The Science And Engineering of Durable Ultralow PGM Catalysts

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FC010

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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)

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

Budget

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

Partners

- Ballard Fuel Cells, UNM, UD
- LANL

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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*
  - *Fernando Garzon*
  - *Ivana Matanovic Gonzalez*
  - *Neil Henson*
  - *Tommy Rockward*
  - *JoseMari Sansiñena*
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  - *Kateryna Artyushkova*
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  - *Andrew DeLaRiva*
  - *S. Michael Stewart*

- ***ORNL***
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  - *Kelly Perry*

- ***BALLARD***
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  - *Dustin Banham*
  - *David Harvey*

- ***UD***
  - *Prof. Yushan Yan*
  - *Shaun Alia*
  - *Yanqi Zhang,*
  - *Zhongbin Zhuang*

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*

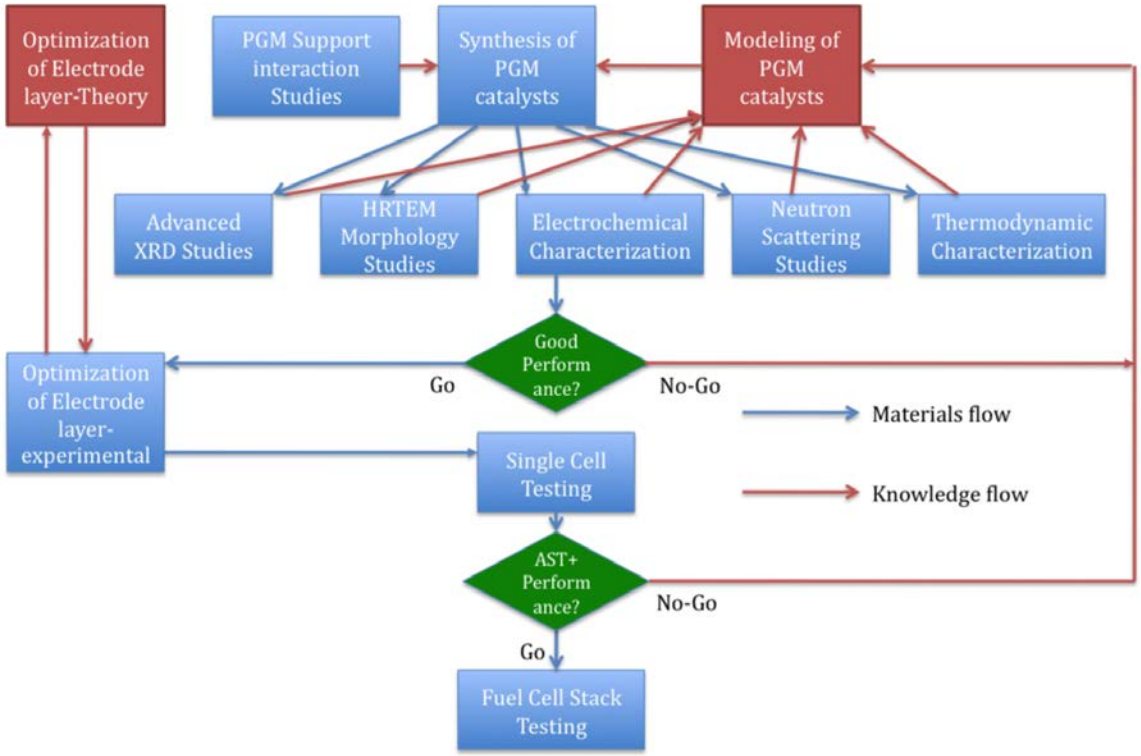
•Understanding the performance degradation mechanisms of high mass activity cathode catalysts – provide insights to better catalyst design. *DFT models for particle reactivity, Free Radical scavenging MEAs LANL, Nanoparticle growth model and experimental validation UNM*

•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

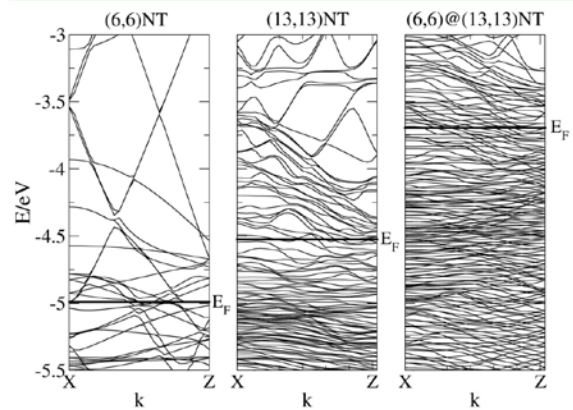
Approach

- 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



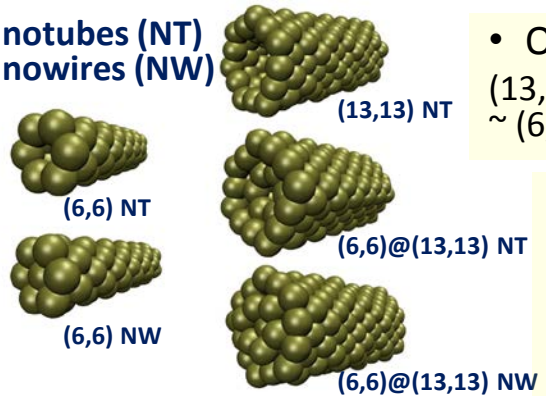
DFT Modeling of Pt Nanotubes & Nanowires

- **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



ELECTRON BAND STRUCTURE

Nanotubes (NT)
Nanowires (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

- 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

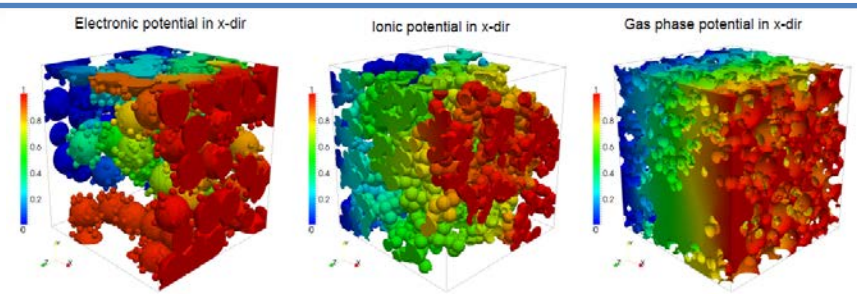
	system	oxygen (fcc site) 0.25 ML E_{ad}/eV	oxygen (fcc site) 0.33 ML E_{ad}/eV	oxygen (fcc site) 0.5 ML E_{ad}/eV	hydroxyl (atop site) 0.25 ML E_{ad}/eV	hydroxyl (atop site) 0.33 ML E_{ad}/eV	hydroxyl (atop site) 0.5 ML E_{ad}/eV	hydroperoxyl (T-T* and atop) 0.25 ML E_{ad}/eV	hydroperoxyl (T-T* and atop) 0.33 ML E_{ad}/eV	d-band center 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

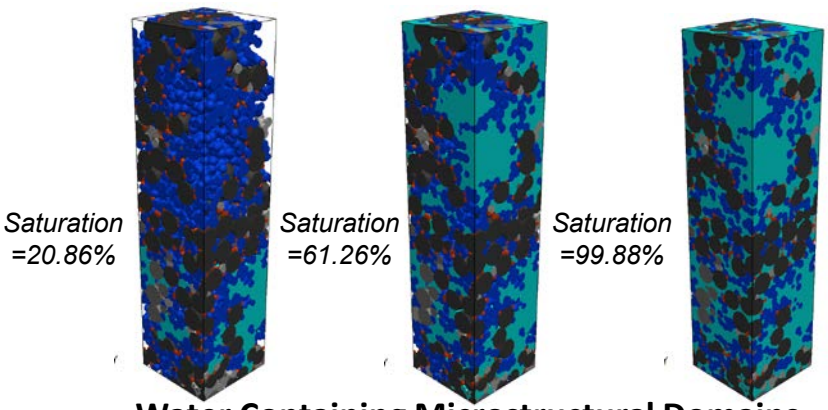
oxygen on (13,13)NT

hydroxyl on (13,13)NT

Catalyst Layer Microstructural Simulations

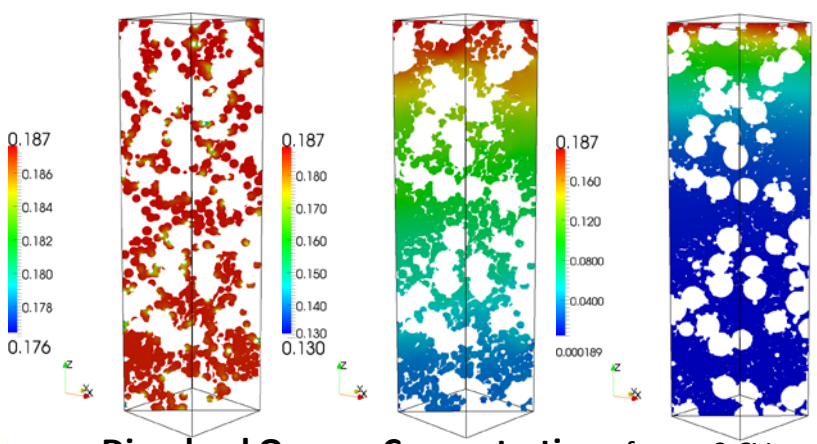
- **Previously**: Computational grids of randomly assigned components were used to derive estimates of effective transport properties
- **Progress**: Method is extended to include water, 1st to predict other transport properties, 2nd to track capillary accumulation



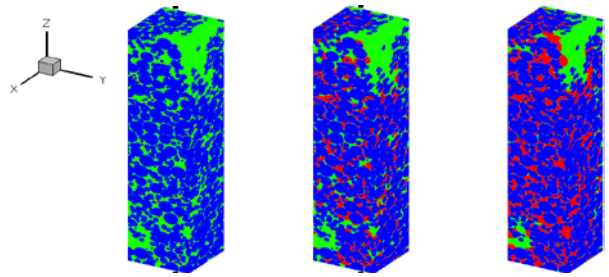


Water Containing Microstructural Domains

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



Dissolved Oxygen Concentrations for η=-0.6V



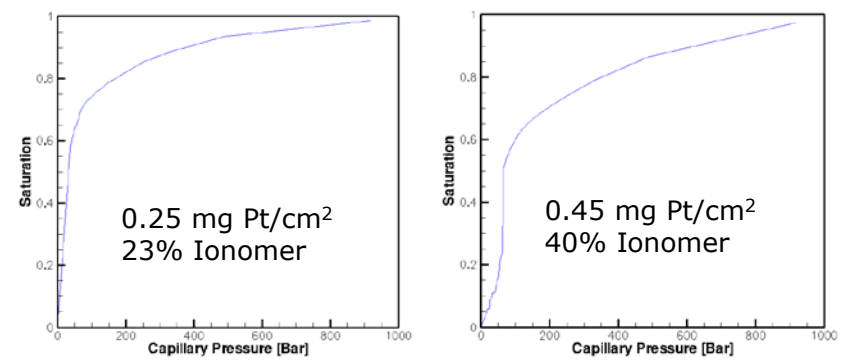
Progression of capillary water accumulation during ORR

Blue: solid phases

Green: open pores

Red: water

Capillary Pressure Catalyst Layer Simulations



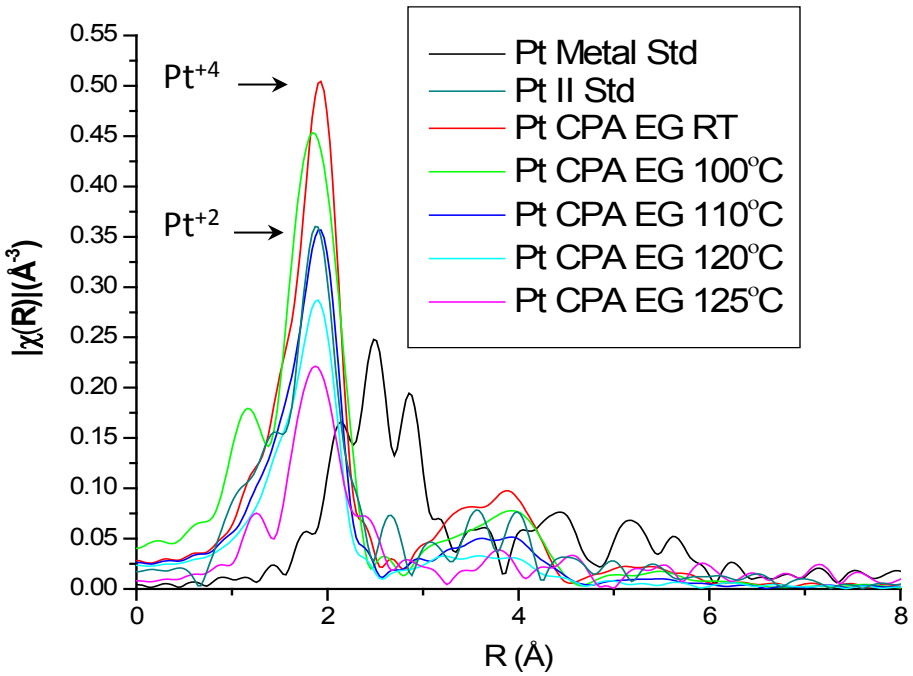
- **Future**: 1) Transient simulations.

2) Tackle transport of water (extremely computationally intensive)

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

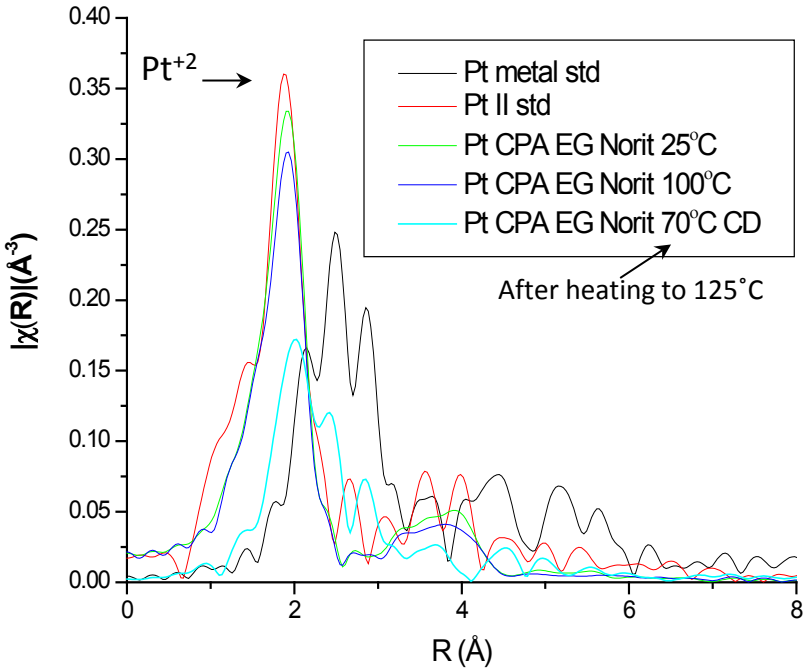
In-situ EXAFS of the Polyol Catalyzation Process

- **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

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

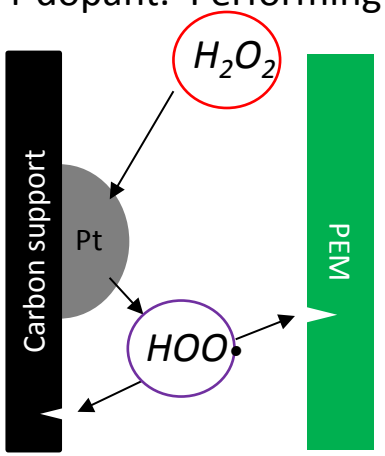


CPA and Norit Carbon in EG, no caustic

- 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

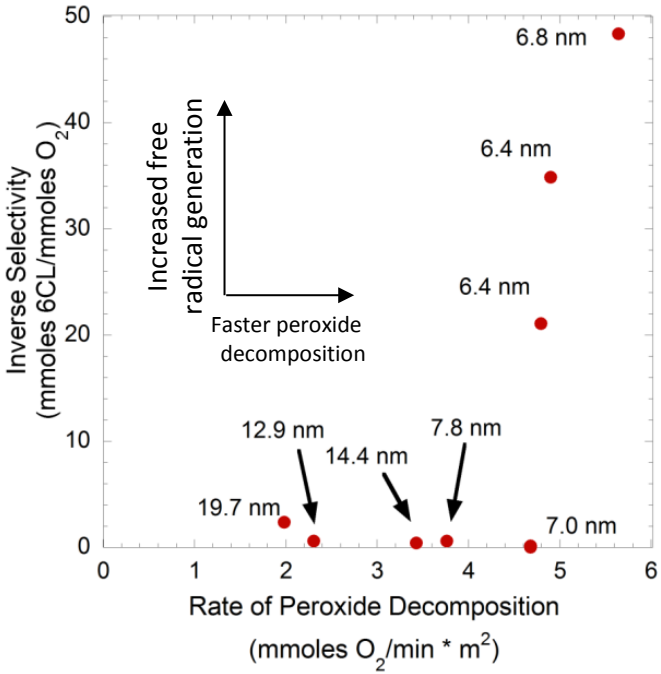
$$Ce^{+4} + H_2O_2 \longrightarrow Ce^{+3} + HOO\bullet + H^+$$

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

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

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

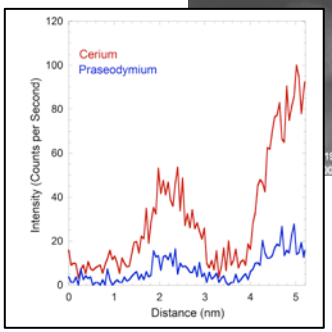


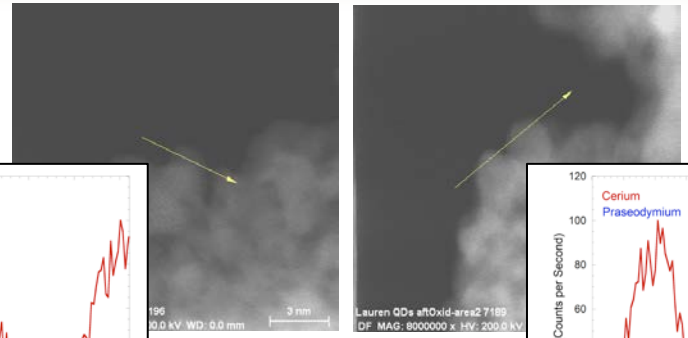
Curve derived from separately measuring the rates of peroxide decomposition and free radical formation (followed spectroscopically using 6-carboxyfluorescein) for different particle sizes of ceria

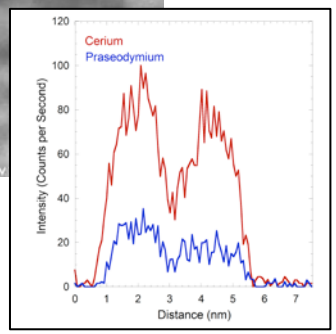
- Cerium cations are currently used to stabilize PEMs
  - Easily leached from the membranes
- Ceria nanoparticles offer a relatively acid stable peroxide decomposition catalyst
- However, free radical formation is also destructive
  - Characterized relative decomposition/formation rates (right)
- The 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

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



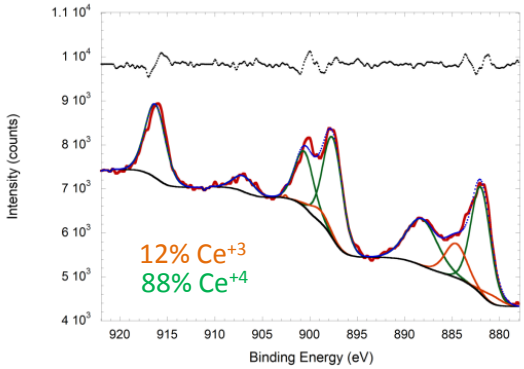


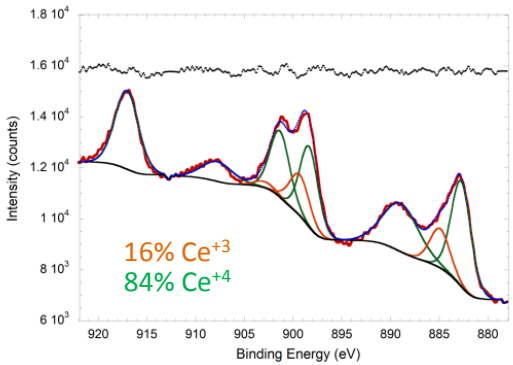


A "flat" composition profile in an EDX line scan suggests surface enrichment

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



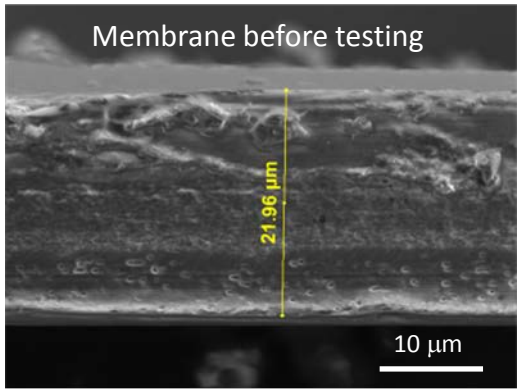


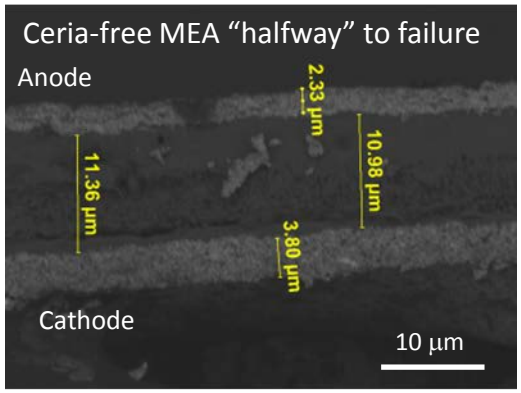
Ce 3d XPS of 15:85 Pr:Ce 5.00 nm particle by solution-precipitation

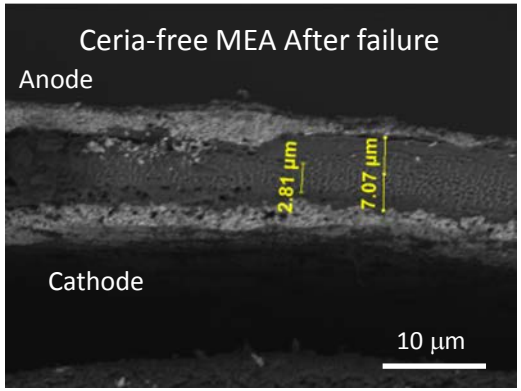
Ce 3d XPS of 15:85 Pr:Ce 5.00 nm particle by ion-exchange resin

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

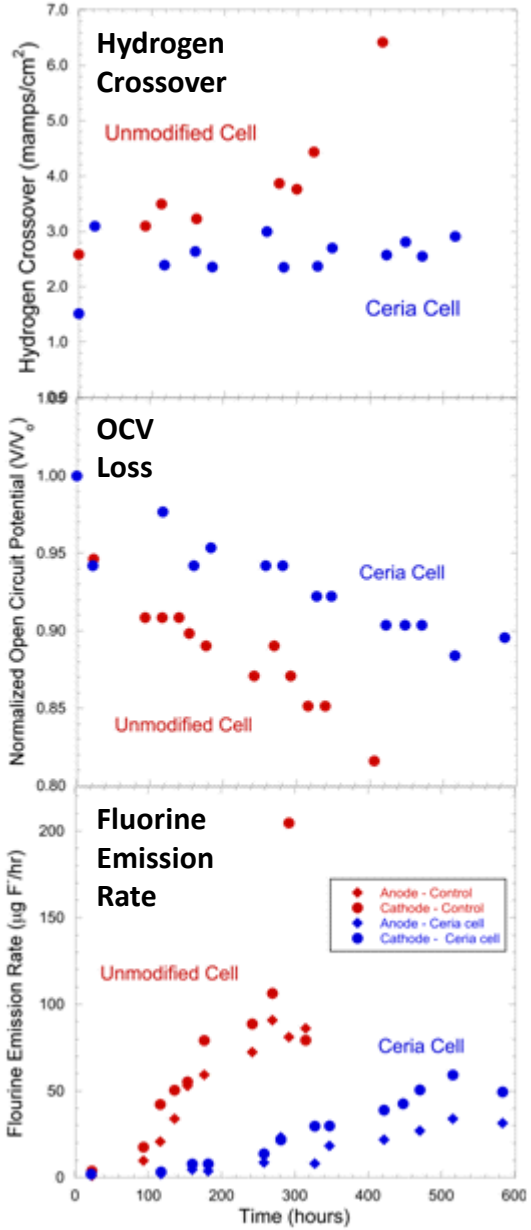
OCV testing with ceria additives



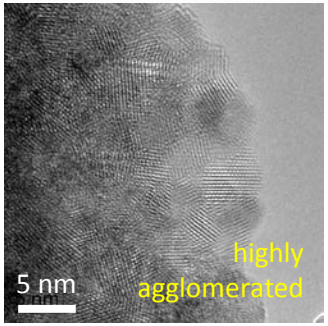




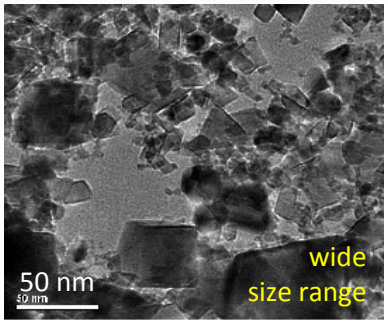
- Results shown for one run (of 4) for each ceria particle size
  - Particle size selective for radical scavenging
- 1.5 wt% ceria in catalyst layer
- Compared to control cells (i.e., ceria-free)
- Tests:
  - Fluorine emission rate (FER)
  - Hydrogen Crossover
  - Open circuit potential (OCV)
  - High 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



Characterizing ceria additives for ASTs

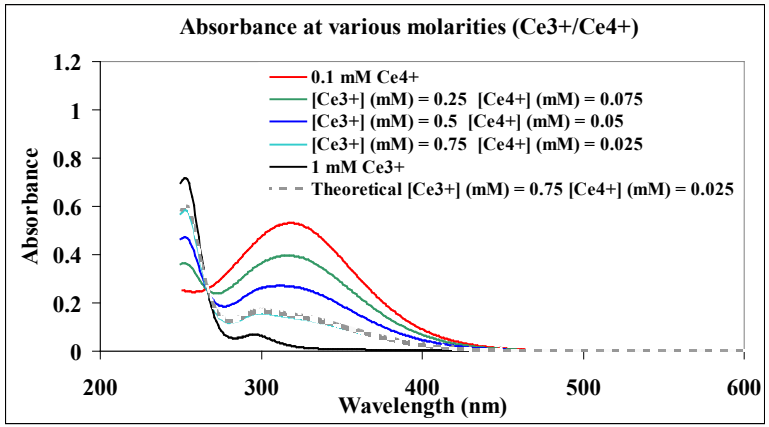


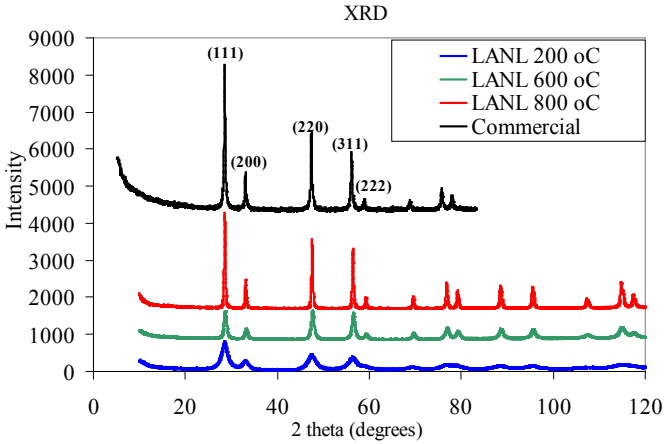
LANL 200˚ ceria



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





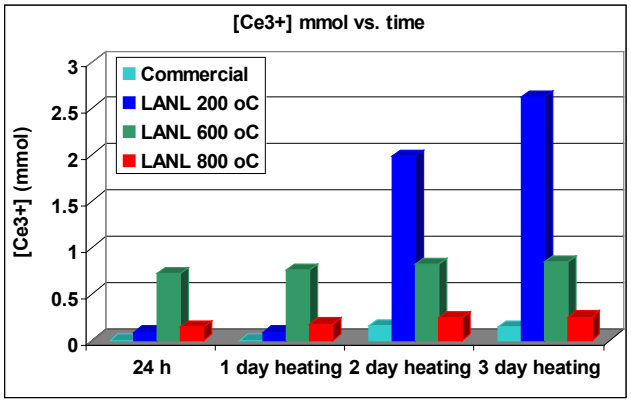
Sample [a]	Cryst. Dia.[b] (nm)	Surf. Area[c] (m^2/g)	Ce^{+3}:Ce^{+4} Surf. Ratio [d]
LANL 200˚	5.6	98	26:74
LANL 250˚	6.4	-	23:77
LANL 300˚	6.8	-	26:74
LANL 400˚	7.0	-	25:75
LANL 600˚	12.9	30	23:77
LANL 800˚	25	9	-
Comm.	31	56	-

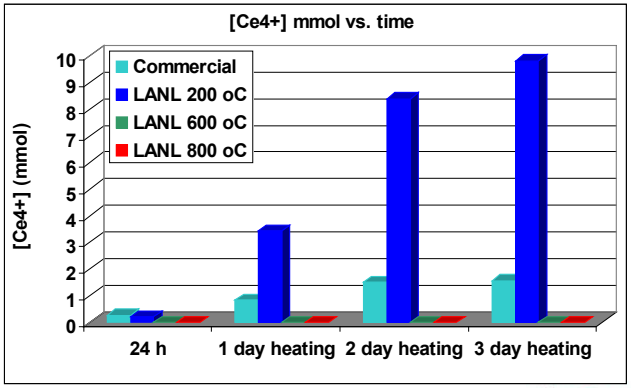
[a] Calcination temp (˚C), [b] XRD, [c] BET, [d] XPS.

- 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>

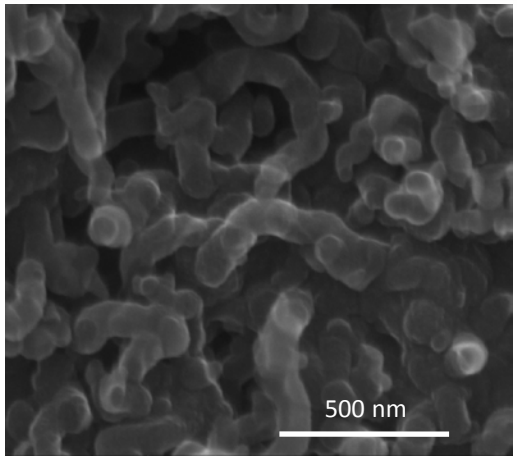
  - 600˚, 800˚Ce^{+4} v. stable
  - Enhanced Ce^{+3} stability in Comm. ceria





PPy nanowire supports

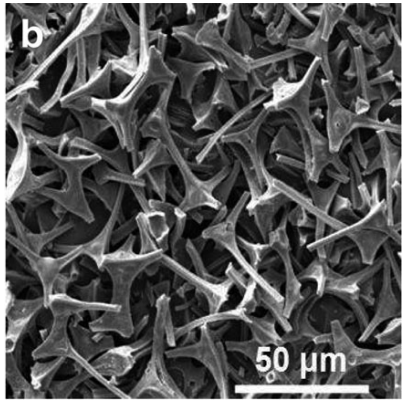
- **Previous Effort**
  - Process
    - Electropolymerize PPy nanowires onto a substrate
    - Pyrolyze
    - Platinize: sputter or impregnate
    - Hot press to membrane
  - Issues:
    - Achieving high Pt dispersions
    - Poor MEA performance (esp. Pt utilization & flooding)



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

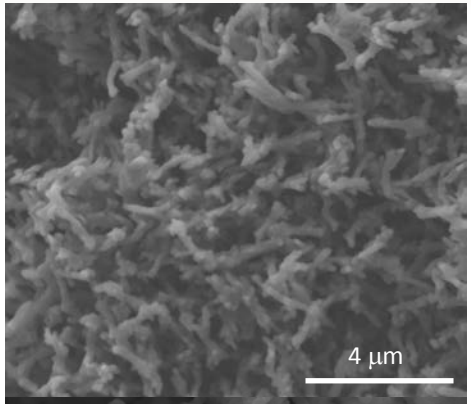
- Advantageous geometry of nanowire network supports
  - Tortuous branched networks maintain open pores but minimal "voids"
    - More free volume available for ionic and mass transport
    - Facilitates ionomer access and dispersion during fabrication
  - Enhances electronic conductivity (including "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

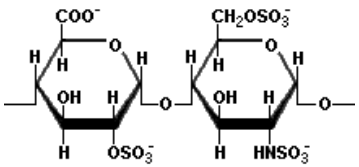


"Tetrapod" Catalyst Structure

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

PPy nanostructures w/ various templates

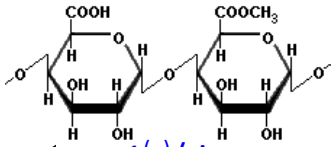




$2^{(-)}$/ring

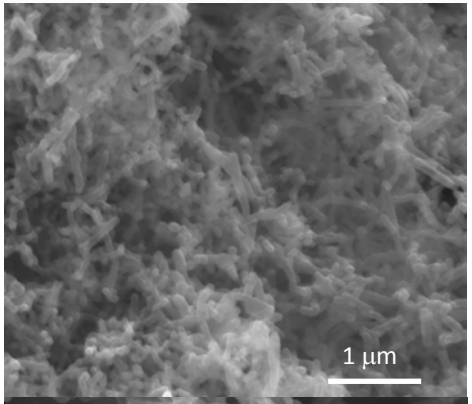
Heparin

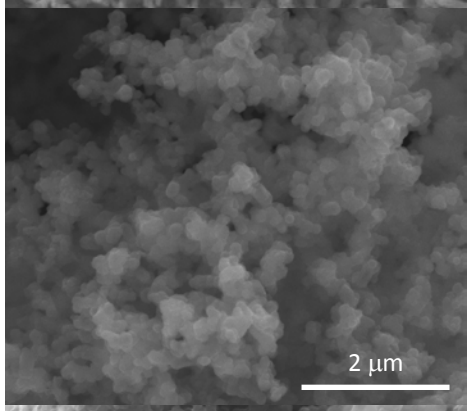
Pectin
(low methoxyl,
+ maltodextrin)

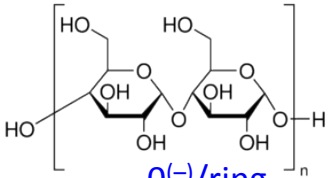


$<1^{(-)}$/ring

50% methoxylated
(0% is polygalacturonic acid)

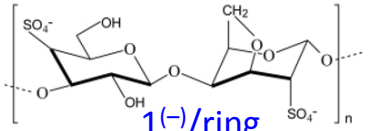






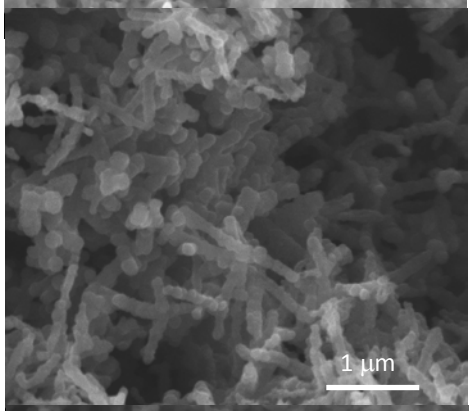
$0^{(-)}$/ring

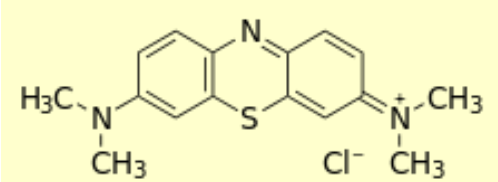
Starch



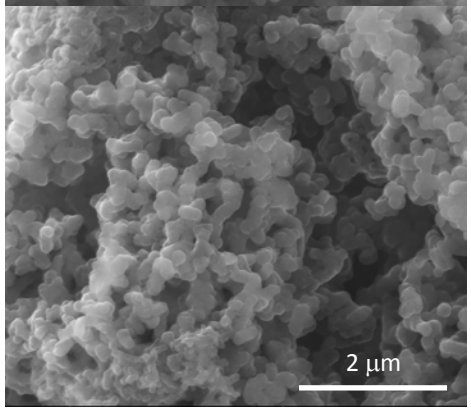
$1^{(-)}$/ring

ι-Carrageenan
(food grade)

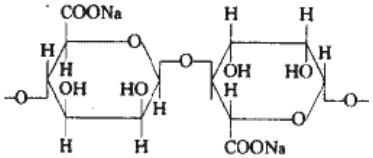




Methylene Blue

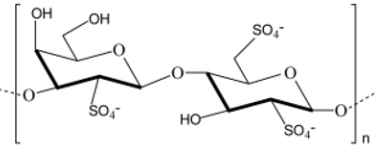


Na⁺ Alginate
(food grade)

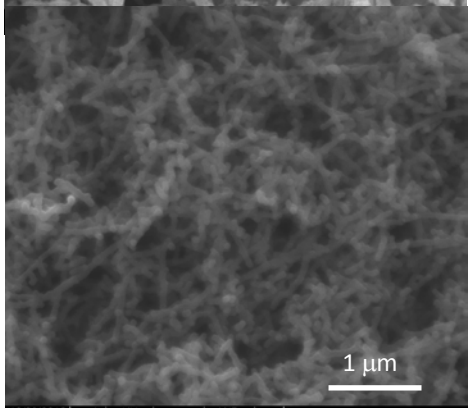


$1^{(-)}$/ring

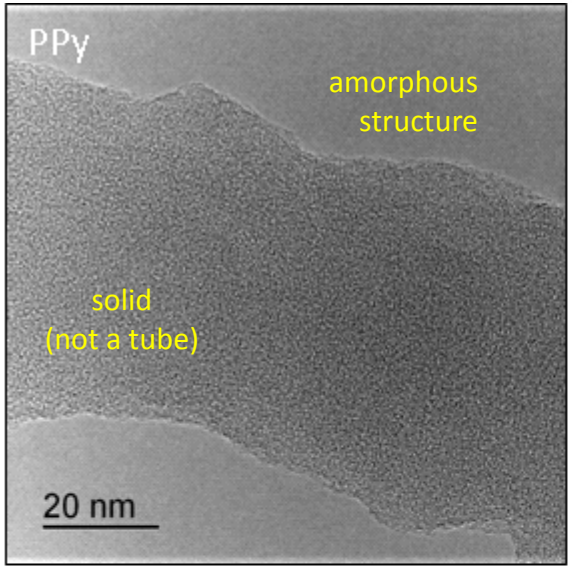
λ-Carrageenan
(food grade)



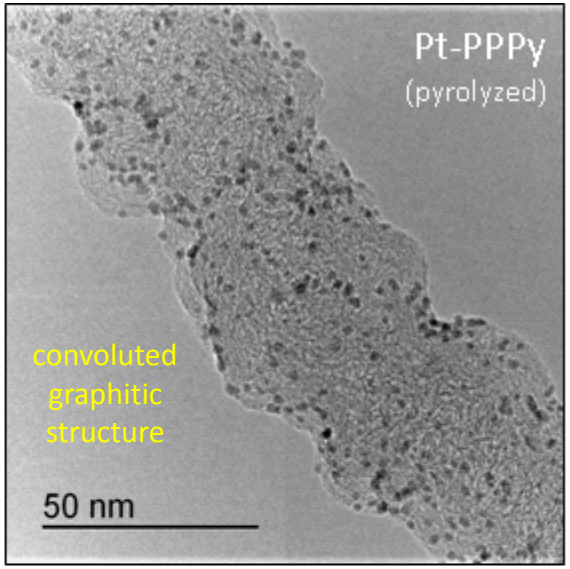
$1.5^{(-)}$/ring

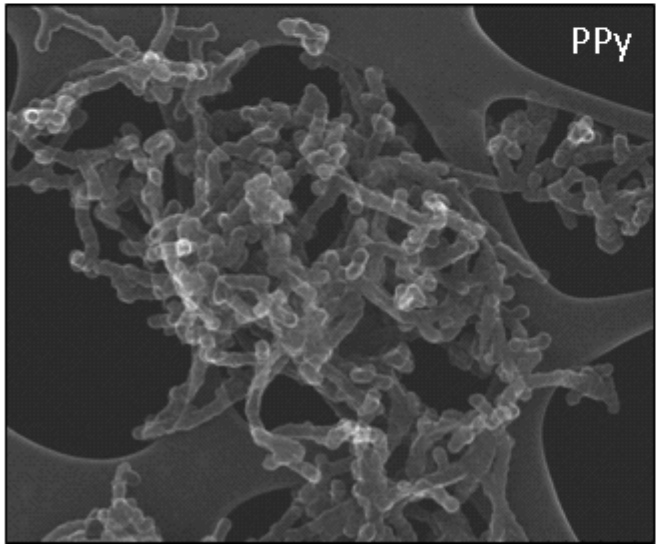


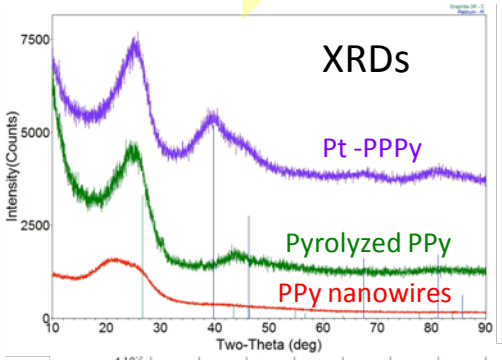
PPy to Pt-PPPy nanowire catalysts

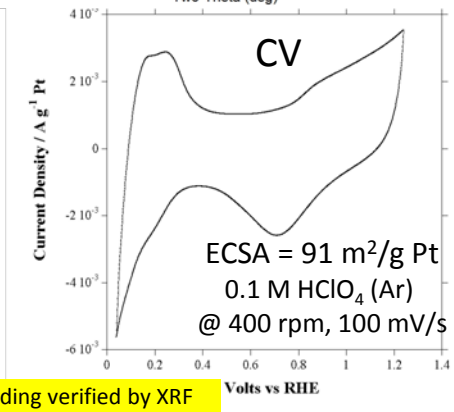


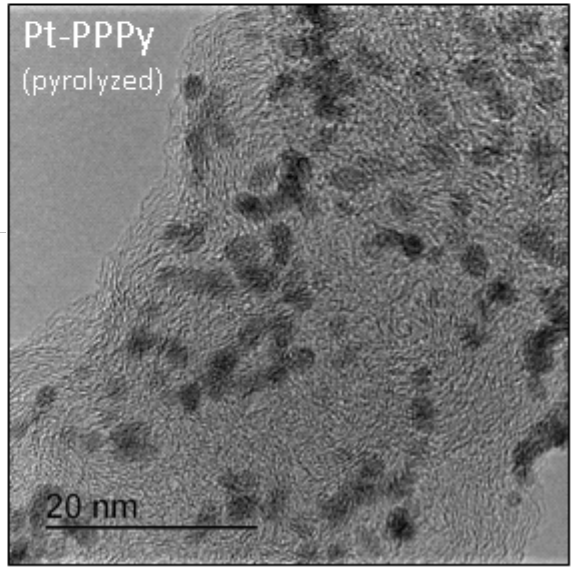
- **Pyrolysis**: 1000˚C, 1h
  - ~ 50% wt loss
  - ~ 10% N content
  - Highly graphitic structure
  - No sulfur detected
- **Platinization:** polyol process
  - Uniformly distributed, due to convoluted surface + N?
  - 13.5 wt% Pt: surface loading
    - ~ 3x 20%Pt/C
  - 2.2 nm particles (TEM)





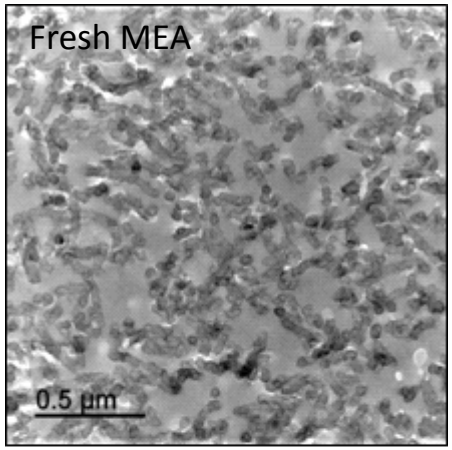




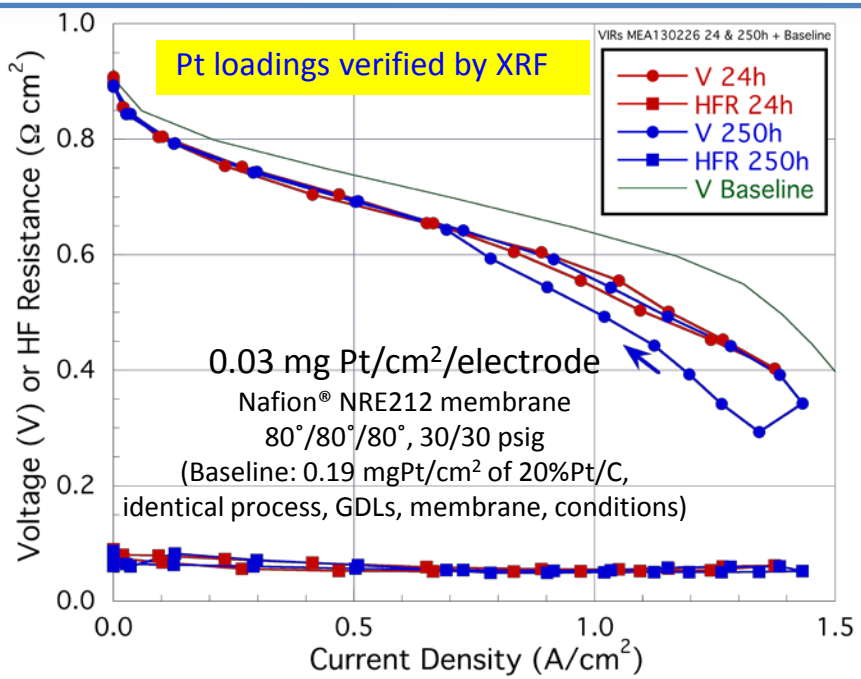


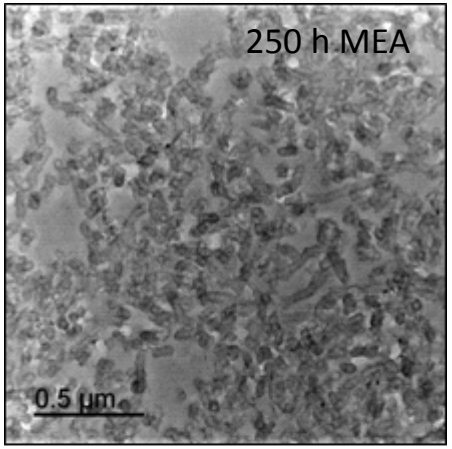
Pt loading verified by XRF

Low-PGM FC performance w/ Pt-PPPy nanowires

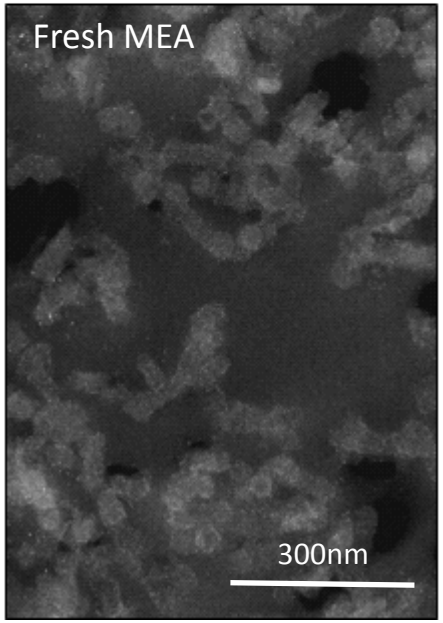


HRTEM Cross-Sections

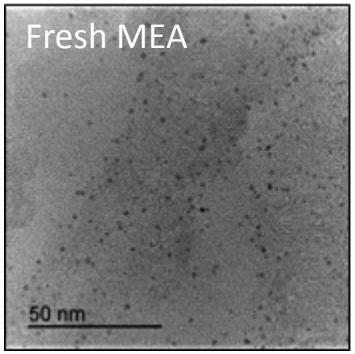


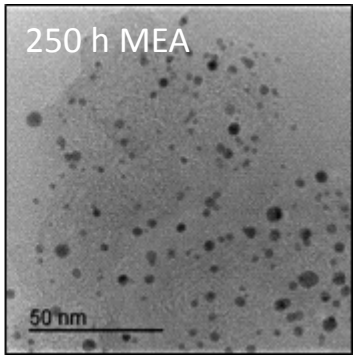


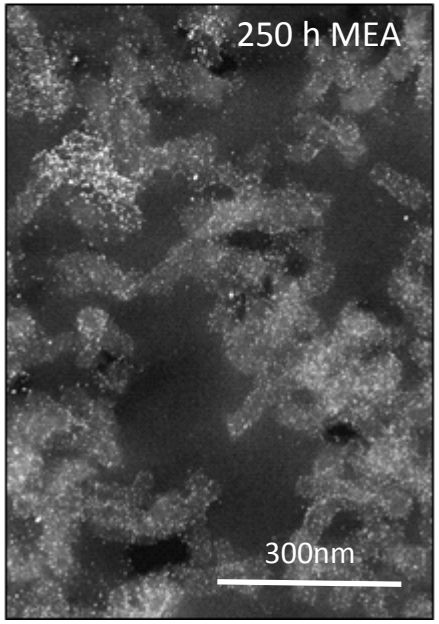
HRTEM Cross-Sections



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







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

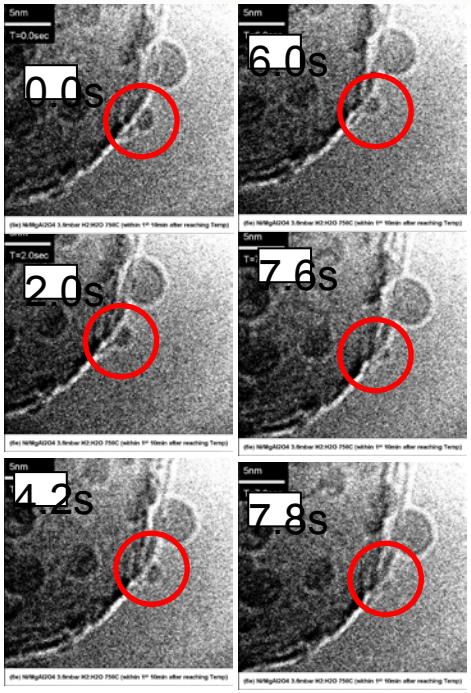
Modeling Details

- 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)

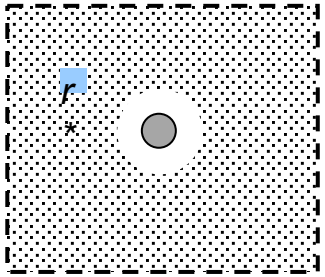
[1] *Choi et al*. ImechE PartA: Journal of Power and Energy, **225**: 183-197 (2011).
[2] *OpenFOAM*: a free, open source CFD software package available at www.openfoam.com.

Modeling of catalyst ripening



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

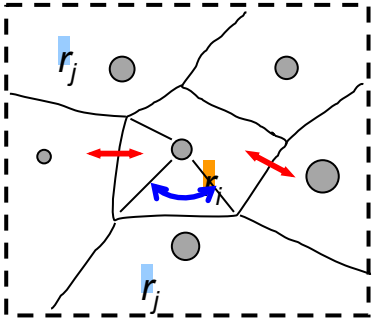
Mean-Field Model



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

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

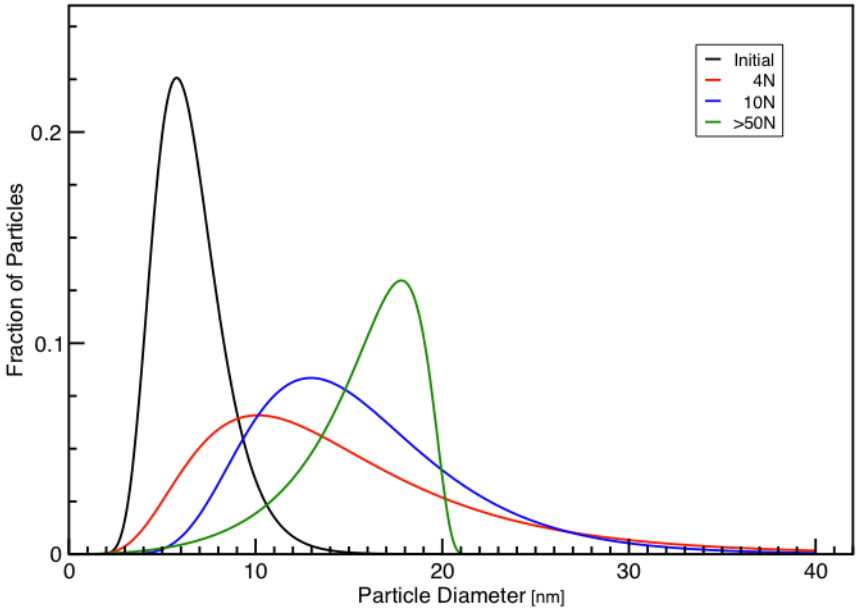
Ripening rate now dictated by local conditions.

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

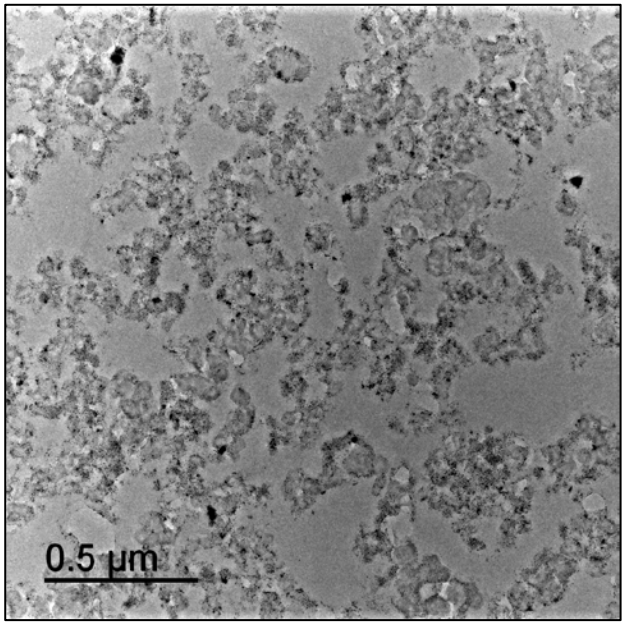
Number of neighbors of a particle steadily decreases until *j*=0 and the size becomes stagnant for **that** particle.

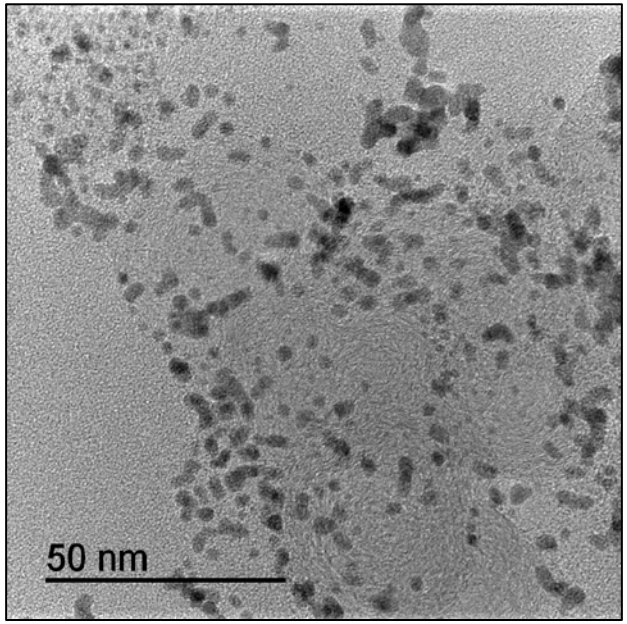
Future: Full model development and analysis

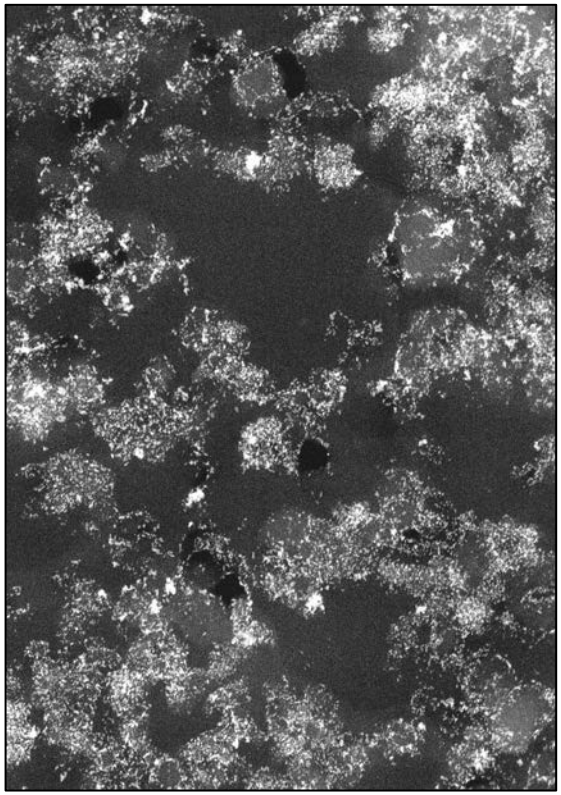
Tie DFT into surface tension calculation



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