The Science And Engineering of Durable Ultralow PGM Catalysts

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THE UNIVERSITY of NEW MEXICO
UNIVERSITY of DELAWARE
OAK RIDGE National Laboratory

Overview

Timeline

- Project start date:03/2010
- Project end date:03/2014
- Percent complete: *75%*

PGM total loading:	0.125 mg/cm^2 (2017 target)
PGM total content:	0.125 g/kW (2017 target)
Loss in initial catalytic activity	< 40% mass activity loss (2017 target)
Electrocatalyst support stability:	< 10 % mass activity loss (2017 target)
Durability: OCV hold 500 h	< 20 mA/cm^2 H_2 X-over < 20 % OCV loss (2017)
Durability with cycling:	5000 h (2017 target)

Budget

- Total project funding
- DOE share: $6M
- Contractor share: $529k
- Funding for FY13: $1.1M

Barriers

- DURABILITY: Free-radicals degrade membranes and catalyst supports
- COST: Unique catalyst geometries improve access and utilization of ultralow precious metal loadings that reduce cost
- PERFORMANCE: More efficient catalyst layer structures improve transport properties and performance

Partners

- Ballard Fuel Cells, UNM, UD
- LANL

Collaborations and Task Assignments

- Theoretical Understanding Of Roles Of PGM Catalyst Shape, Size, Support Interactions And Catalyst Layer Architecture On Cathode Mass Activity And Durability
  - Optimization Of PGM Catalyst Morphology With Guidance From Computational Studies (LANL)
  - Optimization Of Catalyst Layer Architecture With Guidance From Microstructural Simulations (Ballard)
  - Understanding Catalyst Particle Nucleation and Growth (UNM)
- Understanding Catalyst Nucleation And Deposition Processes by EXAFS
  - PGM-Support Interaction Catalyzation Studies (UNM)
- Investigation of Durability Enhancing Additives
  - Synthesis of active and doped nano cerias (LANL, UNM)
  - Peroxide and Free Radical Decomposition Characterization (LANL, UNM)
  - Durability testing (LANL, Ballard)
- Experimental Synthesis And Characterization Of New PGM Catalysts
  - Synthesis of Pt & Support Nanowires LANL, UNM)
- PGM and Ceria Structural Characterization by TEM, XRD, XPS
  - HRTEM Morphology Studies (ORNL, UNM)
  - Advanced X-ray Diffraction Studies (LANL)
  - X-ray Photoelecton Spectroscopy (UNM)
  - Electrochemical Characterization of PGM catalysts (LANL, UD)
- Fuel Cell & Durability Testing Of Novel PGM Catalysts
  - Testing of novel catalysts in fuel cells (LANL, Ballard)
  - Fuel cell post testing materials characterization (LANL, ORNL)

LANL	***UNM***	***ORNL***	***BALLARD***	***UD***
Fernando Garzon	*Prof. Abhaya Datye*	*Karren More*	*Siyu Ye*	*Prof. Yushan Yan*
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Neil Henson	*Sivakumar Challa*		*David Harvey*	*Yanqi Zhang,*
Tommy Rockward	*Andrew DeLaRiva*			*Zhongbin Zhuang*
JoseMari Sansiñena	*S. Michael Stewart*			
Mahlon Wilson				

Project Objectives – Relevance

- Development of durable, high mass activity Platinum Group Metal cathode catalysts -enabling lower cost fuel cells - *Synthesis and characterization of Low PGM catalysts LANL ORNL*

- Elucidation of the fundamental relationships between PGM catalyst shape, particle size and activity-will help design better catalysts - *DFT models for novel Pt nanotubes LANL, Pt nucleation and dispersion on carbons UNM*

- Optimization of the cathode electrode layer to maximize the performance of PGM catalysts-improving fuel cell performance and lowering cost – *Nanowire supports LANL, Advanced microstructural catalyst layer model development Ballard*

- Understanding the performance degradation mechanisms of high mass activity cathode catalysts – provide insights to better catalyst design. *DFT models for particle reactivity, Free Radical scavenging MEAs LANL, Nanoparticle growth model and experimental validation UNM*

- Development and testing of fuel cells using ultra-low loading, high activity PGM catalysts-Validation of advanced concepts *LANL &Ballard*

- IMPACT: This project will help lower the cost and the precious metal loading of PEM fuel cells and improve catalyst durability

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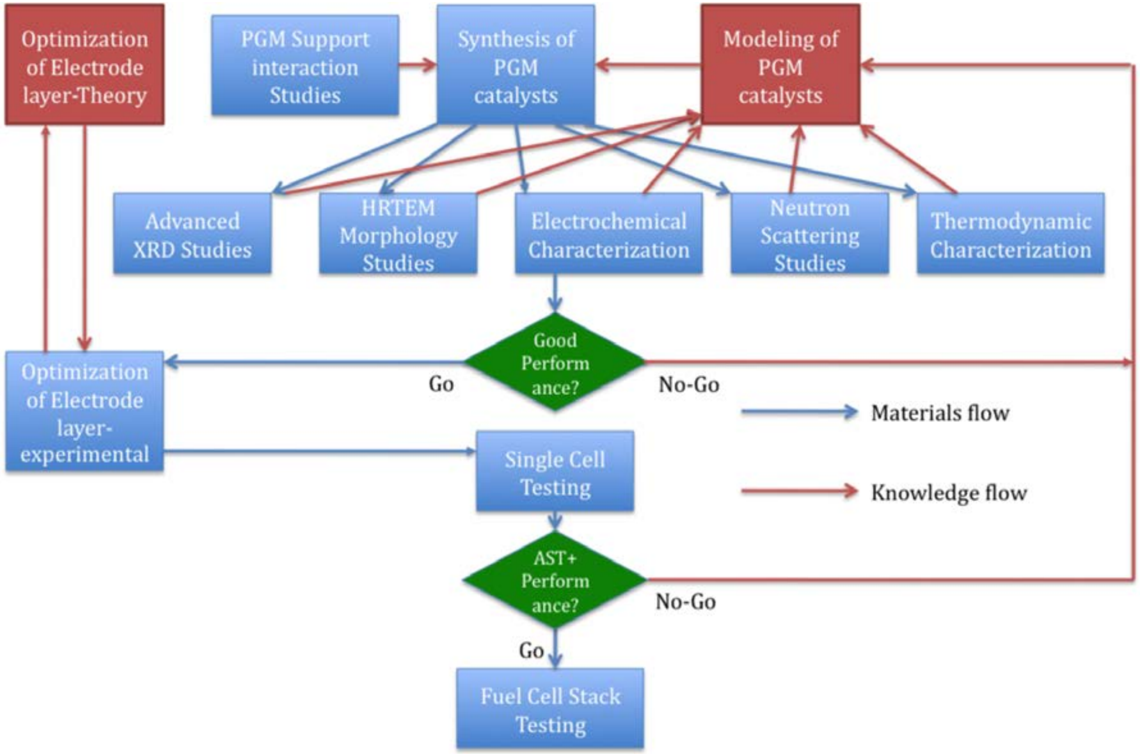
Approach

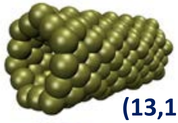
- Use contemporary theoretical modeling and advanced computational methods to understand and engineer new catalysts and catalyst layers
- Model and design appropriate catalyst architectures to maximize the performance of our novel catalysts
- Investigate catalyst-support interactions and their effects on durability and mass activity
- Study and test the performance of the catalysts in electrochemical cells, single cell-fuel cells and fuel cell stacks
- Extensively characterize new materials before and after fuel cell operation



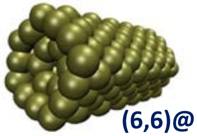
DFT Modeling of Pt Nanotubes & Nanowires

- **Previously**: Pt nanotube (NT) structure & intermediate adsorption energy calculations. NT stability issues.
- **Progress**: Extended calcs to nanowires (NW). Added hydroperoxyl adsorption calculations. Simulated electronic band structures and the d-band centers.
- **Future:** Finish computationally intensive calcs for larger NTs & NWs

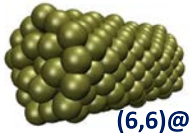
Nanotubes (NT)
Nanowires (NW)


(13,13) NT


(6,6) NT

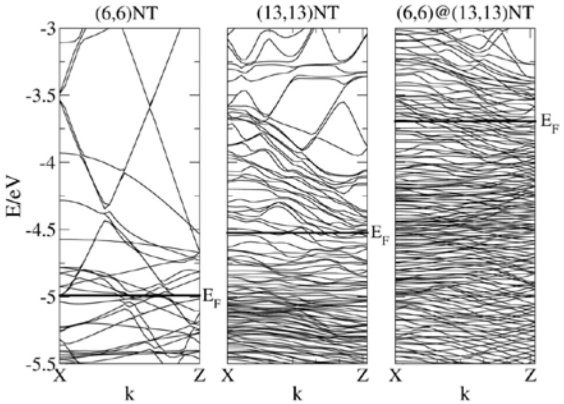

(6,6)@(13,13) NT


(6,6) NW


(6,6)@(13,13) NW

- ORR activities (per E_{ab}'s):

(13,13)NT > Pt(111) ~ (6,6)@(13,13)NW ~ (6,6)@(13,13)NT > (6,6)NW > (6,6)NT



ELECTRON BAND STRUCTURE

- Any HOO• hydroperoxyl free radicals formed on Pt are readily evolved

- No correlation between the shift in the d-band center relative to the Fermi level and the adsorption energies
  - Adsorbate changes the local environment
  - Simple descriptors inadequate to predict activity

ADSORPTION ENERGIES

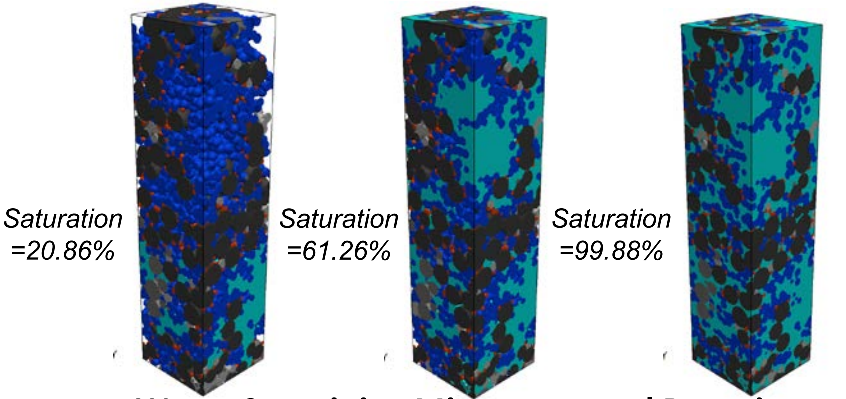
	system	oxygen (fcc site)			hydroxyl (atop site)			hydroperoxyl (T-T* and atop)		d-band center
		0.25 ML E_{ad}/eV	0.33 ML E_{ad}/eV	0.5 ML E_{ad}/eV	0.25 ML E_{ad}/eV	0.33 ML E_{ad}/eV	0.5 ML E_{ad}/eV	0.25 ML E_{ad}/eV	0.33 ML E_{ad}/eV	eV
	Pt(111)	-4.42	-4.25	-4.07	-2.88	-2.92	-3.09	-1.24*/-1.15	-1.27*/-1.20	-1.78
~ 0.5 nm	(6,6)NT	-4.72	-4.41	-4.46	-3.54	-3.53	-3.52	-1.83	-1.78	-1.81
	(6,6)NW	-4.62	-4.38	-4.33	-3.30	-3.42	-3.36	-1.75	-1.69	-1.75
~ 1.0 nm	(13,13)NT	-4.14	-3.90	-3.92	-2.83	-2.87	-2.85	-1.28*/-1.42	-1.47	-2.00
	(6,6)@(13,13)NT	-4.05	-4.21	-4.06	-3.07	-3.13	-3.20	-1.24*/-1.38	-1.41	-2.05
	(6,6)@(13,13)NW	-4.04	-4.02	-3.97	-3.04	-3.10	-3.09	-1.30	-1.36	-2.13


oxygen on (13,13)NT


hydroxyl on (13,13)NT

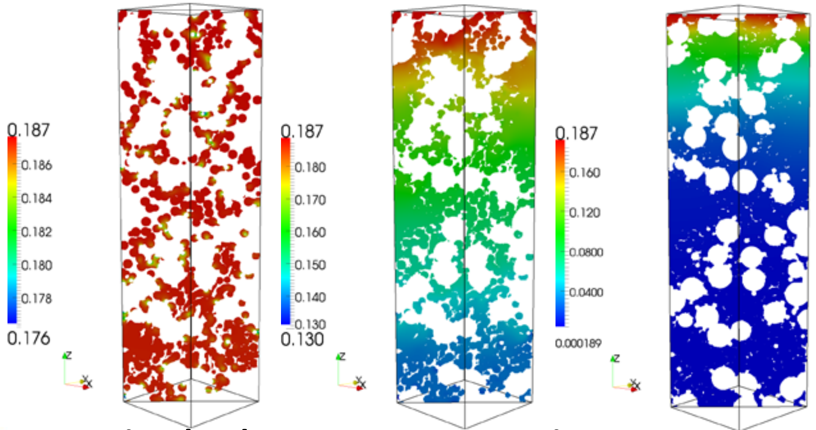
Catalyst Layer Microstructural Simulations

- **Previously**: Computational grids of randomly assigned components were used to derive estimates of effective transport properties
- **Progress**: Method is extended to include water, 1st to predict other transport properties, 2nd to track capillary accumulation

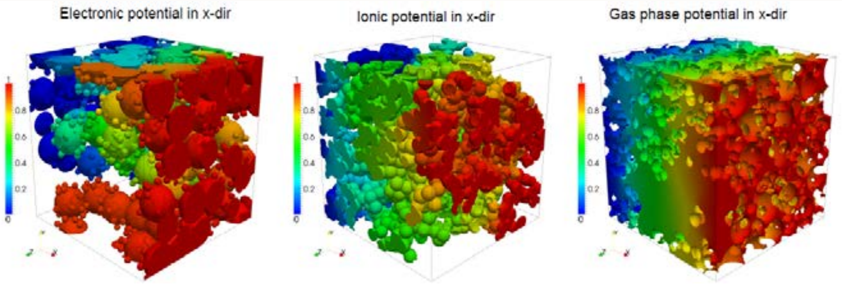


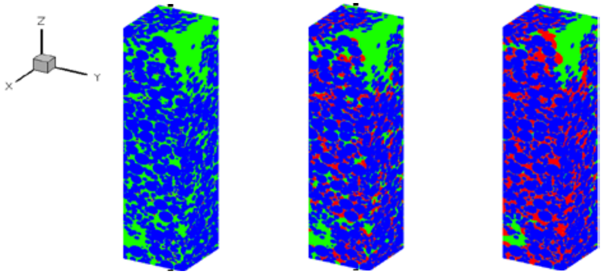
Water Containing Microstructural Domains

Black: carbon, Red: Pt, Dark-blue: Ionomer, Lt.-blue: water



Dissolved Oxygen Concentrations for η=-0.6V





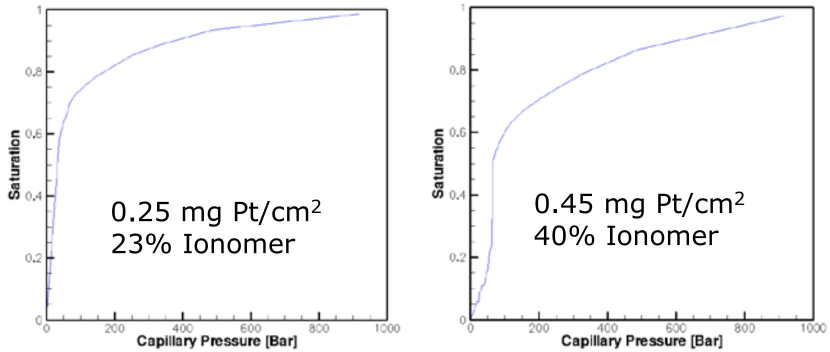
Progression of capillary water accumulation during ORR

Blue: solid phases

Green: open pores

Red: water

Capillary Pressure Catalyst Layer Simulations



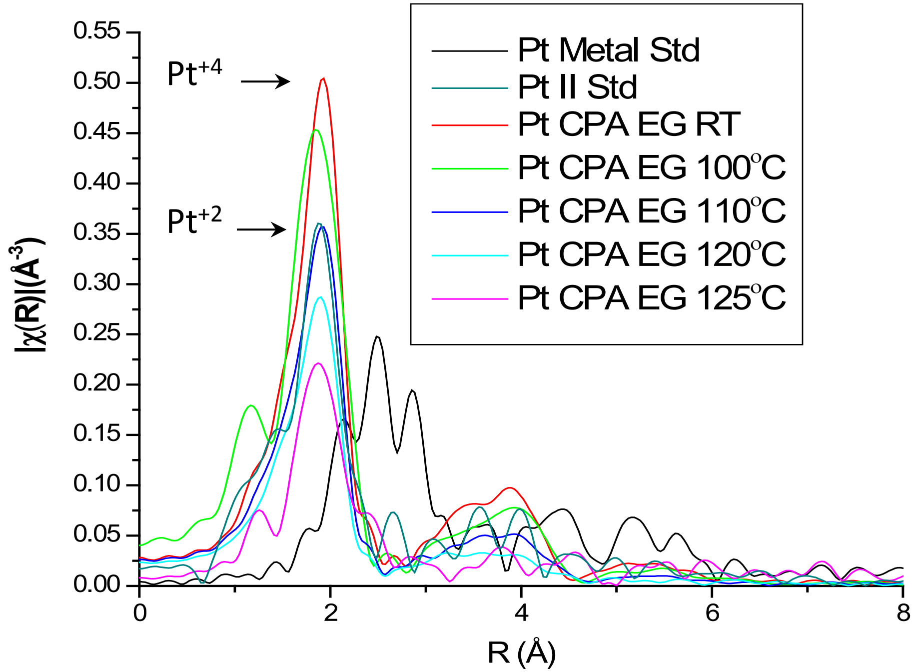
- **Future**: 1) Transient simulations.

2) Tackle transport of water (extremely computationally intensive)

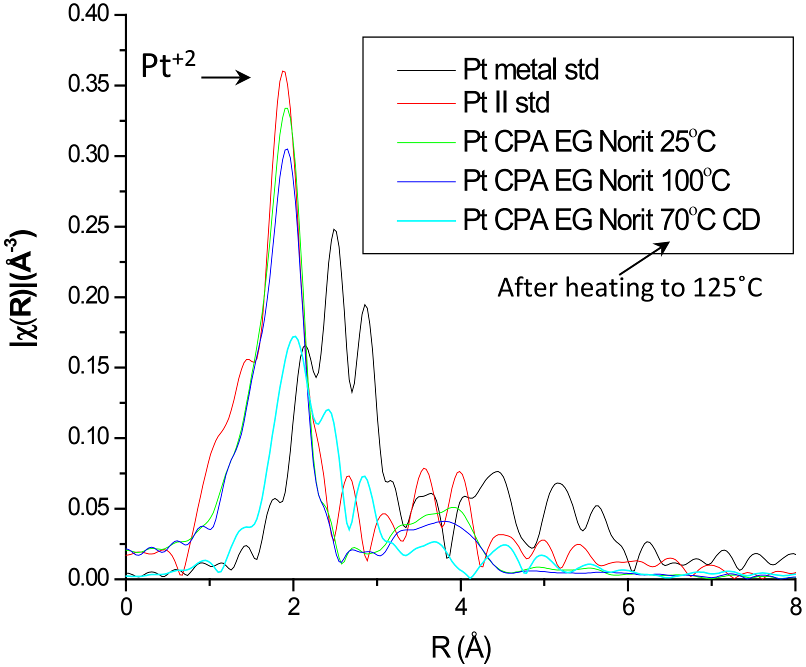
3) Introduce catalyst layer structures of interest to this project (i.e., nanowire networks)

In-situ EXAFS of the Polyol Catalyzation Process

- **Previously**: Observed that Pt(IV) in chloroplatinic acid (CPA) is immediately reduced to Pt(II) in the presence of carbon. Not clear the functions of carbon and caustic in the polyol process
- **Progress**: In-situ EXAFs to 125˚C with and without carbon and caustic in the polyol process.
- **Future**: Measurements at higher temps and with higher CPA concentrations to discern roles of carbon and caustic wrt Pt nucleation & particle size. Explore stirring mixtures in the beamline.



CPA in ethylene glycol (EG), no caustic



After heating to 125˚C

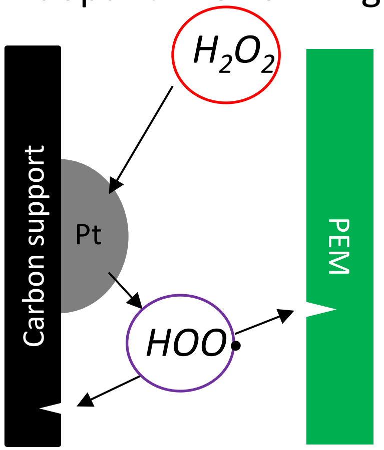
CPA and Norit Carbon in EG, no caustic

- CPA not reduced to Pt(II) until ~ 110˚C.
- Pt particles fall out of the beam

- CPA reduced instantly to Pt(II) when C added.
- With caustic, still Pt(II) at 125˚C (not shown)

Ceria additives for improving durability

- **Previously**: Originally developed ceria impregnated carbon supports, switched to additives
- **Progress**: Controlled synthesis of ceria crystallite size. Determined peroxide decomposition and free radical generation rates. Characterized surface concentrations of Ce^{+3} and Ce^{+4} with and w/o Pr dopant. Performing OCV tests and initiated AST's of MEAs w/ and w/o ceria.



Peroxide generation and degradation into hydroperoxyl free radicals attack the carbon support and PEM

$$Ce^{+4} + H_2O_2 \longrightarrow Ce^{+3} + HOO\bullet + H^+$$

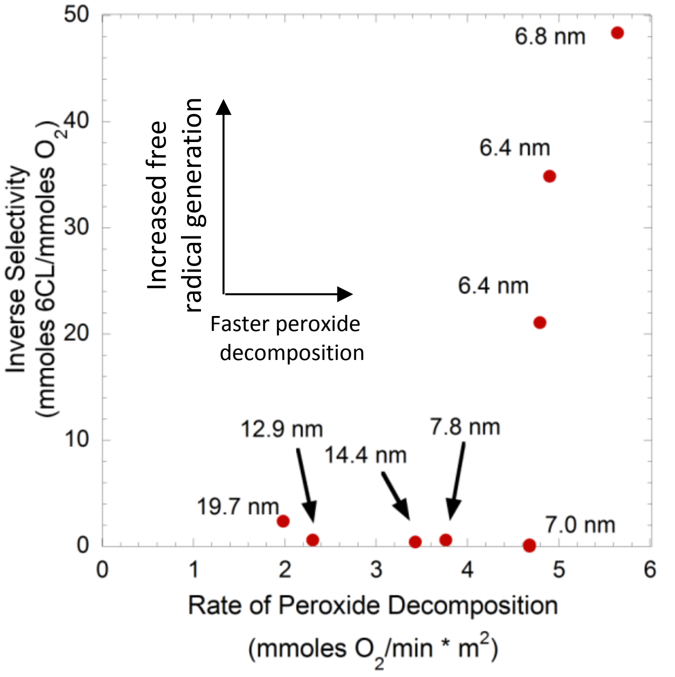
$$Ce^{+4} + HOO\bullet \longrightarrow Ce^{+3} + O_2 + H^+$$

$$Ce^{+3} + HOO\bullet + H^+ \longrightarrow Ce^{+4} + H_2O_2$$

Karakoti et al., Chem. Soc. Rev., 39. 4422-4432 (2010)

Ceria both decomposes peroxide and scavenges free radicals. The Ce^{+3}/Ce^{+4} ratio at the particle surface is thus expected to influence efficacy

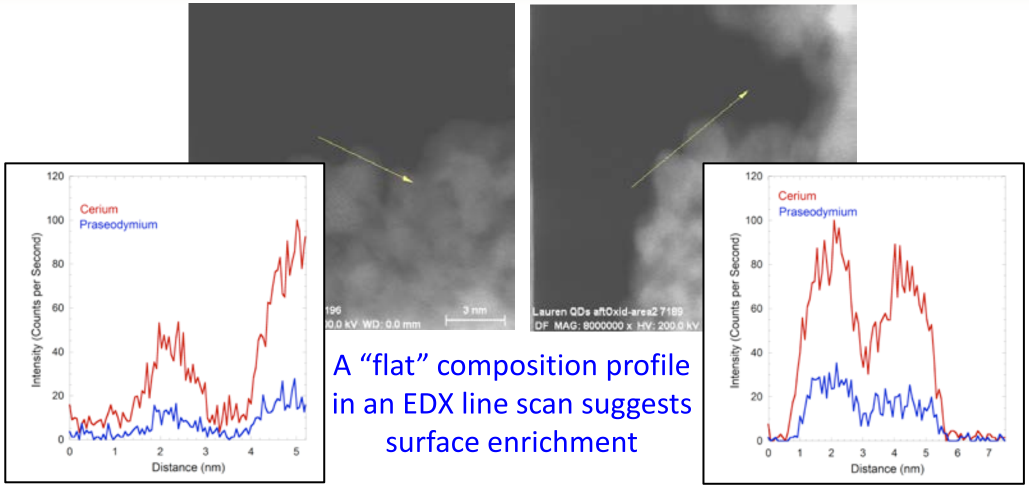
- Cerium cations are currently used to stabilize PEMs
  - Easily leached from the membranes
- Ceria nanoparticles offer a relatively acid stable peroxide decomposition catalyst
- However, free radical formation is also destructive
  - Characterized relative decomposition/formation rates (right)
- The Ce^{+3}/Ce^{+4} ratio should affect the selectivity of these processes and needs to be characterized & understood
  - Doping the ceria influences the surface oxidation states



Curve derived from separately measuring the rates of peroxide decomposition and free radical formation (followed spectroscopically using 6-carboxyfluorescein) for different particle sizes of ceria

Doped ceria scavengers

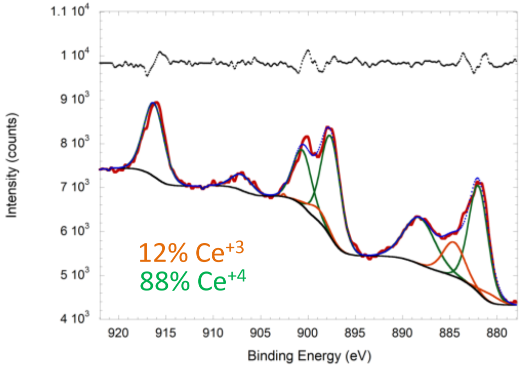
- Ceria dopants may increase chemical resistance and may also improve the performance of ceria as a scavenger by imparting ionic or electronic conductivity
  - Gd increases ionic conductivity
  - Pr increases ionic & electronic
- Pr-doped ceria was synthesized by two separate processes and investigated how Pr affects the surface composition
- Energy dispersive X-ray spectroscopy (EDX) suggests that Pr segregates to the surface of the ceria (top figures).
- X-ray photoelectron spectroscopy (XPS), however, indicates that the Ce^{+3} surface content is decreased (undoped ceria is typically ~ 23% Ce^{+3})
  - Ostensibly affects free radical scavenging negatively,
- Will investigate the effects the Pr dopant and the lower Ce^{+3}/Ce^{+4} ratio will have on acid stability, peroxide decomposition and selectivity, and ultimately fuel cell lifetime



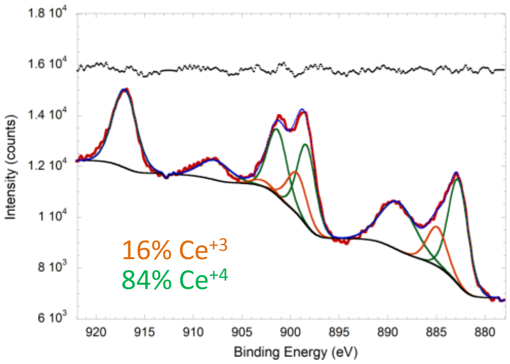
A “flat” composition profile in an EDX line scan suggests surface enrichment

EDX line scan of 15:85 Pr:Ce 5.00 nm particle by solution-precipitation with path in HRTEM shown above

EDX line scan of 15:85 Pr:Ce 5.00 nm particle by ion exchange resin with path in HRTEM shown above



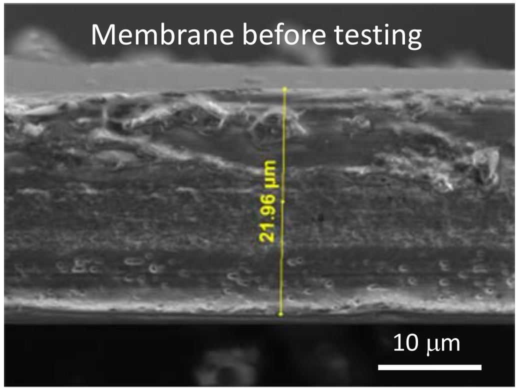
Ce 3d XPS of 15:85 Pr:Ce 5.00 nm particle by solution-precipitation



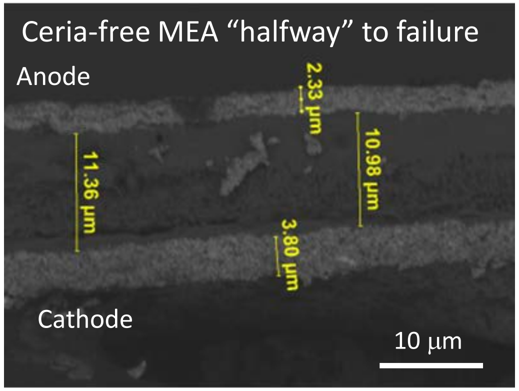
Ce 3d XPS of 15:85 Pr:Ce 5.00 nm particle by ion-exchange resin

While Ce^{+3}s are lower than in undoped ceria (~ 23%), Pr^{+3} /Pr^{+4} contents and ratios are unknown

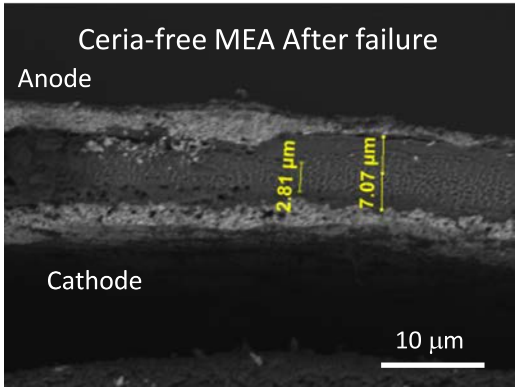
OCV testing with ceria additives



Membrane before testing

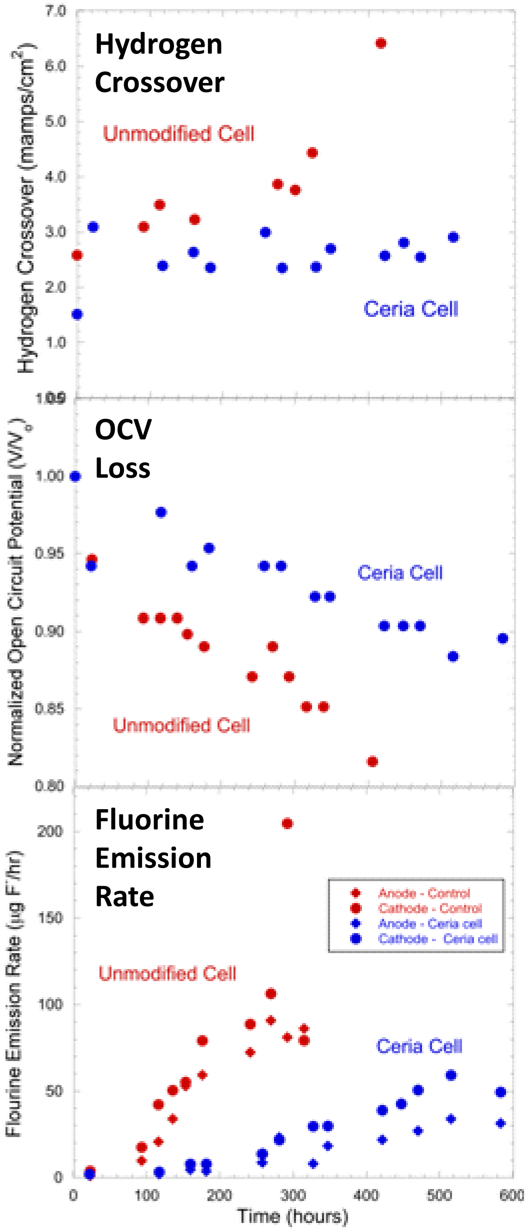


Ceria-free MEA “halfway” to failure



Ceria-free MEA After failure

- Results shown for one run (of 4) for each ceria particle size
  - Particle size selective for radical scavenging
- 1.5 wt% ceria in catalyst layer
- Compared to control cells (i.e., ceria-free)
- Tests:
  - Fluorine emission rate (FER)
  - Hydrogen Crossover
  - Open circuit potential (OCV)
  - High frequency resistance (HFR)
- Test result comparisons:
  - Ceria decreased hydrogen cross-over (but both < 20 mA/cm^2)
  - Ceria decreased OCV loss (from > 25% to ~ 10%)
  - Ceria substantially decreases amount and rate of fluorine emission
- SEMs illustrate membrane thinning of ceria-free control cell
  - Membrane thinning is uniform
  - Less catalyst layer loss on the anode side

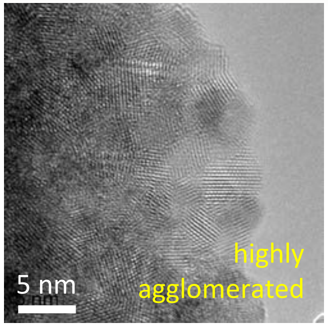


Hydrogen Crossover

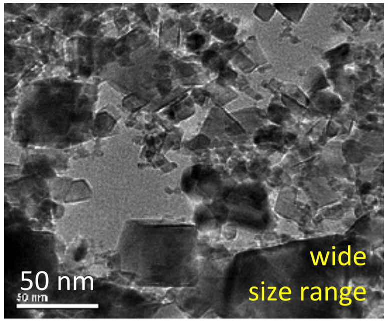
OCV Loss

Fluorine Emission Rate

Characterizing ceria additives for ASTs

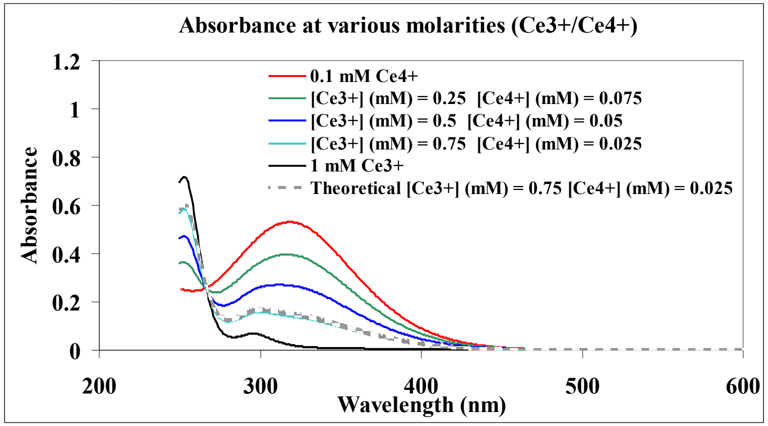


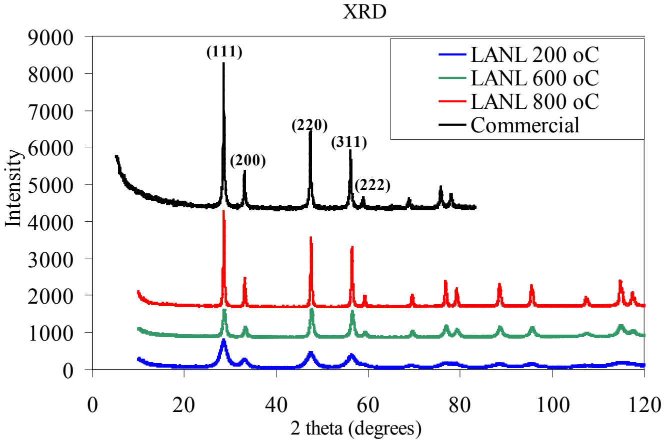
LANL 200˚ ceria



Commercial nano ceria

UV-vis spectra for various conc's of cerium salts in 1M sulfuric acid. Individual Ce^{+3}/Ce^{+4} conc's can be resolved





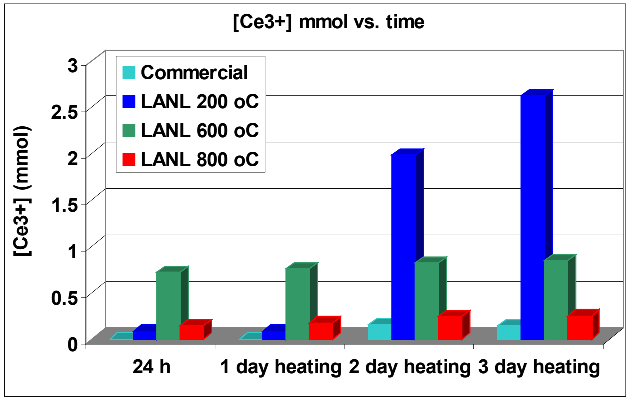
Sample [a]	Cryst. Dia.[b] (nm)	Surf. Area[c] (m^2/g)	Ce^{+3}:Ce^{+4} Surf. Ratio [d]
LANL 200˚	5.6	98	26:74
LANL 250˚	6.4	-	23:77
LANL 300˚	6.8	-	26:74
LANL 400˚	7.0	-	25:75
LANL 600˚	12.9	30	23:77
LANL 800˚	25	9	-
Comm.	31	56	-

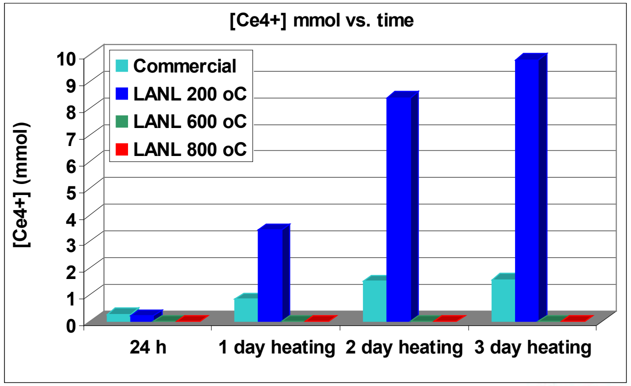
[a] Calcination temp (˚C), [b] XRD, [c] BET, [d] XPS.

- UV-vis investigated for measuring Ce^{+3}/Ce^{+4} conc's in solution
  - Indistinguishable in perchloric
  - Clear diff in sulfuric
- Several LANL & the commercial cerias tested for dissolution in 1 M acid
  - Minimal in perchloric
  - Varies in sulfuric
- Stability in sulfuric
  - Overall:

<u>800˚>600˚>Comm.>200˚</u>

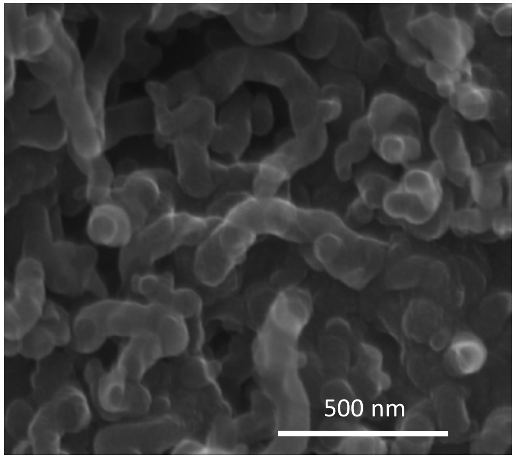
  - 600˚, 800˚Ce^{+4} v. stable
  - Enhanced Ce^{+3} stability in Comm. ceria





PPy nanowire supports

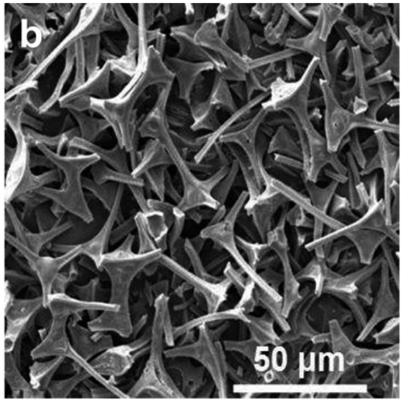
- **Previous Effort**
  - Process
    - Electropolymerize PPy nanowires onto a substrate
    - Pyrolyze
    - Platinize: sputter or impregnate
    - Hot press to membrane
  - Issues:
    - Achieving high Pt dispersions
    - Poor MEA performance (esp. Pt utilization & flooding)



Electropolymerized PPy nanowires

- **New Direction**
  - Process
    - Bulk synthesis of PPy nanowires
    - Pyrolyze to form powder
    - Platinize using polyol process
    - Prepare catalyst ink
    - Coat decals (or membrane)
    - Hot-press
  - Advantages
    - Conventional MEA manufacture
    - Greatly improved MEA performance

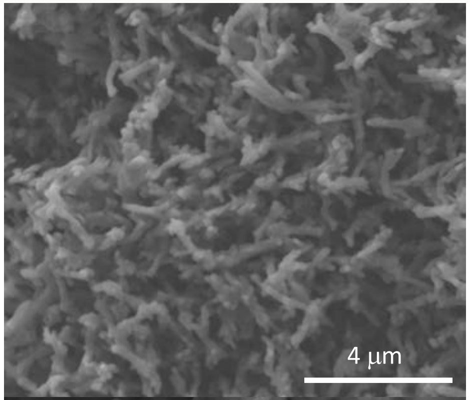
- Advantageous geometry of nanowire network supports
  - Tortuous branched networks maintain open pores but minimal “voids”
    - More free volume available for ionic and mass transport
    - Facilitates ionomer access and dispersion during fabrication
  - Enhances electronic conductivity (including “z” direction)
    - Minimizes electronically stranded catalyst
- Comparison with other carbon tube/fiber/wire support options
  - Nanotubes/fibers (vapor grown): expensive, not branched
  - Polyaniline nanowires: easily made, but pyrolyze poorly
  - Polypyrrole nanowires: readily graphitize
    - Synthesis by potentially low-cost “soft” template processes
    - Good results with Heparin:Methylene Blue soft template (Wei et al., *Synth. Met.* 160 (9–10), 849-854 (2010))
      - Some control of fiber diameter possible by varying the Hep:MB ratio

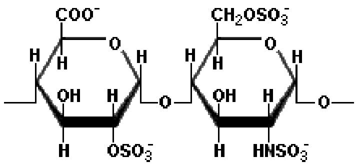


“Tetrapod” Catalyst Structure

Lee et al., Angew. Chem. Int. Ed., 52, 1026 (2013)

PPy nanostructures w/ various templates

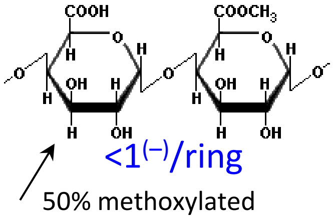




2$^{(-)}$/ring

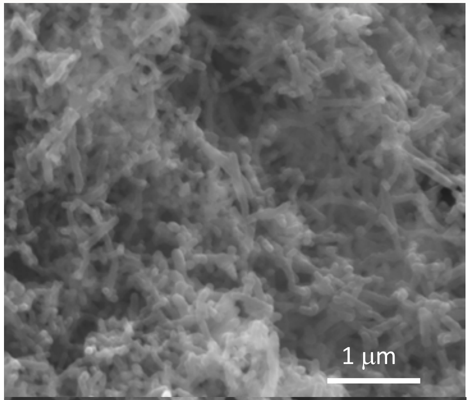
Heparin

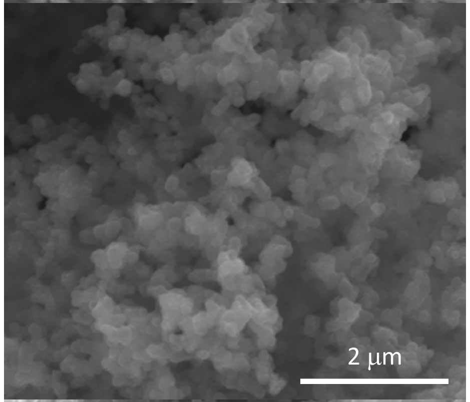
Pectin
(low methoxyl,
+ maltodextrin)

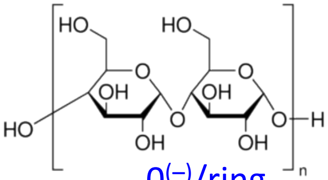


<$1^{(-)}$/ring

50% methoxylated
(0% is polygalacturonic acid)

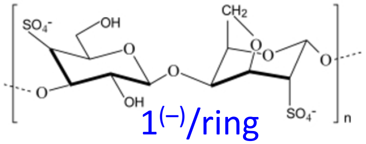






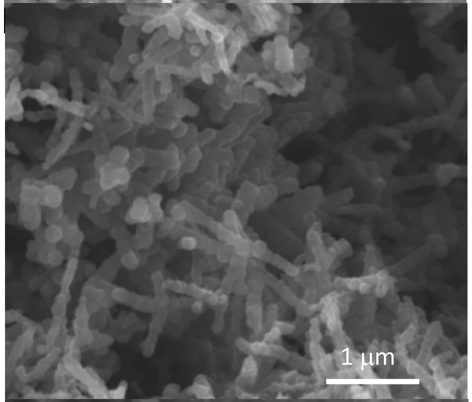
0$^{(-)}$/ring

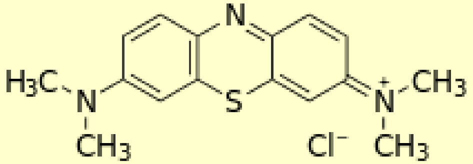
Starch



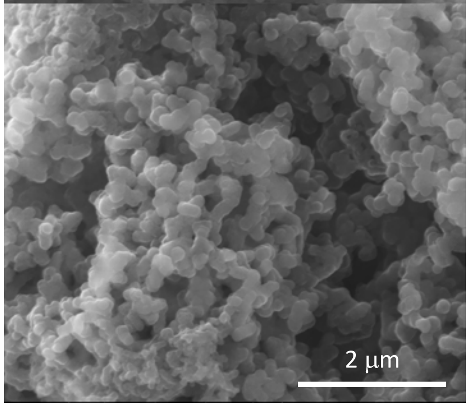
1$^{(-)}$/ring

ι-Carrageenan
(food grade)

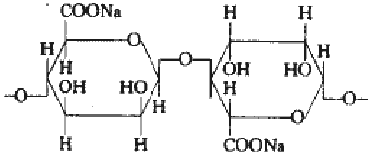




Methylene Blue

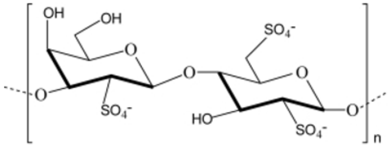


Na$^+$ Alginate
(food grade)

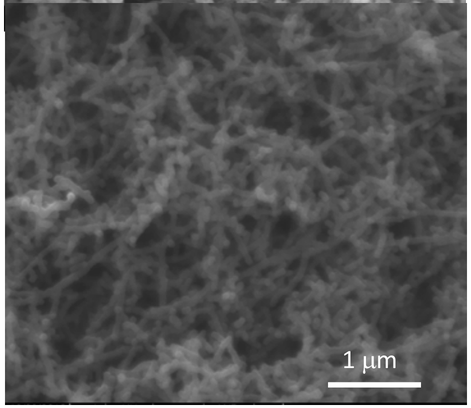


1$^{(-)}$/ring

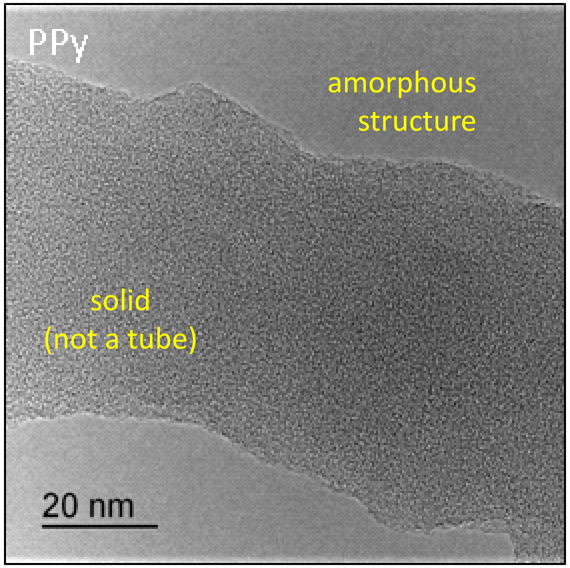
λ-Carrageenan
(food grade)

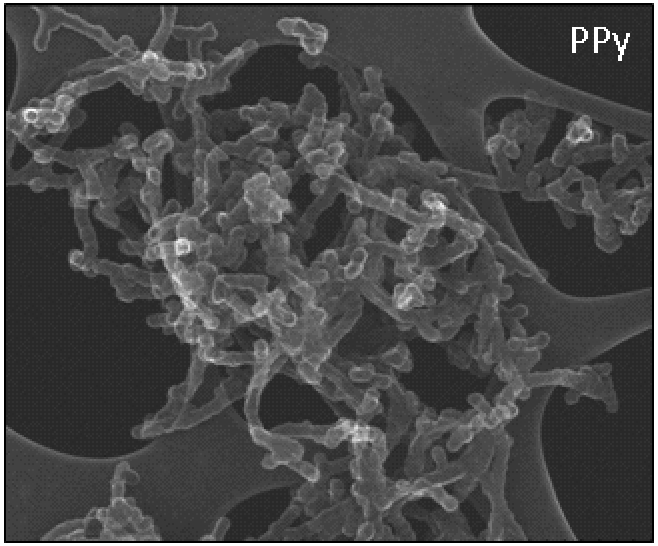


1.5$^{(-)}$/ring

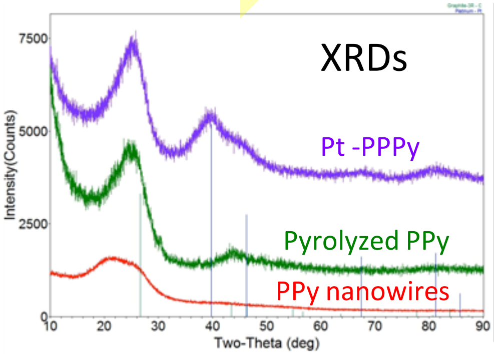


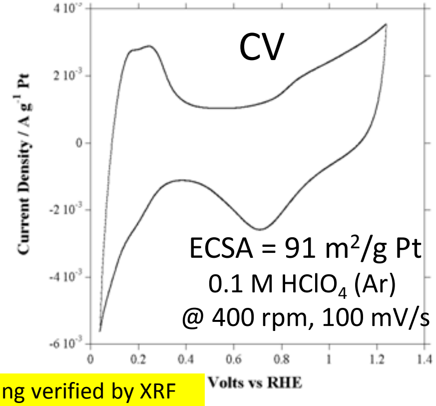
PPy to Pt-PPPy nanowire catalysts





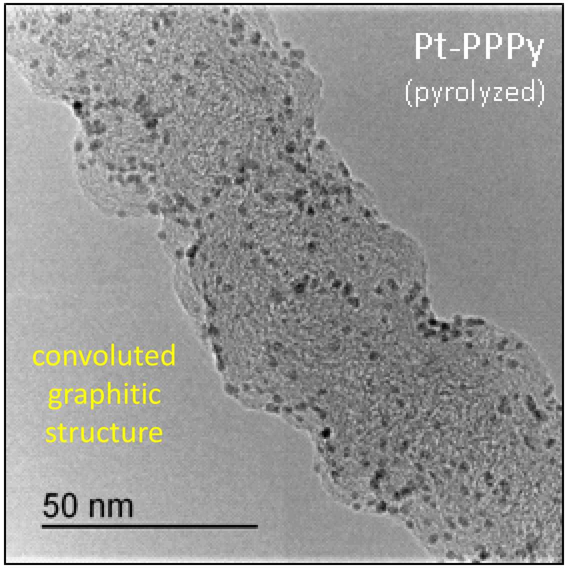
- **Pyrolysis**: 1000˚C, 1h
  - ~ 50% wt loss
  - ~ 10% N content
  - Highly graphitic structure
  - No sulfur detected
- **Platinization:** polyol process
  - Uniformly distributed, due to convoluted surface + N?
  - 13.5 wt% Pt: surface loading
    - ~ 3x 20%Pt/C
  - 2.2 nm particles (TEM)

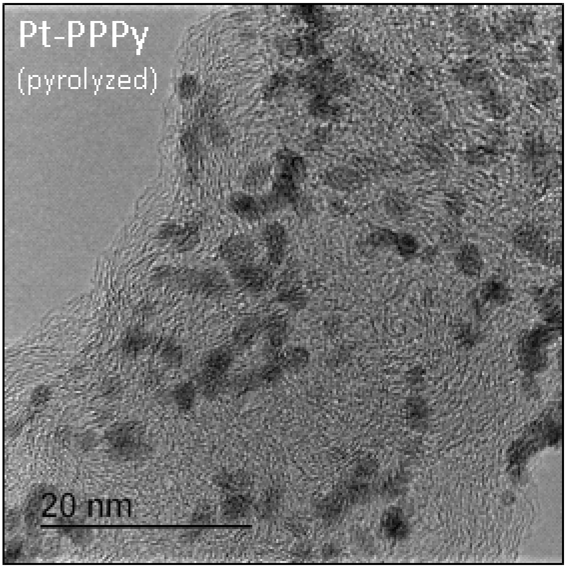




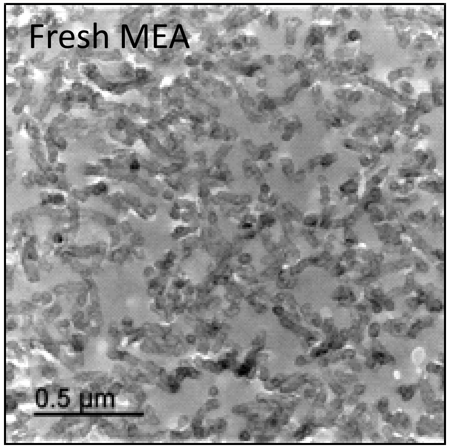
ECSA = 91 m^2/g Pt
0.1 M $HClO_4$ (Ar)
@ 400 rpm, 100 mV/s

Pt loading verified by XRF

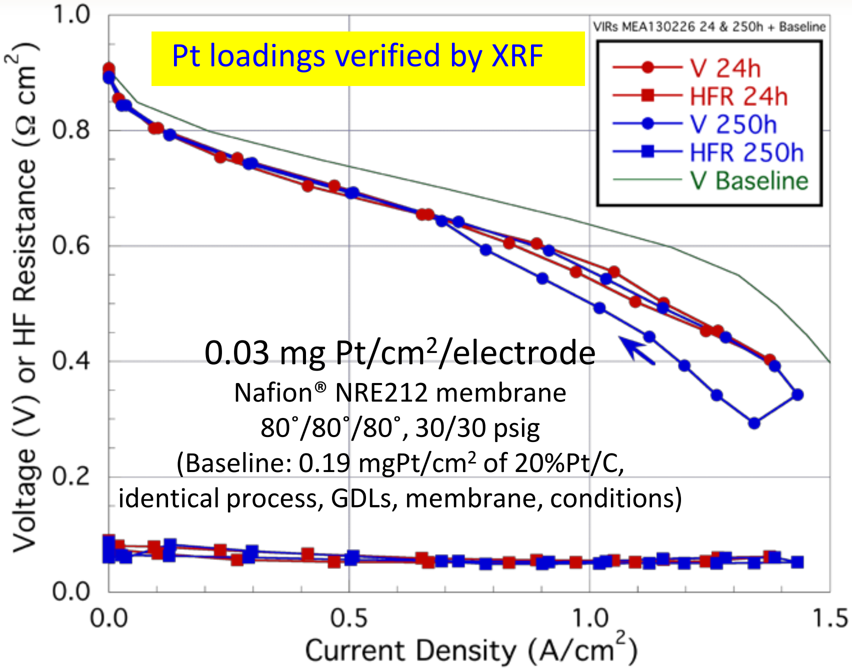




Low-PGM FC performance w/ Pt-PPPy nanowires

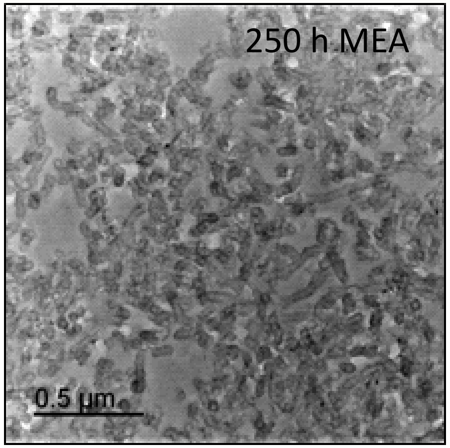


HRTEM Cross-Sections

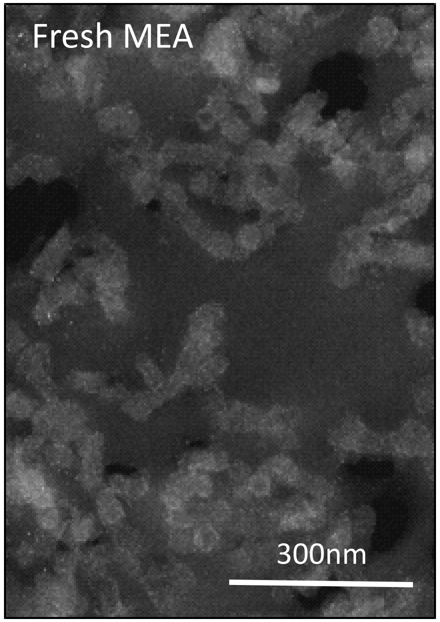


Pt loadings verified by XRF

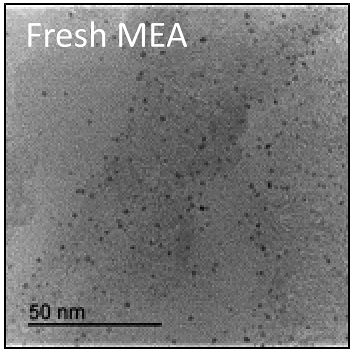
0.03 mg Pt/cm²/electrode
Nafion® NRE212 membrane
80˚/80˚/80˚, 30/30 psig
(Baseline: 0.19 mgPt/cm² of 20%Pt/C,
identical process, GDLs, membrane, conditions)

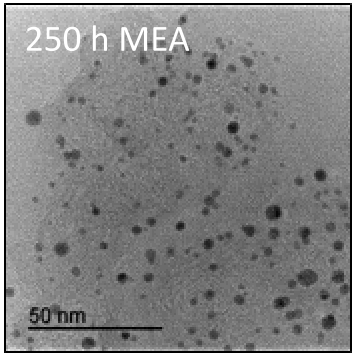


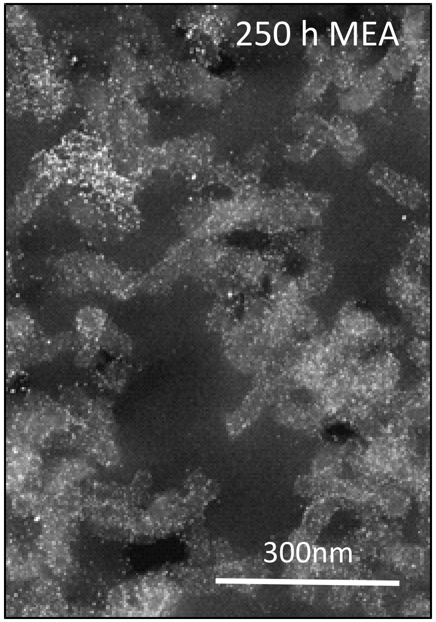
HRTEM Cross-Sections



- Initial performance promising (still evolving process)
- After 250 h, hysteresis, but no loss despite considerable Pt coarsening. No obvious carbon corrosion.







Los Alamos NATIONAL LABORATORY EST. 1943
BALLARD power to change the world
THE UNIVERSITY of NEW MEXICO
UNIVERSITY of DELAWARE
OAK RIDGE National Laboratory

Milestones & No-Go Decisions

- **Milestones**
  - Dec 2012
    - Achieve preparation of MEAs with novel nanowire PGM catalyst layers < 25 µm thick with < 0.1 mg Pt/cm^2 and an ESA > 70m^2/g –LANL *Achieved*
    - Optimize Pt-Ceria-ratios for low free radical generation catalysts with less than 10% difference in FC performance at 0.6V from non ceria catalysts –UNM & LANL *Achieved (w/ ceria additive)*
  - Feb 2013
    - Complete HRTEM imaging of novel nanowire PGM catalysts- ORNL *Achieved*
  - July 2013
    - Complete optimization of fuel cell components using novel nanowire PGM catalysts to demonstrate single cell performances with << 0.1 mg Pt/cm^2 that equal or exceed conventional MEAs with 0.2 mg Pt/cm^2 – LANL *On track*
    - Complete AST testing of MEAs incorporating free-radical scavengers – LANL & Ballard *First series will be completed, but further testing will continue*
  - Sept 2013
    - Complete characterization (XRF, SEM, HRTEM, XRD, X-ray tomography) of AST testing samples – LANL & ORNL *First series will be completed, but further testing will continue*
    - Complete the extension of modeling on the optimization of catalyst architecture extended to ultra-low catalyst loading geometries - Ballard *On track*
    - Complete the extension of VASP DFT modeling to larger structures that better approximate the dimensions of experimental materials – LANL *On track*
- **No-Go Decisions**
  - Ceria/carbon composite Pt supports – <~8 nm ceria counterproductive
  - Electrosynthesis of PPy nanowires – chemical synthesis approach proved superior
  - Pt_3Sc & Pt_3Y catalysts - ORNL microanalysis indicated HSA materials were oxides

Proposed Future Work

- Modeling
  - DFT modeling of nanotubes/wires:
    - Complete computations on larger Pt tubes/wires
  - Catalyst Layer Microstructural Calculations:
    - Transient simulations
    - Incorporate water generation & transport
    - Investigate nanowire supports
  - Catalyzation and particle growth modeling (see Back-up slides)
    - Perform simulations & correlate with experimentation
- Catalyzation studies
  - EXAFs of polyol at higher temps and Pt concentrations, including on new carbons
- Ceria free-radical scavenger additives
  - Free radical and peroxide decomposition studies of doped cerias
  - FC lifetime OCV testing with differing ceria particle sizes, dopants
  - AST studies of prime candidates
- Pyrolyzed PPy nanowire supports
  - Synthesize finer nanowires
  - Determine PPPy nanowire functionality and durability
    - If needed, modify pyrolyzed nanowire composition
  - Catalyst layer composition and processing optimization
  - Comprehensive FC and AST testing
    - Synthesize large Pt-PPPy batches

Summary

- Modeling
  - some aspects are coming to closure, others are progressing nicely
- Ceria free-radical scavengers
  - Identified particle size range that maximizes scavenging
  - Structurally characterized non- and Pr-doped cerias
  - Early FC OCV testing results already meet durability technical target
    - 2017 Durability Target: OCV hold 500 h
      - < 20 mA/cm^2 H_2 X-over (achieve < 5 mA/cm^2)
      - < 20 % OCV loss (achieve about 10%)
  - AST testing is underway
- Pt-PPPy nanowire catalysts
  - Developed potentially low-cost soft-template PPy nanowire synthesis process
  - Pyrolyzed PPy nanowires provide desirable properties
    - Tortuous branched network with high void volume
    - Highly graphitic
    - Convoluted graphitic surface with high N functionality (ideal for nucleation)
  - Achieved high Pt dispersions with high surface loadings on highly graphitic surfaces
  - Using “conventional” MEAs, early results indicate promising catalyst layer properties

- Conclusion: Progress in durability enhancement additives and more efficient catalyst layers further contribute to the realization of durable, ultra-low PGM fuel cells

Technical Back-Up Slides

Modeling Details

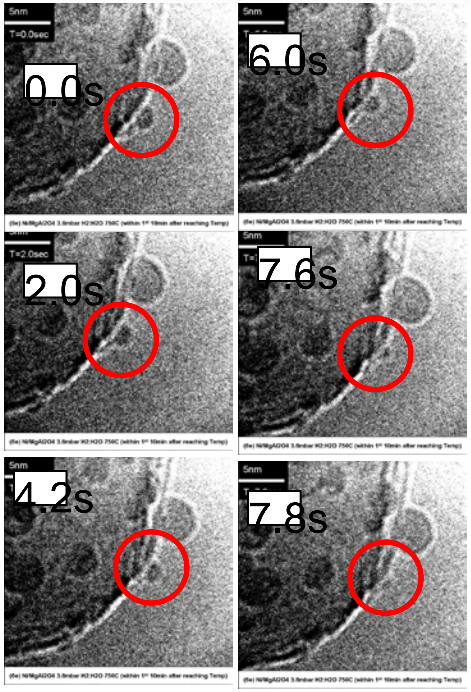
- DFT
  - VASP program (Vienna ab-initio simulation package)
  - DFT with PAW method using GGA approximation with PW91 exchange-correlation term
  - 23 Å x 23 Å x n*L* cell, vacuum space twice the tubes diameter
  - (1 x 1 x 4) – (1 x 1 x 21) k-point Monkhorst-Pack mesh
  - plane-wave basis with a cutoff energy of 400 eV
  - Methfessel-Paxton smearing of order 2 with sigma value of 0.2 eV

- Catalyst layer microstructural simulations
  - Sample structure generated by random addition of spherical components
    - First carbon, then Pt, then ionomer
    - Follow simple populating rules (e.g., Pt adds onto carbon)
  - Surface triangulation of sample structure converted to discretized volume
  - Volume is discretized by cut-cell based unstructured grids using MicroFOAM[1] based on OpenFOAM[2]
  - Discretized volume consists of 4 distinctive phases (Carbon, Pt, Ionomer, Pore)

[1] *Choi et al*. ImechE PartA: Journal of Power and Energy, **225**: 183-197 (2011).

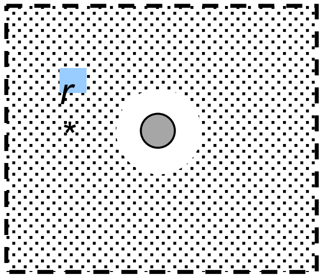
[2] *OpenFOAM*: a free, open source CFD software package available at www.openfoam.com.

Modeling of catalyst ripening



ETEM Study of the Ostwald Ripening of Nanoparticles, de la Riva *et al.* (UNM)

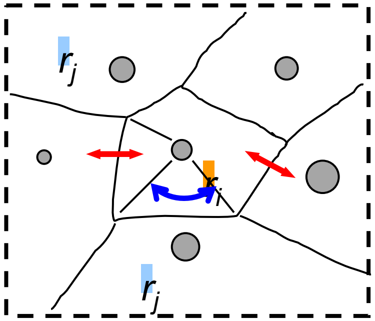
Mean-Field Model



$$\text{flux} \propto \frac{1}{r}\left[\exp\left(\frac{r_c}{r_*}\right) - \exp\left(\frac{r_c}{r_i}\right)\right]$$

Over estimates ultimate particle sizes

Non-Mean-Field Model



$$\text{flux} \propto \frac{1}{r_i}\sum_j\left[\exp\left(\frac{r_c}{r_j}\right) - \exp\left(\frac{r_c}{r_i}\right)\right]\alpha_{ij}$$

$\alpha=\theta/2\pi$
Introduces a surface tension factor

Better predictions of particle size distribution will be obtained with the physically more realistic model

N. C. Bartelt *et al.*, *Phys. Rev. B* **54** 11741 (1996)

Previous: Mean-Field Model

Progress: Introduce Non-Mean-Field Model

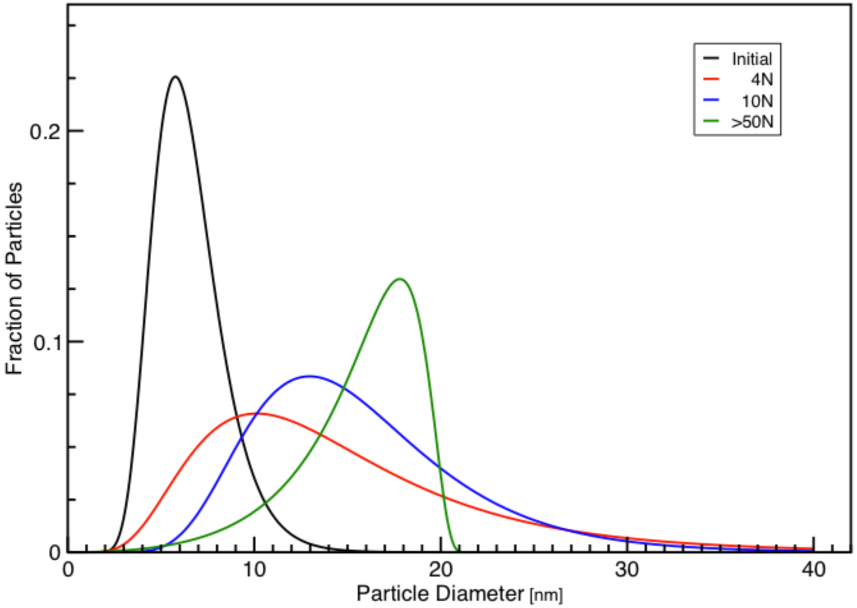
Ripening rate now dictated by local conditions.

Space divided into randomly angled Voronoi polygons centered around individual particles with *j*=6 randomly chosen neighbors.

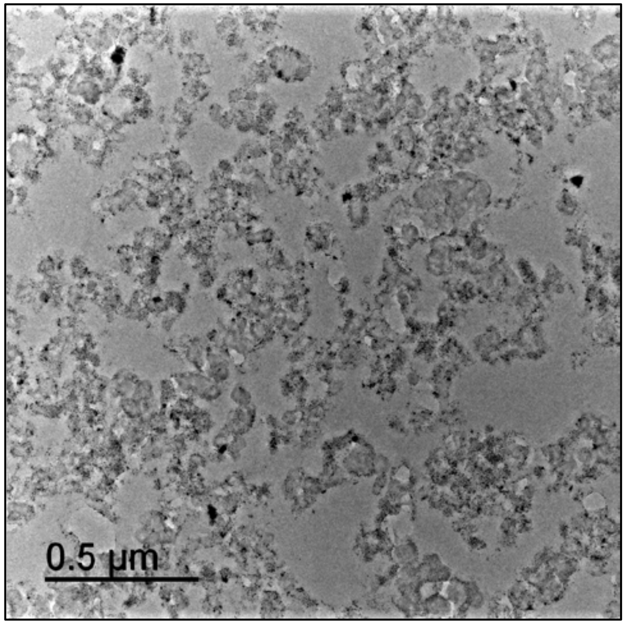
Number of neighbors of a particle steadily decreases until *j*=0 and the size becomes stagnant for **that** particle.

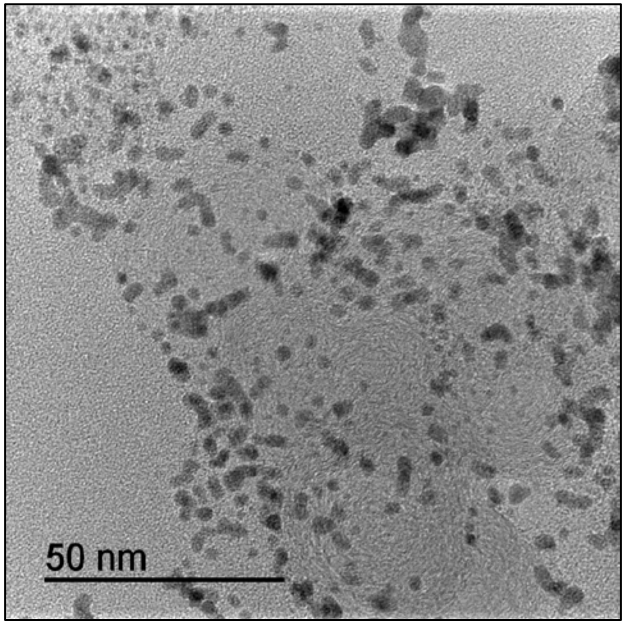
Future: Full model development and analysis

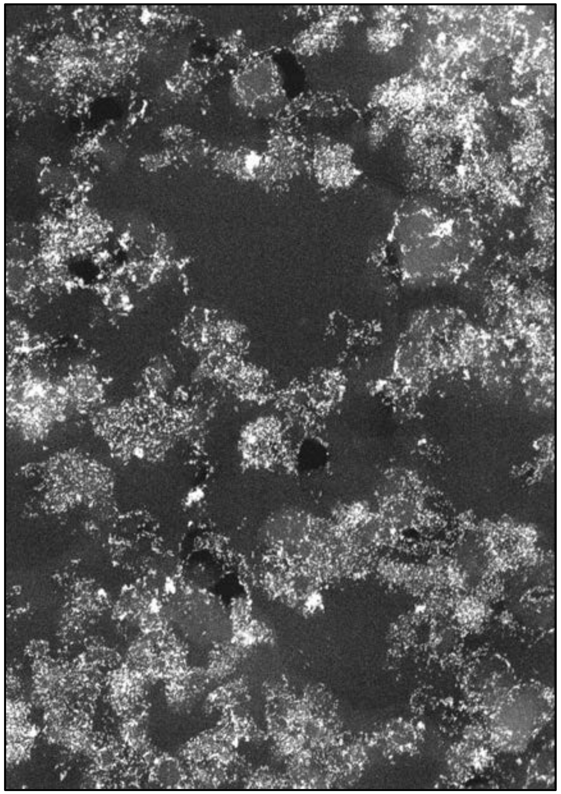
Tie DFT into surface tension calculation



HRTEM of conventional fresh Pt-C MEA







- Fresh MEA using Pt on Vulcan® XC-72
- For comparison with HRTEM results on Pt-PPPy nanowires
  - Note considerably larger Pt particles with Pt-XC72
    - Surface affinity a factor in stabilizing particles during processing?
  - Note the greater possibility of stranded particles with the Pt-XC72 MEA