

# The Science And Engineering of Durable Ultralow PGM Catalysts

Fernando Garzon

Los Alamos National Laboratory

May 10<sup>th</sup> 2011

FC010

This presentation does not contain any proprietary, confidential, or otherwise restricted information

# Overview

## Timeline

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

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

## 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)

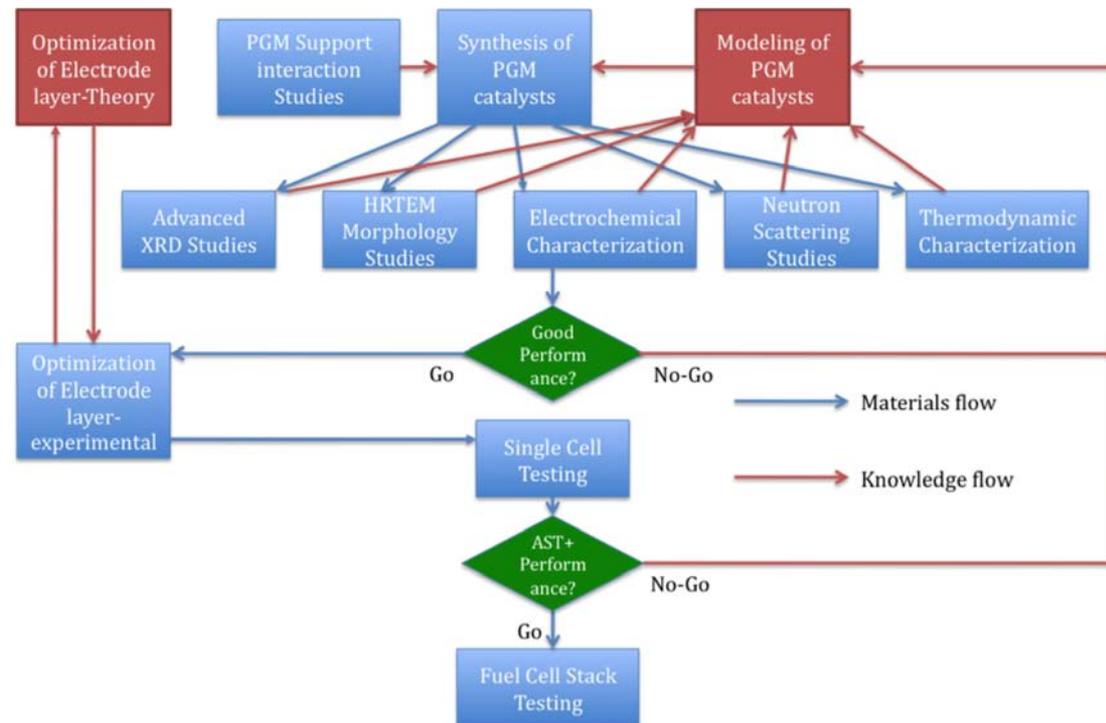


- |                     |                       |               |                |                    |
|---------------------|-----------------------|---------------|----------------|--------------------|
| • LANL              | • UNM                 | • ORNL        | • BALLARD      | • UCR              |
| – 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



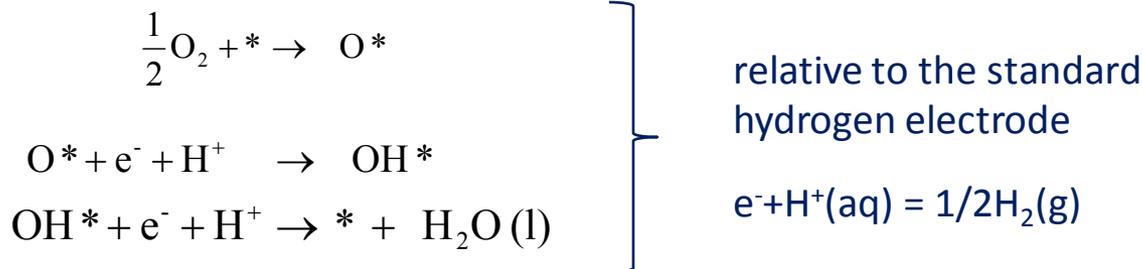
# Milestones

- 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

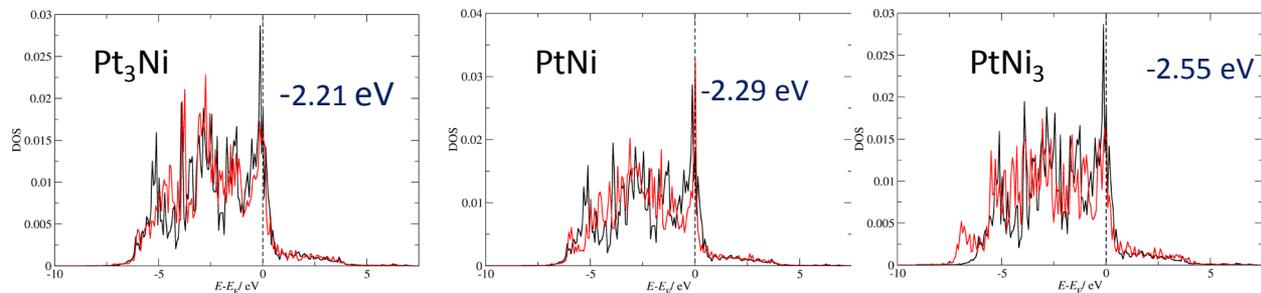


Gibbs free energy of the reactions (Norskov et al. J. Phys. Chem. B 2006, 110, 21833 )

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

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

- Calculate d-band center for: Pt( -1.97 eV), Pt<sub>3</sub>Ni, PtNi, PtNi<sub>3</sub>
- Pt surface atoms only, no Ni in top layer
- Shift corresponds to weakening of oxygen binding



	OH* + e <sup>-</sup> + H <sup>+</sup>	O* + 2(e <sup>-</sup> + H <sup>+</sup> )	H* - e <sup>-</sup> + H <sup>+</sup>
<b>Pt(111)</b>			
$\Delta E_{\text{w,water}}$	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
<b>Pt<sub>3</sub>Ni(111)seg</b>			
$\Delta E_{\text{w,water}}$	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
<b>PtNi(111)seg</b>			
$\Delta E_{\text{w,water}}$	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
<b>PtNi<sub>3</sub>(111) seg</b>			
$\Delta E_{\text{w,water}}$	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

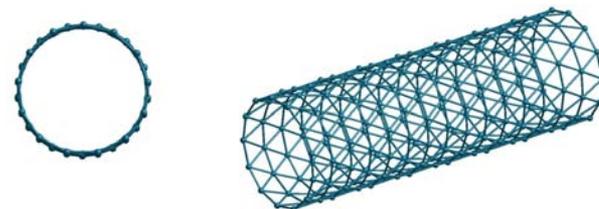
# Theoretical Modeling of Novel Pt Shapes- Nanotubes

- DFT calculations of stability of Pt structures:

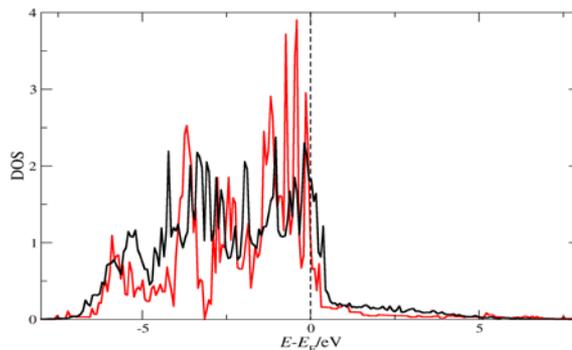
(6,6) Pt SWNT,  
d=5.18 Å, E=-4.97 eV/atom



(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)

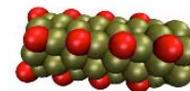
adsorption energies in eV of atomic oxygen for  
fcc site

	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



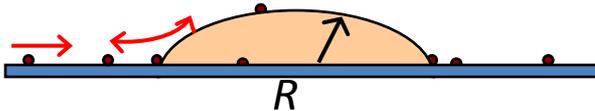
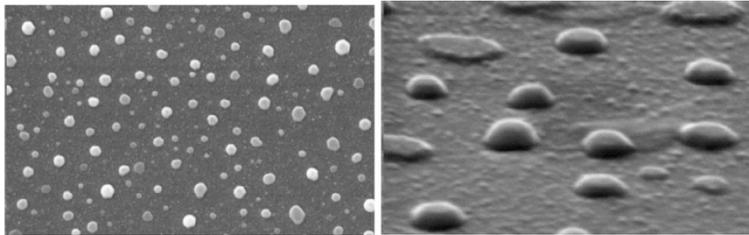
(13,13) Pt SWNT



# 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)



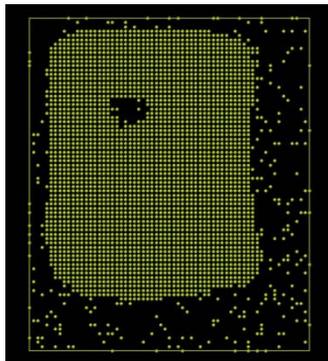
## Modeling Change of Particle Size

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

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

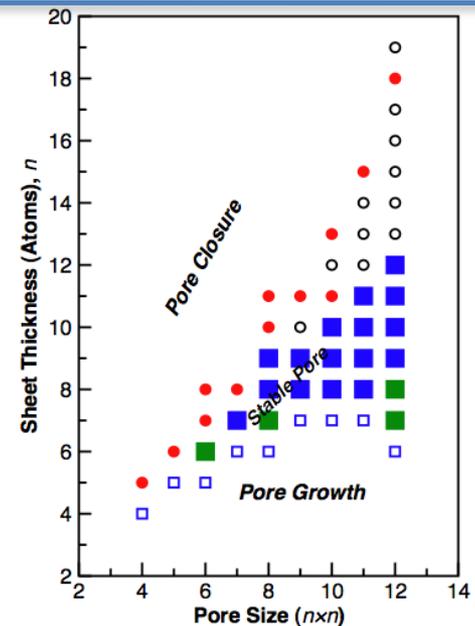
- Campbell model (below) predicts lower heats of adsorption for smaller particles than Gibbs Thompson (above)

## Stability of a Pore in a Pt Nanosheet



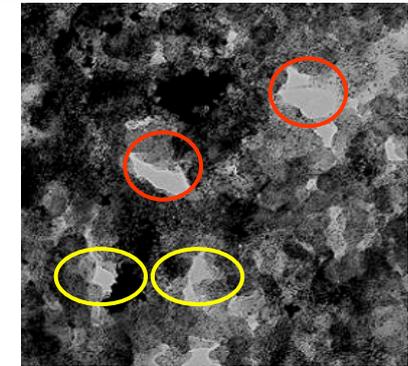
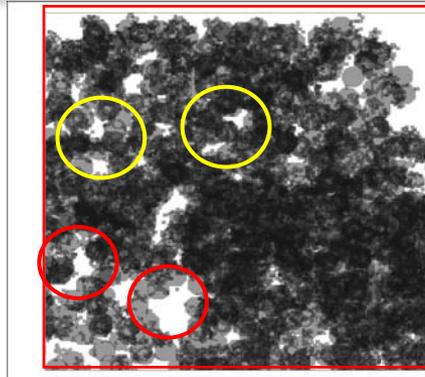
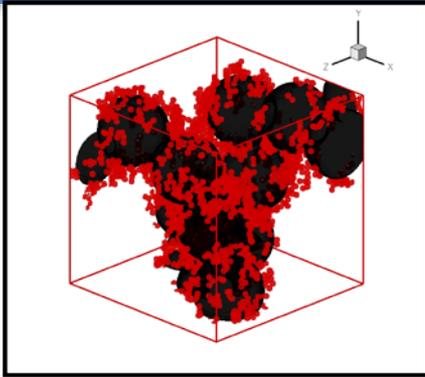
A region of sintering-resistant Nanostructures exists:

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.%

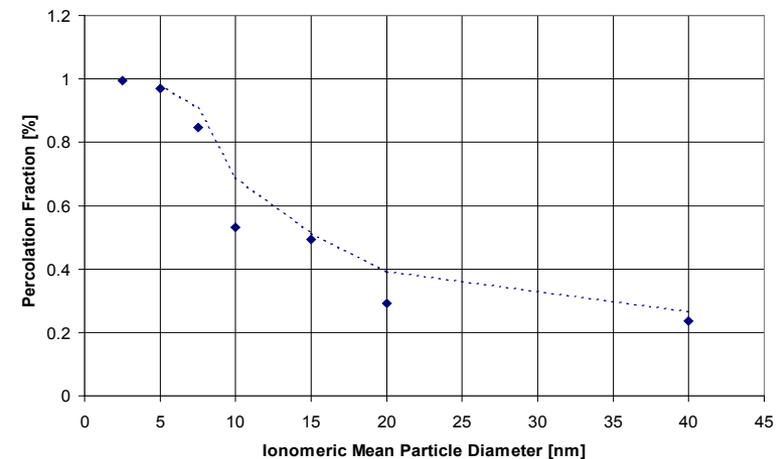
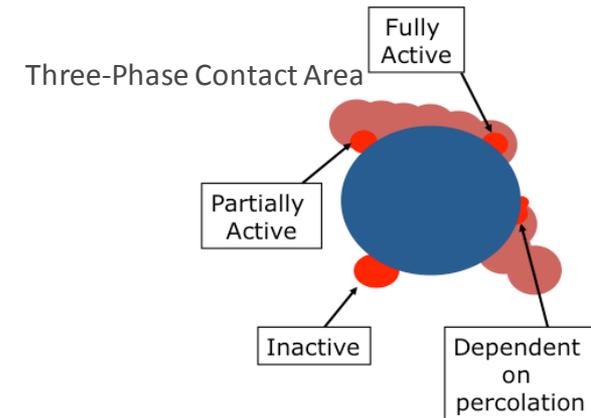
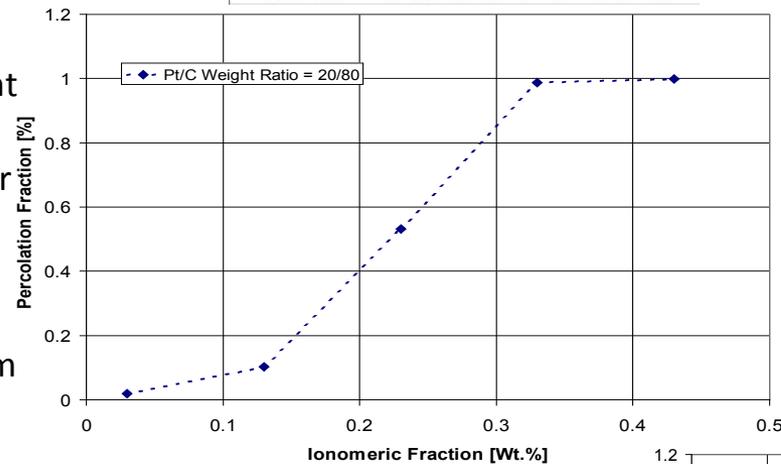
- Decreases with increasing Particle Size

- 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

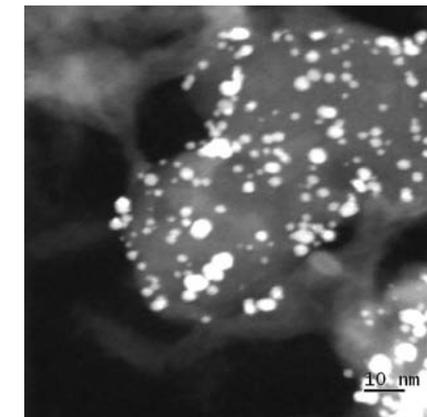
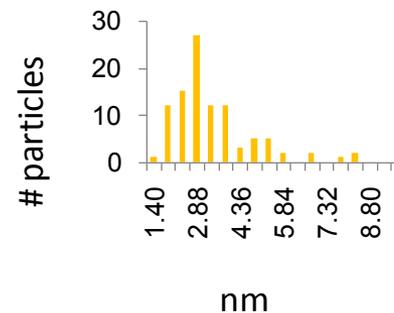
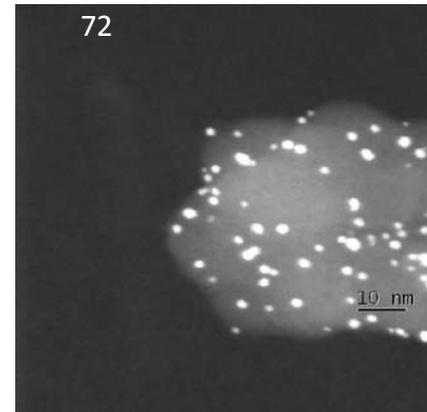
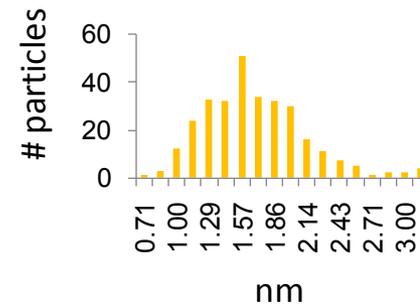
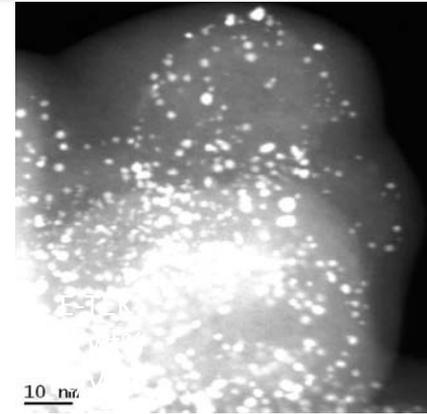
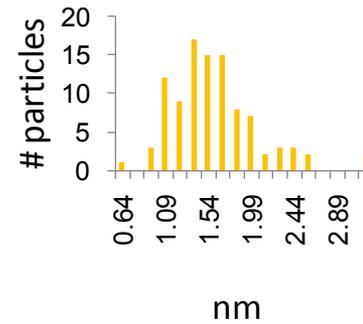


# Pt Dispersion On Carbon Supports

• 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 (Å) increases with loading
- Number of Pt particles/area only changes by changing carbon

Catalyst	Number of particles/cm <sup>2</sup> ( $10^{-11}$ )
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:

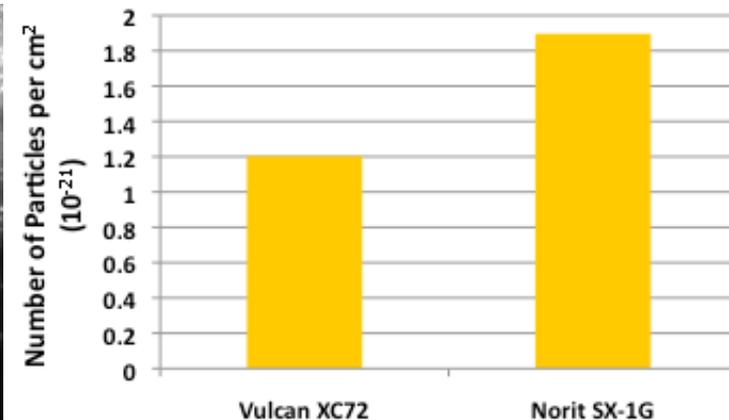
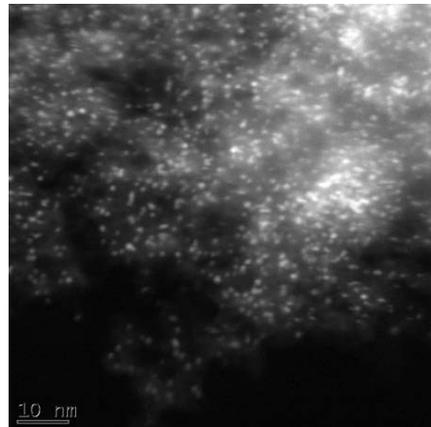
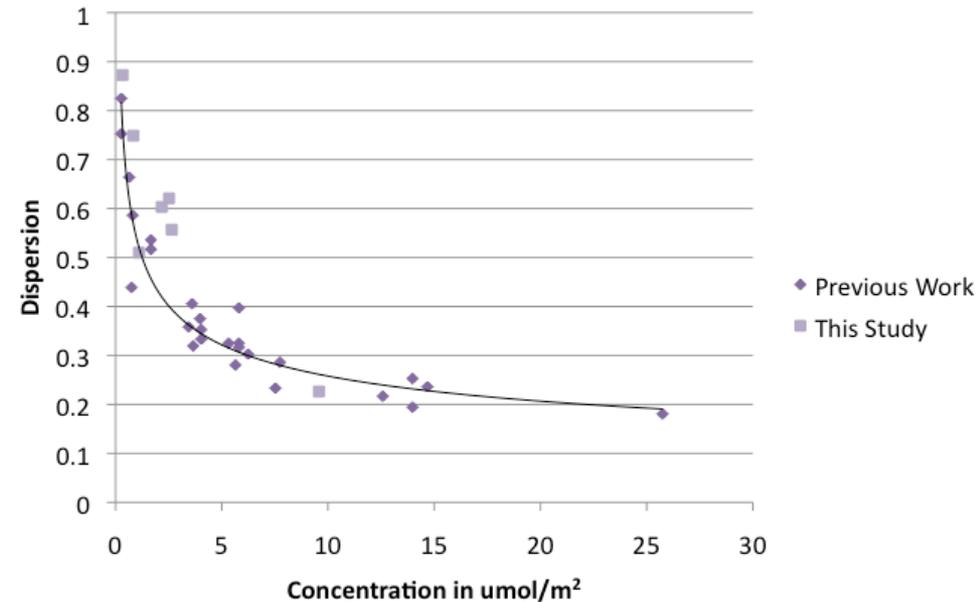
- Independent of furnace carbon type and surface area

- Nucleation site density is the same!

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

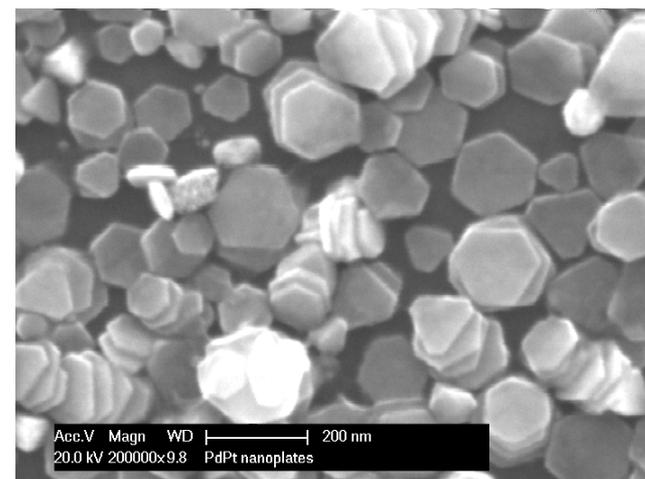
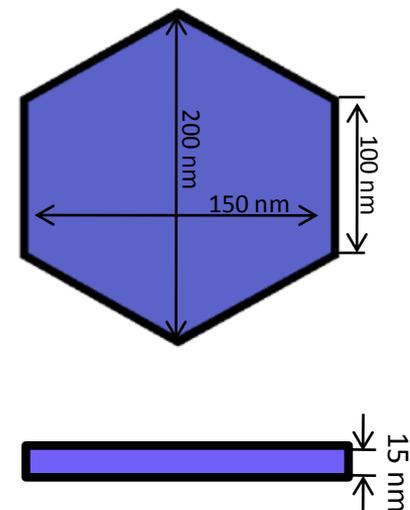
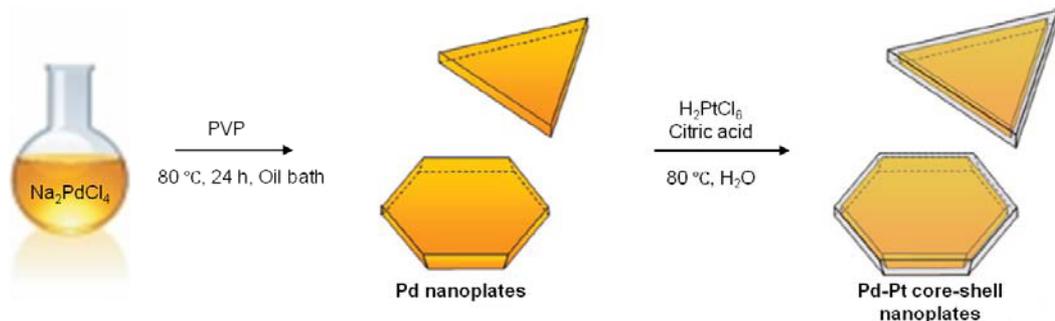
- These carbons oxidize very easily; poor corrosion resistance

- 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:



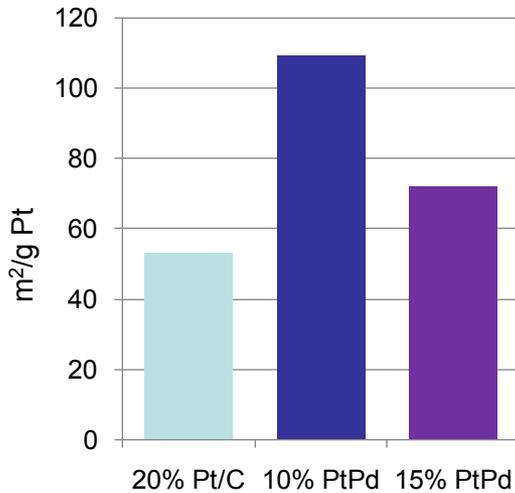
SEM image of Pt/Pd Nanoplates

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

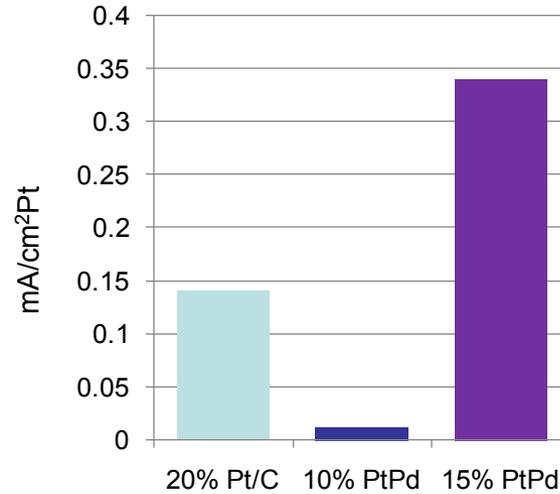
Samples with different Pt content:  
 2 layers 10.5% 3 layers 15.5%

# Electrochemical Characterization of Pt/Pd Nanoplates

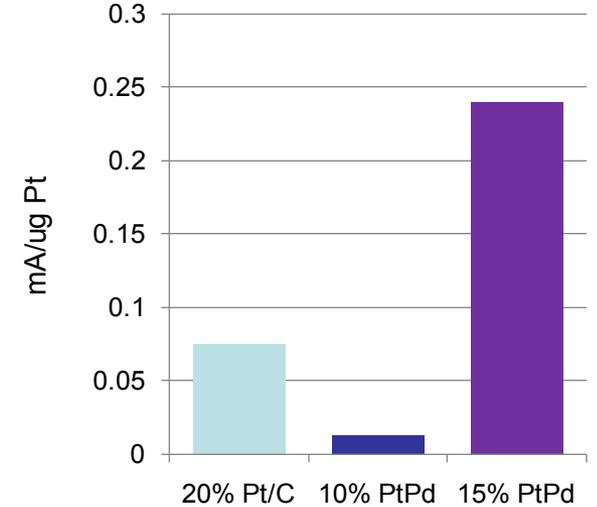
## Surface area



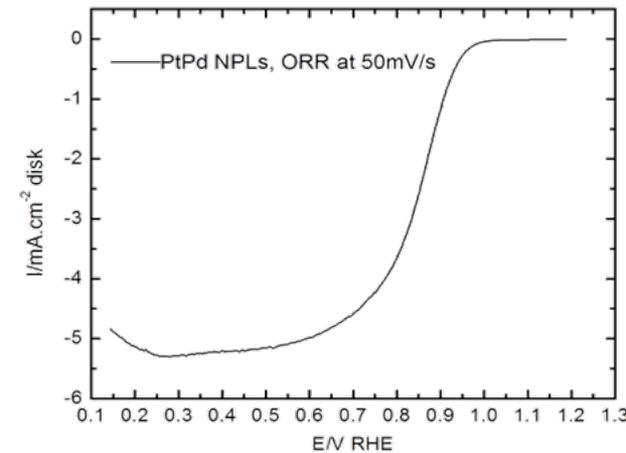
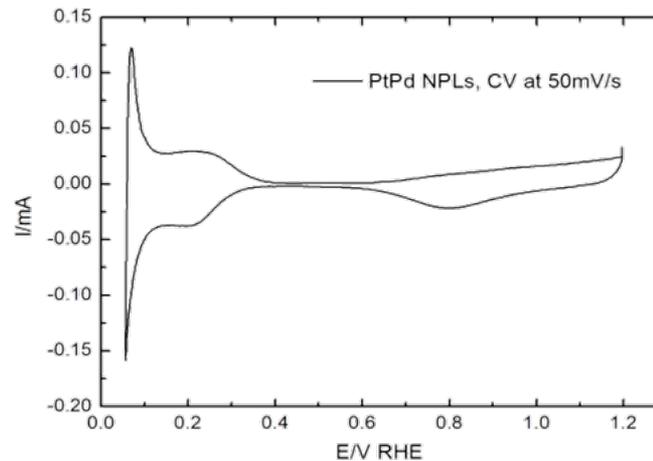
## Specific activity



## Mass activity

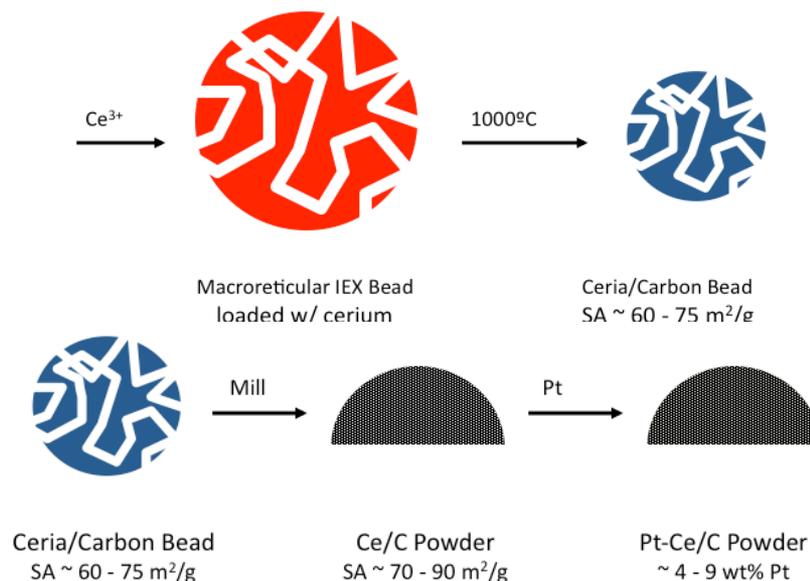
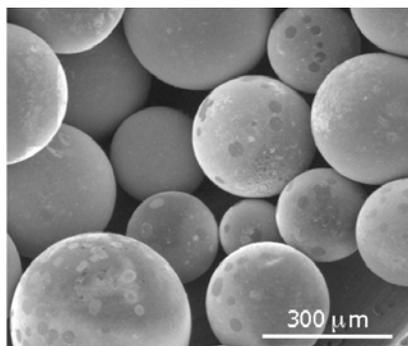


- Surface area for 15% PtPd is slightly higher than Pt/C, the activity is more than 2 times higher for both specific and mass activity
- Surface composition has a great effect on the activity



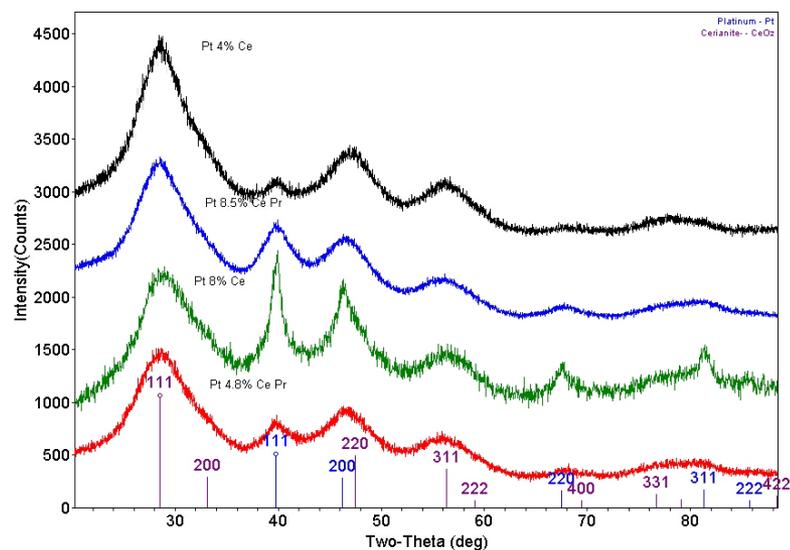
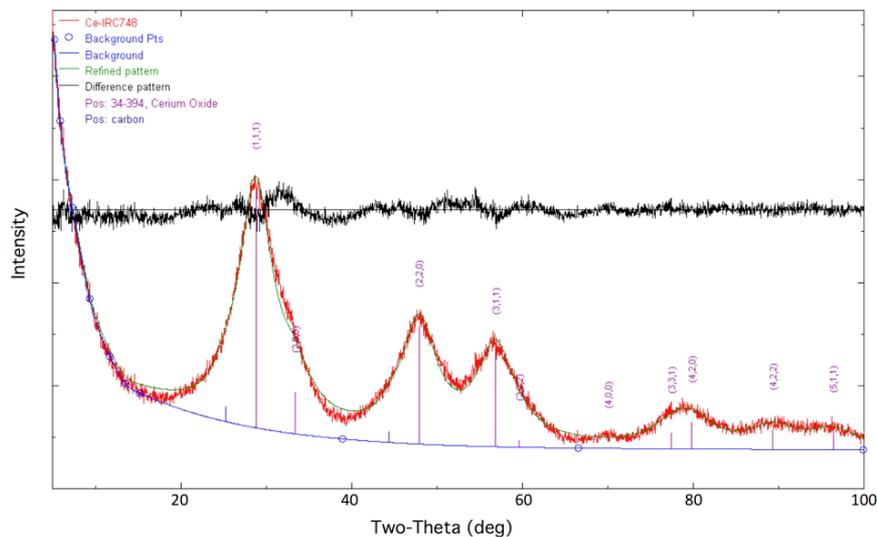
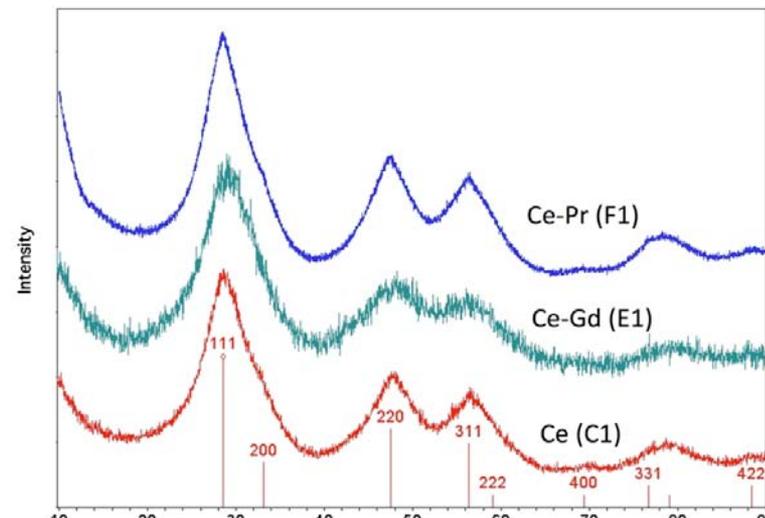
# Pt/ Cerium Oxide /Carbon Catalysts

- 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  $H_2PtCl_6$



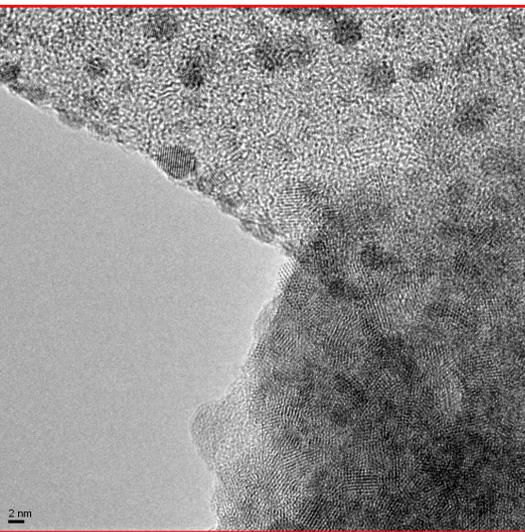
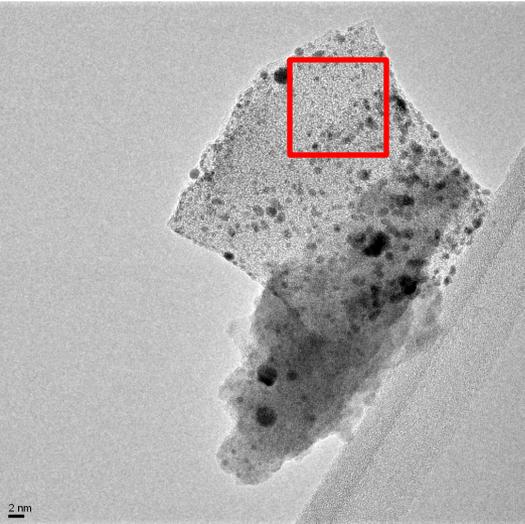
Batch/ Furnace Run	IEX Resin	Metal Cation(s)	Salt* (wt%)	Air Pre- treatment	Oxide (wt%)	Carbon Yield (wt%)	Crystal Size† (nm)
A1	IRC748	Ce	12.5	none	30	16	1.4
A2	IRC748	Ce	12.5	225° 3h	24	21	1.3
B1	IRC748	Ce	12.5	none	30	16	1.0
C1	IRC748	Ce	25	none	41	22	1.1
C2	IRC748	Ce	25	225° 3h	36	27	-
D1	IRC748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

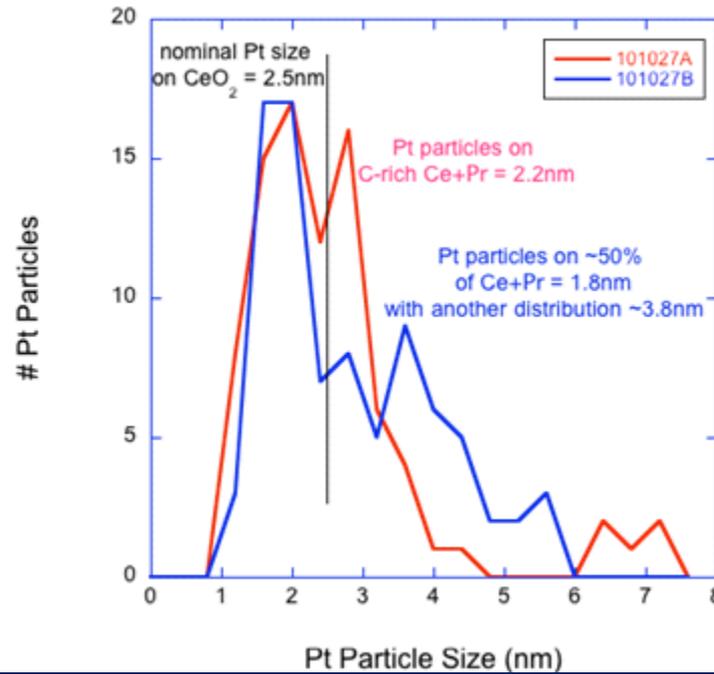
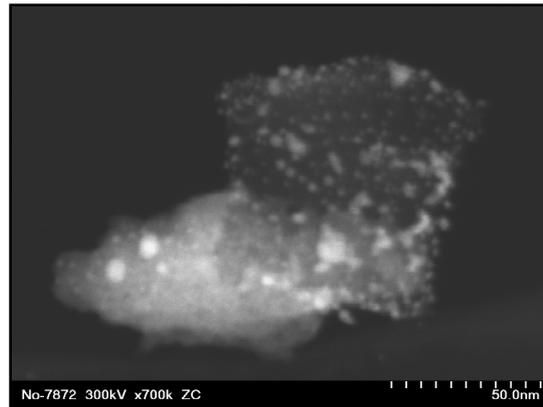


- Milestone nm scale Pt on nm size Ceria supports achieved and verified by XRD and TEM

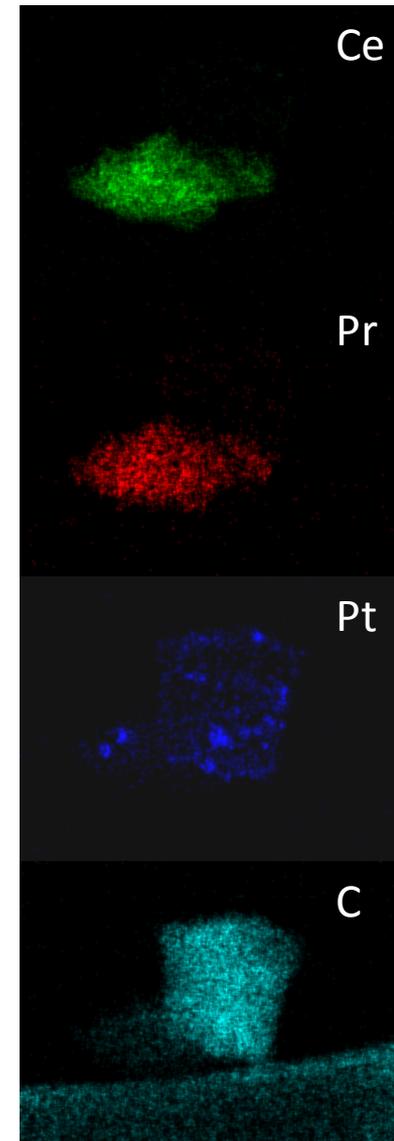
## HRTEM



## HAADF-STEM



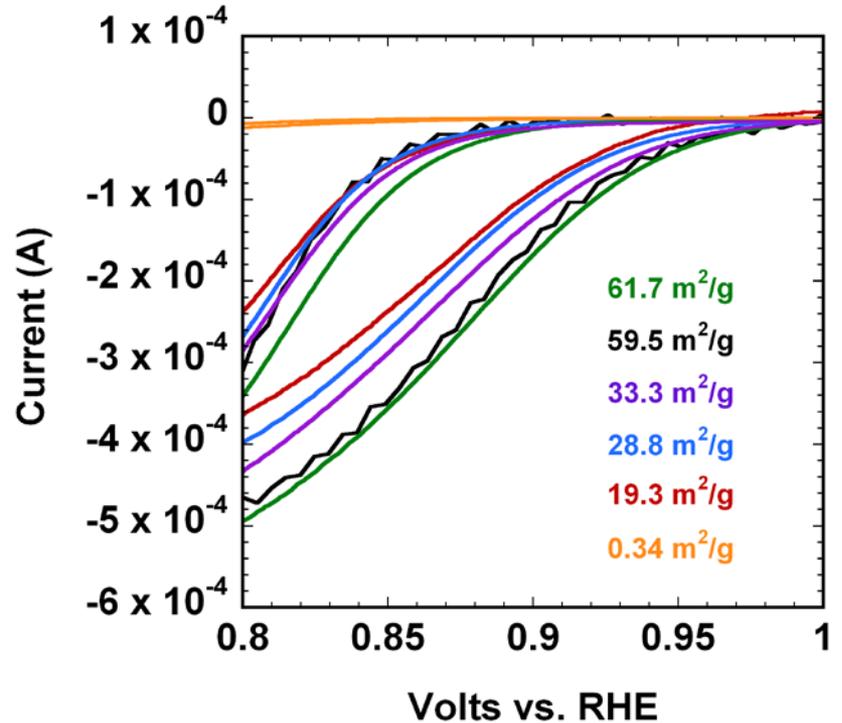
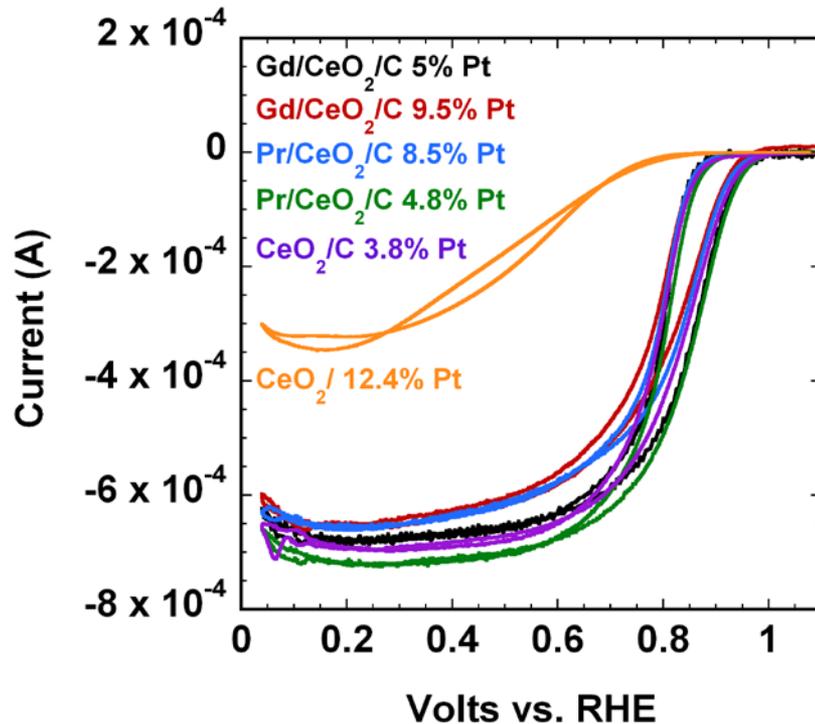
## EDS-X ray Maps



• Nanometer Pt deposition achieved on Pt/Ceria/ Carbons

# RRDE Oxygen Reduction Kinetics

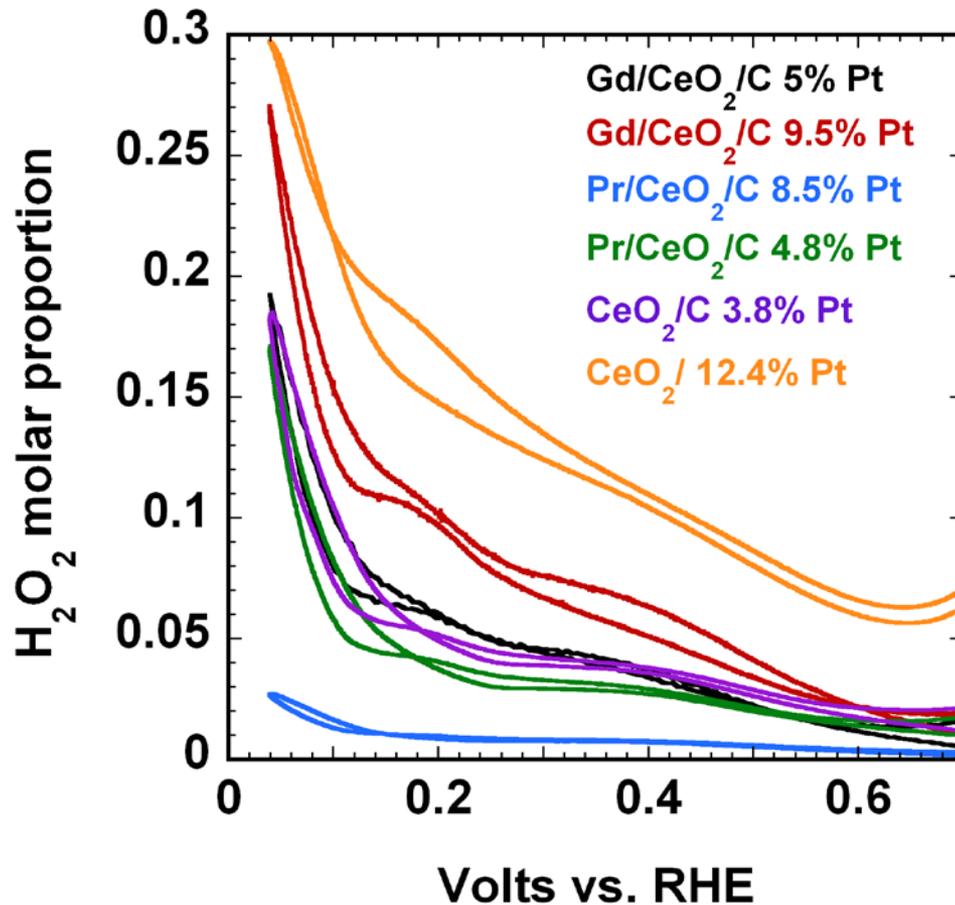
0.5 M H<sub>2</sub>SO<sub>4</sub>, ~50 μg<sub>Pt</sub>/cm<sup>2</sup>, 900 rpm



- 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<sub>2</sub>SO<sub>4</sub>, ~50 μg<sub>Pt</sub>/cm<sup>2</sup>, 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 CeO<sub>2</sub> support

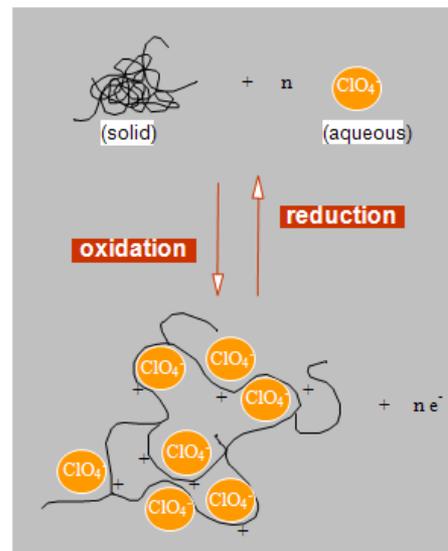
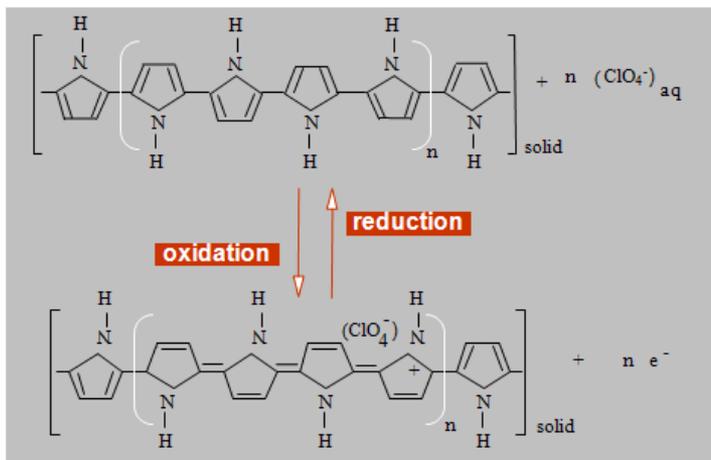
• Extremely low peroxide generation on Pt-ceria praseodymium-supported catalysts

# Surface Areas and Specific Activities Pt/Ceria/C

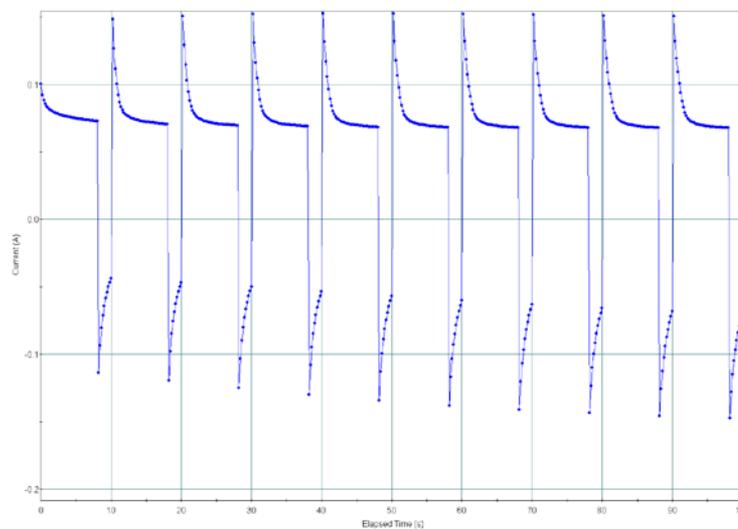
	IPA inks uniform electrode coverage				
	Specific surface areas m <sup>2</sup> /g			Mass activity at 0.9 V vs. RHE A/g	Specific activity at 0.9V vs. RHE mA/cm <sup>2</sup>
	H UPD	CO with bckgnd	CO w/o bckgnd		
Pt 101006 on CeO <sub>2</sub> /Gd/C 7.6%Pt					
Pt 101027A on CeO <sub>2</sub> /Pr/C 4.8%Pt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

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

# Electrochemical Oxidation/Reduction of Polypyrrole

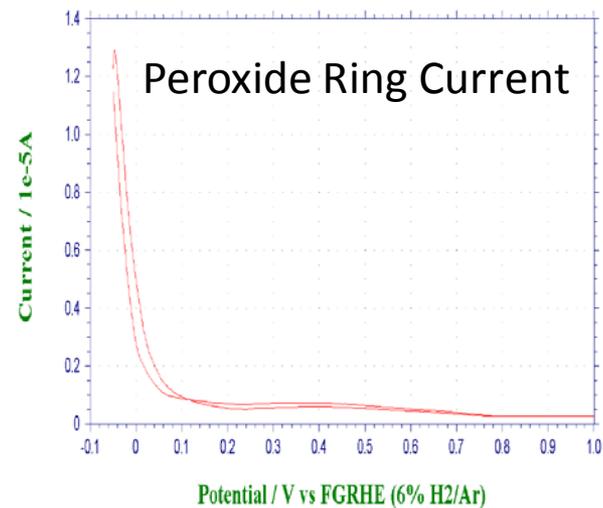
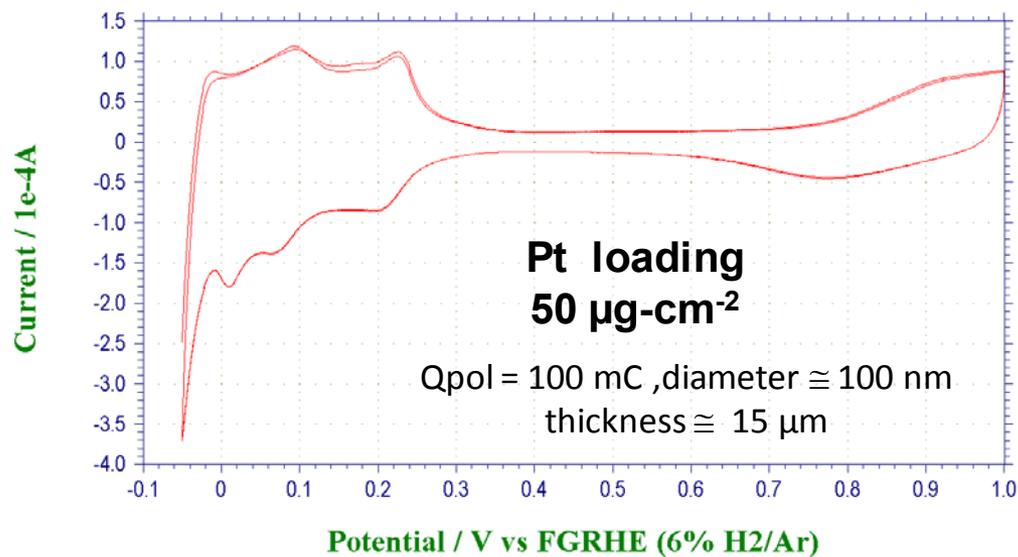
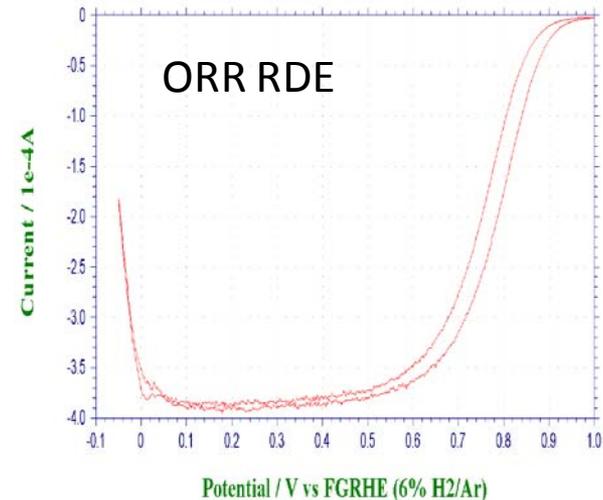
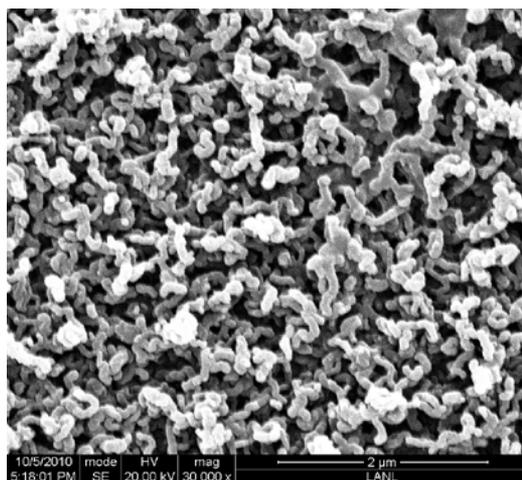
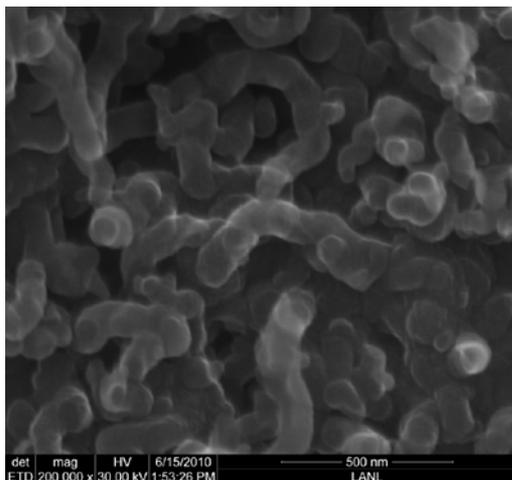


## Electrochemical Cell



PPy +  
 $\text{LiClO}_4$

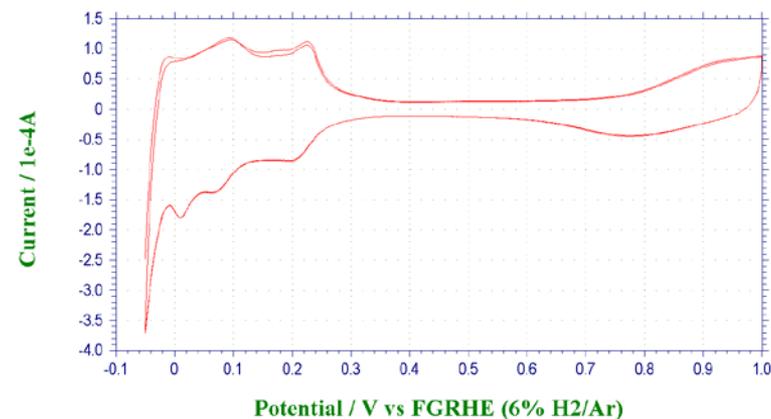
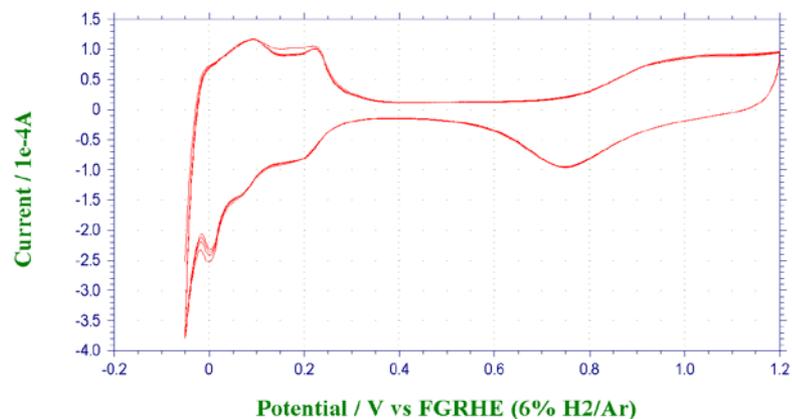
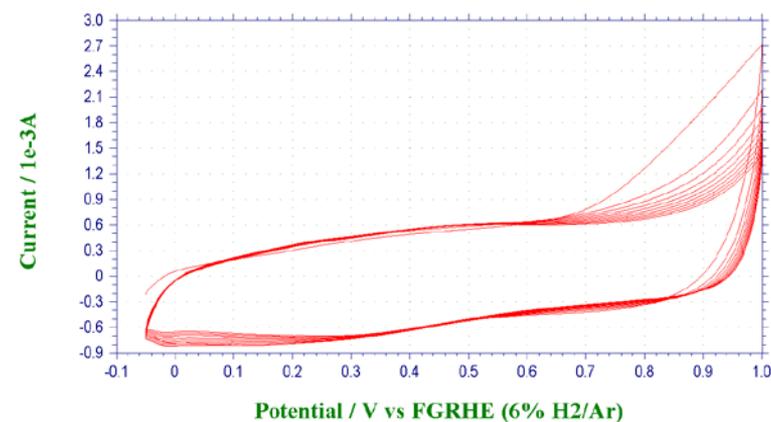
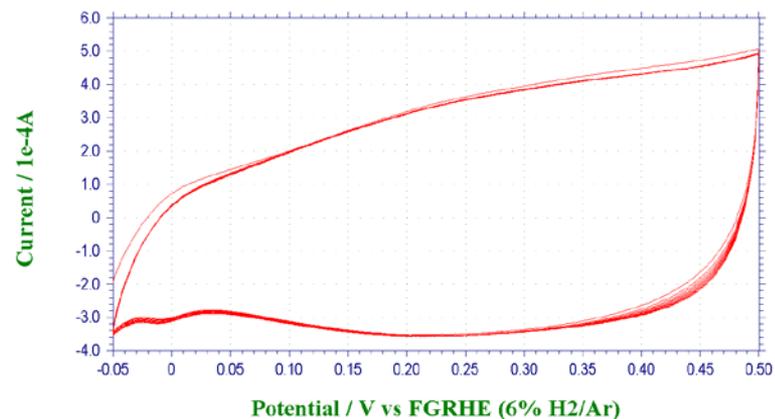
Multipotential  
steps  
+1V (8s) / -0.1V (2s)  
vs RHE



- Surface area corresponds to ~14 m<sup>2</sup>/gram; 20 nm thick Pt layer

# Electrochemistry of Pt Coated PPY/starch Nanowires

Q<sub>pol</sub> = 100 mC  
 diameter  $\cong$  100 nm  
 thickness  $\cong$  15  $\mu$ 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

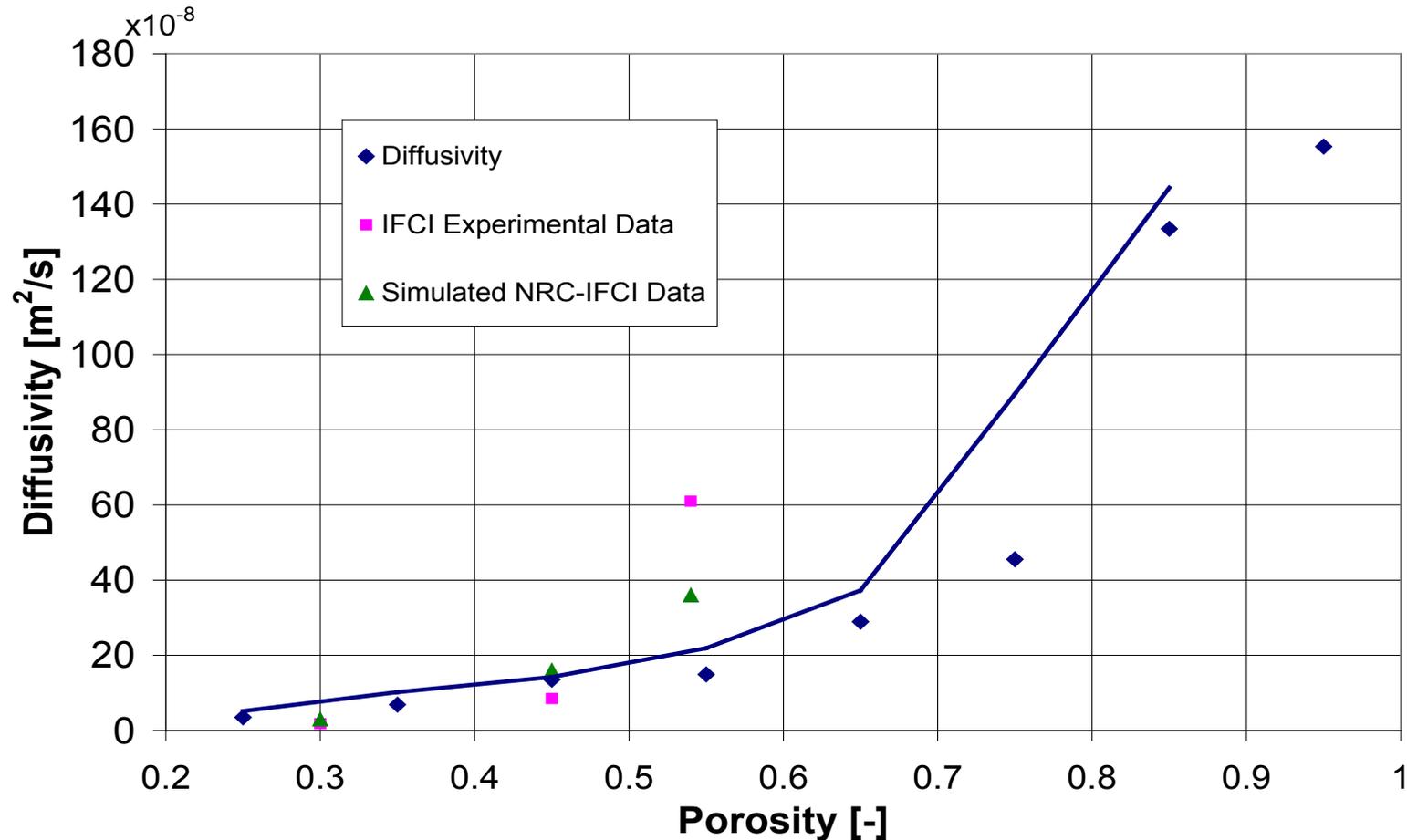
# Acknowledgement

*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

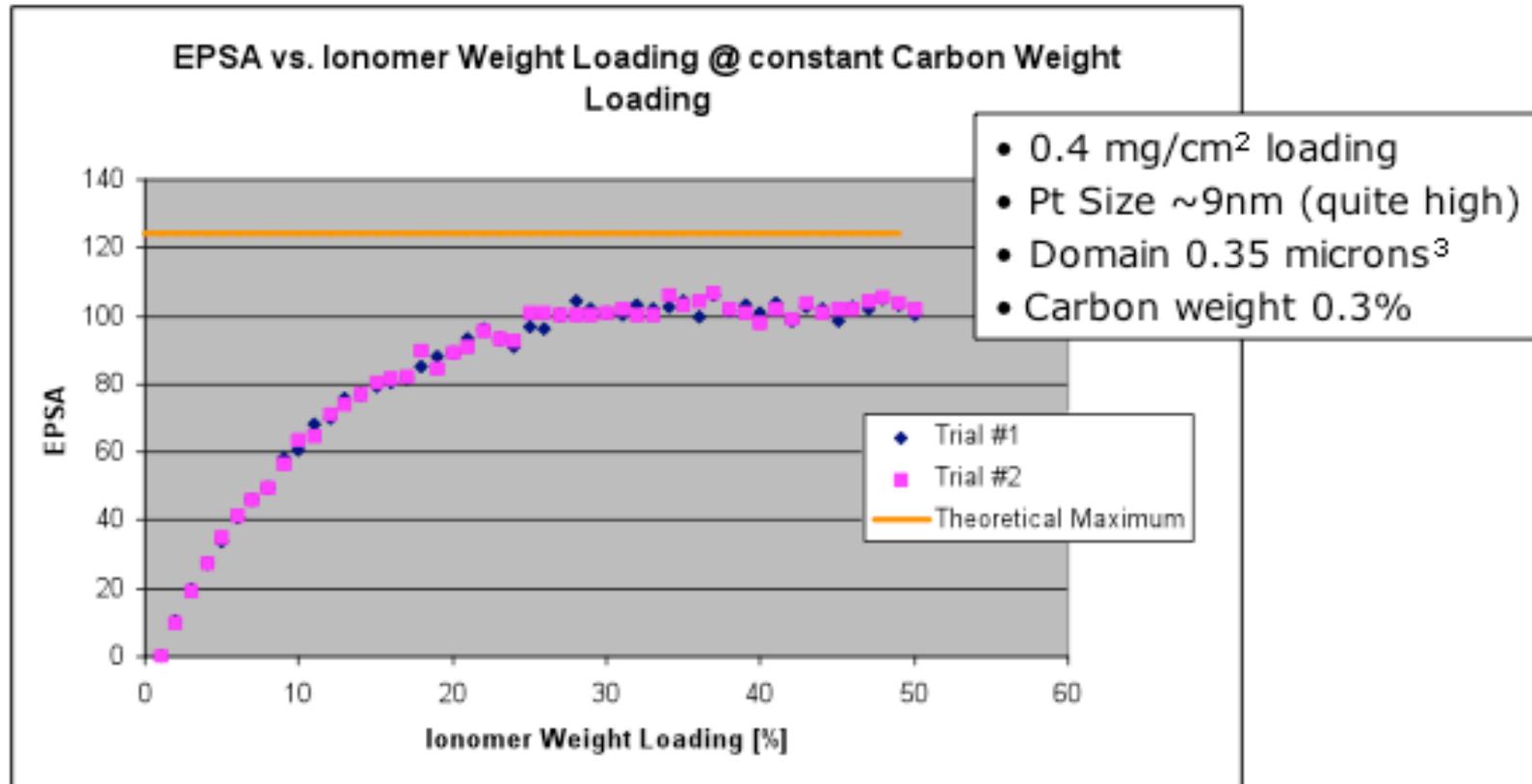
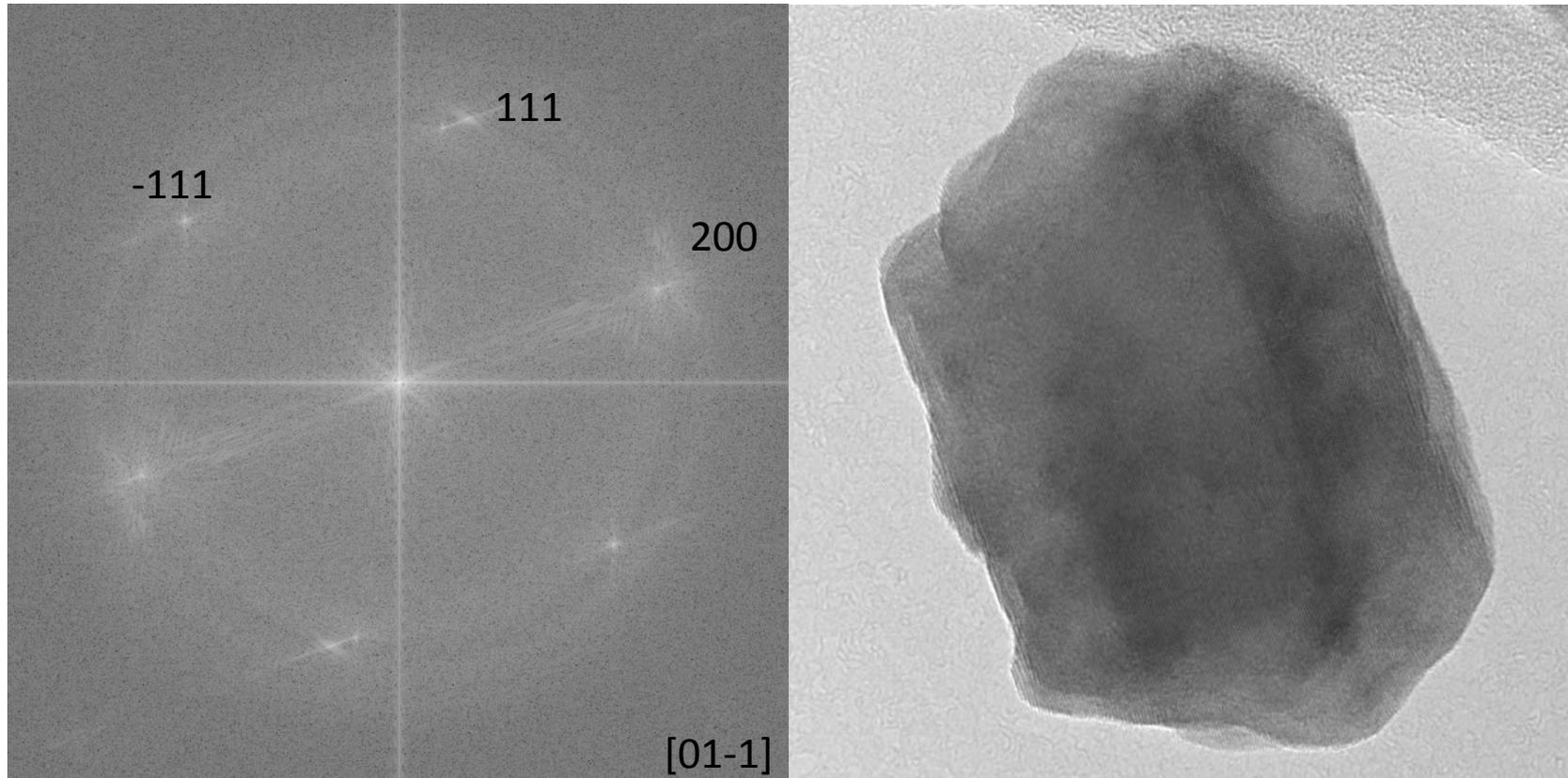


Illustration of the effect of ionomer wt loading on maximization of the available surface area of Pt.

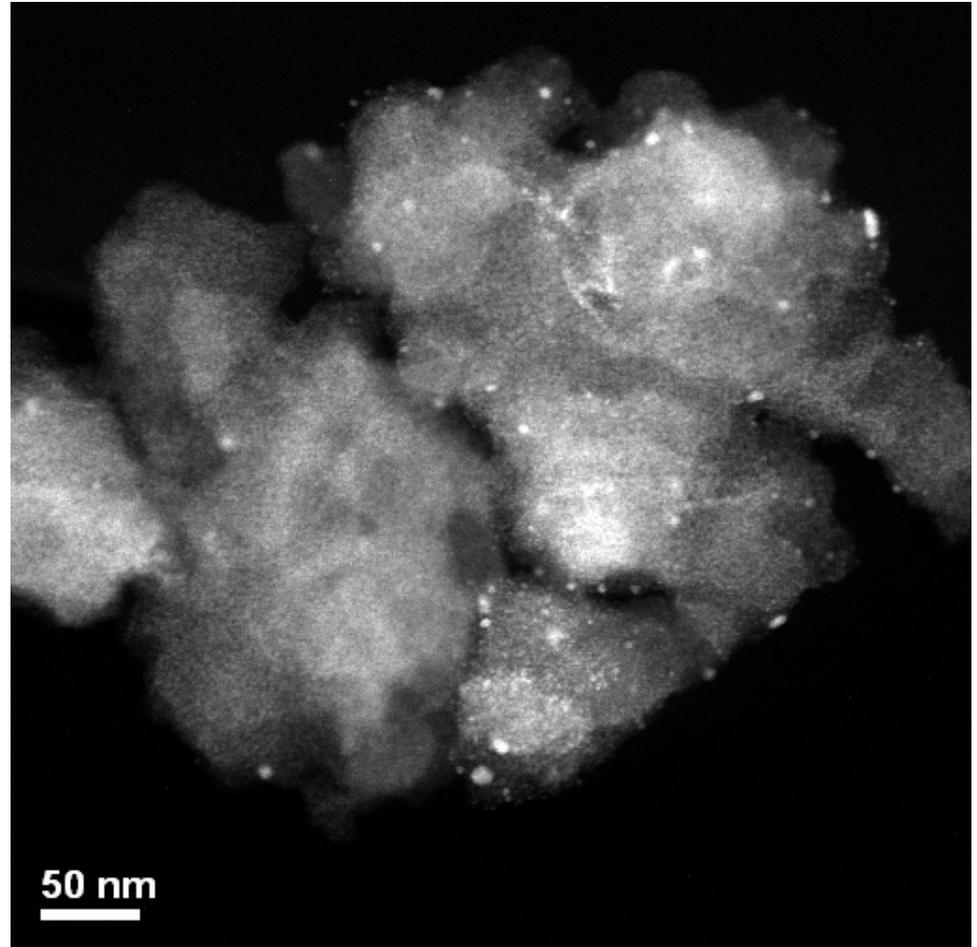
The maximum surface area is typically achieved at ~30 wt%

# HRTEM PtPd Nanoplates

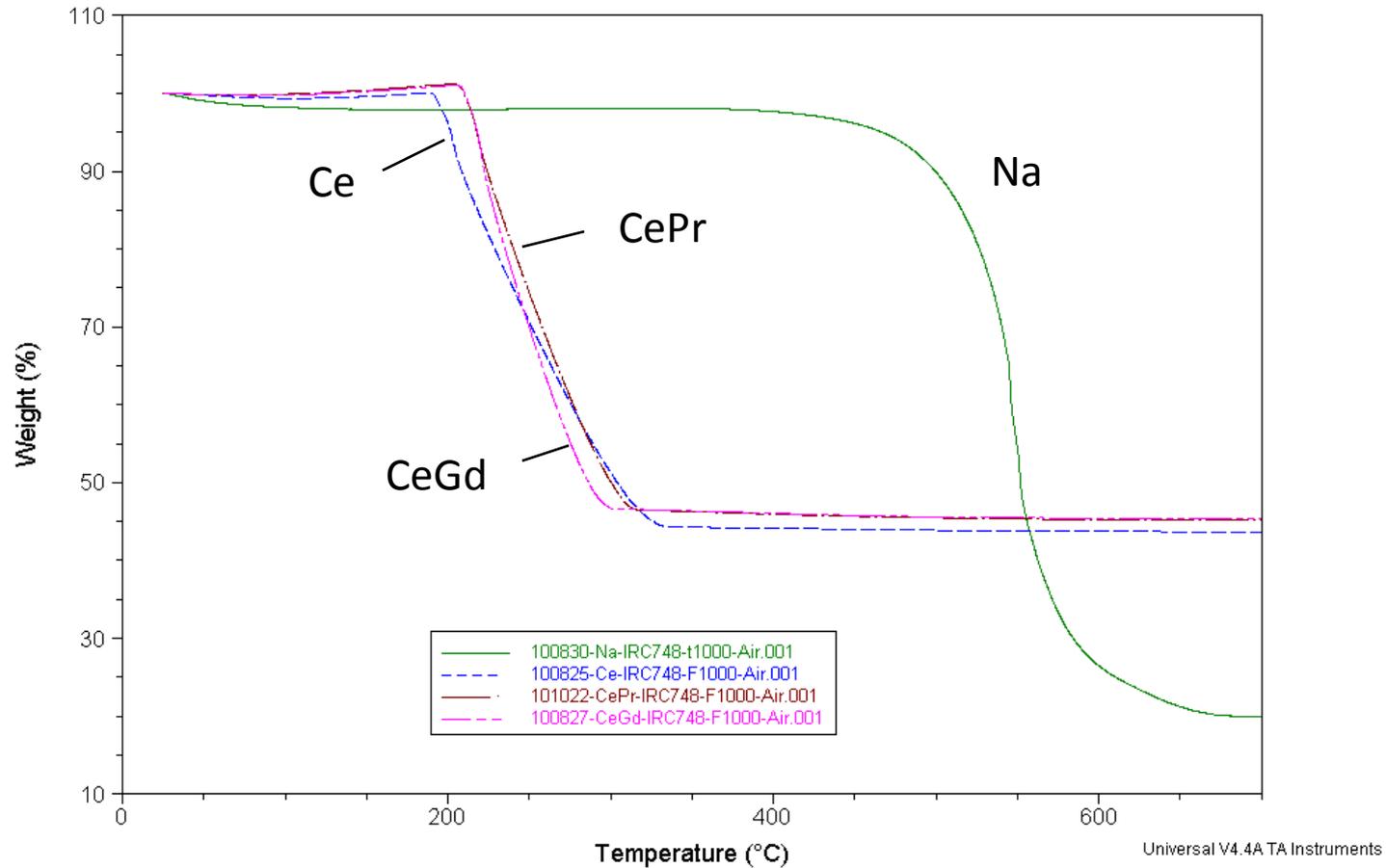


High resolution TEM of PtPd nanoplates

- HAADF-STEM image showing adjacent CeO<sub>2</sub>+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  $\sim 200^{\circ}\text{C}$