

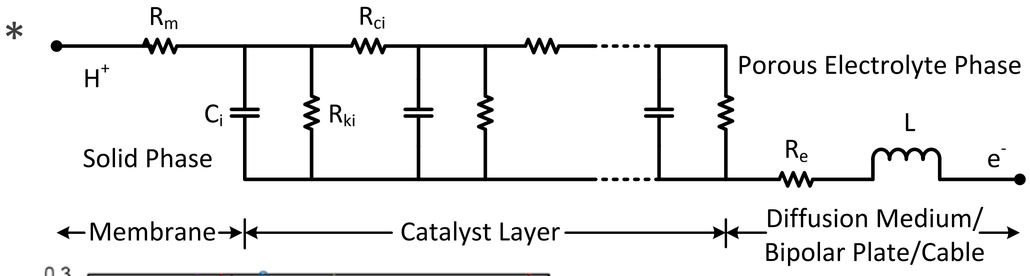
*After two week extensive performance testing at UTRC

Accomplishments: Microscopy and EDAX of d-PtNi/C in MEA



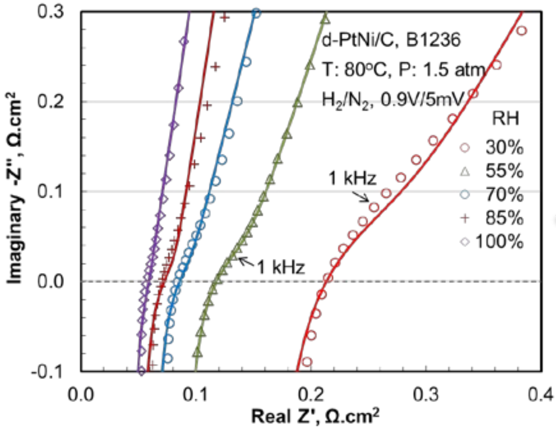
- Ni EDAX signal observed in particles and around particles
- Ionomer is more associated with catalyst particles than with carbon (Fluorine EDAX)

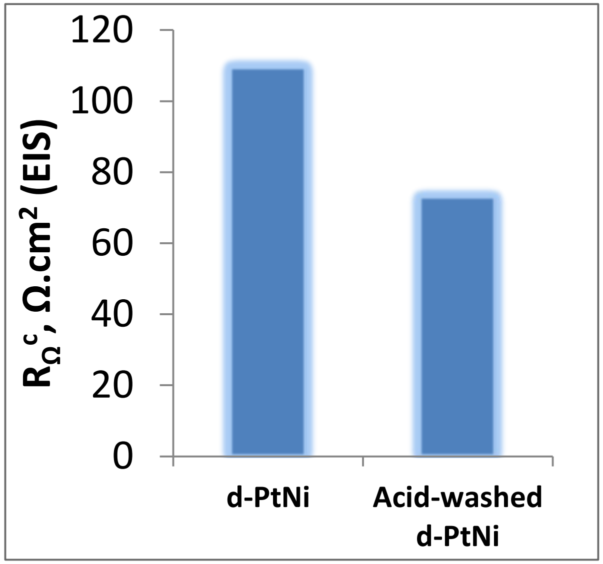
Accomplishments: Impact of Ni^{2+} in ionomer on cathode resistance and ionomer oxygen permeability

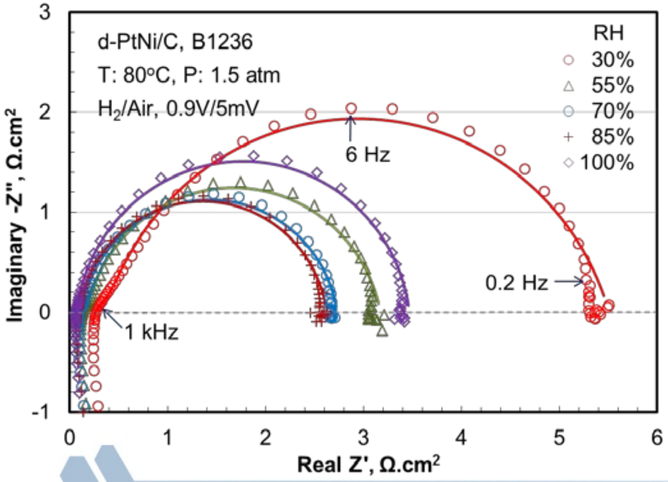


$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} + \frac{1}{i_f} = \frac{1}{i_k} + \frac{1}{BC_o w^{1/2}} + \frac{L}{nFC_fD_f}$$

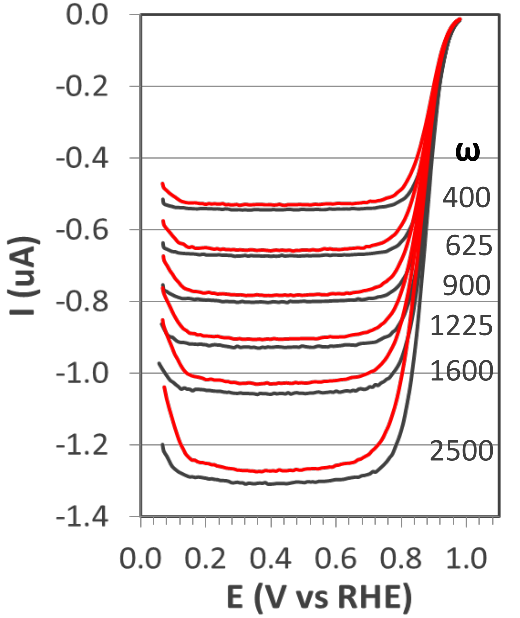
$C_fD_f(Ni^{2+})/C_fD_f(w/o\ Ni^{2+}) = 0.94$





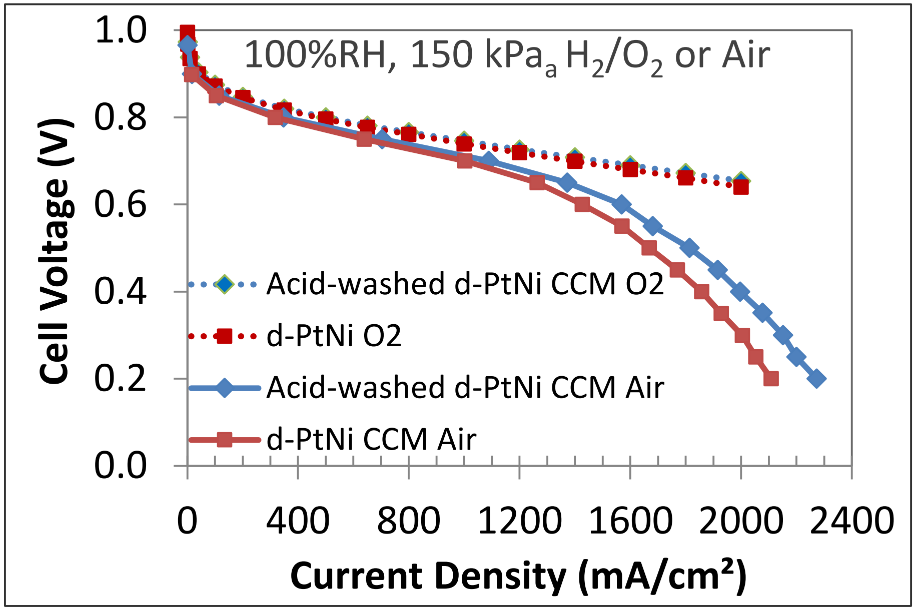


ORR on Ionomer-coated Poly Pt with (red) and w/o 10 mM Ni^{2+} (black)

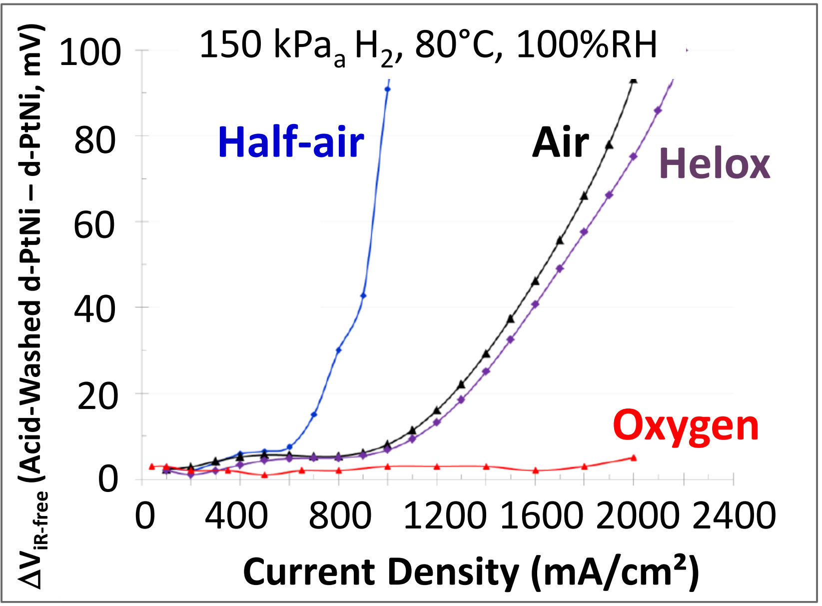


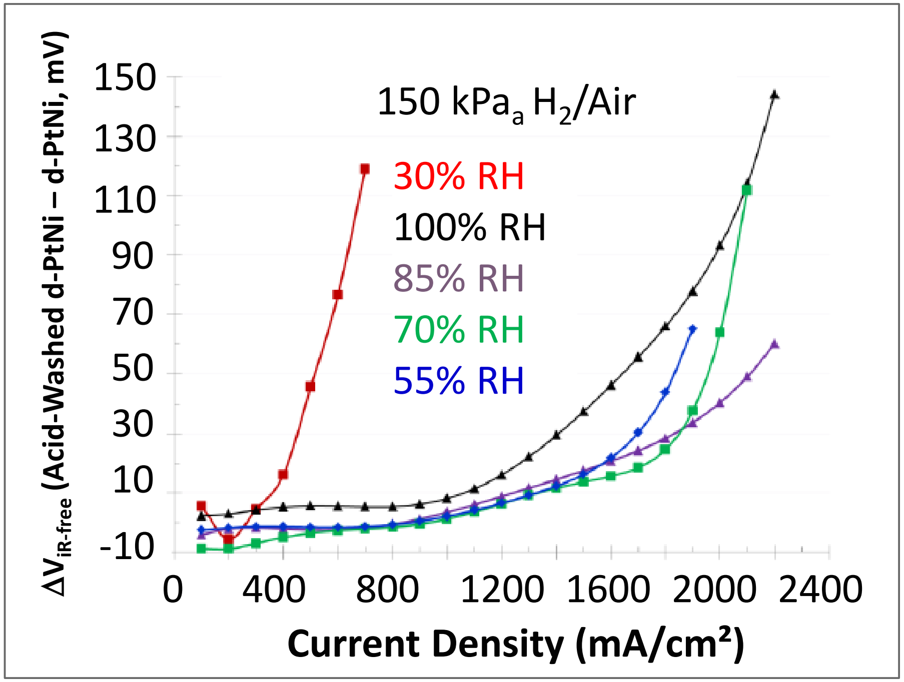
*R. Makharia, M. T. Mathias, and D. Baker, "Measurement of Catalyst Layer Electrolyte Resistance in PEFCs using Electrochemical Impedance Spectroscopy," JECS, 152 (5) A970-A977 (2005)

Accomplishments: Effect of acid treatment on d-PtNi CCM performance



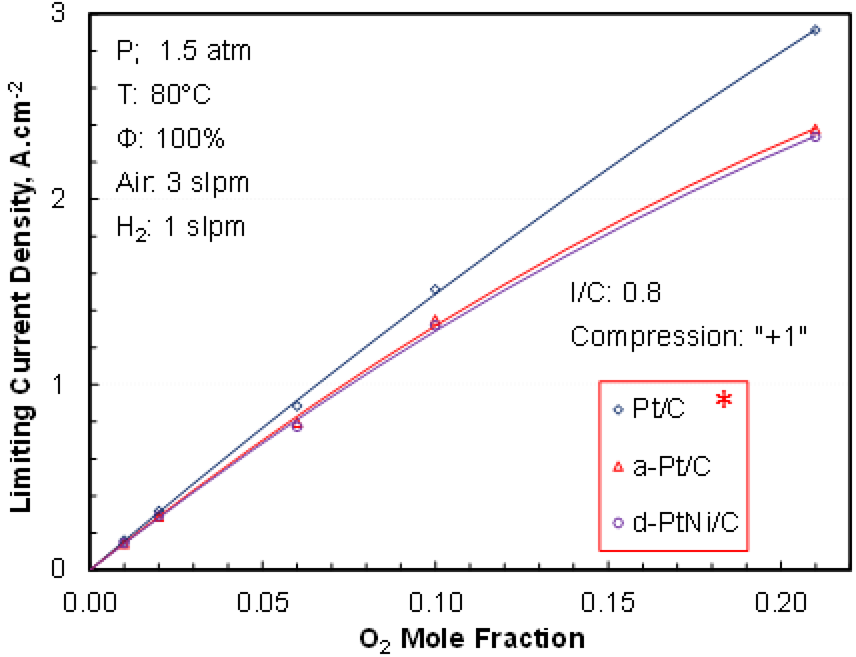
- Acid washing d-PtNi MEAs
  - Did not effect the catalyst's ORR activity
  - Lowered the membrane resistance, by 8% at 100%RH and by 15% at 55%RH and 30%RH
  - Lowered the mass transport losses on air and on lower pO_2 cathode gases, especially at 30% RH
  - **Increased H_2/Air power density by 89 W/cm²**
- Comparison of air and helox data indicates that acid-washing improves mass transport in condensed phase rather than gas phase

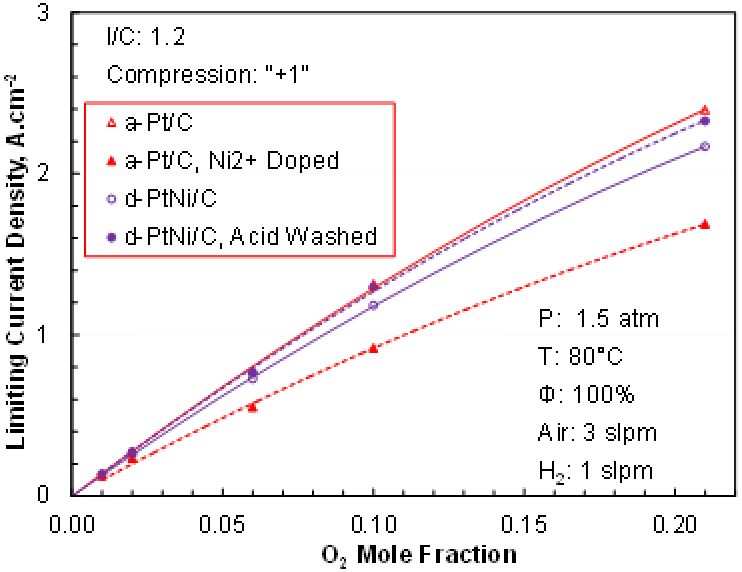


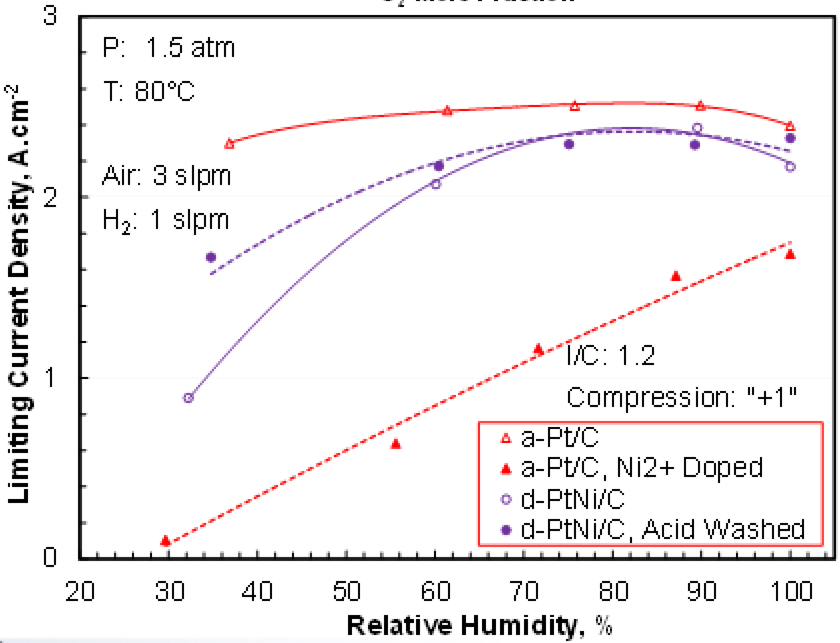


Summary of limiting currents: effect of catalyst type, Ni^{2+} doping, and acid-washing of CCM

*Pt/C does not meet lifetime targets due to small Pt particle size





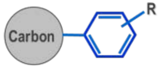


- Limiting current densities* (I_L) at 100% RH for An-Pt/C and d-PtNi/C are similar and are lower than I_L for Pt/C
  - I_L correlates with the absolute ECA (cm^2) of catalyst
  - I_L increases at higher pressures and at higher pO_2
  - I_L is lower for d-PtNi/C at low RH; acid-washing removes this limitation

***I_L defined as the current density at which the mass transfer overpotential equals 450 mV**

Accomplishments: Impact of -SO_3H functionalization of support

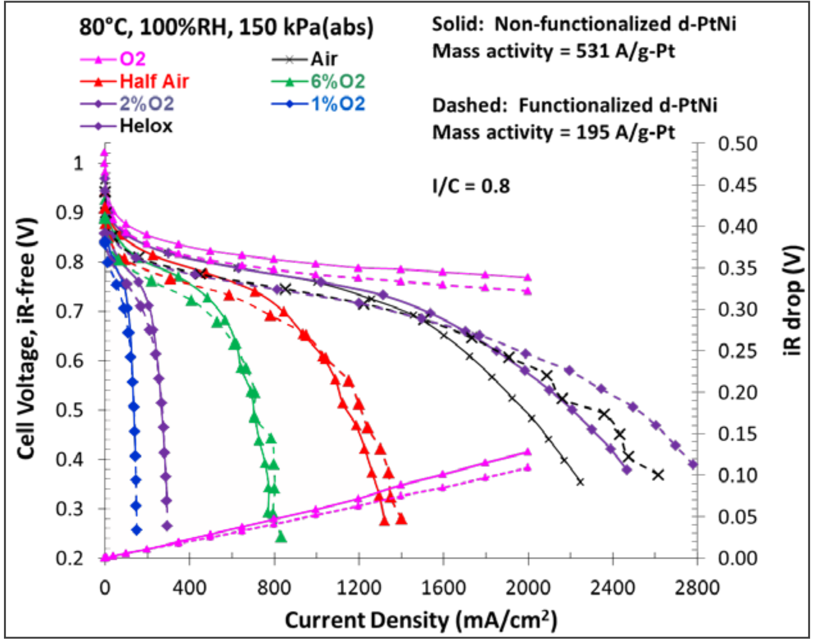
- Functionalizing carbon support decreases the mass activity and kinetic performance of d-PtNi/C, but improves mass transport and mid- to low-RH performance

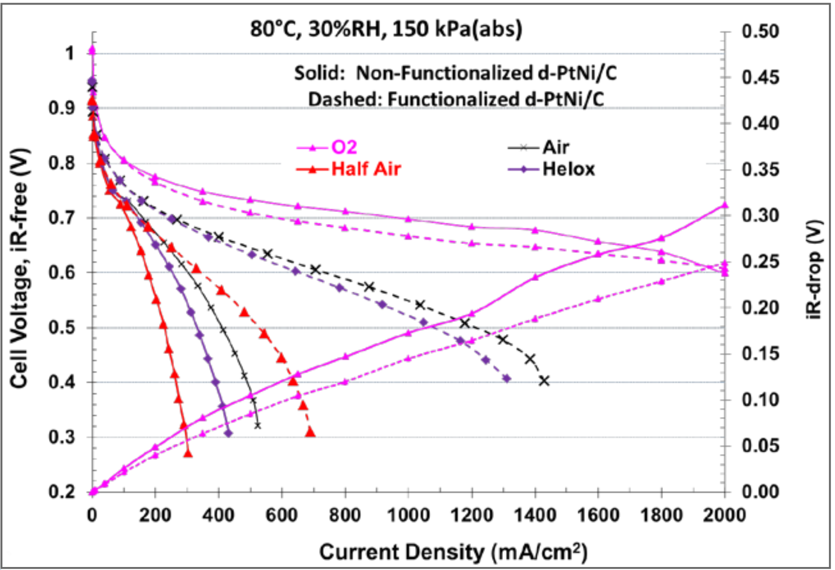


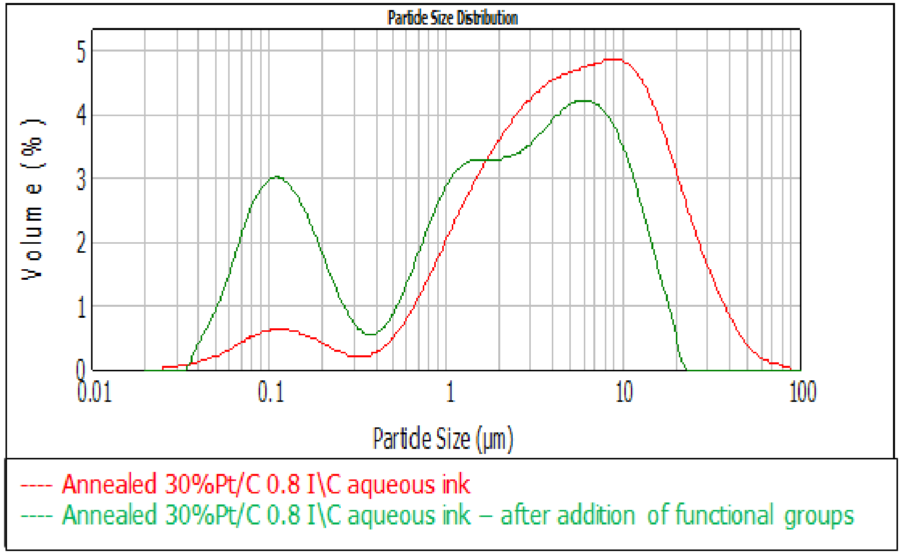
IUPUI

- RDE measurements confirm decrease of ORR mass activity due to functionalization (by 55%)
- Light scattering of dilute inks shows that functionalization aids in break up of carbon agglomerates
- Porosimetry of catalyst powder shows functionalization decreases number of 0.1 to 1 µm pores and eliminates 4 to 50 µm pores

Non-functionalized: 0.092 mg-Pt/cm^2
Functionalized: 0.139 mg-Pt/cm^2







Summary of Results

- 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=0.8
  - Reactant transport to d-PtNi/C at 100% RH is linked to low absolute catalyst ECA (same as for An-Pt/C). At low RH, additional mass transport losses are observed which are unique to d-PtNi/C.
- Ni^{2+} is leached from d-PtNi into ionomer during ink preparation and MEA fabrication:
  - Ni^{2+} in ionomer decreases O_2 permeability and decreases catalyst layer ionic conductivity
  - Acid-washing CCM improves mass transport in d-PtNi/C catalyst layer, improving H_2-Air performance at 0.675 V by 90 mA/cm^2 to 1225 mA/cm^2 and greatly improving low RH performance
- Organic solvent vs. aqueous solvent in catalyst-ionomer inks:
  - Increases breakup of carbon agglomerates, increasing fraction of small agglomerates (70-100 nm)
  - 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 Ni^{2+} in the “free” ionomer
  - “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 (see supplemental material for USAXS results)
  - Primarily enhances cathode performance at high and low RH – extent of effect is pO_2 dependent
- Increased ionomer content (I/C ratio) in inks:
  - Increases breakup of carbon agglomerates, increasing fraction of small agglomerates (70-100 nm)
  - Decreases catalyst layer pore volume fraction and permeability
  - Enhances the MEA performance under dry and wet conditions, except for d-PtNi/C at 100%RH where it increased mass transport on air
- Functionalization of carbon support with -SO_3H groups improves low RH performance, but decreases catalyst mass activity

Remaining Challenges/Barriers/Next Steps

- Issues with the d-PtNi/C-containing catalyst are drop-off in performance at >1 A/cm^2 (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, due to:
  - Note: Near one-dimensional conditions used for diagnostic and modeling purposes in this project exacerbate the issues at low relative humidity
  - 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, can be partially mitigated with increased ionomer content and organic solvents which improve dispersion of d-PtNi/C particles, and can be greatly improved with acid treatment of CCM
  - Results thus far indicate that Ni^{2+} in ionomer, leached during ink and CCM fabrication is altering agglomerate structure of cathode catalyst layer, decreasing mass transport, especially at low RH
    - *More aggressive leaching of Ni^{2+} prior to ink synthesis and CCM fabrication can improve d-PtNi/C cathode performance, especially under dry conditions*

- Next steps in characterization/understanding:
  - USAXS tomography for spatial distribution of agglomerates in catalyst layers
  - Nano-X-ray tomography for spatial distribution of pore and agglomerates in catalyst layers
  - Continued analysis of electrochemical impedance spectroscopy data for proton conductivity of all electrode layer compositions and electrode loss breakdown
  - Solid state cell measurements of permeability of oxygen through ionomer and impact of Ni^{2+} on permeability/solubility
  - 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

Response to Previous Year's Reviewers' Comments

- *The project should have started with a well-designed durable catalyst, such as one developed at the end of the GM project. It takes too much effort to develop a working catalyst that is unlikely to be employed in practical fuel cells.*
- *The catalyst with so many problems needs to be replaced by a more stable, highly active catalyst.*
- *The project team should change the scope to investigate the stability of the alloy catalysts in operating fuel cells.*
  - The catalyst used in this project **is** the one developed in the GM project.
  - The catalyst used in this project has mass activity exceeding the DOE targets and can reach the kinetic performance stability targets, as shown in the GM project (FC-087).
- *It is necessary to conduct a durability study of the rationally designed catalyst layer even if it is not in the scope of work.*
  - Durability studies are planned in the next fiscal year on the optimized d-PtNi/C-based MEA
- *While it seems clear that dealloyed catalysts will play an important role in next-generation catalyst materials, it is unclear whether this team's approach has advantages over other approaches (e.g., 3M nanostructured thin film). It would have been useful to have an assessment of the synthesis methodology and its scalability.*
  - A key team member (Johnson Matthey) is an industrial supplier of fuel cell catalysts. They have developed catalyst synthesis techniques, internally and within the GM-led catalyst project, that are scalable. Strategic Analysis conducted a cost study on this catalyst and presented these results at the 2014 AMR.

Collaborations and acknowledgment

- Project team (subs) within DOE H_2 and Fuel Cells 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

Thanks!

DOE, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office

- Nancy Garland (Technology Development Manager)

Backup Slides

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 (45°C, 60°C, 70°C, 80°C, and 90°C)
    - Back pressures (100, 150, and 250 kPa abs)
    - RHs (100%, 85%, 70%, 55%, and 30%)

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

Performance Model

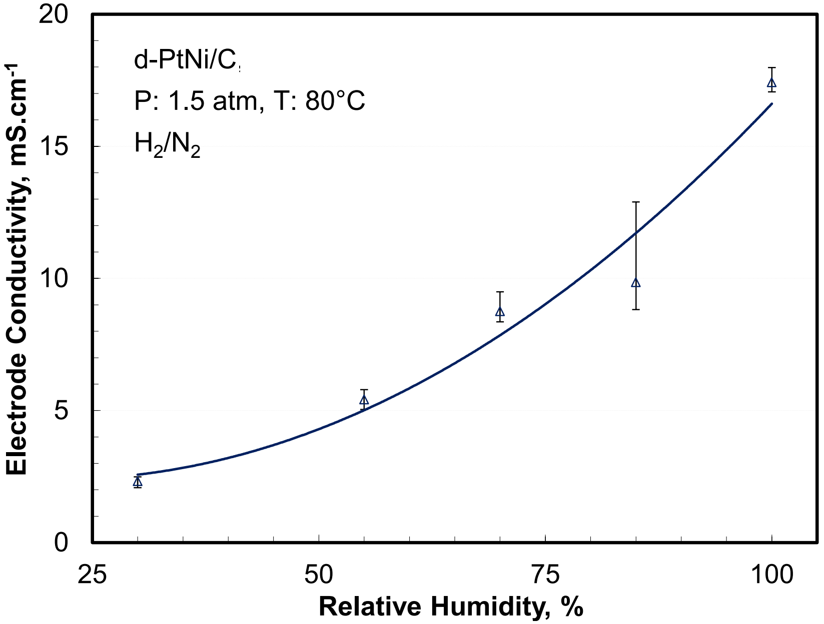
$$E = E_N - iR_\Omega - (iR_\Omega^c + \eta_c^c + \eta_m^c) - (iR_\Omega^a + \eta_c^a + \eta_m^a)$$

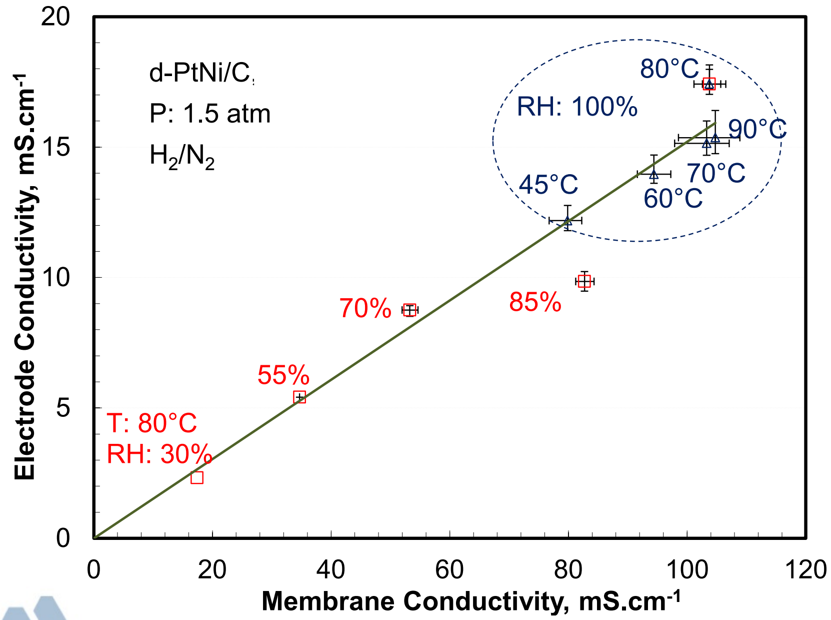
- R_Ω: High frequency resistance as measured by the current interrupt method. It includes membrane and contact resistances.
- η_c^c: ORR kinetic overpotential as determined from a kinetic model formulated using H_2/O_2 polarization data. It includes any kinetic effects due to limited O_2 solubility in 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

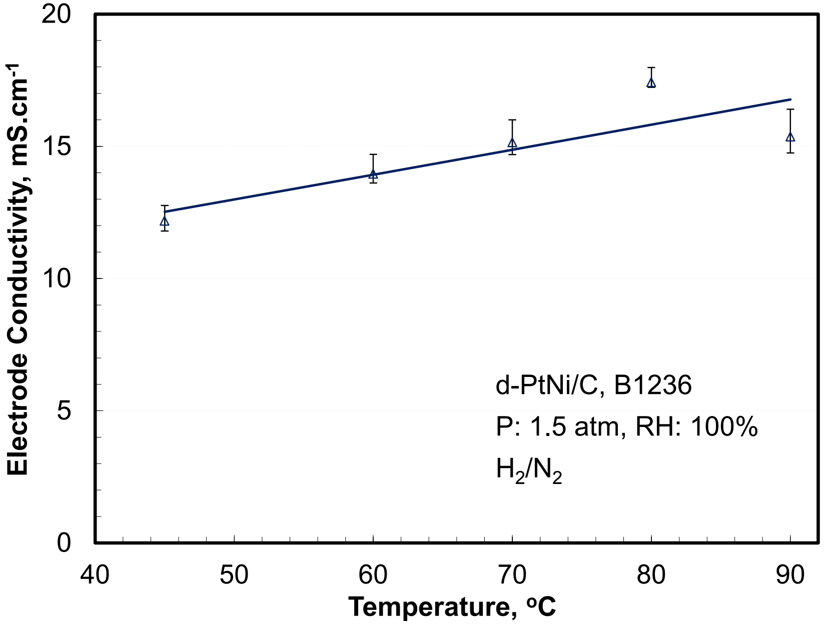
Electrode Conductivity

Electrode conductivity (σ_i) derived from electrode resistance (R_c) determined using electrochemical impedance spectroscopy and assuming that the cathode catalyst layer is 10-µm thick: $\sigma_i = \delta_c / R_c$

- σ_i has similar temperature and RH dependence as σ_m
- σ_i is >75% smaller than σ_m
- Almost linear correlation between electrode and membrane conductivities: $\sigma_i = \sigma_m f(\varepsilon_i, \tau)$







All data for I/C = 1.2

Structure of free ionomer in An-Pt/C and d-PtNi/C-ionomer inks

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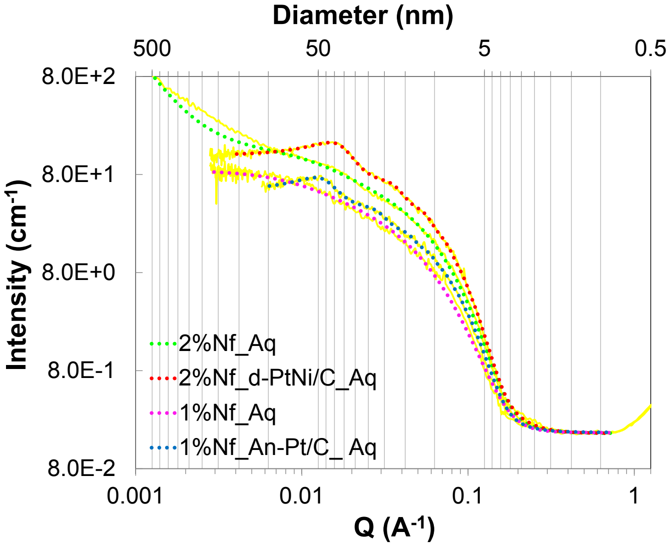
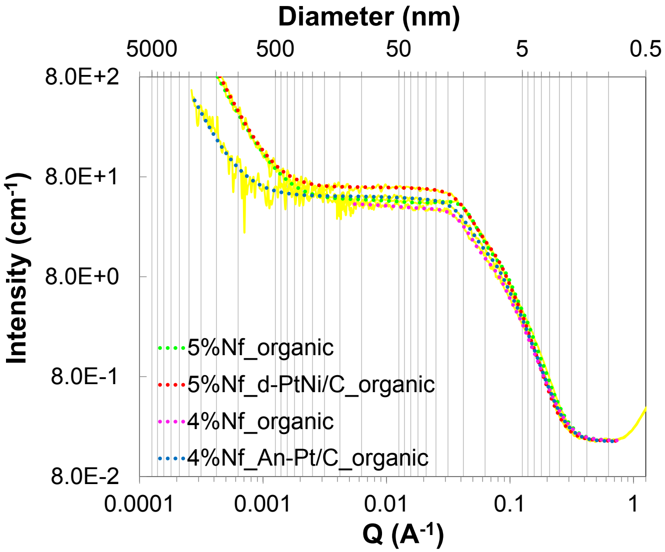
An-Pt/C



d-PtNi/C



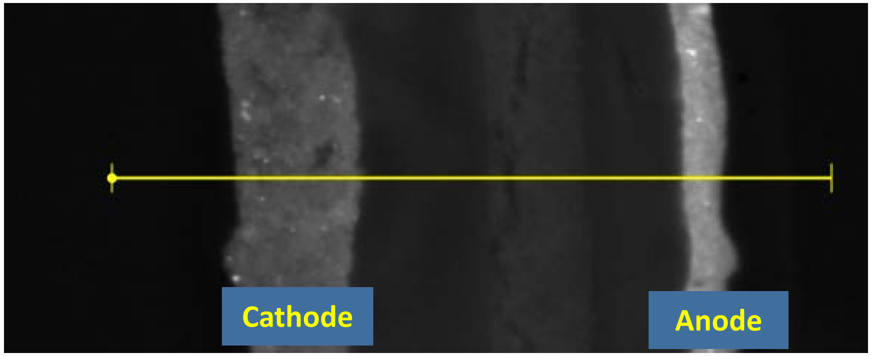
Ionomer solution	Mean Size (nm)
2% Nf_Aq	5.6
2%Nf_d-PtNi_Aq	5.7
1%Nf_Aq	5.7
1%Nf_An-Pt/C_Aq	5.3

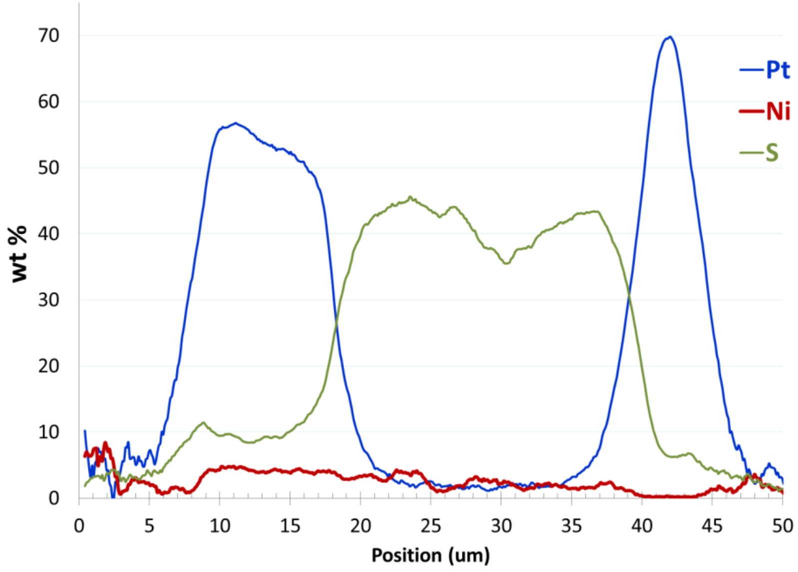
Ionomer solution	Mean Size (nm)
5%Nf_organic	3.7
5%Nf_d-PtNi_organic	4.2
4%Nf_organic	3.6
4%Nf_An-Pt/C_organic	3.8

- More free ionomer with organic vs. aqueous inks and with d-PtNi vs. An-Pt/C inks
- Plateau in USAXS data indicates ionomer has a rod-like structure in solution
- Oscillations in data for aqueous extracted ionomer are caused by interferences of hydrophilic domains of rods
- Ionomer rods in aqueous solvent have larger diameter than ionomer rods in organic solvent
- Ionomer extracted from d-PtNi/C inks has a larger diameter than that extracted from An-Pt/C inks

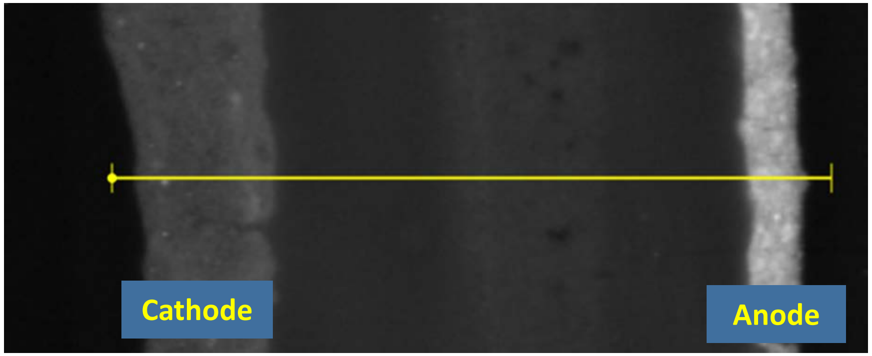
Ni^{2+} moves throughout MEA during testing

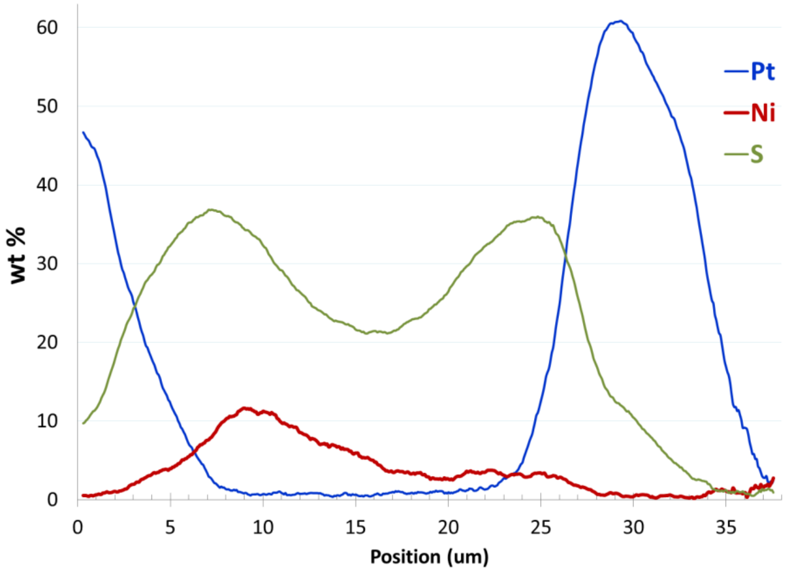
d-PtNi, I/C=1.2, After Testing





Ni^{2+}-doped An-Pt/C, I/C=1.2, After Testing

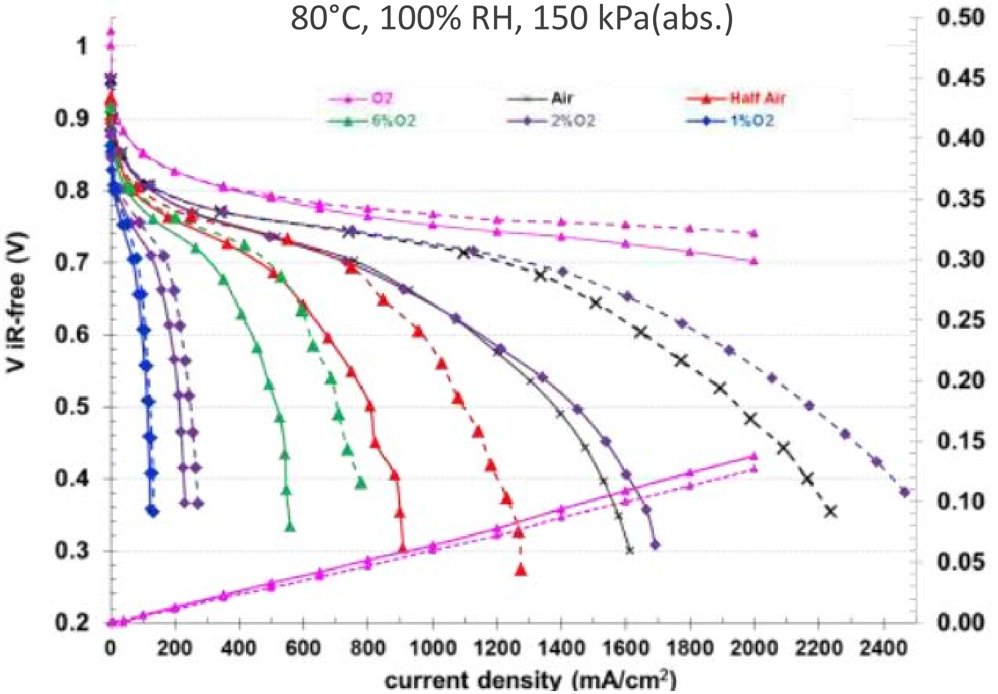




- Ni^{2+} is primarily in cathode for d-PtNi cathode, but Ni^{2+} is observed in membrane with concentration decreasing from cathode side to anode side.
- Added Ni^{2+} is more concentrated in the membrane close to the cathode.

Effect of Ni^{2+} contamination on An-Pt/C cathode performance

Solid Lines – Ni^{2+}-doped An-Pt/C;
Dashed Lines – An-Pt/C
80°C, 100% RH, 150 kPa(abs.)



Summary of effect of Ni^{2+} doping:

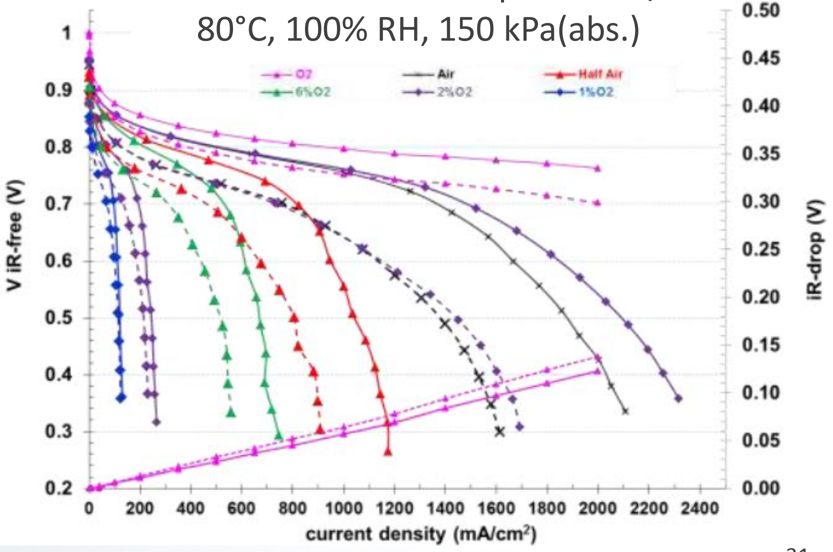
Membrane resistance

- Increased slightly under high RH
- Effect is exacerbated at mid and low RH

Mass transport resistance

- Increased at high current densities
- Helox measurements show loss is in condensed phase
- Much higher loss under mid and low RH conditions

Solid Lines – d-PtNi/C
Dashed Lines – Ni^{2+}-doped An-Pt/C
80°C, 100% RH, 150 kPa(abs.)



Summary of effect of Ni^{2+} doping vs. d-PtNi/C:

- Ni^{2+}-doping into an An-Pt/C cathode showed an amplification of the losses observed for d-PtNi/C cathode