

The Science And Engineering of Durable Ultralow PGM Catalysts

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FC010

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Overview

Timeline

- Project start date: 10/ 2009
- Project end date: 10/2013
- Percent complete: **40%**

Precious metal loading:	~0.2 mg/cm ² (2015 target)
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Cost:	< 3\$/kW (2015 target)
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Activity (precious-metal based catalyst):	0.44 A/mgPt @ 0.90 V
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Surface area activity:	720 μ A/cm ² @ 0.90 V
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Electrocatalysis support loss:	<30 mV after 100 hrs @1.2V
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Electrochemical surface area (ESA) loss:	<40% (after cycling protocol)
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Budget

- Total project funding
 - DOE share: \$6M
 - Contractor share: \$529K
 - Funding received in FY10: \$1.5M
 - Funding for FY11: \$1.5M

Barriers

- **COST:** High performance catalysts enabling ultralow precious metal loadings are required to reduce cost
- **PERFORMANCE:** Voltage losses at the cathode are too high to meet efficiency targets. Loss of electrochemical surface area can occur as a result of catalyst migration and agglomeration

Partners

- Ballard Fuel Cells, UNM, UCR
- 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)
- Experimental Synthesis And Characterization Of New Geometry PGM Catalysts
 - Synthesis of Novel Pt Nanoparticles (UCR, UNM, LANL)
 - Synthesis of Pt Nanowires (UCR, UNM, LANL)
- PGM Structural Characterization by TEM, XRD, Neutron Scattering
 - HRTEM Morphology Studies (ORNL) (UNM)
 - Advanced X-ray Diffraction Studies (LANL)
 - Neutron Scattering Studies (LANL)
 - Thermal and Thermodynamic Characterization of PGM catalysts (UNM, LANL)
 - Electrochemical Characterization of PGM catalysts (LANL, UCR)
- Understanding Catalyst Nucleation And Support Interactions
 - Inverse Chromatography Studies Of Precursor-Support Interactions (LANL, UNM)
 - PGM-Support Interaction Studies (UNM)
- Fuel Cell Testing Of Novel PGM Catalysts (LANL, Ballard)
 - Testing of novel catalysts in fuel cells (LANL, Ballard)
 - Fuel cell post testing materials characterization (LANL, ORNL)

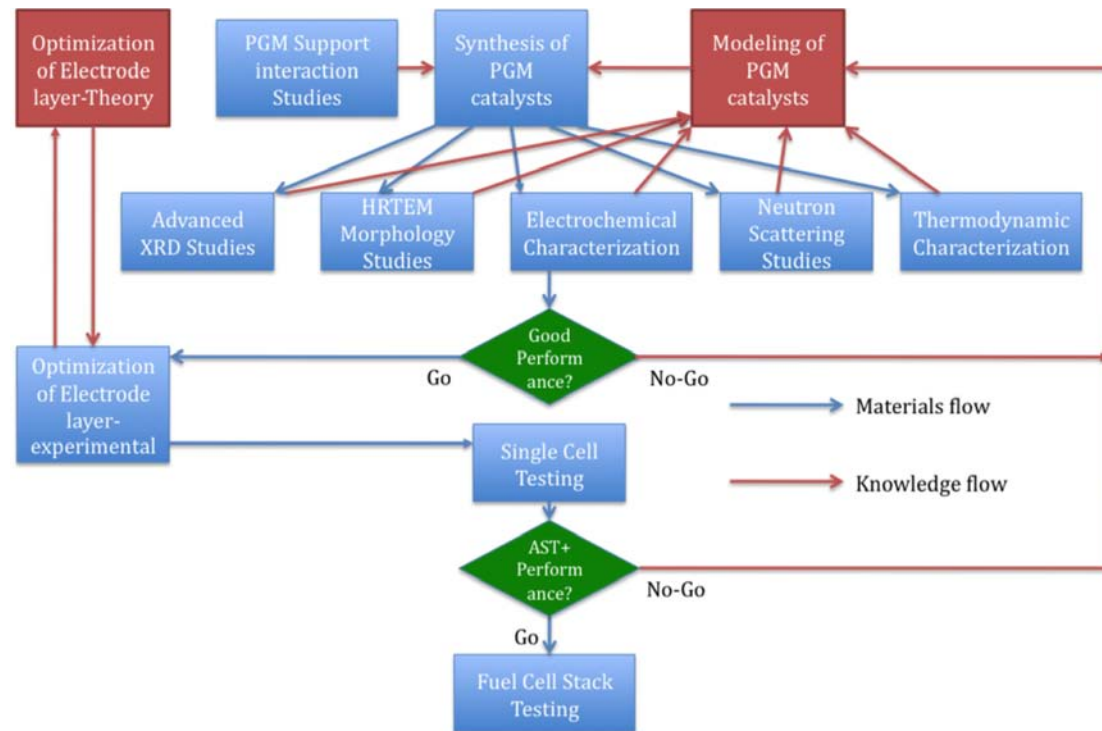


- | • LANL | • UNM | • ORNL | • BALLARD | • UCR |
|---------------------|-----------------------|---------------|----------------|--------------------|
| – Fernando Garzon | – Prof. Abhaya Datye | – Karren More | – Siyu Ye | – Prof. Yushan Yan |
| – JoseMari Saniñena | – Elena Berliba-Vera | – Kelly Perry | – David Harvey | |
| – Mahlon Wilson | – Andrew DelaRiva | | | |
| – Jerzy Chlistunoff | – Sivakumar R. Challa | | | |
| – Neil Henson | | | | |
| – Ivana Matanovic | | | | |

Project Objectives – Relevance- *Work completed*

- Development of durable, high mass activity Platinum Group Metal cathode catalysts -enabling lower cost fuel cells-*Synthesis and characterization of three new families of Low PGM catalysts [LANL](#) [UCR](#) [ORNL](#)*
- Elucidation of the fundamental relationships between PGM catalyst shape, particle size and activity-will help design better catalysts-*New state of the art DFT models for novel nanoparticle shapes [LANL](#). Pt nucleation and dispersion on carbon study completed [UNM](#)*
- Optimization of the cathode electrode layer to maximize the performance of PGM catalysts- improving fuel cell performance and lowering cost-*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 [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. *Single Cell Fuel Cell Testing [LANL](#)*
- IMPACT: [This project will help lower the cost and the precious metal loading of PEM fuel cells and improve catalyst durability](#)

- Use contemporary theoretical modeling and advanced computational methods to understand and engineer the 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



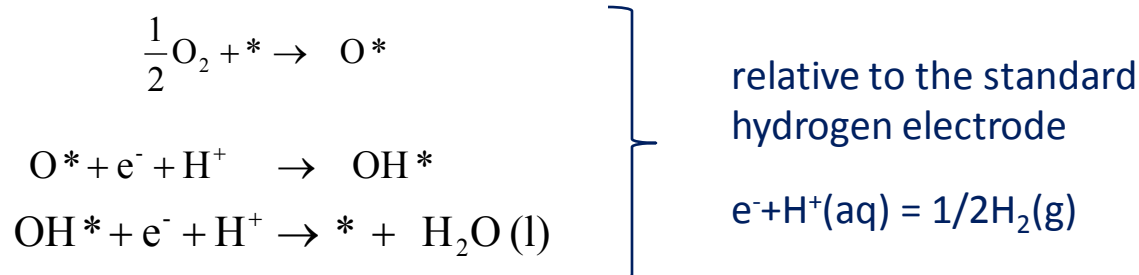
Milestones

- Synthesis of high activity catalysts
 - Pt Pd Nanoplates *completed Q2*
 - Pt ceria carbons *completed Q2*
 - Pt Polypyrrole Nanowires *completed Q1*
- Electrochemical characterization of high activity catalysts
 - Pt Pd Nanoplates *completed Q3*
 - Pt ceria carbons *completed Q3*
 - Pt Polypyrrole Nanowires *completed Q2*
- XRD characterization (Whole Profile Fitting) of new catalysts
 - Analysis of Pt/ceria/C catalysts *completed Q2*
- TEM of New Catalysts
 - HRTEM, STEM and SEM-EDS imaging of Pt-Ceria catalysts *completed Q3*
- Thermal characterization
 - TGA studies of Pt/ceria/C catalysts *completed Q2*
- DFT modeling of Novel Pt shapes
 - Electrochemical Reactions incorporated into model *completed Q1*
 - Pt Ni catalyst study completed *completed Q2*
 - Stability calculations of nanotubes *completed Q3*
- Pt Particle Ripening Modeling
 - Modified Bond Additivity Model *completed Q2*
 - Monte Carlo particle growth model *completed Q1*
- Nucleation of Pt on supports study
 - Pt particle density study on multiple carbon supports completed *completed Q2*
- Microstructure Model Development
 - Cathode Layer Microstructural Model developed *completed Q1*

DFT Model – Study of ORR Mechanism VASP

PtNi alloys experimentally show better ORR than Pt- R. Stamenkovic et al. Science,315,493 (2007)

Reactions connecting different states of the metal surface in the ORR mechanism

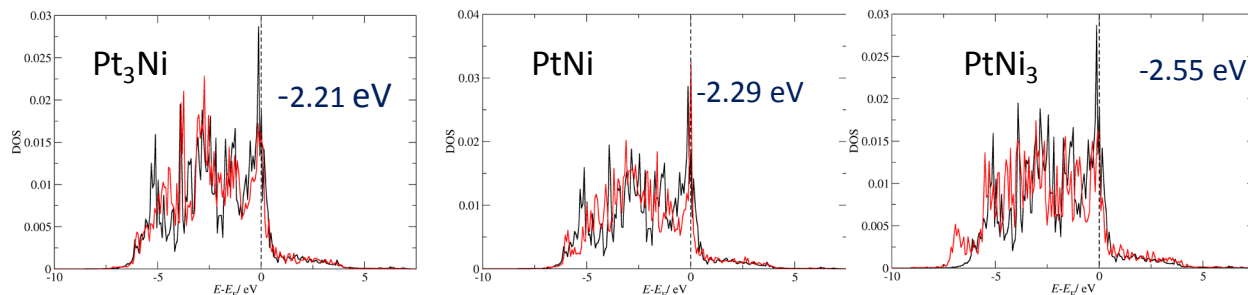


Gibbs free energy of the reactions (Norskov et al. J. Phys. Chem. B 2006, 110, 21833)

$$\Delta G_{\text{w,water}} = \Delta E_{\text{w,water}} + \Delta \text{ZPE} + T\Delta S$$

$$\Delta G_{298} = \Delta G_{\text{w,water}} - eU + kT \ln(10) \text{pH}$$

- Calculate d-band center for: Pt(-1.97 eV), Pt₃Ni, PtNi, PtNi₃
- Pt surface atoms only, no Ni in top layer
- Shift corresponds to weakening of oxygen binding

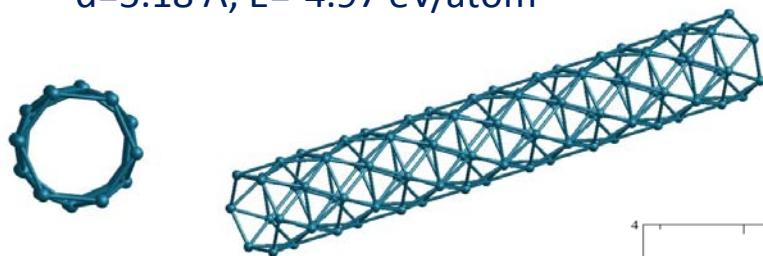


	OH* + e ⁻ + H ⁺	O* + 2(e ⁻ + H ⁺)	H* - e ⁻ + H ⁺
Pt(111)			
$\Delta E_{\text{w,water}}$	0.45 eV	1.43 eV	-0.38 eV
$\Delta G_{\text{w,water}}$	0.80 eV	1.48 eV	-0.14 eV
U_f	0.8 V	0.74 V	0.14 V
Pt₃Ni(111)seg			
$\Delta E_{\text{w,water}}$	0.74 eV	2.04 eV	-0.16 eV
$\Delta G_{\text{w,water}}$	1.09 eV	2.09 eV	0.08 eV
U_f	1.1 V	1.40 V	-0.08 V
PtNi(111)seg			
$\Delta E_{\text{w,water}}$	0.97 eV	2.34 eV	-0.01 eV
$\Delta G_{\text{w,water}}$	1.32 eV	2.39 eV	0.23 eV
U_f	1.32 V	1.20 V	-0.23 V
PtNi₃(111) seg			
$\Delta E_{\text{w,water}}$	1.05 eV	2.43 eV	0.10 eV
$\Delta G_{\text{w,water}}$	1.40 eV	2.48 eV	0.34 eV
U_f	1.4 V	1.24 V	-0.34 V

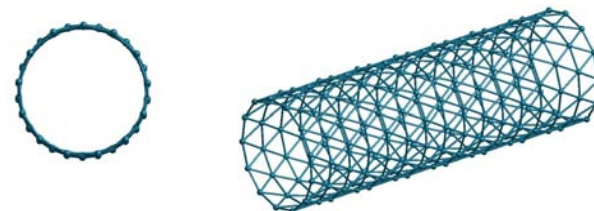
Theoretical Modeling of Novel Pt Shapes- Nanotubes

- DFT calculations of stability of Pt structures:

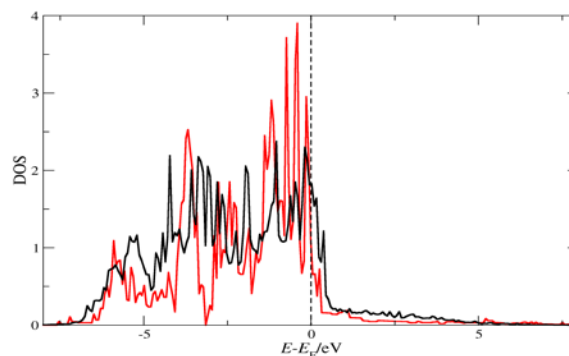
(6,6) Pt SWNT,
d=5.18 Å, E=-4.97 eV/atom



(13,13) Pt SWNT,
d=10.83 Å, E=-5.15 eV/atom



Density of states – black: Pt(111) surface and red achiral(6,6) tube



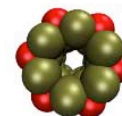
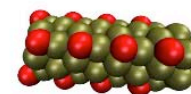
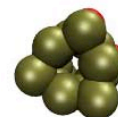
- DFT modeling show smaller Pt nanotubes are stable only for larger coverage and symmetric structures
- (6,6) Pt nanotube binds O more strongly than Pt(111)
- (13,13) Pt nanotube binds O similar or slightly weaker than Pt(111)

adsorption energies in eV of atomic oxygen for fcc site

	Pt(111)	(6,6) SWNT	(13,13) SWNT
1/4	-4.42	-4.72	-4.57
1/3	-4.25	-4.44	-4.11
1/2	-4.07	-4.24	-4.06
2/3	-3.79	-4.28	

(6,6) Pt SWNT

(13,13) Pt SWNT



Modeling of Particle Ripening

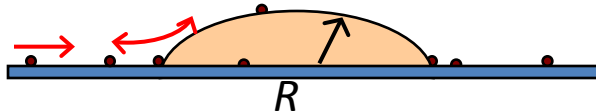
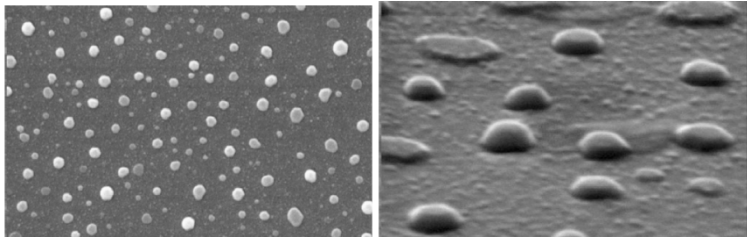
Critical Assumption – How Does Surface Energy Vary With Particle Diameter?

Two models – Gibbs Thompson (GT) also known as the Kelvin equation & Modified Bond Additivity (MBA)

Modeling Change of Particle Size

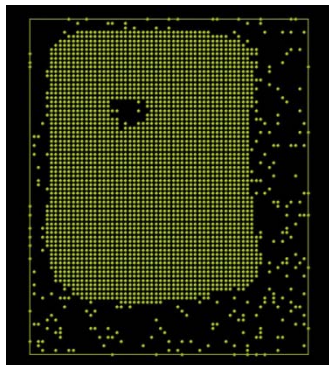
$$\frac{dR}{dt} = K \exp\left(\frac{-E_{tot}}{kT}\right) \frac{1}{R} \left(\exp\left[\frac{2\gamma\Omega}{kTR^*}\right] - \exp\left[\frac{2\gamma\Omega}{kTR}\right] \right)$$

$$\frac{dr}{dt} = (K/r) \exp\left(\frac{-E_{tot}}{k_b T}\right) \left[\exp\left(\frac{\mu(r^*) - \mu(\infty)}{k_b T}\right) - \exp\left(\frac{\mu(r) - \mu(\infty)}{k_b T}\right) \right]$$



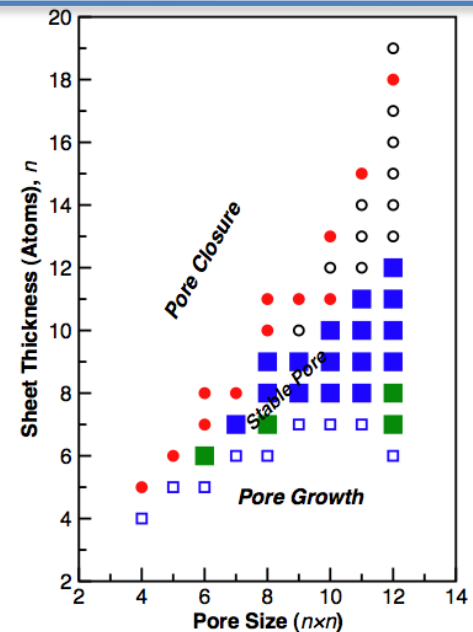
- Campbell model (below) predicts lower heats of adsorption for smaller particles than Gibbs Thompson (above)

Stability of a Pore in a Pt Nanosheet



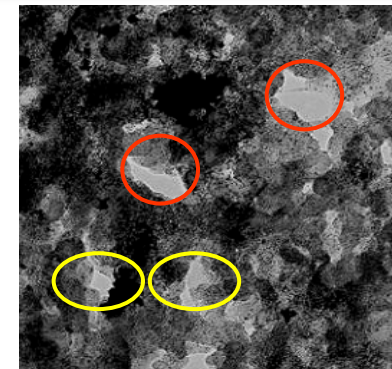
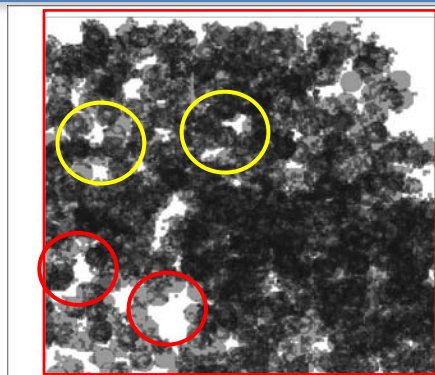
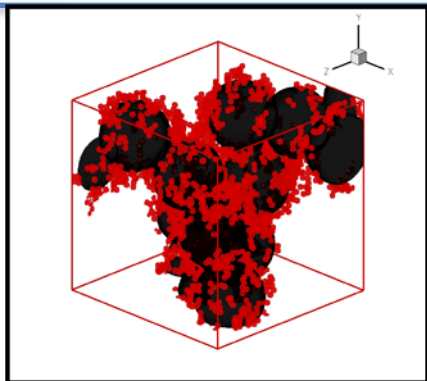
A region of sintering-resistant Nanostructures exists:

Monte Carlo computer simulation of pore stability



• Driving force for ripening can be reduced by having both negative curvature and positive curvature!

Microstructure Model of Cathode Catalyst Layer



- Percolation Fraction Increases with increasing Ionomer Content

- Percolating Fraction approaches 100% after 33 wt.%

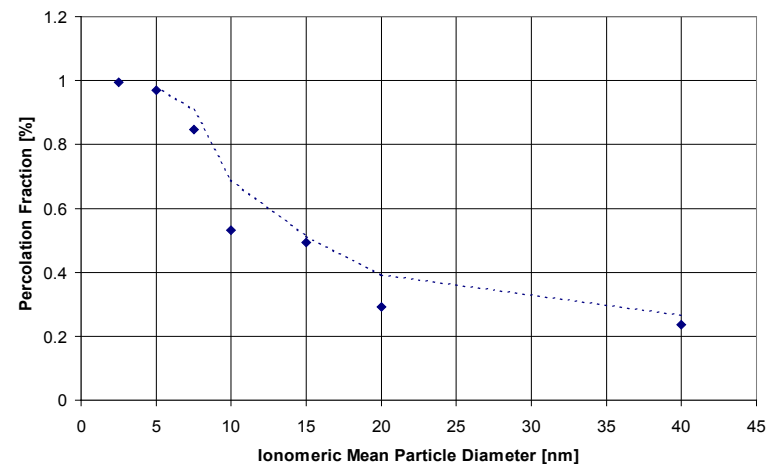
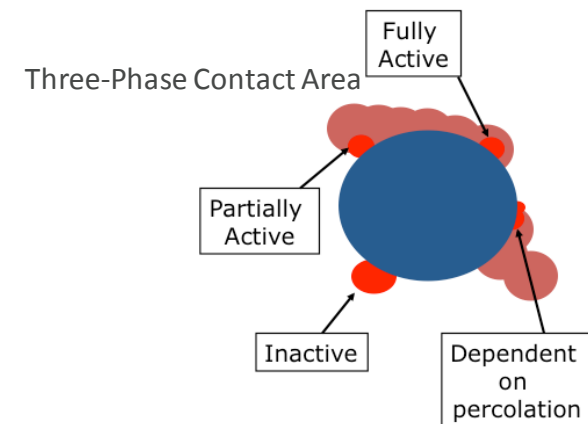
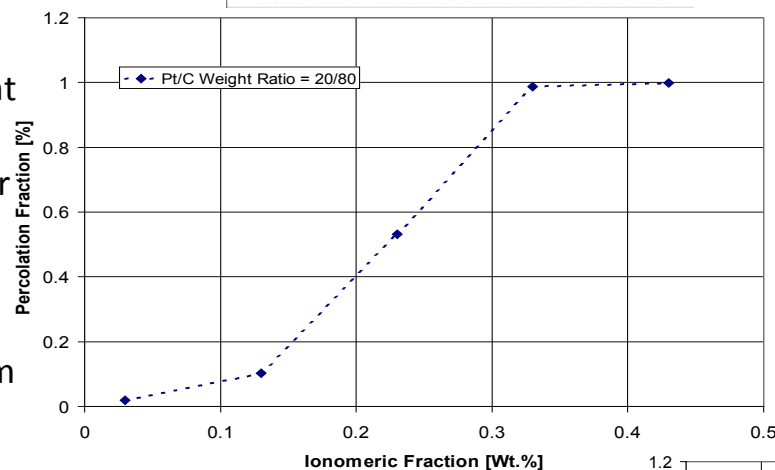
- Decreases with increasing Particle Size

- Fewer particles to form pathways

- Rapid increase with smaller particles

- Small reductions in particle size, yield large benefits

- Model can be used to optimize performance

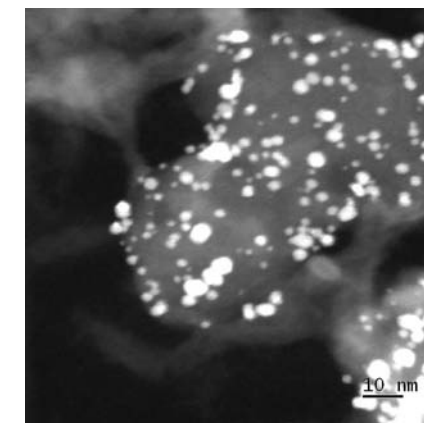
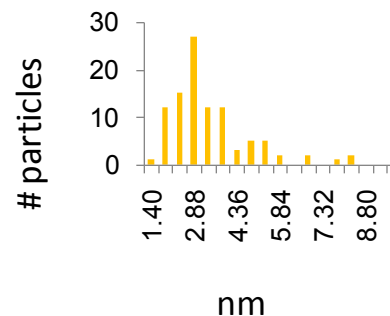
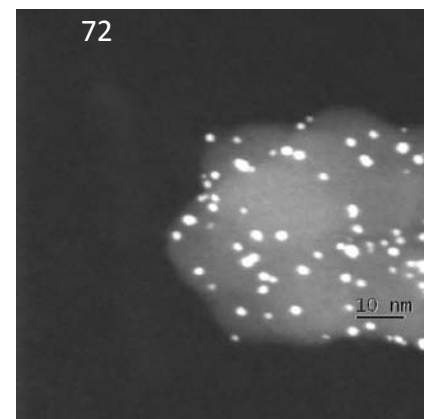
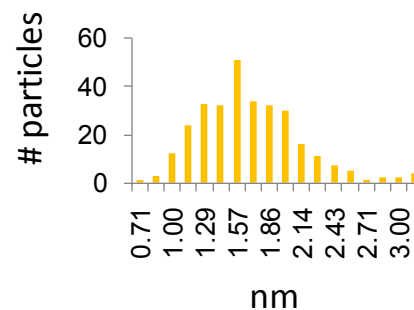
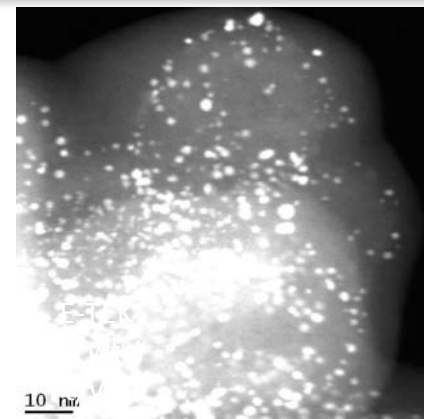
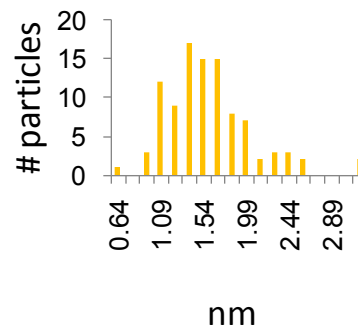


Pt Dispersion On Carbon Supports

• Modeling results show it would be desirable to increase the number of Pt particles per unit area of carbon surface, without increasing mean particle size

- decreases volume of catalyst phase, more space for ionomer and pore volume
- Particle size (\AA) increases with loading
- Number of Pt particles/area only changes by changing carbon

Catalyst	Number of particles/cm ² (10^{11})
E-TEK 5 wt% Pt/Vulcan XC-72R	1.042
E-TEK 20 wt% Pt/Vulcan XC-72R	0.838
E-TEK 30 wt% Pt/Vulcan XC-72R	0.748



Pt Dispersion and Pt Particle Surface Density

- Work agrees with limited earlier study: All furnace blacks (Vulcans, Cabot, Acetylene Blacks) fit on same dispersion curve:

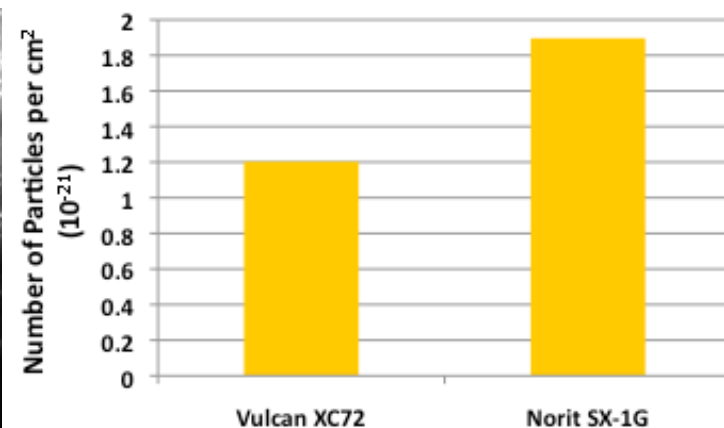
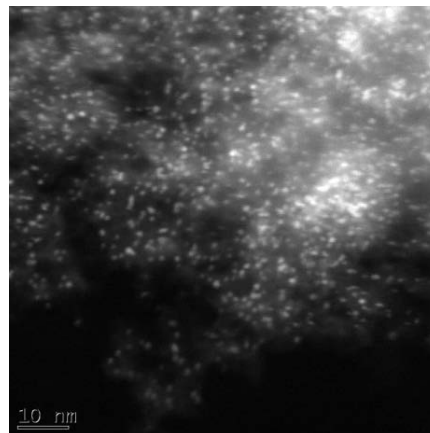
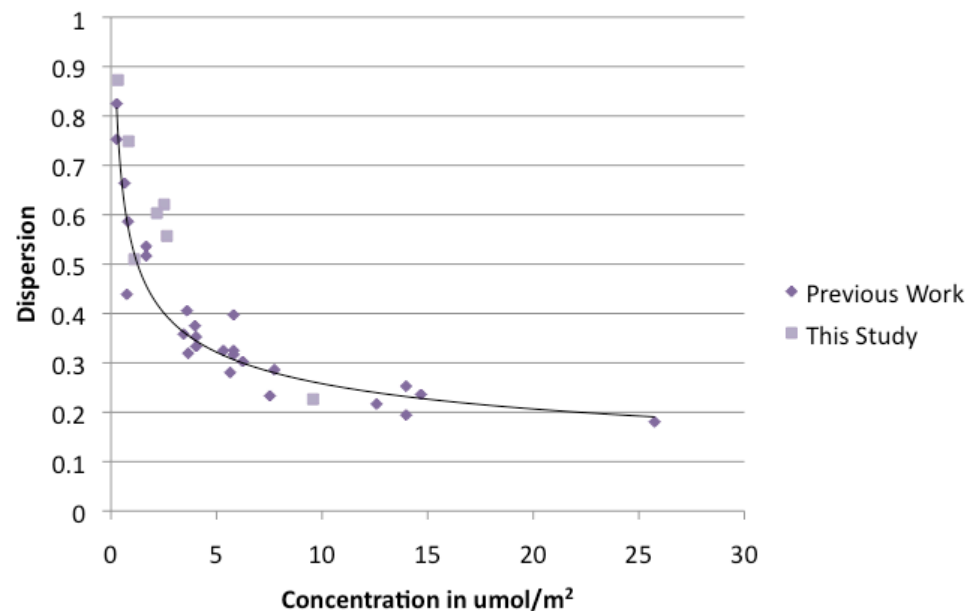
- Independent of furnace carbon type and surface area

- Nucleation site density is the same!

- Only Pt on Norit steam activated carbons show an increase in the number Pt particles/area

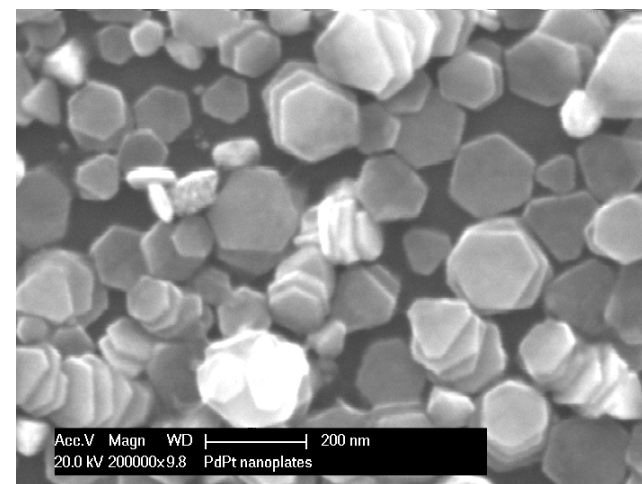
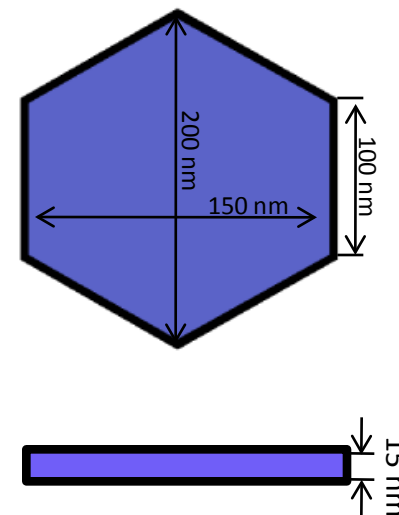
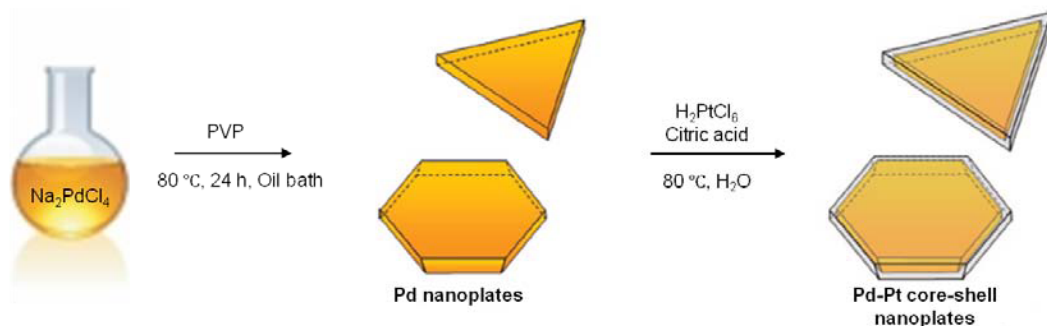
- These carbons oxidize very easily; poor corrosion resistance

- Need to increase nucleation site density on more corrosion resistant carbons



New Catalyst Development: Pt on Pd Nanoplates

- Pt on Pd has enhanced ORR properties as compared to Pt
- J. Zhang and R.R.Adzic, **Angew. Chem. Int. Ed.** 2005, 44, 2132-2135)
- Platelets give more surface area than spheres:



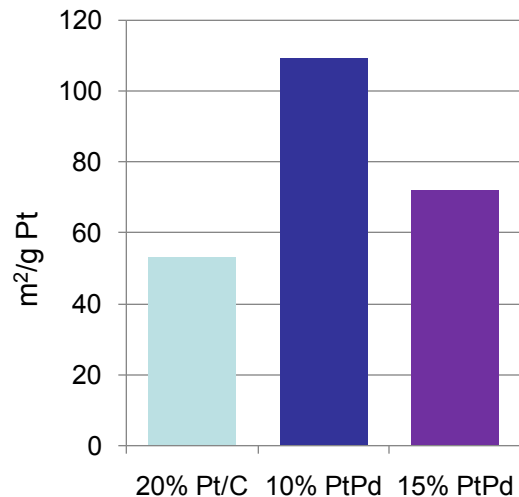
SEM image of Pt/Pd Nanoplates

Theoretical surface area:	13 m ² /g M
Pt content for 1 layer:	5.3%
Surface area of Pt:	245 m ² /g Pt

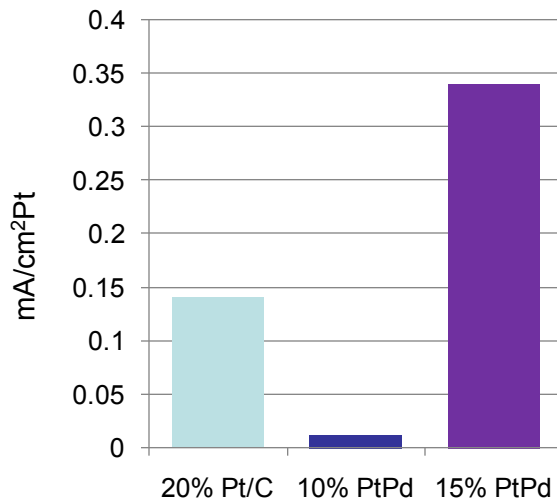
Samples with different Pt content:
2 layers 10.5% 3 layers 15.5%

Electrochemical Characterization of Pt/Pd Nanoplates

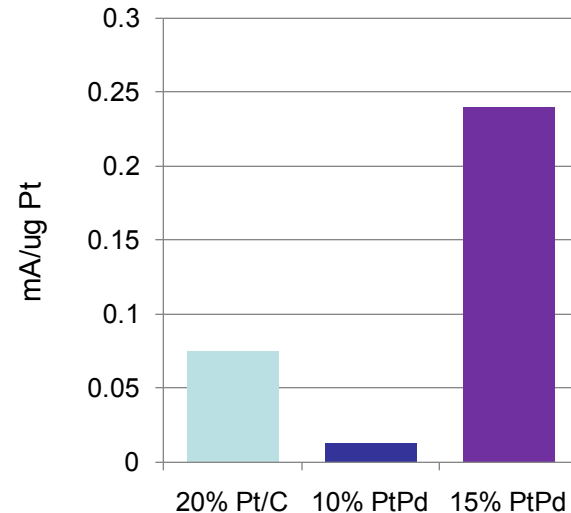
Surface area



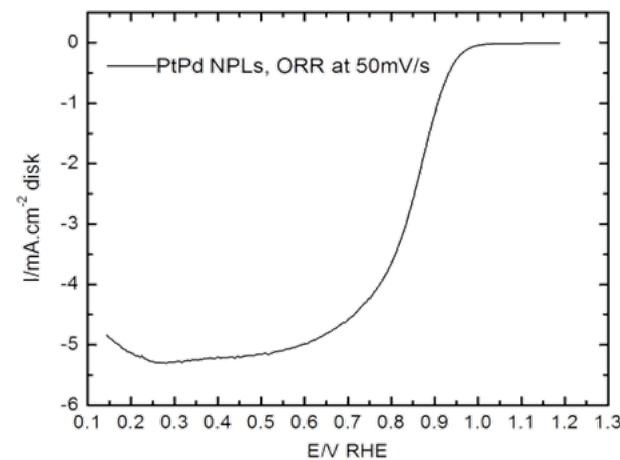
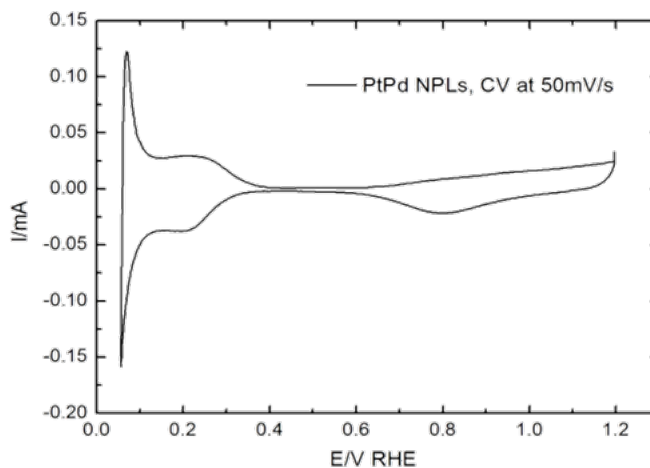
Specific activity



Mass activity

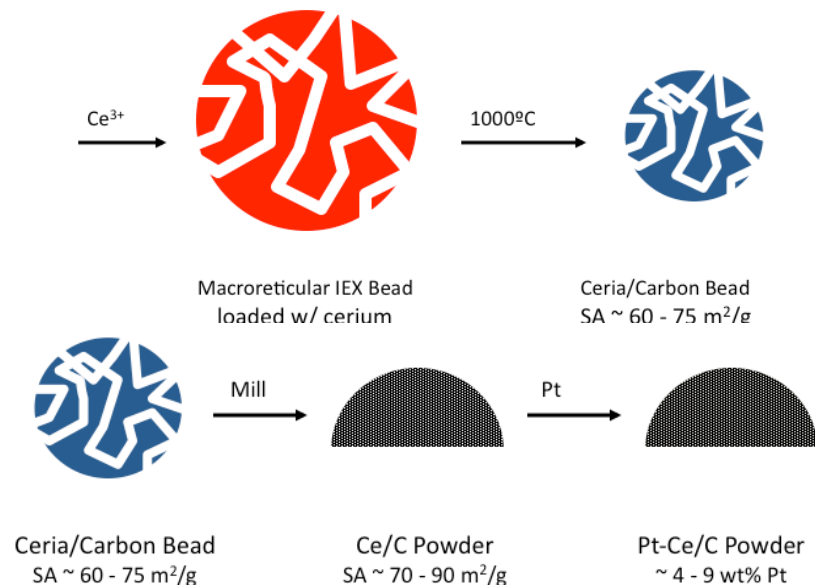
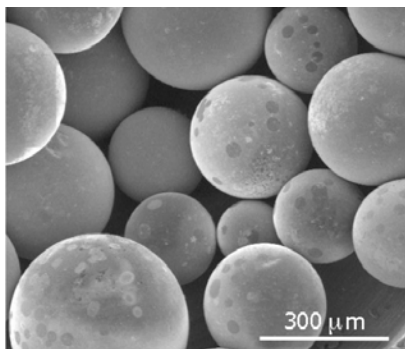


- Surface area for 15% PtPd is slightly higher than Pt/C, the activity is more than 2 times higher for both specific and mass activity
- Surface composition has a great effect on the activity



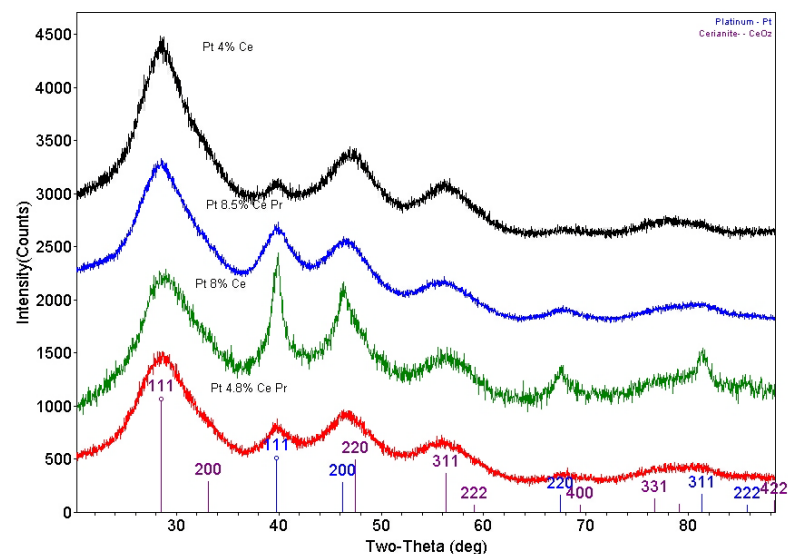
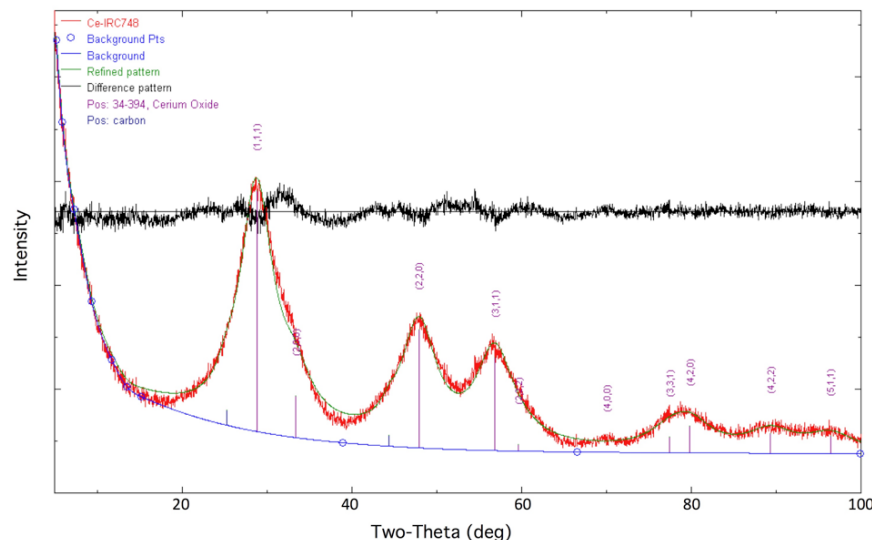
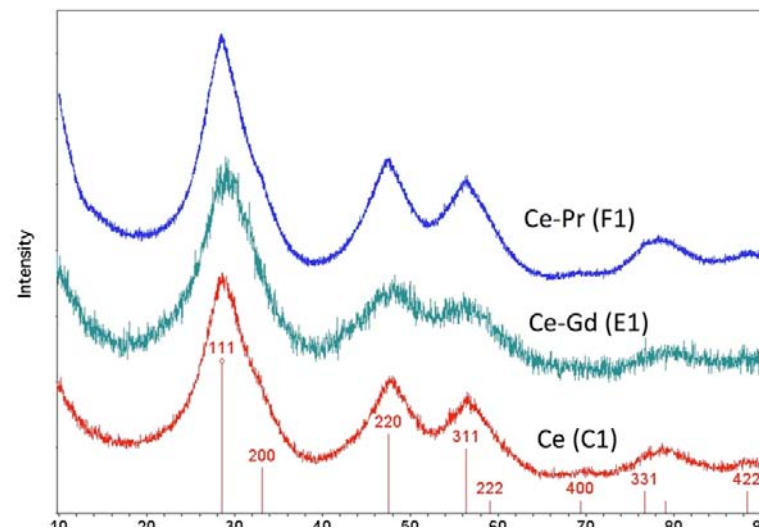
Pt/ Cerium Oxide /Carbon Catalysts

- Pt supported on metal oxides - improved catalytic properties and free radical scavenging
 - Poor electronic conductivity hampers cell performance
 - Intimate mixtures of Pt/metal oxide on carbon may solve problem
- A sorb precursor solutions into carbonaceous sorption media then pyrolyze to form nanocomposites
- Ceria, Gd doped Ceria, and Pr doped Ceria supports synthesized
 - Pt deposition from acetone H_2PtCl_6



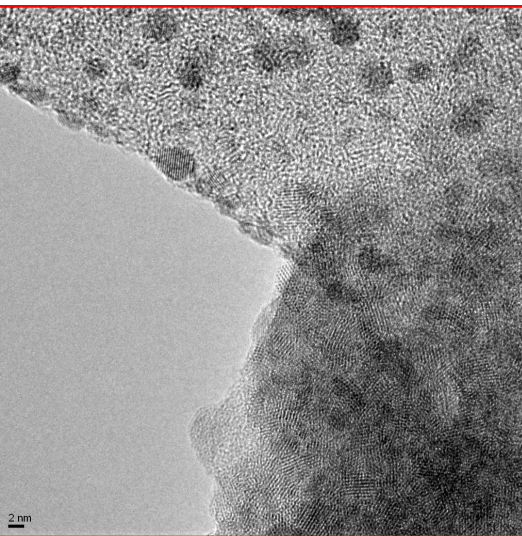
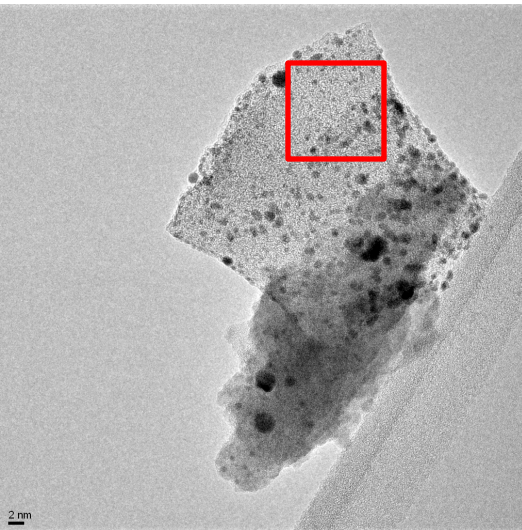
Batch/ Furnace Run	IEX Resin	Metal Cation(s)	Salt* (wt%)	Air Pre- treatment	Oxide (wt%)	Carbon Yield (wt%)	Crystal Size† (nm)
A1	IRC748	Ce	12.5	none	30	16	1.4
A2	IRC748	Ce	12.5	225° 3h	24	21	1.3
B1	IRC748	Ce	12.5	none	30	16	1.0
C1	IRC748	Ce	25	none	41	22	1.1
C2	IRC748	Ce	25	225° 3h	36	27	-
D1	IRC748	Ce	25	none	43	20	1.1
E1	IRC748	Ce _{0.81} Gd _{0.19}	25	none	45	19	1.2
F1	IRC748	Ce _{0.85} Pr _{0.15}	25	none	45	19	1.3
G1	IRP64	Ce	21	225° 3h	38	18	1.0

- Full profile (Retivield) refinement of all patterns
- No unreacted phases
- Lattice parameter shifts indicated Ln doping of ceria occurred
- XRD and TEM in good agreement, <2 nm ceria, 2-8 nm Pt depending on deposition conditions
- Carbon content controllable from 0-80%

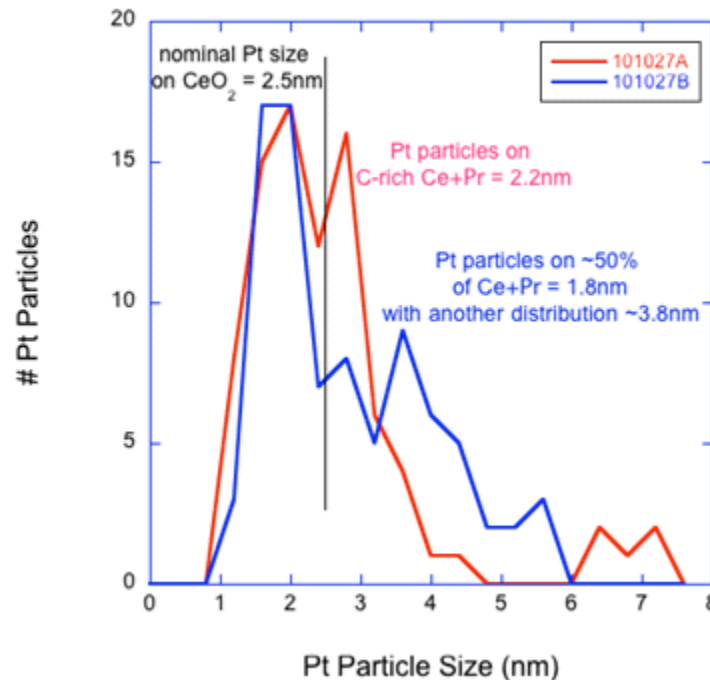
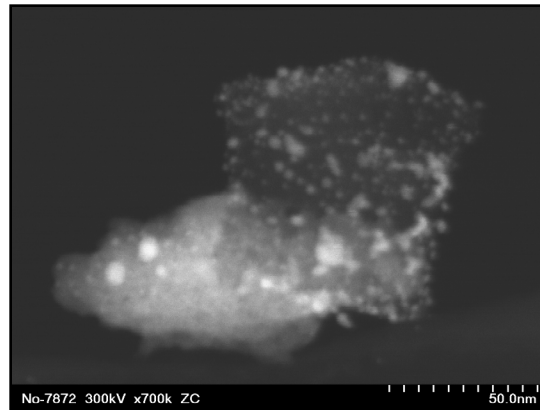


- Milestone nm scale Pt on nm size Ceria supports achieved and verified by XRD and TEM

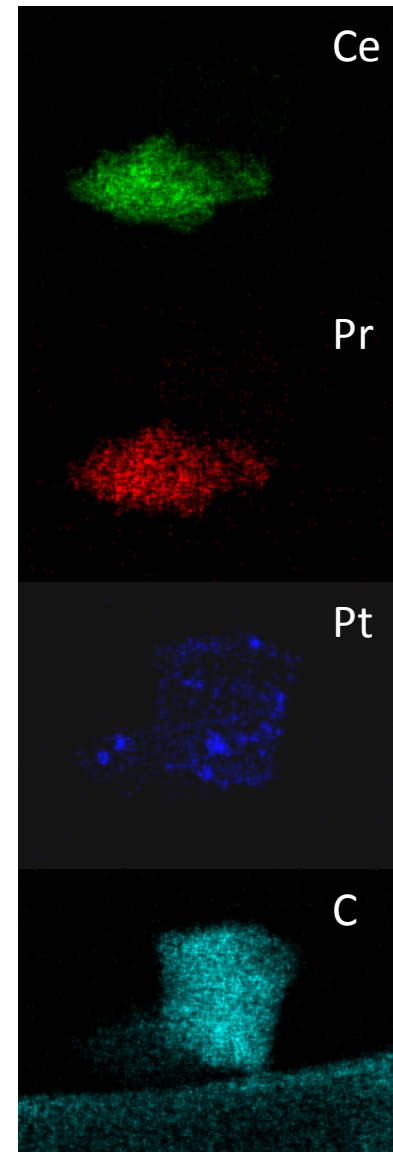
HRTEM



HAADF-STEM



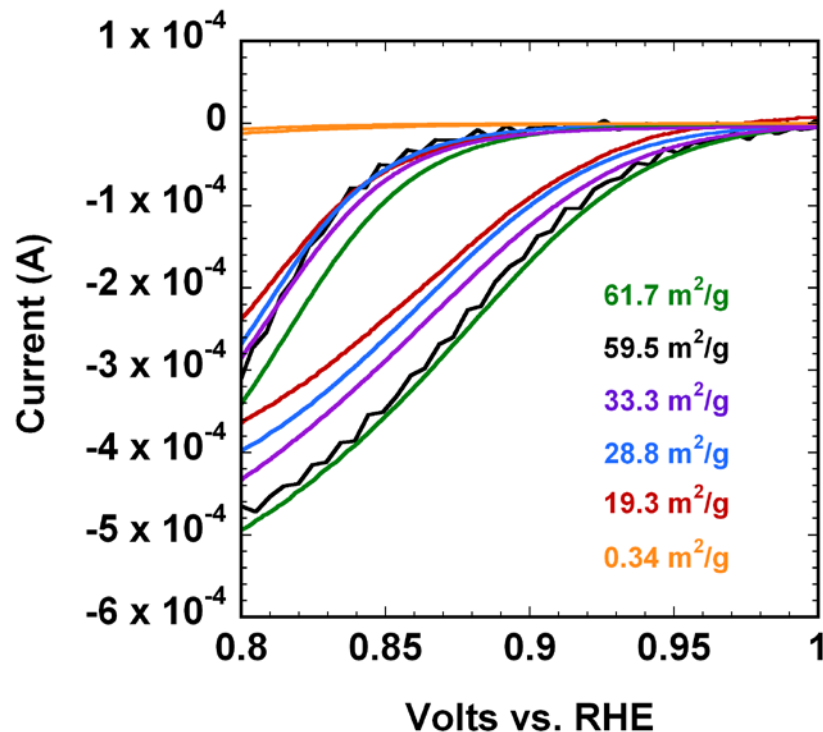
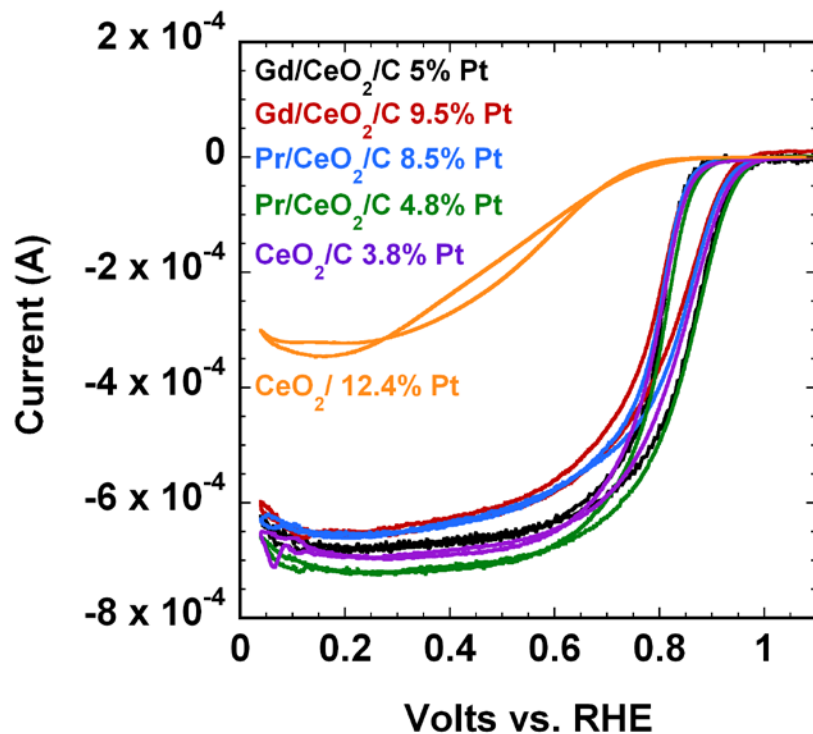
EDS-X ray Maps



- Nanometer Pt deposition achieved on Pt/Ceria/ Carbons

RRDE Oxygen Reduction Kinetics

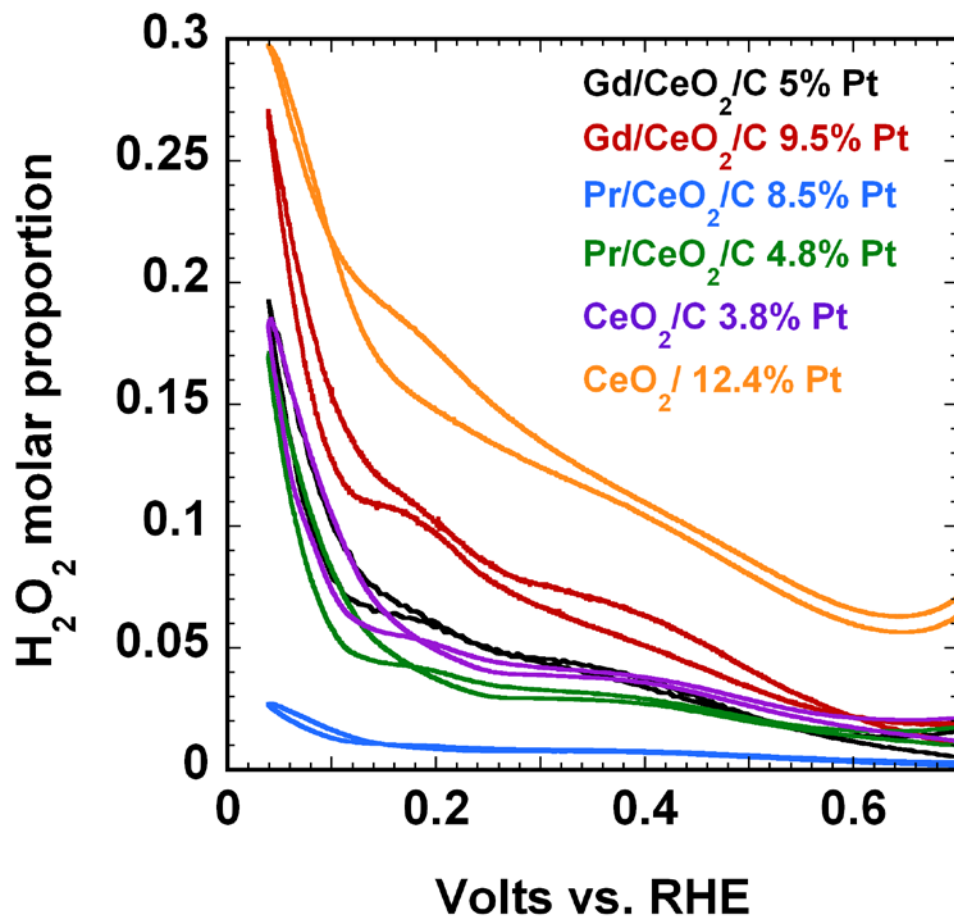
0.5 M H₂SO₄, ~50 μg_{Pt}/cm², 900 rpm



- All disk electrode loadings verified by X-ray Fluorescence spectroscopy!
- Apparent ORR kinetics correlates with specific surface area from hydrogen UPD for all supports

Catalyst Selectivity For 2-Electron Oxygen Reduction

0.5 M H_2SO_4 , $\sim 50 \mu\text{g}_{\text{Pt}}/\text{cm}^2$, 900 rpm



- No correlation between peroxide generation and Pt content or Pt surface area
- Lowest peroxide generation for Pr-doped supports
- Highest peroxide for pure CeO₂ support

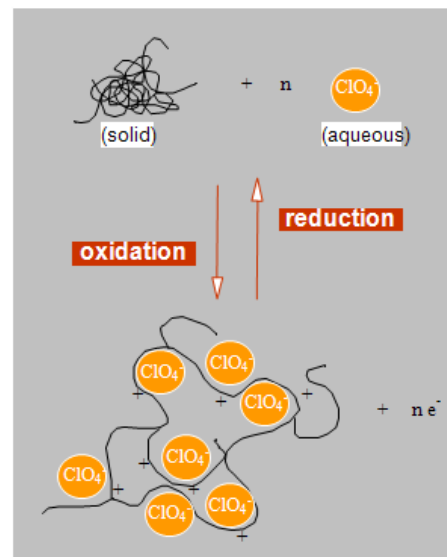
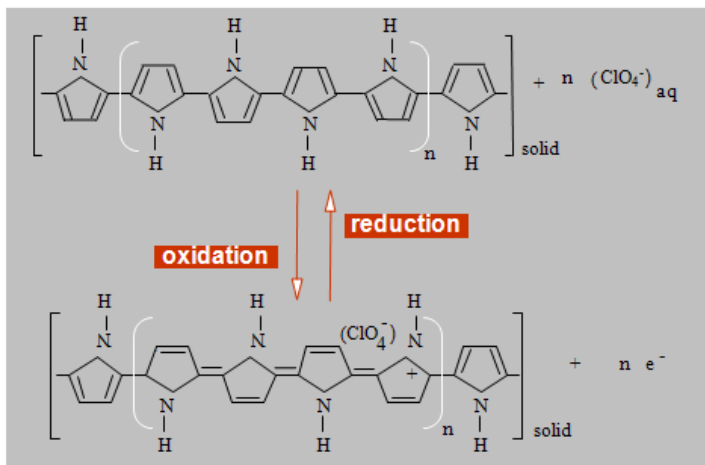
• Extremely low peroxide generation on Pt-ceria praseodymium-supported catalysts

Surface Areas and Specific Activities Pt/Ceria/C

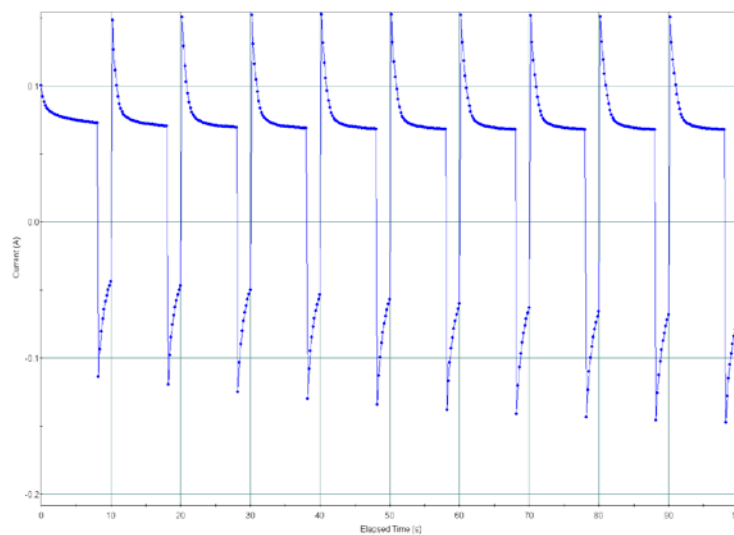
	IPA inks uniform electrode coverage				
	Specific surface areas m ² /g			Mass activity at 0.9 V vs. RHE A/g	Specific activity at 0.9V vs. RHE mA/cm ²
	H UPD	CO with bckgnd	CO w/o bckgnd		
Pt 101006 on CeO ₂ /Gd/C 7.6%Pt					
Pt 101027A on CeO ₂ /Pr/C 4.8%Pt	61.7	30.1	55	30.1	0.049
Pt 101027B on CeO ₂ /Pr/C 8.5%Pt	28.8	10.4	39.3	17.4	0.060
Pt 101104 on CeO ₂ /C 3.8% Pt	33.3	27.2	55.2	20.1	0.060
Pt 101130B on CeO ₂ /Gd/C 9.5% Pt	19.3			11	0.057
Pt 101130A on CeO ₂ /Gd/C 5% Pt	59.5			20	0.034
20% Pt/C E-TEK 2.7nm 1.17M H ₂ SO ₄	87			11	0.010

- Higher mass and surface activities compared to commercial Pt/C catalysts

Electrochemical Oxidation/Reduction of Polypyrrole

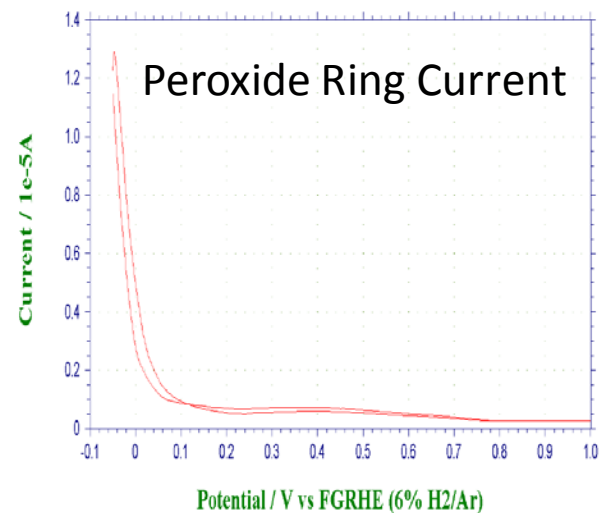
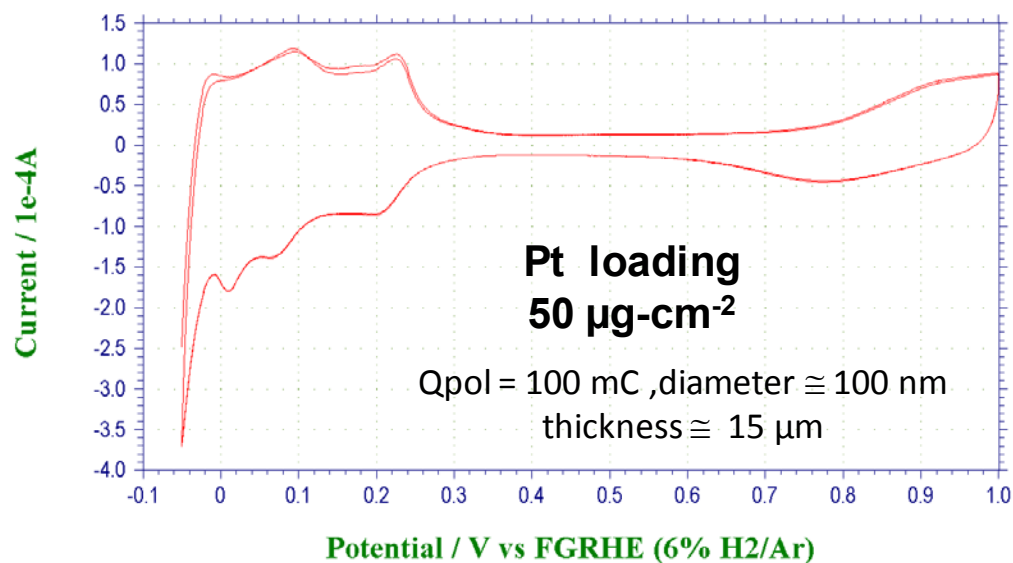
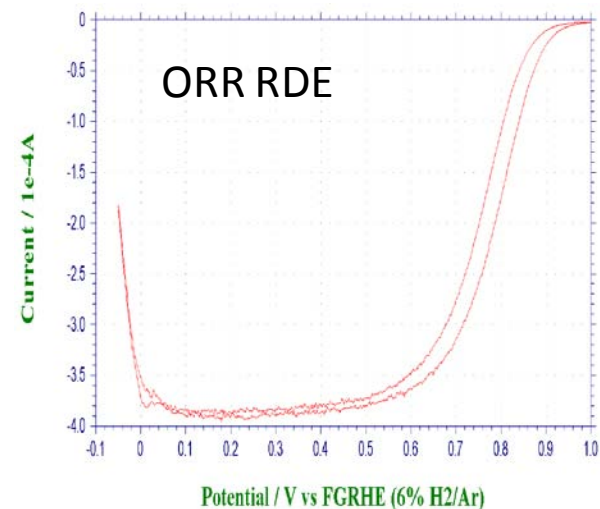
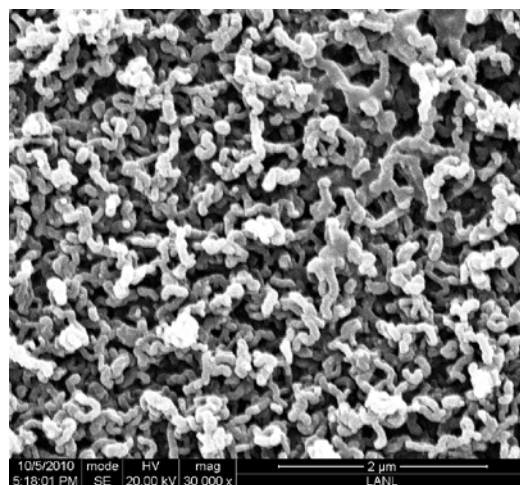
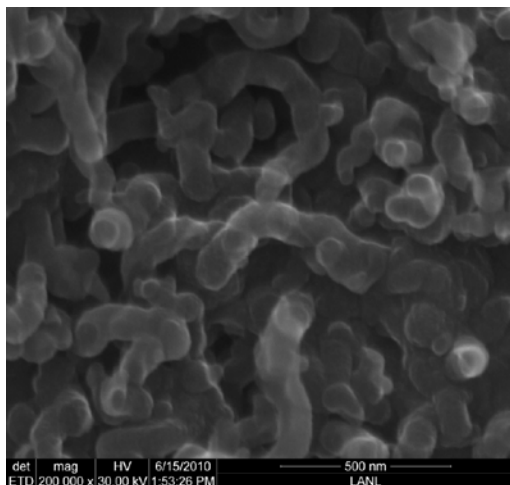


Electrochemical Cell



**PPy +
 LiClO_4**

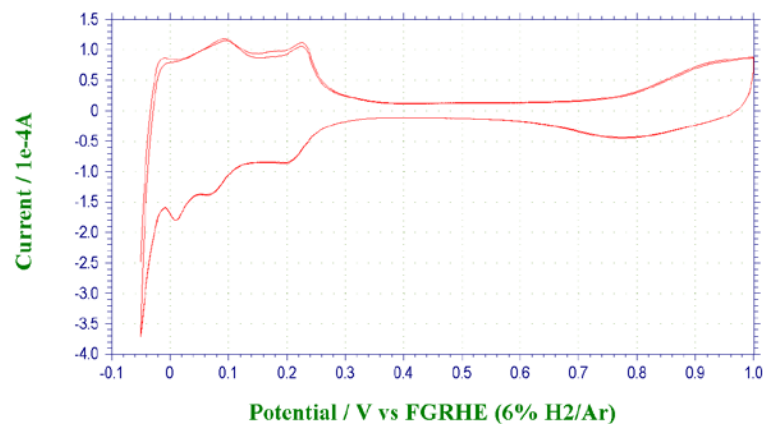
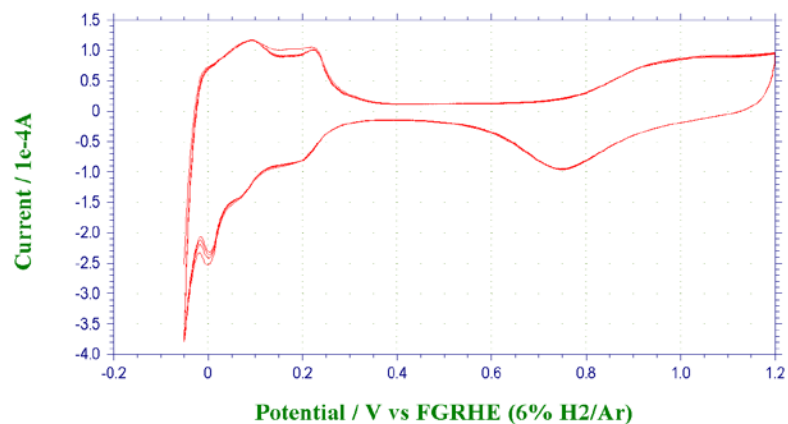
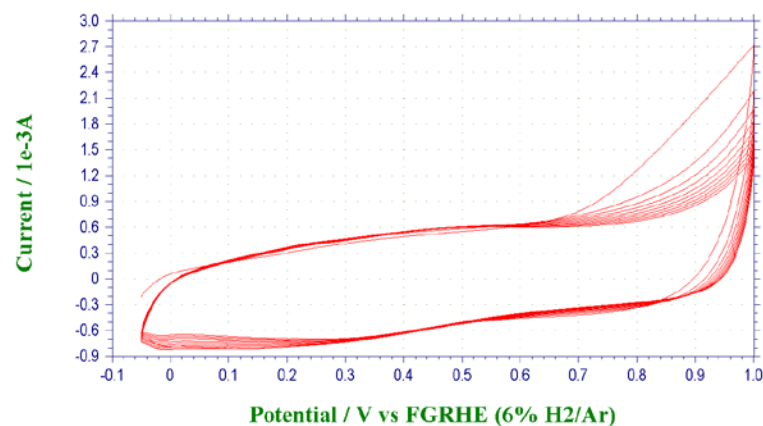
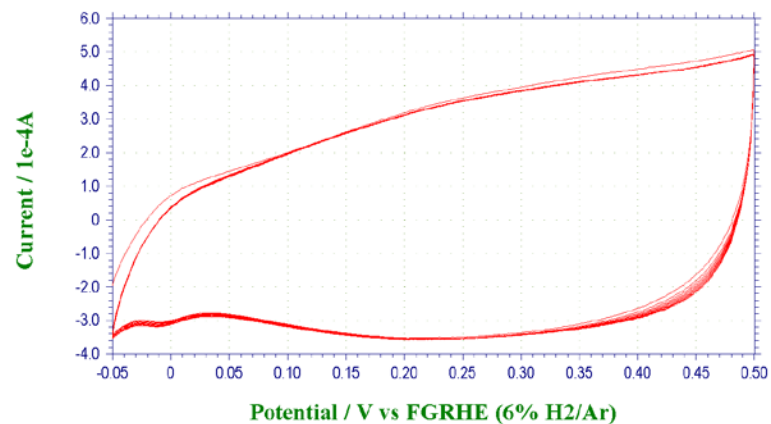
**Multipotential
steps
+1V (8s) / -0.1V (2s)
vs RHE**



- Surface area corresponds to ~14 m²/gram; 20 nm thick Pt layer

Electrochemistry of Pt Coated PPY/starch Nanowires

$Q_{pol} = 100 \text{ mC}$
diameter $\cong 100 \text{ nm}$
thickness $\cong 15 \mu\text{m}$



- Initial voltammograms are dominated by polymer redox, later voltammograms show Pt features

Summary

- Modeling
 - DFT calculations providing insight into ideal alloy compositions, stable shapes
 - Explain high activity of the PtNi family
 - Show instability of very small diameter Pt nanotubes
 - Grain growth models developed
 - show unconventional geometry “sheets with holes” may show enhanced stability
 - Microstructure models developed
 - will aid optimization of catalyst layers
- Nucleation and growth study:
 - Show all furnace carbons have similar nucleation site densities
 - highlights the importance of increasing Pt nucleation site density on carbon surfaces
- Synthesis and Characterization:
 - New Pt/ceria/carbon catalysts developed and characterized by XRD, HRTEM, Cyclic and RRDE voltammetry, and thermogravimetry
 - Show enhanced ORR activity over Pt-C
 - New Pt/Pd nanoplates developed and characterized by TEM and Cyclic and RRDE voltammetry
 - Show enhanced ORR activity over Pt-C
 - Pt/Polypyrrole cathodes electrochemical behavior probed by Cyclic and RRDE voltammetry

Future Work

- Pt/Ceria/C catalyst research
 - Pt/Ceria/catalyst optimization- improve Pt dispersion
 - Pt/Ceria/catalyst neutron scattering
 - Scale up for fuel cell testing
 - Incorporation into catalyst layers and MEA optimization
 - Fuel cell performance and durability testing
- Pt/Polypyrrole catalyst research
 - Decrease nanowire diameter
 - Determine if ORR activity will meet requirements (go-no)
 - Calculate optimal MEA geometries
- Pt/Pd nanoplate research
 - Decrease nanoplate size
 - TEM and XRD characterization
 - Scale up for fuel cell testing
 - Incorporation into catalyst layers and MEA optimization
 - Fuel cell performance and durability testing
- Development of Models and Theory
 - DFT model extension to nanoplates and nanowires
 - Sintering model extension to include dissolution and reprecipitation
 - Microstructural Model Application to Novel catalysts
 - Model Validation

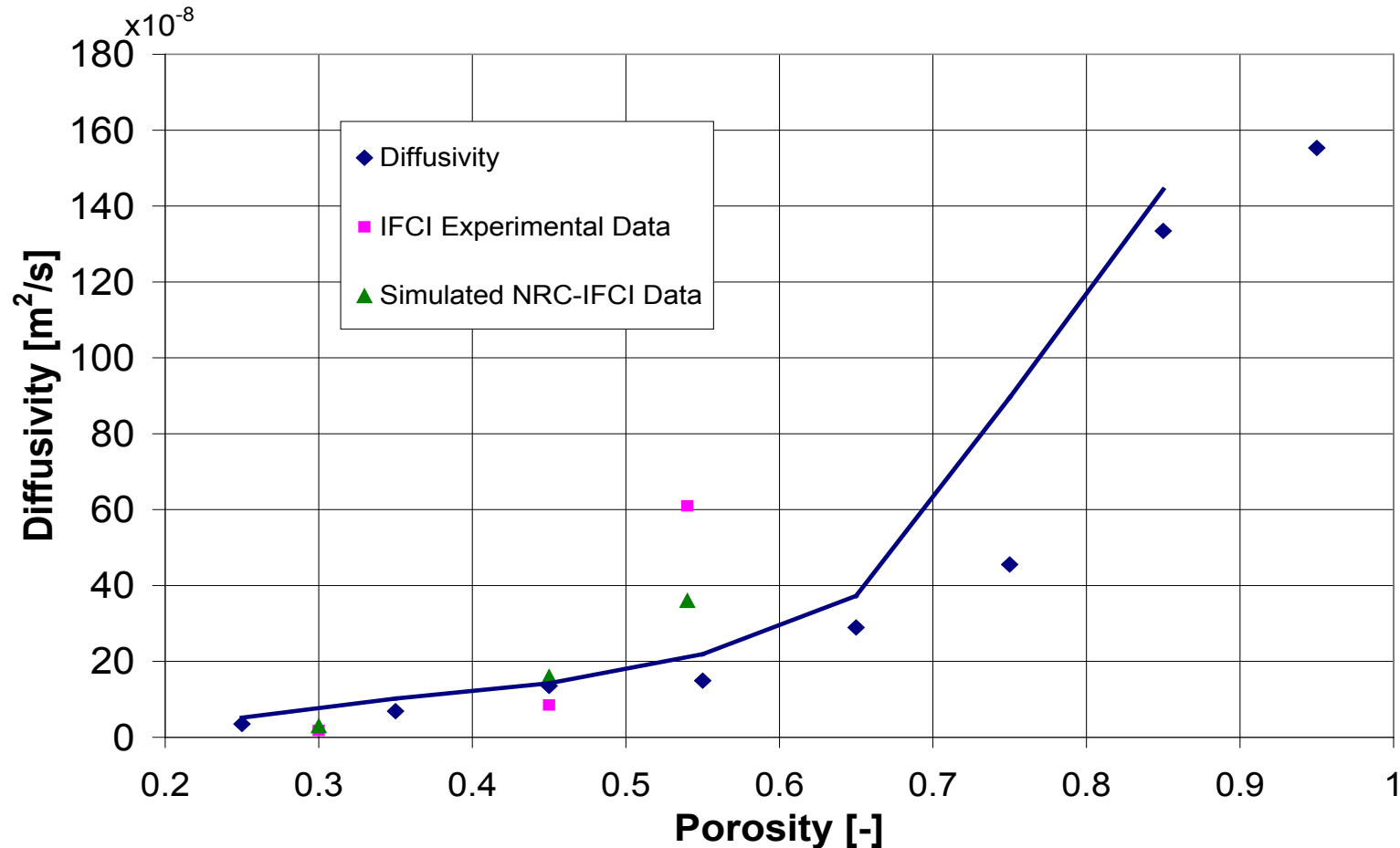
Acknowledgement

*We gratefully acknowledge funding from the US
DOE Office of Fuel Cell Technologies*

Technical Backup Slides

Diffusivity vs. Composition

As expected diffusivity reduces with reduction in fluid porosity



Microstructural Modeling Results

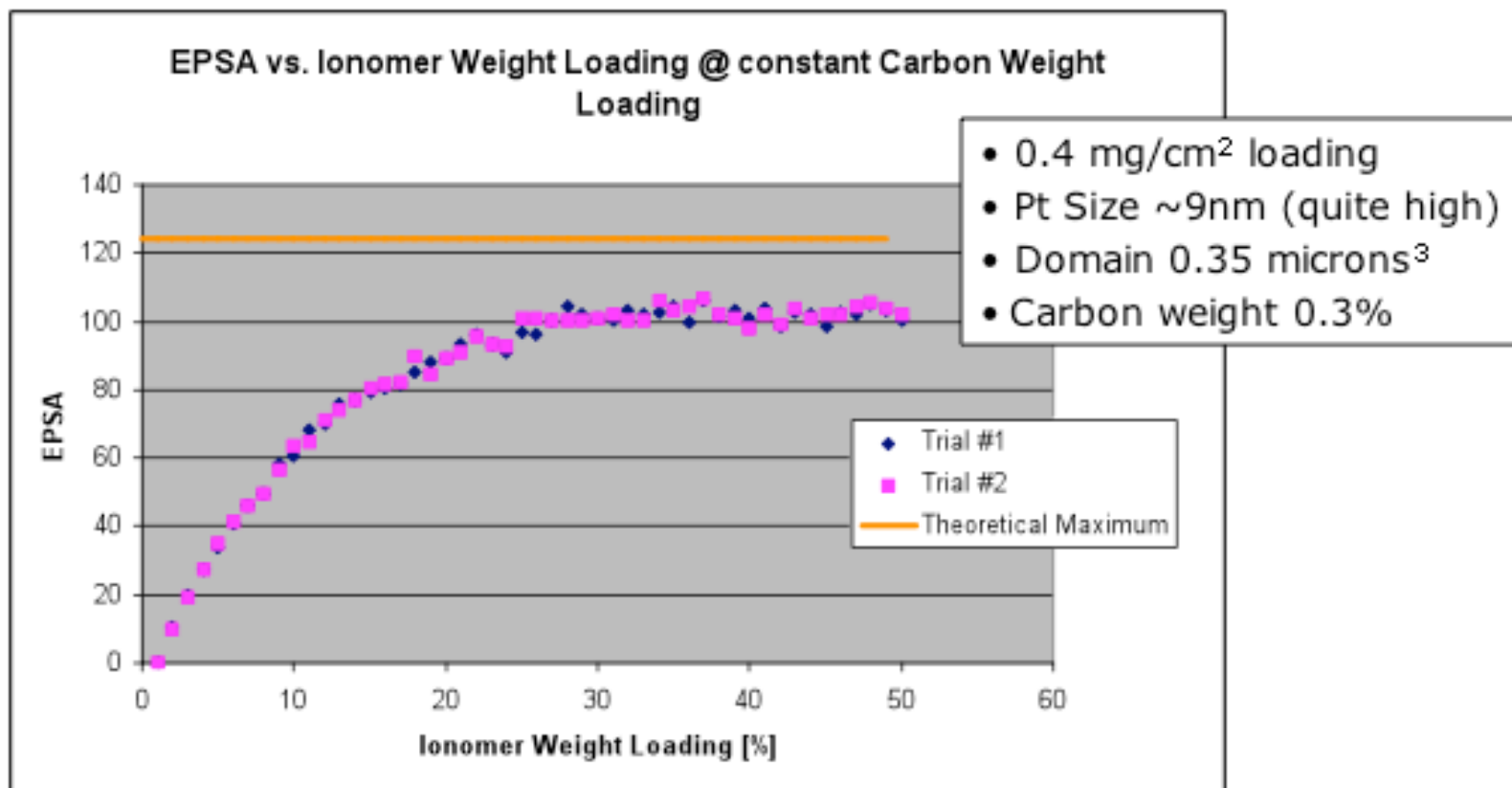
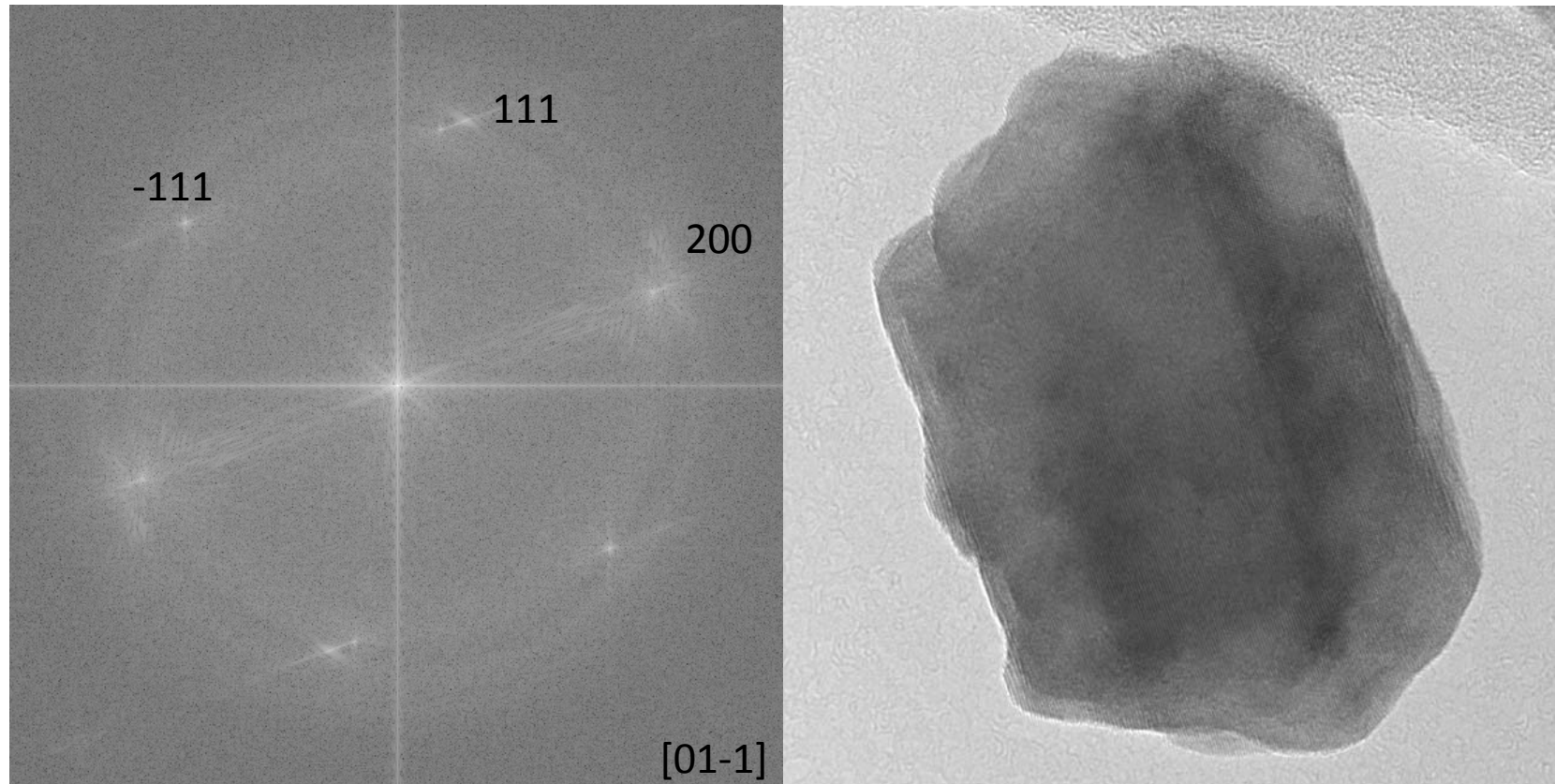


Illustration of the effect of ionomer wt loading on maximization of the available surface area of Pt.

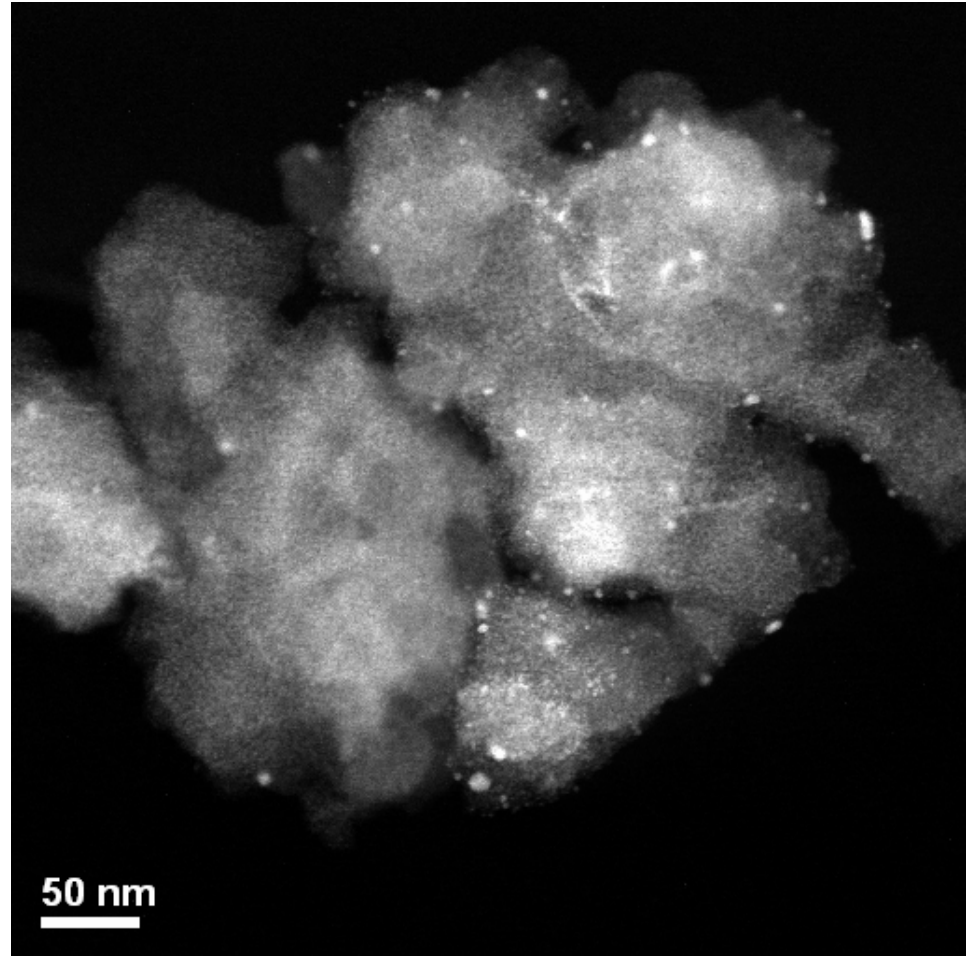
The maximum surface area is typically achieved at ~30 wt%

HRTEM PtPd Nanoplates

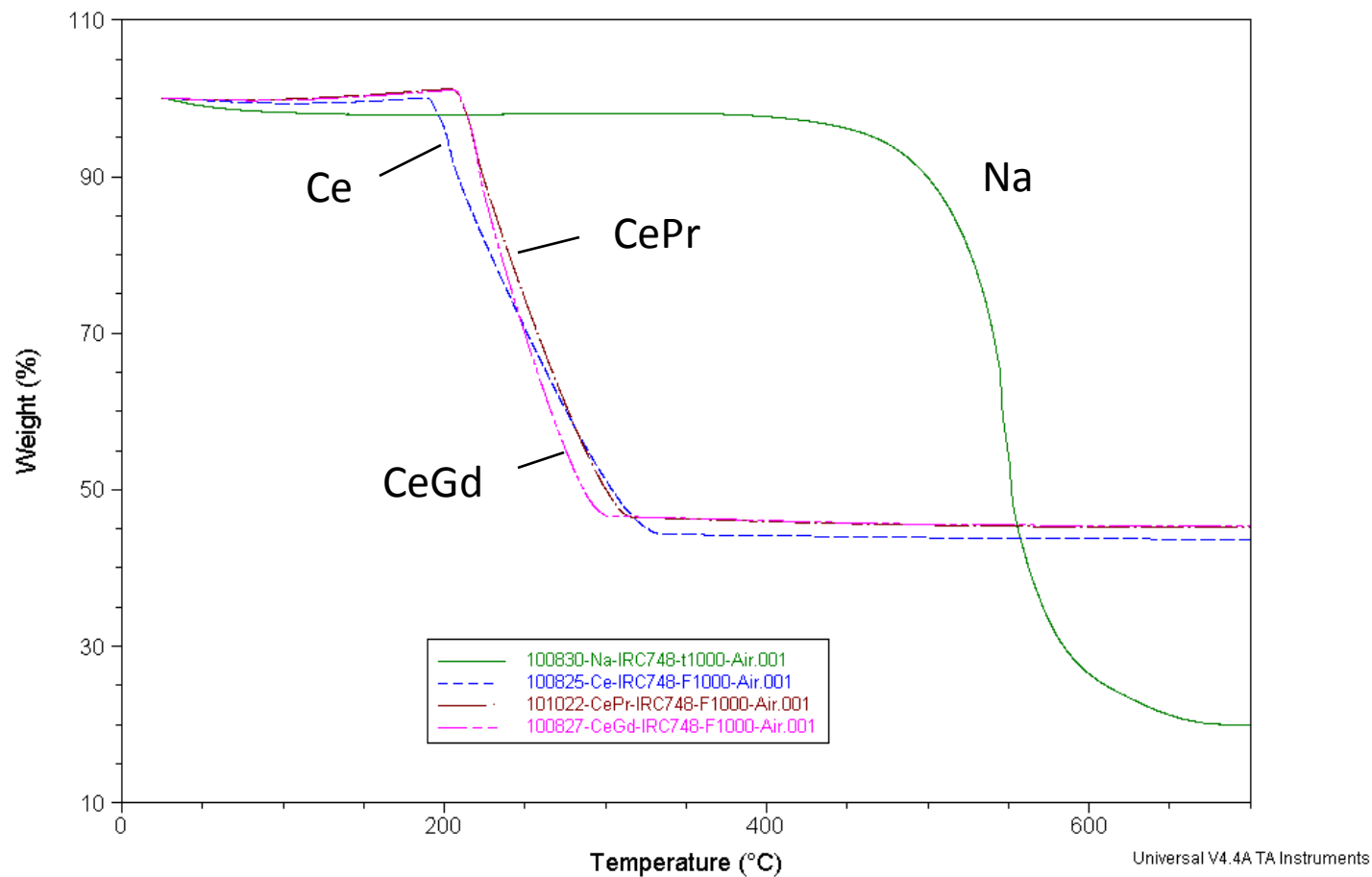


High resolution TEM of PtPd nanoplates

- HAADF-STEM image showing adjacent CeO₂+Gd aggregates with large Pt particles on one aggregate (left) and much smaller Pt nanoparticles on the other aggregate (right).



Air Thermogravimetric Analysis of Ceria/C's



- Nanocerias very active catalysts, light-off at ~ 200°C