

Rationally Designed Catalyst Layers for PEMFC Performance Optimization

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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: 99%

Budget

- FY15 DOE Funding: \$985K
- FY16 Funding: \$101K
- Total DOE Project Value: \$3,480K
- Cost Share Percentage: 20%

Barriers

Barrier	2020 Target
A. Electrode Performance	>300 mA/cm ² at 800 mV >1000 mW/cm ² at rated power
B. Cost	\$5-9/kW _e catalyst, <\$30 kW _e system, <0.125 mg _{PtGM} /cm ²
C. Durability	<40% loss of initial catalytic mass activity at 900 mV on O ₂ ; <30 mV loss at 0.8 A/cm ²

Partners and Project Lead

- **Johnson Matthey Fuel Cells**
 - Jonathan Sharman, Alex Martinez, Dash Fongalland, Brian Theobald, Geoff Spikes, L. Smith, D. Ozkaya, M. Gutierrez, and Graham Hards
- **United Technologies Research Center**
 - Mike Perry and Zhiwei Yang
- **University of Texas at Austin**
 - Paulo Ferreira, Kang Yu, Somaye Rasouli, Andres Godoy, and Daniel Groom
- **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, c. Firat Cetinbas 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



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** ($\leq 0.1 \text{ mg}_{\text{Pt}}/\text{cm}^2$ on cathode and $< 0.025 \text{ mg}_{\text{Pt}}/\text{cm}^2$ on anode)

Impact on DOE Targets

Metric/Units	DOE 2020 Target	Project Status FY'15 AMR*	Current Project Status (high anode loading)	Status (low anode loading)
Mass activity ($\text{A}/\text{mg}_{\text{PGM}}@0.9\text{mV}_{\text{iR-free}}$)	≥ 0.44	0.57	0.59	0.6
Specific activity ($\mu\text{A}/\text{cm}^2_{\text{PGM}}@0.9\text{mV}_{\text{iR-free}}$)	≥ 720	986	1151	1015
PGM total loading ($\text{mg-PGM}/\text{cm}^2_{\text{geo}}$)	≤ 0.125	0.092 cath	0.112 cath	0.1159 cath 0.018 anode
MEA performance ($\text{mA}/\text{cm}^2_{\text{geo}} @ 800 \text{ mV}$) FCTT Pol Curve	≥ 300	347 n/d	347 n/d	371 200
MEA performance ($\text{mW}/\text{cm}^2_{\text{geo}} @ 675 \text{ mV}$) FCTT Pol Curve	≥ 1000	827 n/d	878 n/d	850 672
MEA performance ($\text{mW}/\text{cm}^2_{\text{geo}} @ 600 \text{ mV}$) FCTT Pol Curve	≥ 1000	940 n/d	999 n/d	1025 750

*The results shown here (except where noted) were acquired under test conditions designed for diagnostic and modeling purposes (e.g., differential high flow conditions rather than integral, low stoichiometry conditions)

Approach

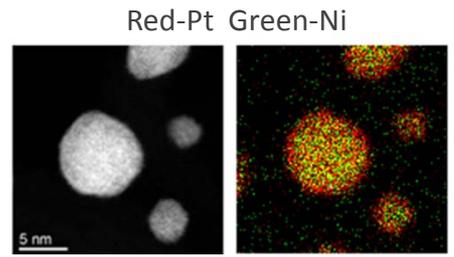
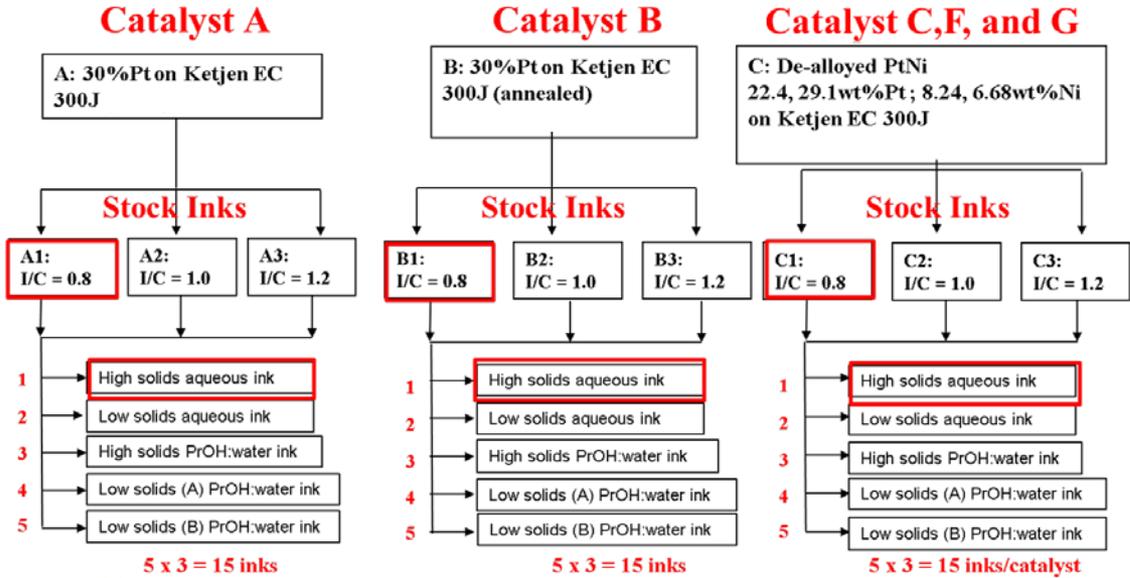
- Determine property of electrode/catalyst that limits the high current density/air performance of electrodes based on advanced Pt-based cathode catalyst
 - The advanced Pt-based catalyst is **dealloyed PtNi (d-PtNi)** developed by Johnson Matthey (**within General Motors-led FC-087 Catalyst Project**). 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**
 - Cost competitive at volume production (B. James, Strategic Analysis, FC018, 2014 AMR presentation)
- 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 particle size distributions
 - 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



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

- Parameters studied:
 - Catalyst type
 - Pt (high surface area and annealed)
 - Dealloyed PtNi; varying Ni content
 - Ionomer to carbon ratio
 - Ink solvent
 - Solids content
 - Equivalent weight of ionomer (750-1100)

Catalyst Code	Catalyst Type/ Annealing Conditions	Wt% Pt	Wt% Ni	Metal area by <i>ex situ</i> 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 "C"	PtNi (45:55) High T	22.4	8.24	52	5.8±2.2
d-PtNi/C "F"	PtNi (57:43) High T	29.1	6.68	50	5.40±1.58
d-PtNi/C "G"	PtNi (56:44) High T	28.5	6.68	54	5.5±3.2



I/C = ionomer to carbon weight ratio
 = inks used for cathodes of baseline catalyst-coated membranes (ccms)

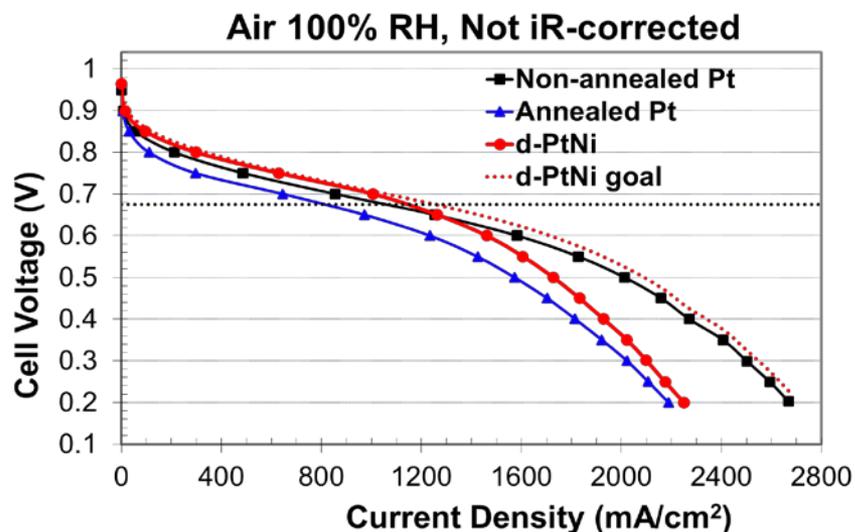
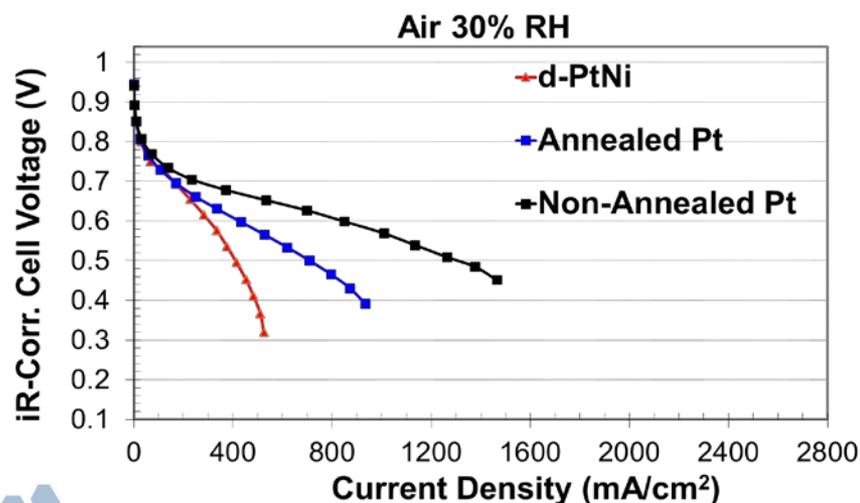
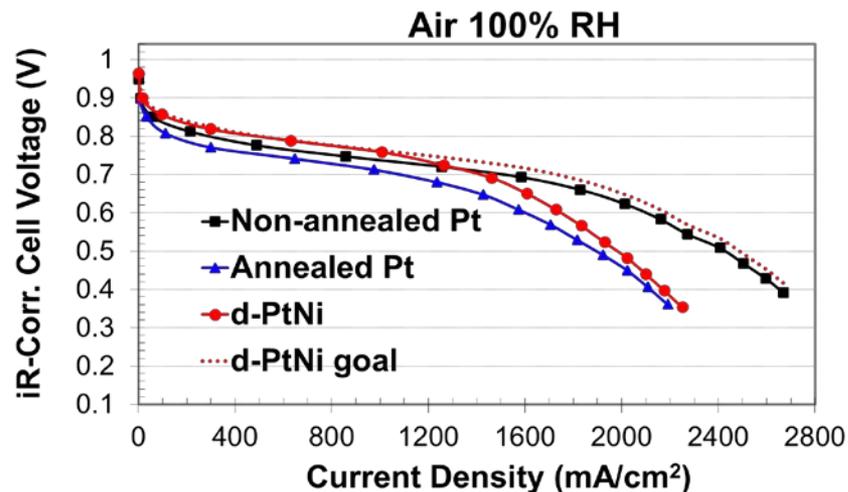
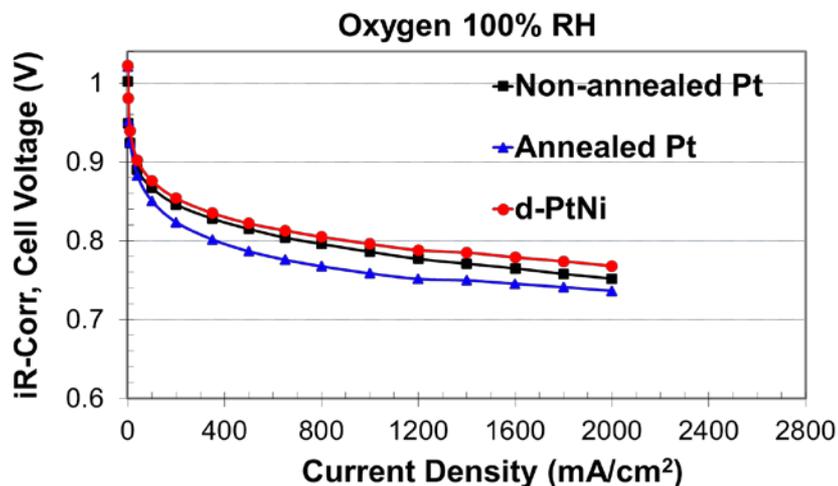
Description of testing and diagnostics of Pt and d-PtNi MEAs

- **Beginning-of-Life (BOL) performance of MEAs (all ~ 0.1 mg/cm²-Pt cathode loading and ~ 0.025 or ~ 0.1 mg/cm²-Pt anode loading):**
- **Cell Builds:**
 - Solid bipolar plates with triple serpentine flow channels
 - Co-flow of hydrogen and oxidant
 - Active area = 12.25-cm²
- **Testing protocol:**
 - Wet-up to reach cells' peak performance
 - BOL diagnostics, including:
 - H₂-pump, H₂-crossover, and ECA by CO stripping
 - Cyclic voltammetry and impedance characterization under nitrogen and air atmosphere
 - BOL performances under various conditions, including:
 - O₂ concentrations (pure O₂ - 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%)
 - Stoichiometry (1 L/min and 3 L/min)
 - Addition since 2015 AMR is Fuel Cell Technical Team Polarization Curve Protocol
 - Accelerated stress tests
 - 0.6 to 0.925 V, 50 mV/s, triangle
 - 0.6 to 1.0 V, 50 mV/s, triangle
 - 0.6 to 0.95 V, 700 mV/s, trapezoid, 6 s/cycle



d-PtNi/C electrode shows unique losses in performance at high current density, especially at lower relative humidity

0.1 mg-Pt/cm² cathode loadings, 80°C, 150 kPa (abs.), high and fixed flow for differential conditions (3 SLPM O₂ or air), baseline CCM formulations



Activities since 2015 AMR

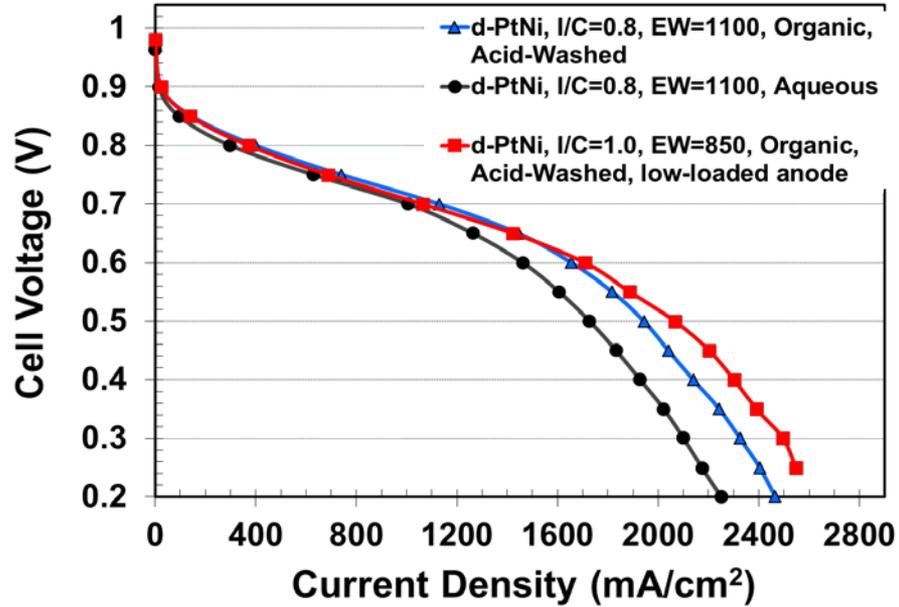
- Effect of ionomer equivalent weight on cell performance and performance durability
- Fabrication and testing of MEAs with low anode loadings (~ 0.125 mg-Pt/cm² cell loading) with catalyst ink composition and CCM treatment giving best overall hydrogen-air performance
 - Polarization curve measurements under differential high flow conditions and using Fuel Cell Tech Team (FCTT) polarization curve protocol
- Performance durability measurements of d-PtNi and annealed Pt-containing CCMs
 - DOE catalyst AST (0.6 to 1.0 V), Modified DOE catalyst AST (0.6 to 0.925 V; General Motors protocol)
 - New FCTT catalyst AST (trapezoid 0.6 to 0.95 V)
- Diagnosis of source of performance losses of d-PtNi with functionalized support
- Effect of doping of An-Pt/C layers with Ni²⁺ at moderate loading
- X-ray scattering measurements of impact of:
 - Ni²⁺ on ionomer structure
 - Catalyst type and Ni²⁺ doping on water uptake of electrodes as a function of RH
 - Solvent removal conditions
- X-ray nano-tomography and TEM of annealed Pt/C and d-PtNi/C electrodes and calculation of porosities and diffusivities from reconstructions and image analysis
- XANES white line, XANES delta-mu analysis of d-PtNi/C and Pt/C in aqueous cell
- Identical location TEM studies of catalyst degradation



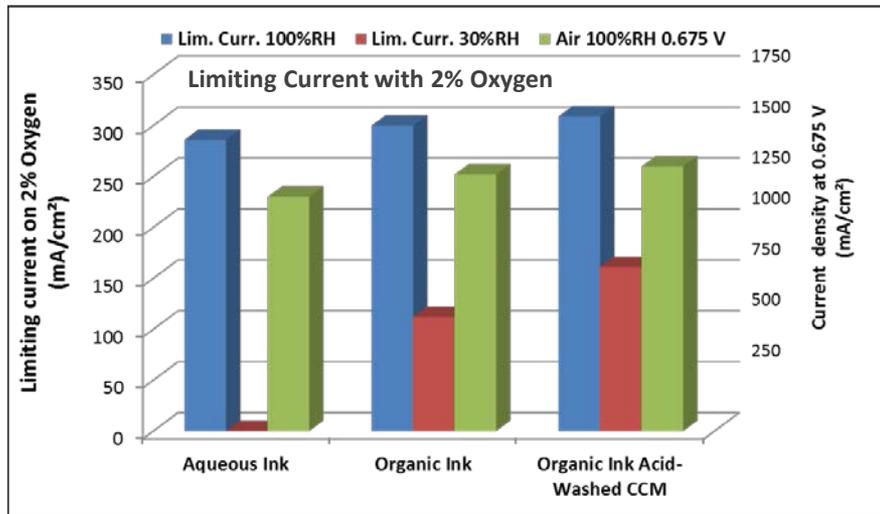
Performance improvement of d-PtNi/C-based cathodes

■ Performance of d-PtNi at high current density improved by:

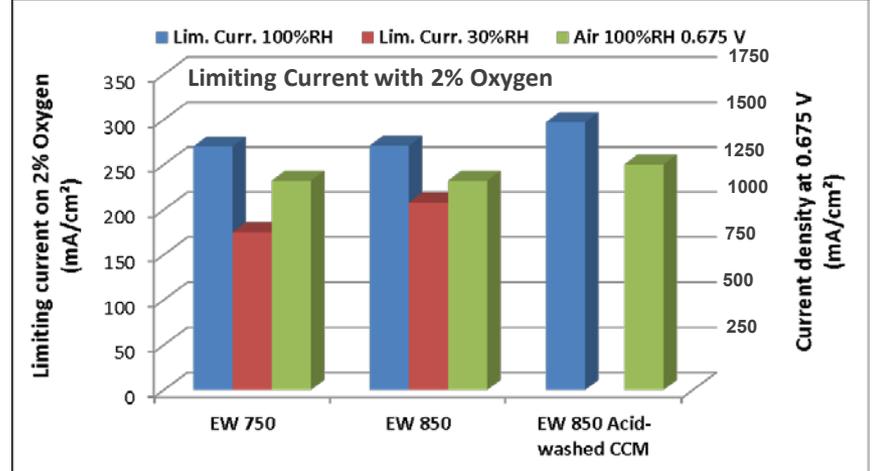
- Decreasing initial Ni content of d-PtNi/C catalyst
- Using organic solvent in catalyst-ionomer ink
- Increasing I/C from 0.8 to 1.0
- Using intermediate EW ionomer (850 EW)
- Acid-washing CCM after fabrication



80°C, 150 kPa, d-PtNi/C (Catalyst “F” or “G”) on cathode at 0.1 mg-Pt/cm², 0.1 mg-Pt/cm² Pt/C anode, I/C=0.8, EW=1100



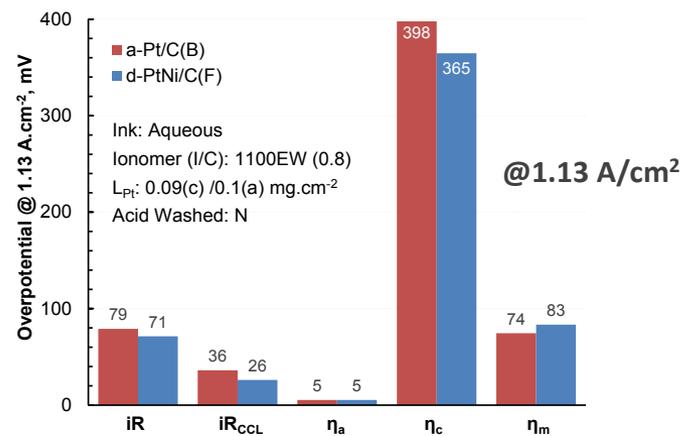
80°C, 150 kPa, d-PtNi/C (Catalyst “G”) on cathode at 0.1 mg-Pt/cm², <0.02 mg-Pt/cm² Pt/C anode, I/C=1.0, Organic Ink



Voltage loss analysis

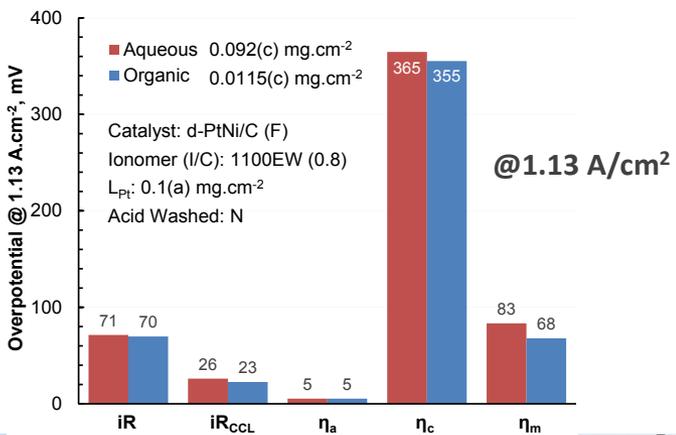
d-PtNi/C vs. An-Pt/C

- Major improvement: ORR overpotential (-33 mV)
- Minor improvement: IR drop in CCL (-10 mV)
- Loss: CCL mass transfer overpotential (+9 mV)



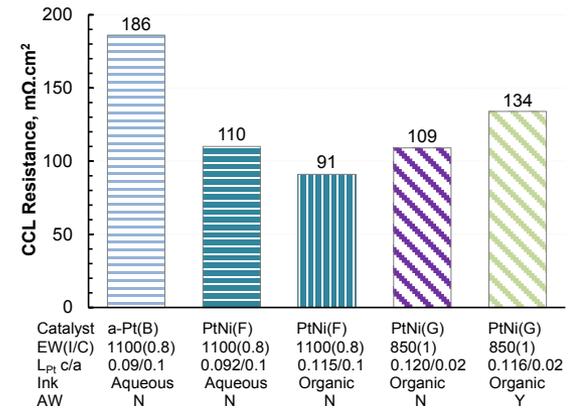
Aqueous vs. Organic Ink for d-PtNi/C

- Reduction in ORR and mass transfer overpotentials with organic ink* (*portion of improvement due to higher Pt loading)



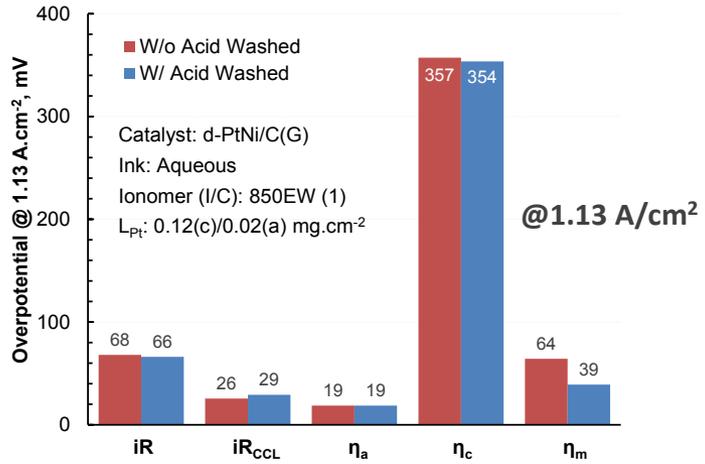
Impedance Analysis An-Pt/C vs. d-PtNi/C electrodes

- Higher proton conductivity in d-PtNi/C electrodes



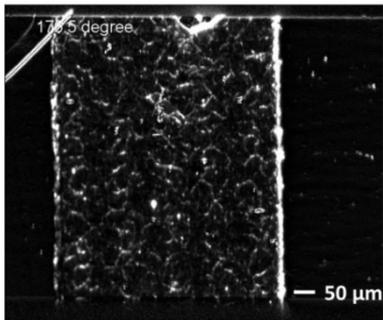
Effect of Acid Washing of d-PtNi/C CCM

- Major improvement in mass transfer overpotential (-25 mV)
- O₂ transport in the ionomer improves with removal of Ni contamination



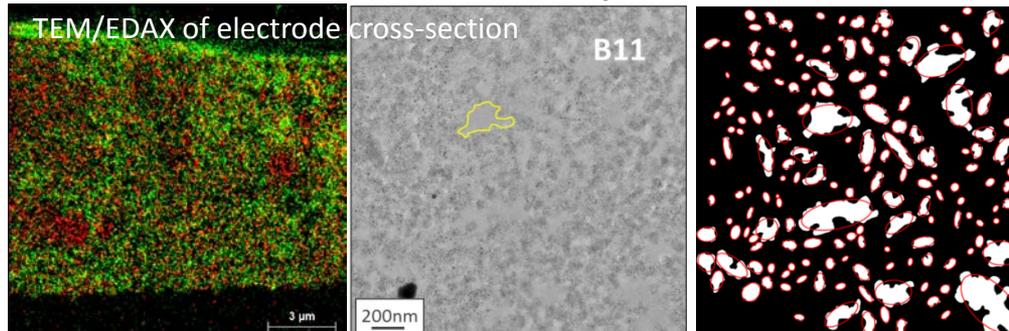
Comparison of An-Pt/C and d-PtNi/C Electrode Micro/Nano-structure

USAXS Imaging of electrode layer at $2e^{-4} \text{ \AA}^{-1}$ ($3 \mu\text{m}$)

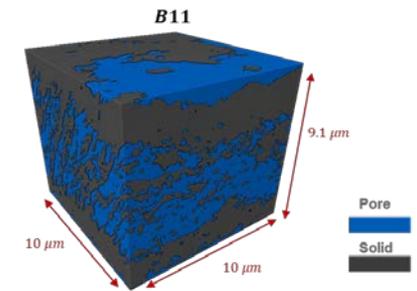


Face-on view

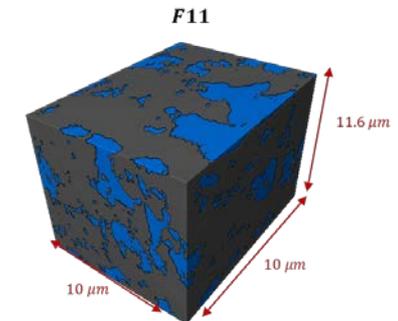
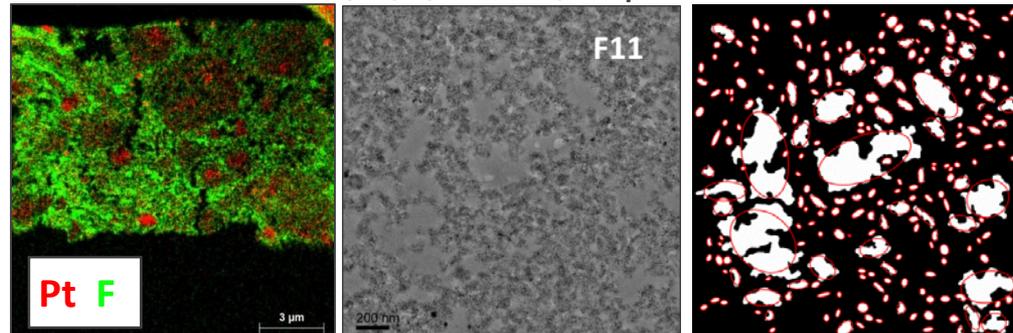
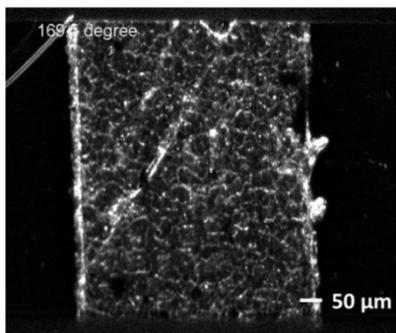
An-Pt/C, I/C=0.8, Aqueous Ink



Nano-X-ray Computed Tomography at ANL/APS 32-ID

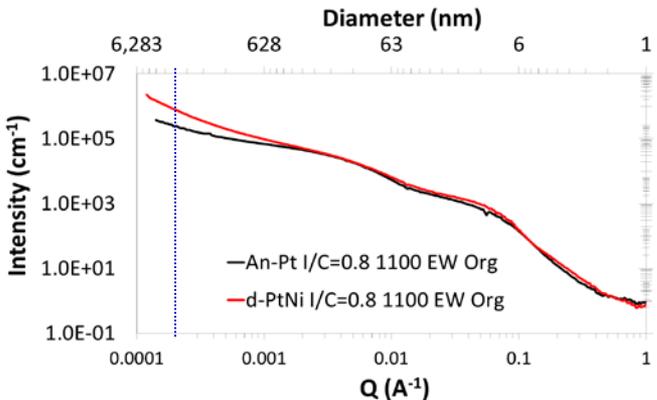


d-PtNi/C, I/C=0.8, Aqueous Ink

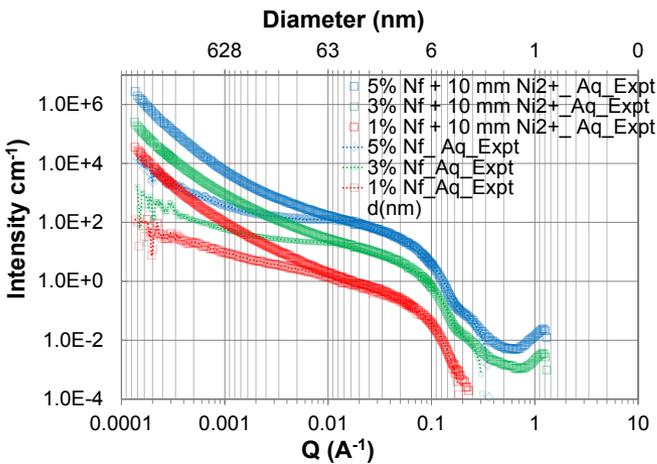
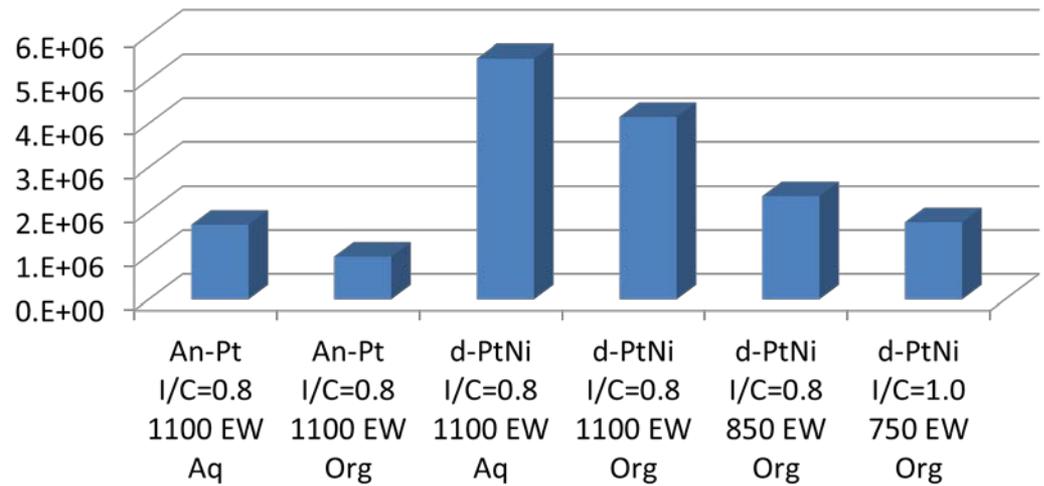


- USAXS imaging shows a dense network of very large aggregates in d-PtNi/C electrode which is not present in An-Pt/C electrode
- TEM/EDAX show dense 1-3 μm d-PtNi/C aggregates with minimal infiltration of ionomer into aggregates; more ionomer infiltration seen in An-Pt/C electrode
- d-PtNi/C electrode has a less homogeneous ionomer distribution than An-Pt/C electrode, smaller primary pores located within agglomerates, and larger secondary pores confined to regions between agglomerates
- Organic solvent vs. aqueous solvent decreases d-PtNi/C aggregate size: 1.47 vs. 2.37 μm average size via TEM analysis

USAXS Structural Analysis of Nafion Dispersions, Electrode Layers



USAXS Scattering at $Q=2E-4$

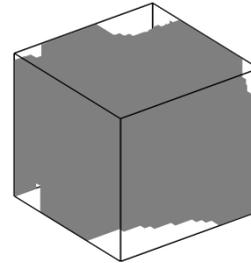


- Ni leaches out of catalyst into solvent/ionomer in inks; extent of leaching dependent on ink composition (low solid aqueous >> high solids organic)
- USAXS shows Ni^{2+} in ionomer dispersions causes PFSA aggregation due to decreased electrostatic repulsion between PFSA strands
- Ionomer forms rod-like structure in solution; diameter of rods larger for d-PtNi inks vs. An-Pt/C inks; diameter of rods smaller in organic ink vs. aqueous ink (4.2 nm vs. 5.7 nm)
- USAXS scattering data at $Q < 0.001 \text{ \AA}^{-1}$ shows aggregate size in electrodes can be controlled using solvent type, I/C, and ionomer EW

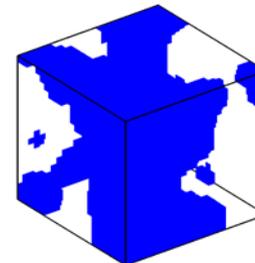
Hybrid Electrode Model: X-ray Tomography/TEM Size Distributions- Numerical Reconstruction-Multi-Physics Model

- Tomography and TEM results at available resolution used as framework for structural model. Numerical reconstruction algorithm builds electrode structure around XCT/TEM-determined structural framework
- Numerical reconstruction used to calculate electrode kinetic and transport properties
 - O_2 and ion transport is modelled along with electrochemical reactions
 - Ion potential drop through domain, O_2 concentration drop in pores and in ionomer film are calculated
 - Model used to calculate effective oxygen diffusivities
 - Results show that the ionomer film is dominating mass transfer resistances
 - Results show significant pore size and diffusivity differences between An-Pt/C and aqueous and organic d-PtNi/C layers

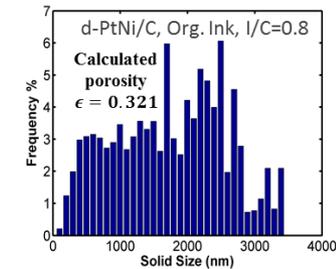
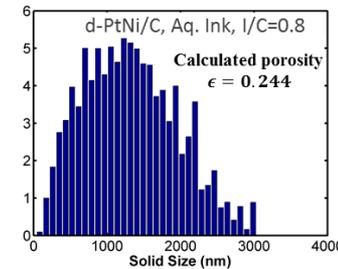
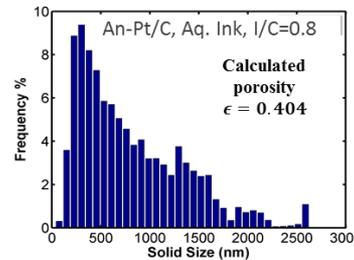
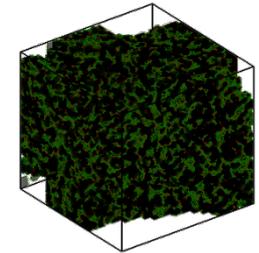
XCT Solid (1 μ m sample)



XCT Pore Space (1 μ m sample)



Extract XCT volume for numerical algorithm

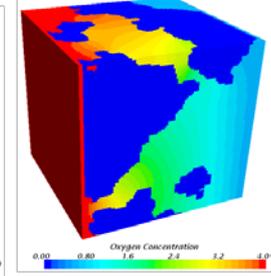
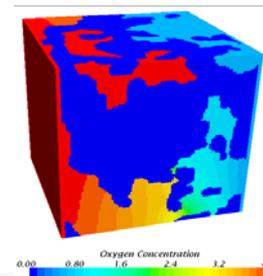


d-PtNi/C, Aq. Ink, I/C=0.8

F11 sample #2, $\epsilon = 0.26$
 $D_{eff} = 7.76e-7 \text{ m}^2 \cdot \text{s}^{-1}$

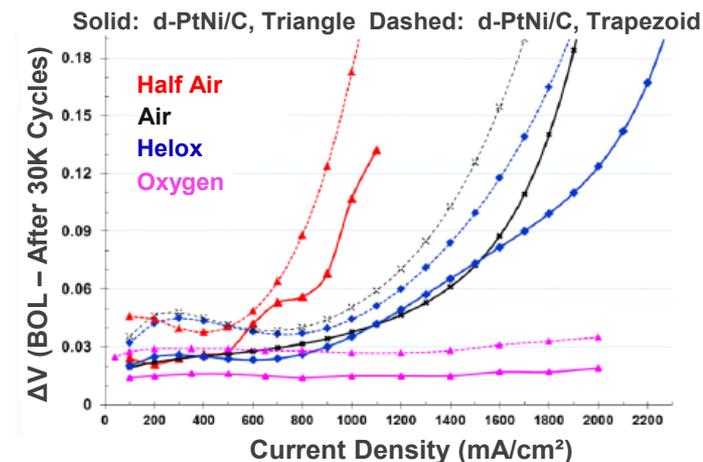
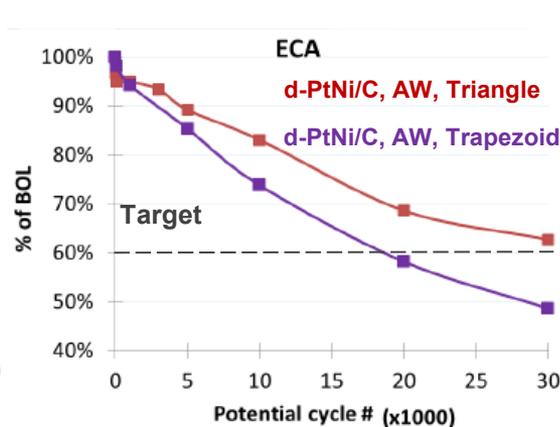
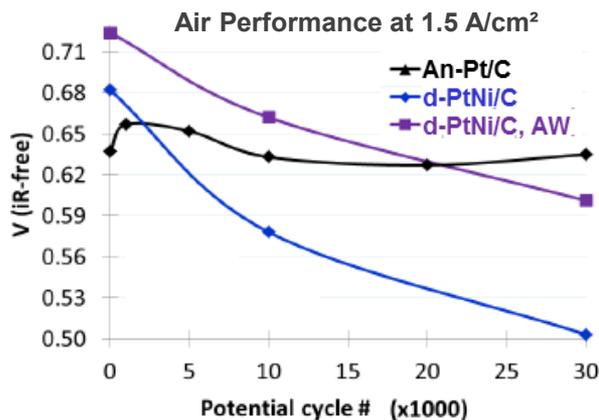
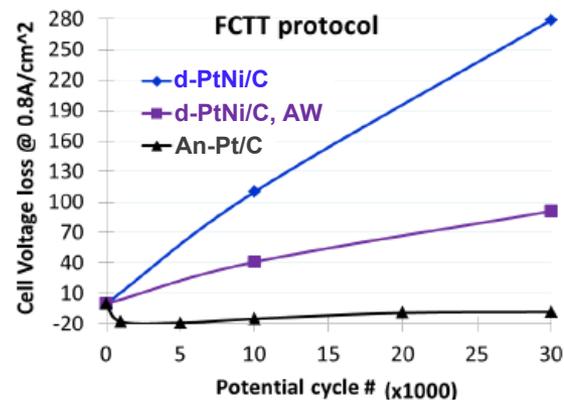
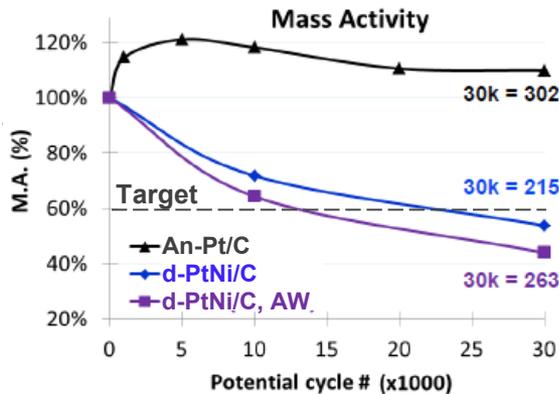
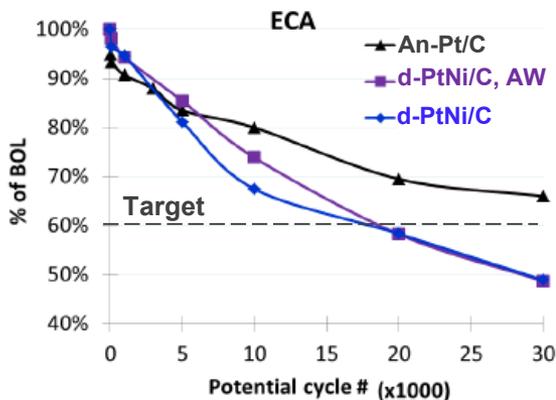
d-PtNi/C, Org. Ink, I/C=0.8

F14 sample #2, $\epsilon = 0.51$
 $D_{eff} = 3.26e-6 \text{ m}^2 \cdot \text{s}^{-1}$



Durability results

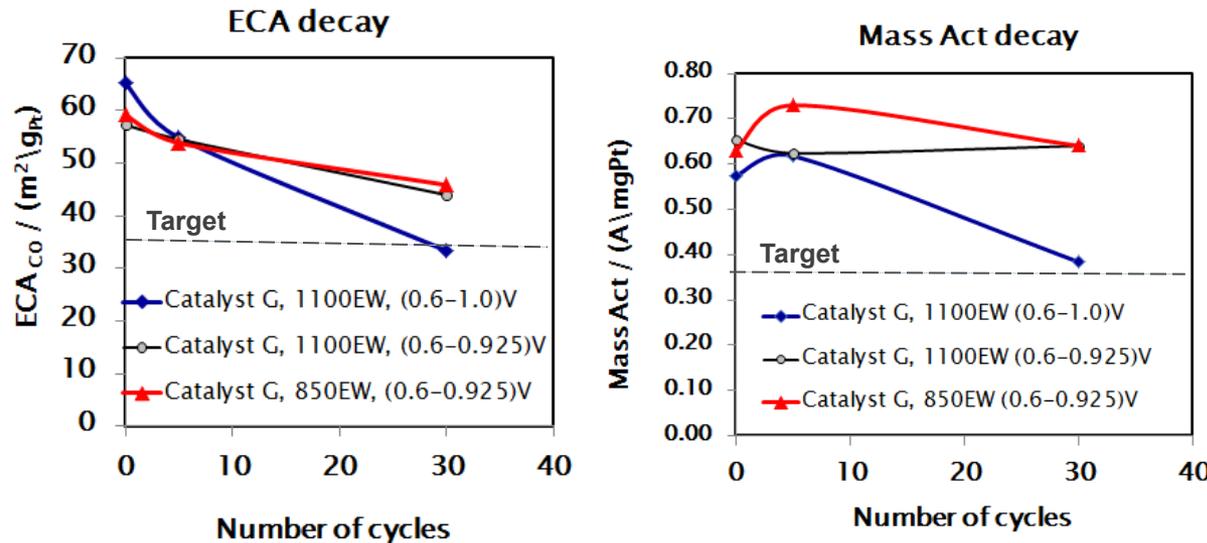
850 EW Ionomer, Organic Ink, d-PtNi/C: Catalyst "G", Anode loading=0.018 mg-Pt/cm²
 AST: 0.6 to 0.95 V Trapezoid, 6 s/cycle



- d-PtNi/C shows higher ECA, mass activity (MA), and high current density performance loss than An-Pt/C, higher than target when using new FCTT AST (0.6 to 0.95 V, trapezoid)
- Acid-washing CCM does not adversely affect ECA and MA decay and decreases low and high current density performance decay
- d-PtNi/C can meet ECA durability target when using GM-developed AST (0.6 to 0.925 V triangle, 50 mV/s)
- New FCTT trapezoid AST causes more degradation of ECA, MA, and air performance than GM-developed triangle AST

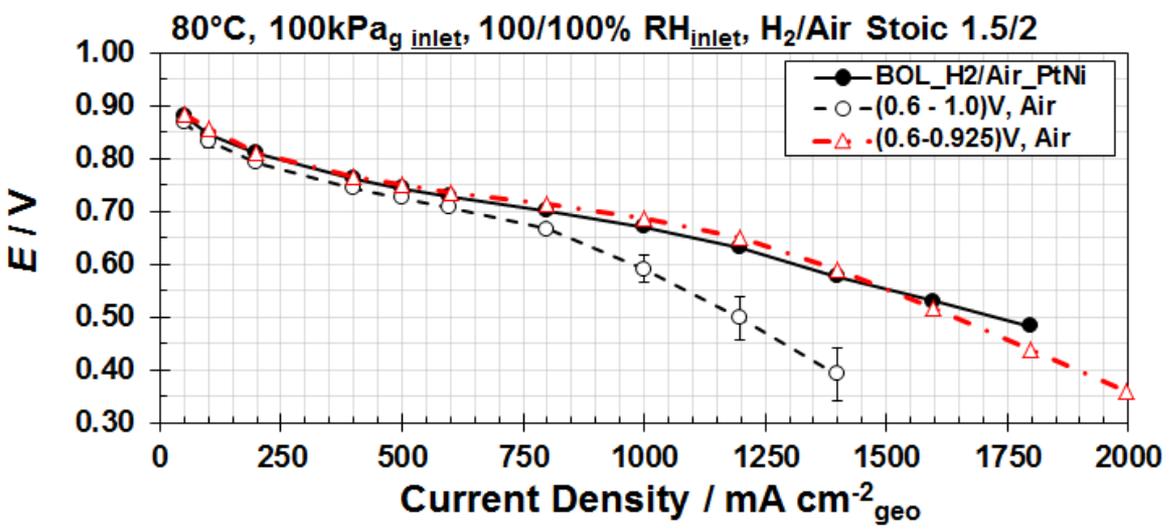


Durability results: ASTs with limited intra-AST diagnostics



d-PtNi/C: Catalyst "G"
 1100 or 850 EW Ionomer, Organic Ink, I/C=0.8
 Anode loading=0.018 mg-Pt/cm²

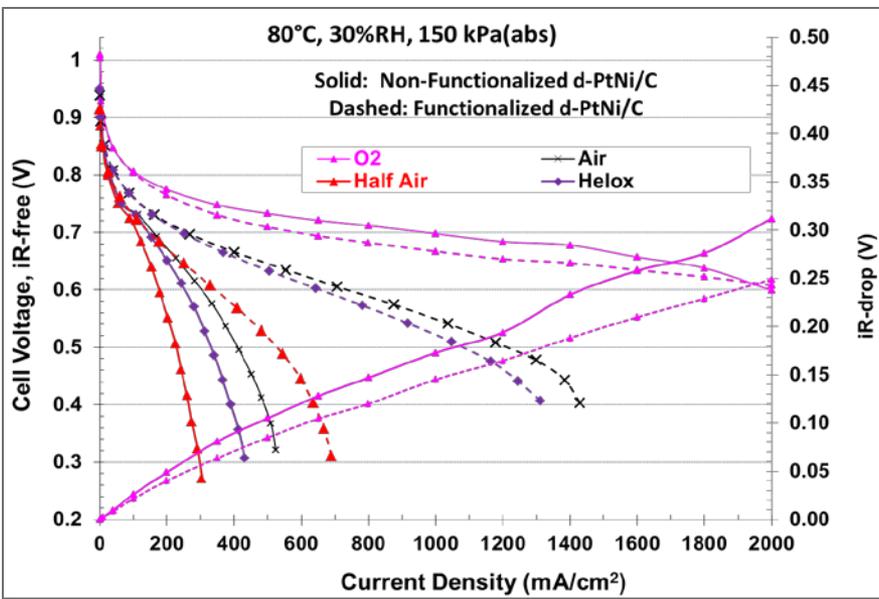
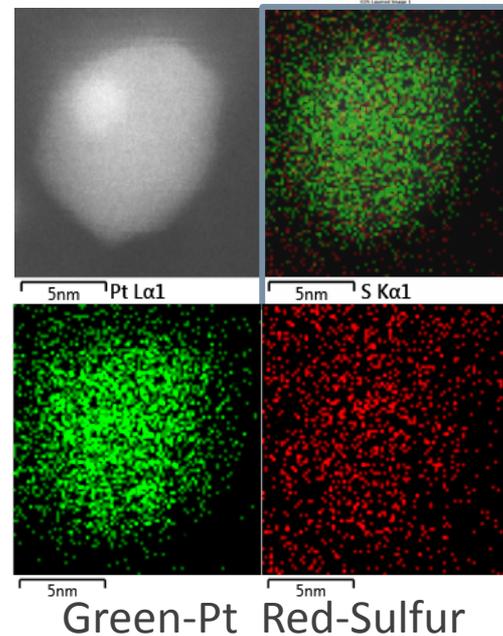
DOE AST: 0.6 to 1.0 V Triangle, 50 mV/s
 Modified DOE AST: 0.6 to 0.925 V Triangle, 50 mV/s



- d-PtNi/C-based electrode layers meet ECA and mass activity durability targets with AST upper potential limits of 0.925 V or 1.0 V
- d-PtNi/C-based electrode layers meet performance durability targets (<30 mV loss) with ASTs to 0.925 V

Impact of -SO₃H functionalization of support

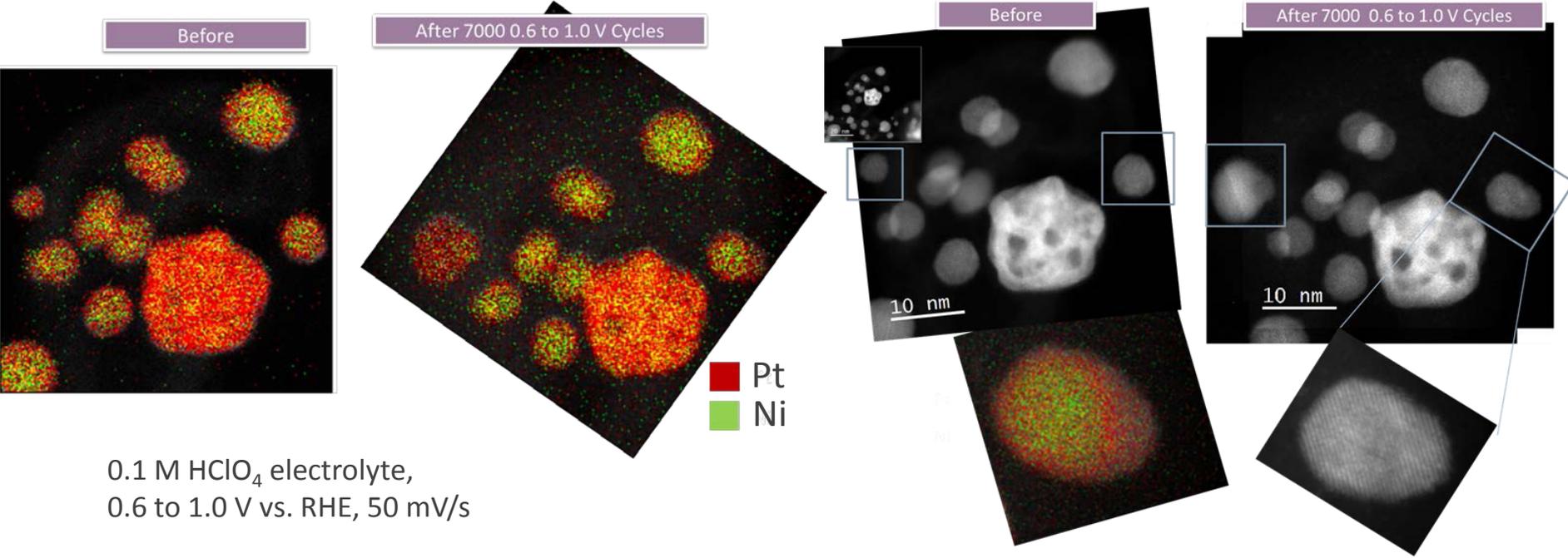
- Functionalizing carbon support decreases the mass activity and kinetic performance of d-PtNi/C, but improves mass transport and mid- to low-RH performance
- Light scattering of dilute inks shows that functionalization aids in break up of carbon aggregates
- Porosimetry of catalyst powder shows functionalization decreases number of 0.1 to 1 μm pores and eliminates 4 to 50 μm pores
- Analysis of powders showed that the functionalization process removes Pt and Ni and poisons catalyst surface with sulfur species



	Pt	Ni
d-PtNi/C	29.5 wt%	5.6 wt%
SO ₃ H-d-PtNi/C	26.4 wt%	4.6 wt%



Identical location TEM d-PtNi/C Intra-Particle Pt and Ni Composition Changes with AST Cycling



0.1 M HClO₄ electrolyte,
0.6 to 1.0 V vs. RHE, 50 mV/s

- Pt skin encasing PtNi core thins with AST potential cycling
- Increased Ni noted on support after AST potential cycling
- Non-isotropic re-deposition of Pt was also observed



FY'16 Milestones

1	<p>Fabricate and test ≤ 0.125 mg-Pt/cm² MEAs with a dealloyed PtNi/C cathode catalyst and a Pt anode catalyst using an alternative electrode composition and/or structure to achieve a hydrogen-air current density of >1250 mA/cm² at 0.675 V under differential cell conditions (high stoichiometries) leading to a current density of >1 A/cm² at 0.675 V when using the U.S. DRIVE Fuel Cell Tech Team (FCTT) Polarization Curve Protocol.</p>	<p>12/23/15 Status: Achieved a hydrogen-air current density of 1240 mA/cm² at 0.675 V with cathode loading of 0.112 mg-Pt/cm² and (total PGM loading of 0.1327 mg-Pt/cm²) under differential conditions. Achieved 1060 mA/cm² at 0.675 V with a total cell 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). Note: Achieved 1259 mA/cm² at 0.675 V under diff. cond. In March, 2016.</p>
2	<p>Fabricate and test 25-50 cm² active area MEAs with a dealloyed PtNi/C cathode catalyst and a Pt anode catalyst with total cell PGM loadings of < 0.125 mg-Pt/cm², determine the performance reproducibility using DOE-recommended polarization curve conditions, and determine the cell durability using DOE-recommended protocols. Performance and durability goals are: 6.5 kW/g-Pt at peak power and <10% drop in power after application of U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Tests.</p>	<p>3/31/16 MEA with dealloyed 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, for a total cell Pt loading of 0.1339 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. A 22% loss in peak power was observed after 30,000 trapezoid cycles (0.6 to 0.95 V, 700 mV/s).</p>

Summary of Results

- d-PtNi/C vs. An-Pt/C :
 - Larger aggregates and less aggregate breakup
 - Less infiltration of ionomer into catalyst aggregates/agglomerates
 - 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 and to mass transport in ionomer. Mass transport issues in d-PtNi/C electrodes are magnified under low RH conditions.
- Ni²⁺ is leached from d-PtNi into ionomer during ink preparation and MEA fabrication:
 - Ni²⁺ in ionomer decreases O₂ permeability
 - Acid-washing CCM improves O₂ and proton mass transport in d-PtNi/C catalyst layer, improving H₂/Air performance at 0.675 V 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 Ni²⁺ in the “free” ionomer
 - “Free” ionomer in inks has rod-like structure and diameter of rods is larger in aqueous inks than in organic inks and is also larger in d-PtNi/C inks than in An-Pt/C inks
 - Primarily enhances cathode performance at high and low RH due to lower mass transport resistance
- Increased ionomer content (I/C ratio up to 1.2):
 - 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 <100% RH conditions



Summary of Results (continued)

- Lower equivalent weight ionomer in inks:
 - In general causes greater break-up of agglomerate structure than EW 1100, effect is dependent on I/C
 - Best overall cell performance observed for lowest equivalent weight ionomer and intermediate I/C (1.0)
- Functionalization of carbon support with $-\text{SO}_3\text{H}$ 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 (high-loaded anode):
 - Differential conditions, organic ink, I/C=0.8, acid-washed CCM: 1.30 A/cm² at 0.675 V
- Performance Status (low-loaded anode):
 - Differential conditions, organic ink, I/C=1.0, 850 EW, acid-washed CCM: 1.259 A/cm² at 0.675 V
 - FCTT polarization curve:
 - 1060 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 (low-loaded anode):
 - Mass activity loss: 34%; ECA loss: 49% (0.6 to 1.0 V, 50 mV/s, triangle, limited diagnostics)
 - Mass activity loss: 0-2%; ECA loss: 22-25% (0.6 to 0.925 V, 50 mV/s, triangle, limited diagnostics)
 - Mass activity loss: 46%; ECA loss: 51% (0.6 to 0.95 V, 700 mV/s trapezoid, extensive diagnostics)



Remaining Challenges/Barriers/Next Steps

- Issues with the d-PtNi/C-containing catalyst are drop-off in performance at $>1 \text{ A/cm}^2$ (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:
 - Mass transport to low loadings of large particles
 - *Can be mitigated with smaller particles that are $>\sim 4 \text{ nm}$ 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
 - Results 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*
 - Leaching of Ni from particles continues during ASTs, especially when upper potential of 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*
- Next steps in characterization/understanding:
 - Reconstruction of all X-ray nano-tomography data, including high-surface-area Pt/C; correlation with TEM data
 - Additional nano-, phase-contrast X-ray tomography for spatial distribution of pore and agglomerates in catalyst layers
 - Input of all structural data from USAXS, X-ray tomography, and electron microscopy into electrode structural model
 - Complete analysis of EIS and cell performance data
- Work to be continued during no-cost extension, under auspices of FC-PAD, and in new General Motors catalyst project (FC144)

Response to Previous Year's Reviewers' Comments

- *Previously unidentified effects may be uncovered with durability testing, and it is unlikely that durability will be effectively addressed in this project.*
 - The scope of the project was modified this year to emphasize durability testing over stack fabrication
- *The work on inks was interesting, but it needs some further clarification; modeling would help. In addition, it is unclear whether there is any beam damage that may be altering the profiles with drying.*
 - All of the USAXS data collected have been modeled and particle size distributions have been determined for all scattering regions. Only the raw data was presented to more clearly illustrate trends.
- *The use of RDE studies for determining permeability of the ionomer is questionable because the environment is different.*
 - The RDE experiments have been repeated using a solid-state micro-electrode cell. The permeability results were qualitatively similar.
- *More cell diagnostics are needed to provide understanding as well as visualization of the catalyst layer, where the only presented work came from outside of this project.;The coordination appears to be correct, but it may be improved by using all the characterization techniques and resources offered in FC-020 (K. More).*
 - Numerous cell diagnostics are performed, which haven't been presented due to time limitations. (see slide 6)
 - A greater emphasis was placed on visualization this year using both TEM and X-ray tomography.
- *The collaborations among several industry, academic, and national laboratory partners are very impressive. It is unclear whether the catalyst dealloying was done at ANL or at JMFC.*
 - All catalyst treatment, processing, and CCM fabrication were performed by JMFC. UTRC performed the post-fabrication acid-washing of the CCMs
- *The functionalization is quite interesting and should be continued with more focus on what is occurring. Perhaps there is a way to do the functionalization before making the catalyst.*
 - The catalyst must be heat-treated to drive the alloying process and this removes the support functional groups.
- *The project contains a lot of data and diagnostics, but there needs to be further analysis of all of the data.*
 - Greater emphasis was placed on analysis this year and analysis will continue under the auspices of FC-PAD

Collaborations and acknowledgments

- Project team (subs) within DOE H₂ 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, assistance/collaboration on delta-mu XANES analysis

▪ Naval Research Laboratory (D. Ramaker and K. Swider-Lyons)

▪ NIST (F. Zhang and L. Levine)

▪ LANL (D. Spornjak and R. Borup)

▪ ORNL (K. More and David Cullen)

Thanks!

Jan Ilavsky, Robert Winarski, Vince De Andrade, ANL-APS

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

– Nancy Garland (Technology Manager)

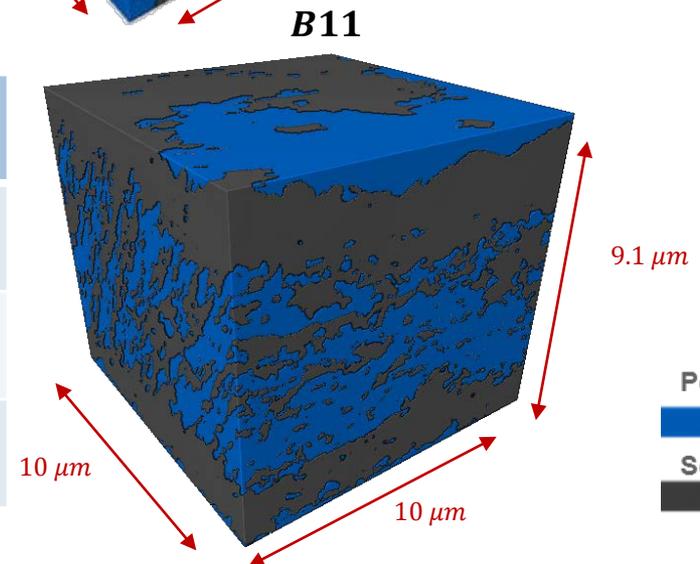
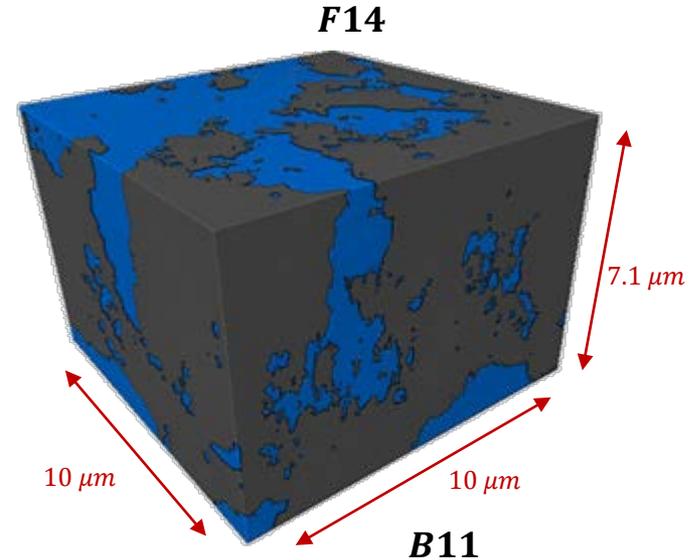
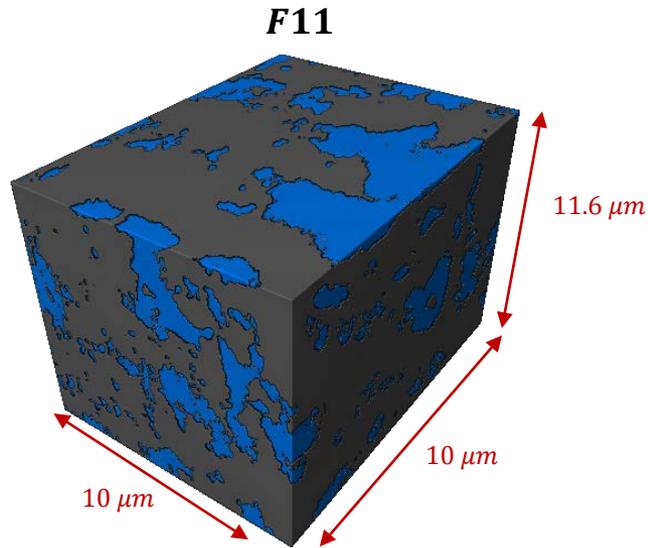


Back-up Slides



X-ray Tomography Results

- The nano-morphology (with 41.48 nm voxel) of different electrodes has been studied using X-ray tomography at the Advanced Photon Source

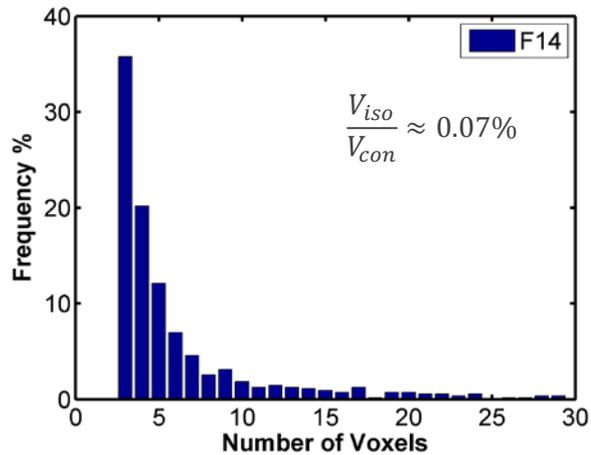
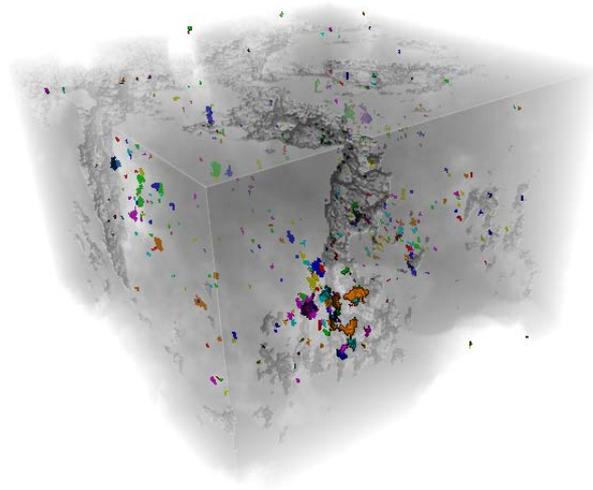


Catalyst/Ink Code	Wt% Pt	Wt% Ni	I/C	Ink Type
F11	29.1	6.68	0.8	High solids aqueous
F14	29.7	6.68	0.8	Low solids organic:aqueous
B11	29.7	-	0.8	High solids aqueous

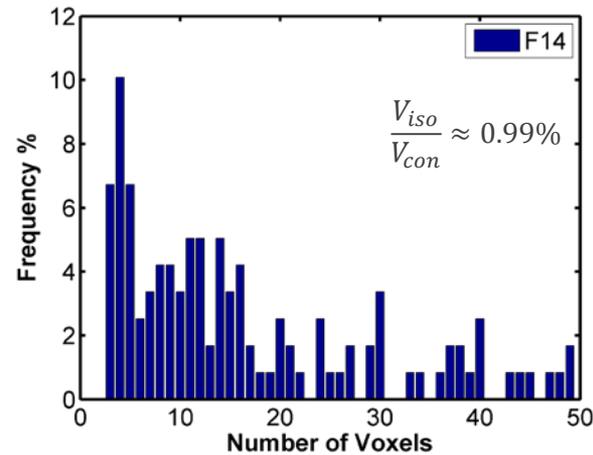
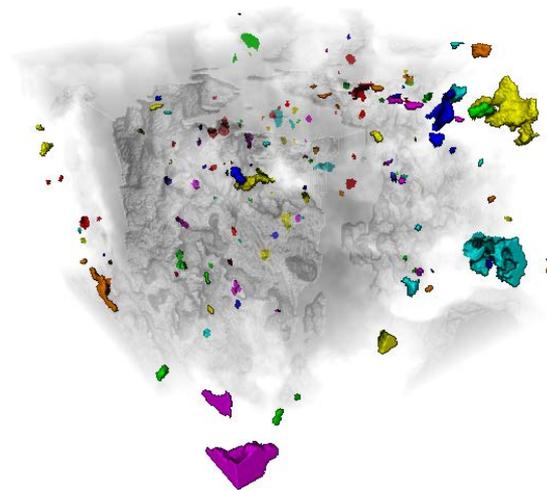
X-ray Tomography Results

- Connectivity of solid mixture (C, Pt, ionomer) and pore space for F14

F14 Solid Connectivity

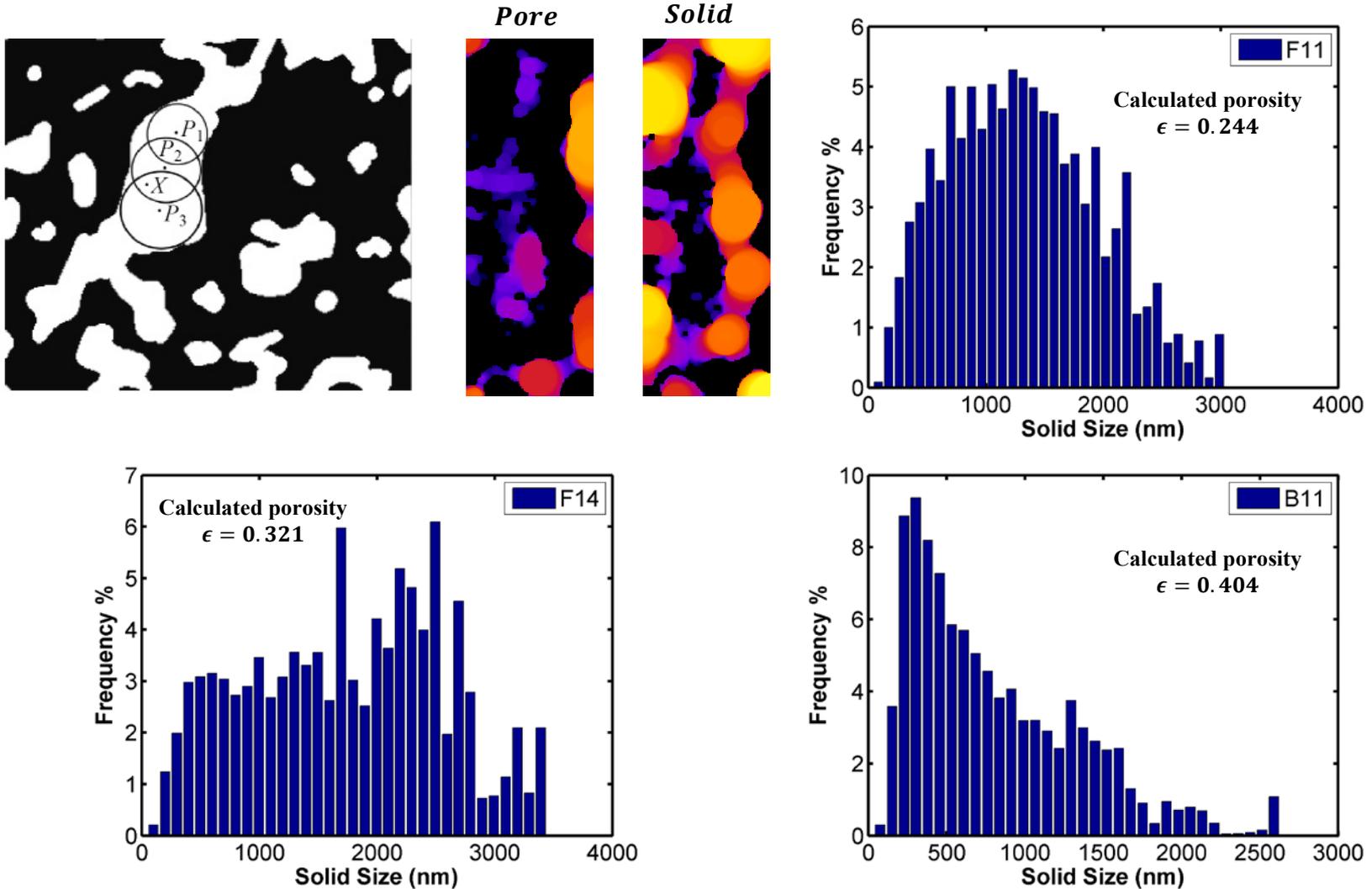


F14 Pore Space Connectivity



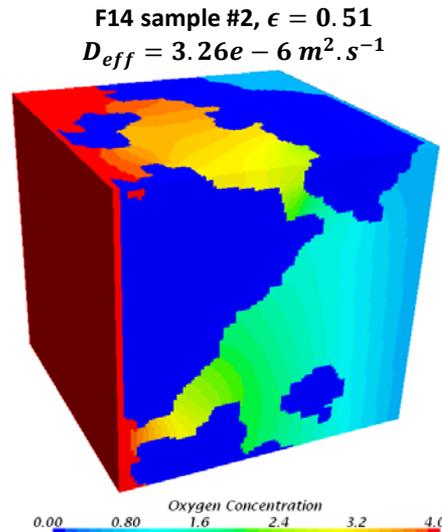
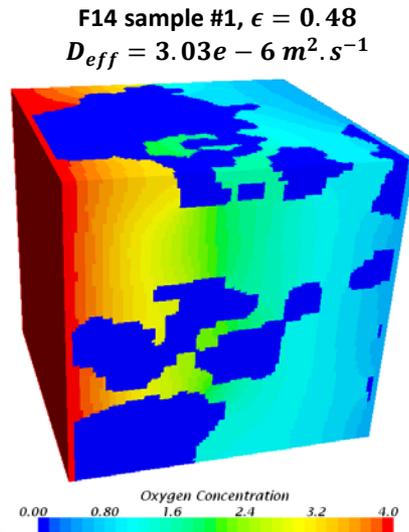
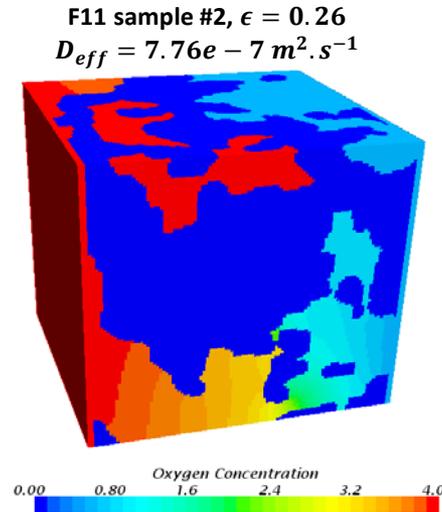
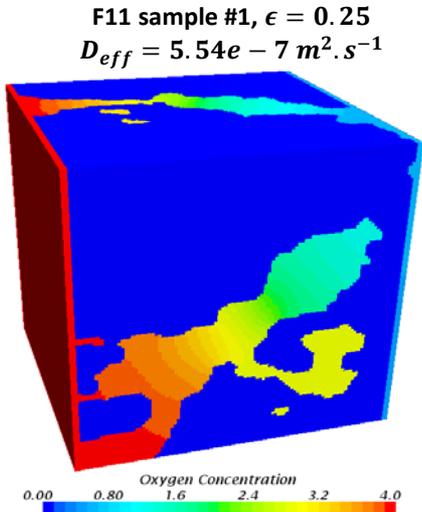
X-ray Tomography Solid Size Distributions

- Local size distributions are calculated using sphere fitting method



X-ray Tomography Effective Diffusivity

- Effective diffusivities are calculated for 4184 nm size cubic samples



- Diffusion equation is solved in through thickness direction
- Two layers of transport cells are added to both ends and Dirichlet boundary conditions are assigned
- Effective diffusivity is calculated based on Fick's law

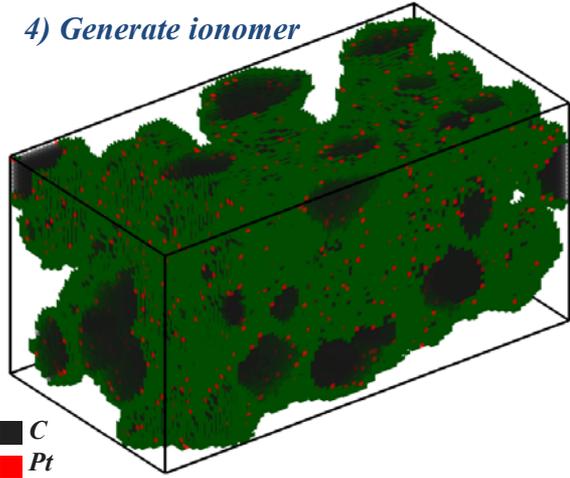
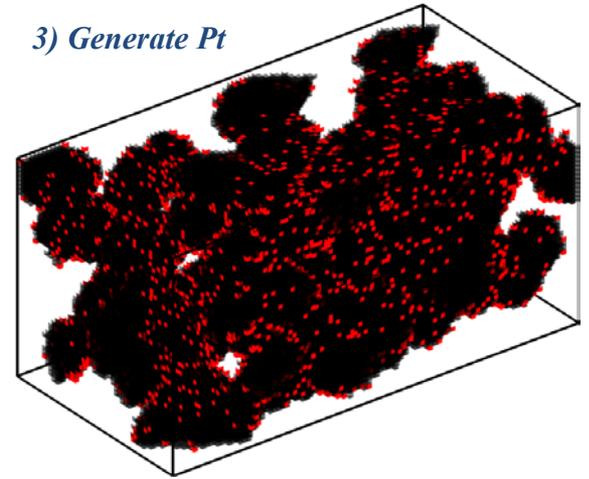
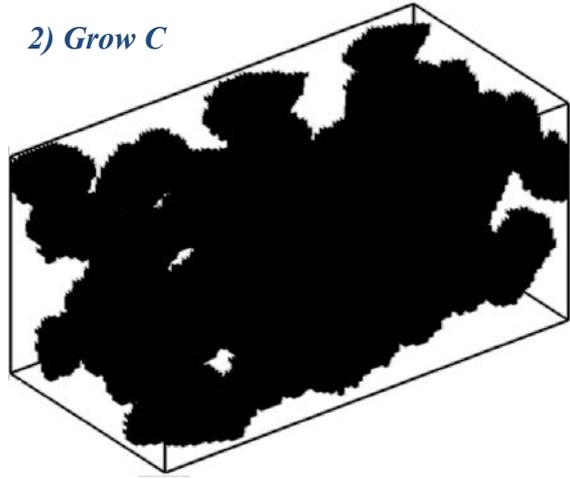
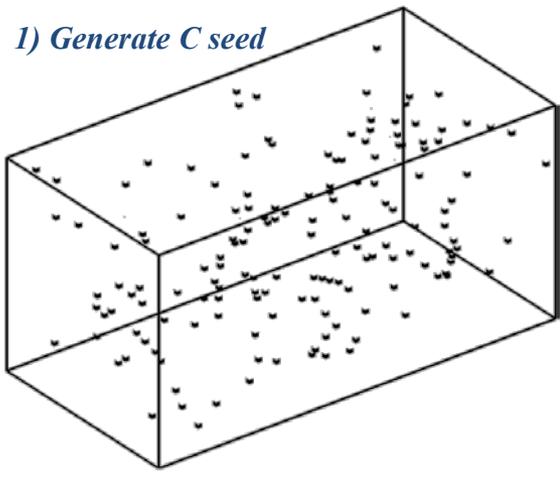
$$\nabla \cdot (D_{pore} \nabla C_{O_2}) = 0$$

$$D_{pore} = \left(\frac{1}{D_{bulk}} + \frac{1}{D_{Kn}} \right)^{-1}$$

$$D_{eff} = j \frac{t_{cl}}{\Delta C_{O_2}}$$

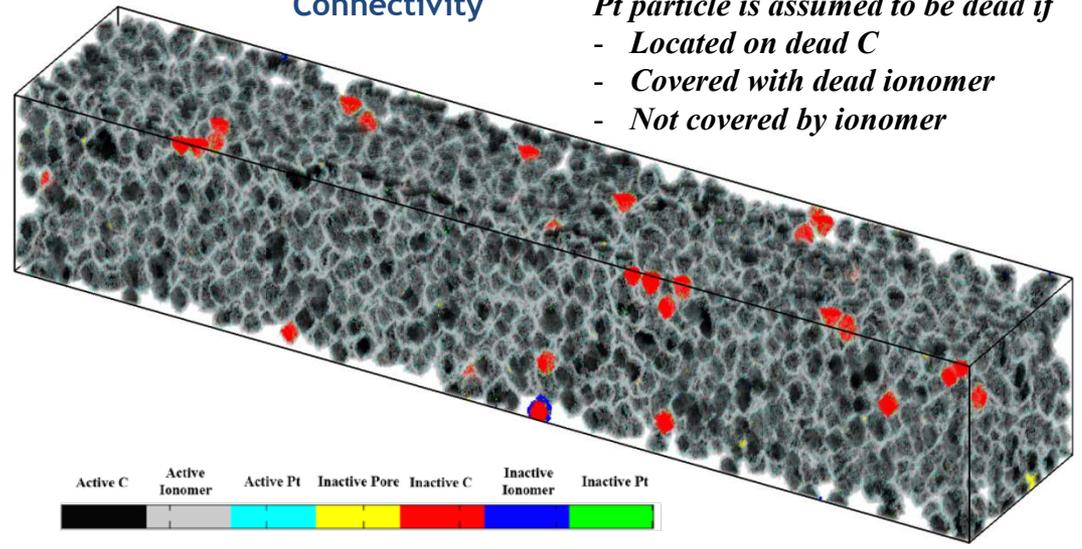
Numerical Reconstruction Algorithm

- The stacking and mixing of CL components in electrode is a random process



C
 Pt
 Ionomer

Connectivity



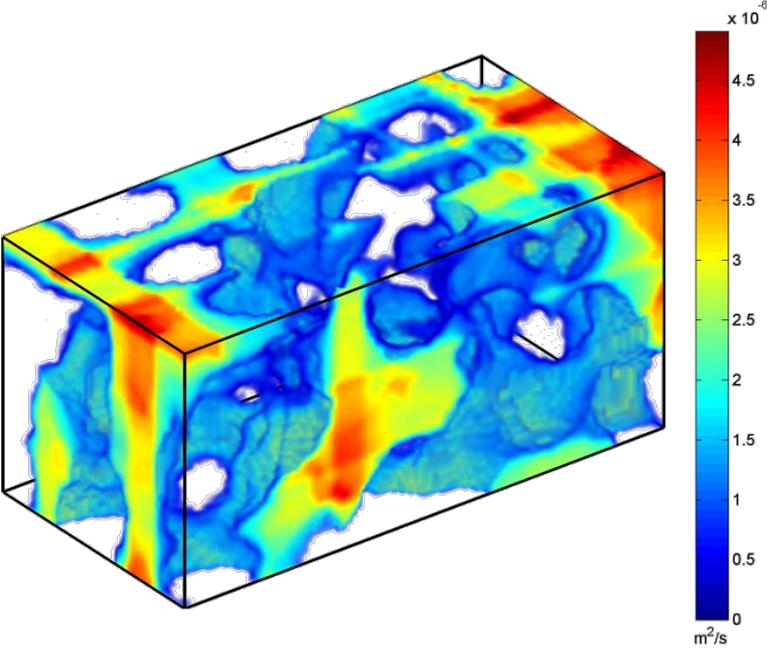
- Pt particle is assumed to be dead if*
- Located on dead C
 - Covered with dead ionomer
 - Not covered by ionomer

Active C	Active Ionomer	Active Pt	Inactive Pore	Inactive C	Inactive Ionomer	Inactive Pt

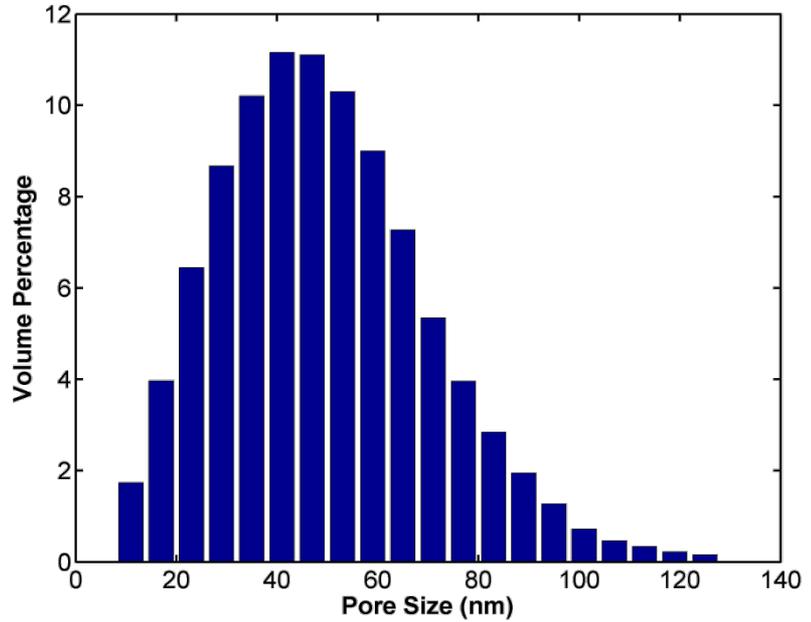


Numerical Reconstruction Algorithm: Pore Size Distribution

- Local size distributions are obtained by averaging chord lengths in 6 directions

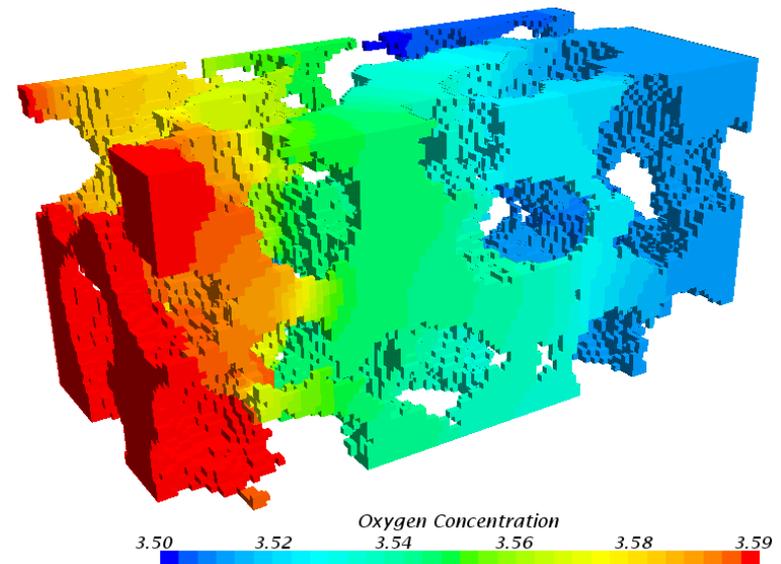
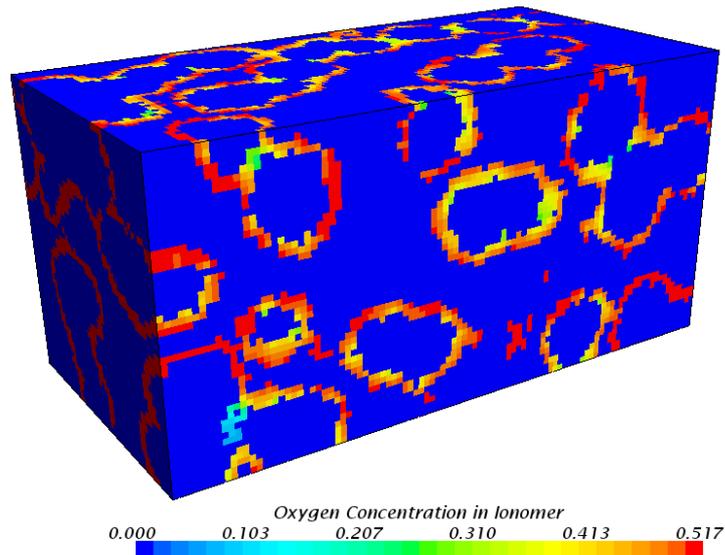
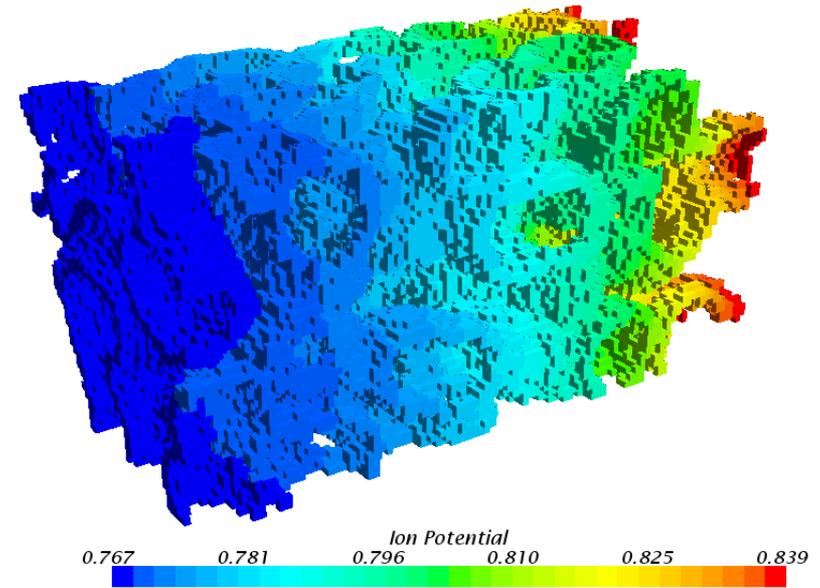


Diffusivity (m^2/s) in pores is a function of local pore size based on Knudsen effect



Numerical Reconstruction Algorithm: Multi-physics model

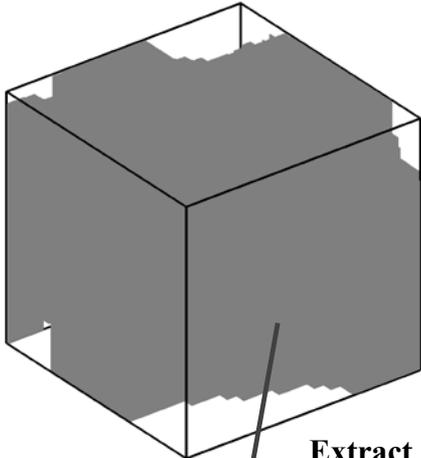
- O_2 and ion transport is modelled along with electrochemical reactions
- Ion potential drop through domain, O_2 concentration drop in pores and in ionomer film are obtained as shown
- Results show that the ionomer film is the dominating mass transfer resistance (no flooding)



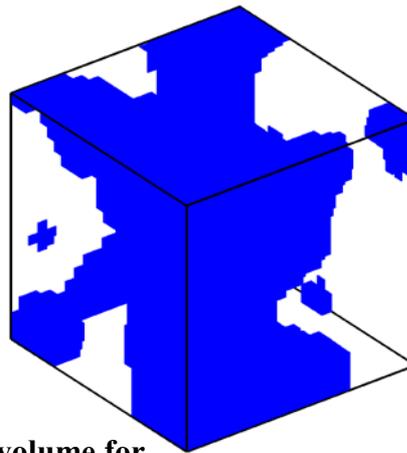
Hybrid Approach: Numerical Model coupled with Imaging Results

- A hybrid approach may help to resolve smaller pores and distinct phases

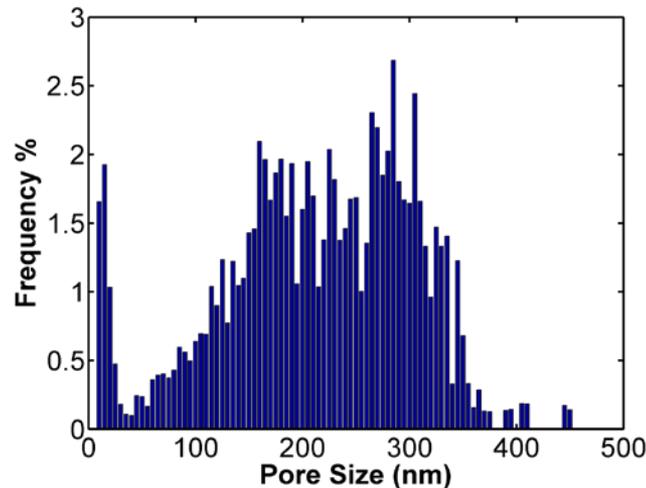
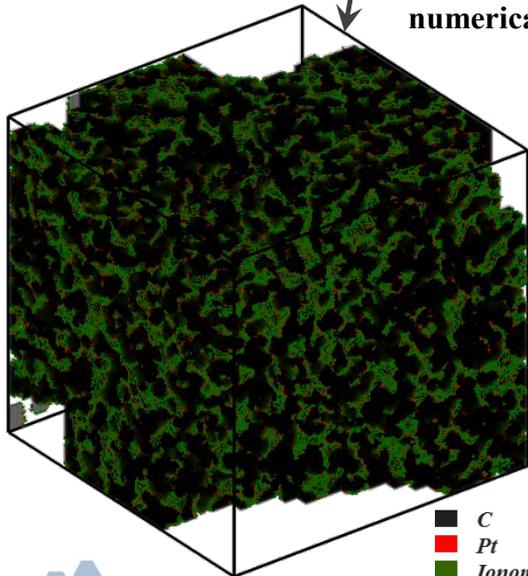
X-ray Solid
(1 μm sample)



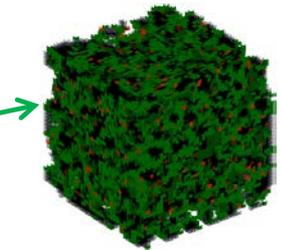
X-ray Pore Space
(1 μm sample)



Extract X-ray volume for
numerical algorithm



Another approach, X-ray coupled with
sub-grid scale model for reactions



Sub-grid scale active
cell model