

# Advanced Cathode Catalysts

PI - Organization

|                                  |   |  |
|----------------------------------|---|--|
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| <b>Karren More</b>               | - | <b>Oak Ridge National Laboratory</b>           |
| <b>Debbie Myers</b>              | - | <b>Argonne National Laboratory</b>             |
| <b>Andrzej Wieckowski</b>        | - | <b>University of Illinois Urbana-Champaign</b> |
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*Project ID: FCP 27*

# Project Timeline & Budget

## Timeline

- **Start date** – New project started in FY07
- **End date** – Four-year duration

## Budget

| Period | Amount, \$                         |                  |                     |
|--------|------------------------------------|------------------|---------------------|
|        | DOE Share                          | Contractor Share | Total Funding       |
| FY06   | <i>New project started in FY07</i> |                  |                     |
| FY07   | 1,980,000<br>(96%)                 | 80,000<br>(4%)   | 2,060,000<br>(100%) |

# Technical Targets & Barriers

## DOE Technical Targets

- Precious metal loading: **~ 0.25 mg/cm<sup>2</sup>**  
*(with ~ 0.05 mg/cm<sup>2</sup> anode)*
- Cost: **< 5 \$/kW**
- Activity (precious-metal based catalysts): **0.44 A/mg<sub>Pt</sub> at 0.90 V<sub>iR-free</sub>**  
**720 μA/cm<sup>2</sup> at 0.90 V<sub>iR-free</sub>**
- Activity (precious-metal free catalysts): **> 130 A/cm<sup>3</sup> at 0.80 V<sub>iR-free</sub>**
- Durability with cycling: **5,000 hours at T ≤ 80°C**  
**2,000 hours at T > 80°C**
- Electrochemical surface area (ESA) loss: **< 40%**

## Technical Barriers Addressed

- **A. Durability** (catalyst, electrode layer)
- **B. Cost** (catalyst, MEA)
- **C. Electrode Performance** (ORR overpotential, O<sub>2</sub> mass transport)

# Participating Organizations & Roles



## – catalysts with ultra-low Pt content

R. Adzic (PI), K. Sasaki, M. Shao, M. Vukmirovic, J. Wang, J. Zhang



## – new-generation chalcogenides

A. Wieckowski (PI), P. K. Babu, B. Wang



## – non-precious metal composites

P. Zelenay (PI), R. Bashyam, E. Brosha, J. Chlistunoff, S. Conradson, F. Garzon, C. Johnston, R. Mukundan, J. Spendelow, J. Valerio, M. Wilson



The University of New Mexico

## – open-frame catalyst structures

P. Atanassov (PI), K. Artyushkova, T. Olson, S. Pylypenko, E. Switzer



## – nanostructure catalyst supports

Y. Yan (PI), L. Xu, Z. Chen



## – characterization & durability

D. Myers (PI), A. J. Kropf



## - characterization; *planned start in FY08*

K. More (PI)



CABOT

## – fabrication & scale-up

P. Atanassova (PI), B. Blizanac, Y. Sun

# Objectives

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## Main objective:

Develop oxygen reduction reaction (ORR) catalyst, alternative to pure platinum, capable of fulfilling cost, performance and durability requirements established by the DOE for the polymer electrolyte fuel cell (PEFC) cathode

## Other objectives:

- Investigate new catalyst supports and electrode structures for maximum catalyst utilization
- Determine ORR mechanisms on newly developed catalysts through extensive physicochemical characterization, electrochemical and fuel cell testing
- Optimize catalysts, supports, and electrode structures for maximum activity and/or utilization
- Determine catalyst stability and minimize performance loss over time
- Assure path forward for fabrication and scale-up of viable catalysts

## Three classes of ORR catalysts

- Oxygen catalysts with ultra-low platinum content
- New-generation chalcogenides
- Non-precious metal/heteroatomic polymer nanocomposites

## Novel electrode structures for cathode catalysts

- Open-frame catalyst structures
- Conductive-polymer nanofibers and nanotubes for non-precious metal cathode structure

## Extensive catalyst characterization

### Catalyst performance durability

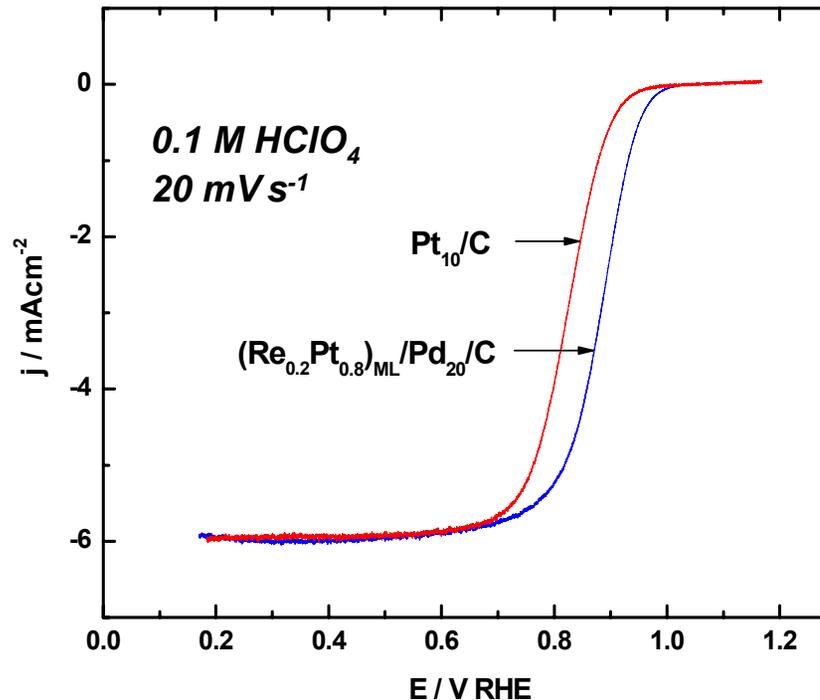
- Fuel cell performance durability
- Catalyst dissolution rates and mechanisms

## Fabrication & scale-up of practically viable cathode catalysts

# Catalysts with Ultra-low Pt Content

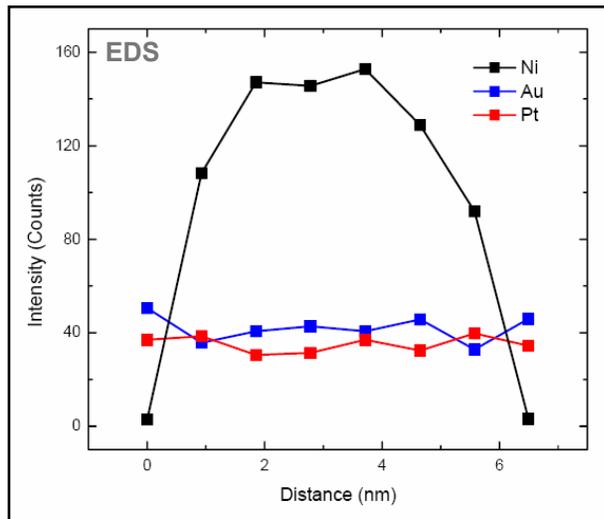
Stabilization of  $\text{Pt}_{\text{ML}}/\text{Me}/\text{C}$  and  $\text{Pt}/\text{C}$ , and reduction of precious metal content in  $\text{Pt}_{\text{ML}}$  catalysts using:

- mixed Pt-metal monolayer catalysts,
- non-precious-metal core/precious-metal shell nanoparticle catalysts
- stabilization of  $\text{Pt}/\text{C}$  by Au clusters
- Pd alloy catalysts

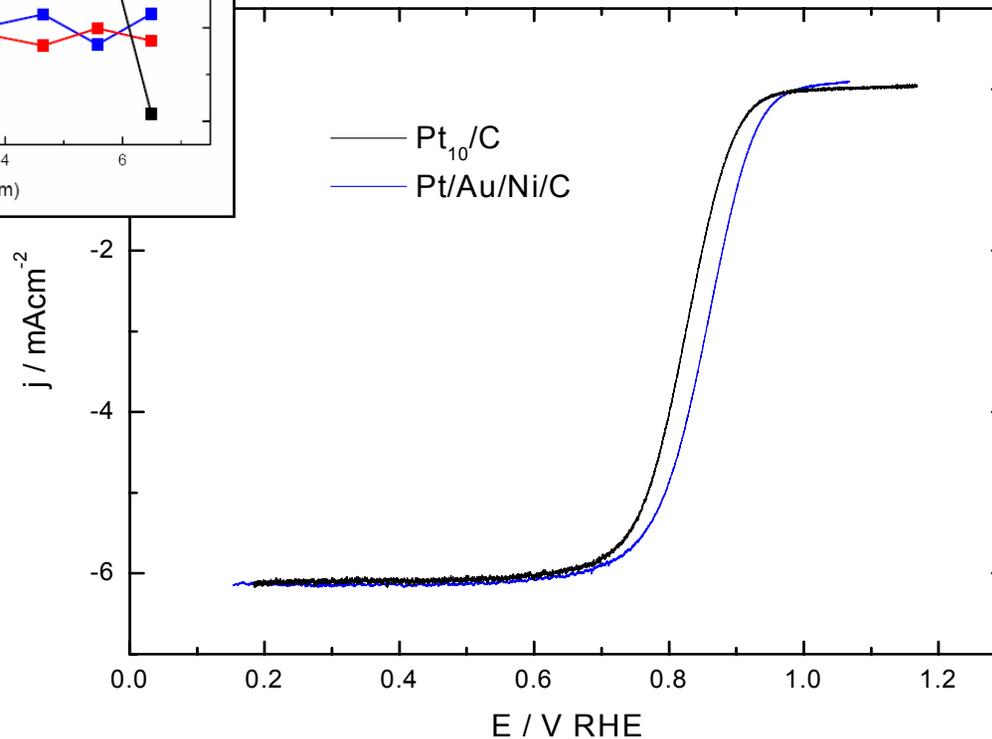


*Pt mass-activity of a mixed  $\text{Pt}_{0.8}\text{Re}_{0.2}/\text{Pd}/\text{C}$  catalyst  $\sim 20\times$  that of  $\text{Pt}/\text{C}$*

# Catalysts with Ultra-low Pt Content: Core-Shell Catalysts

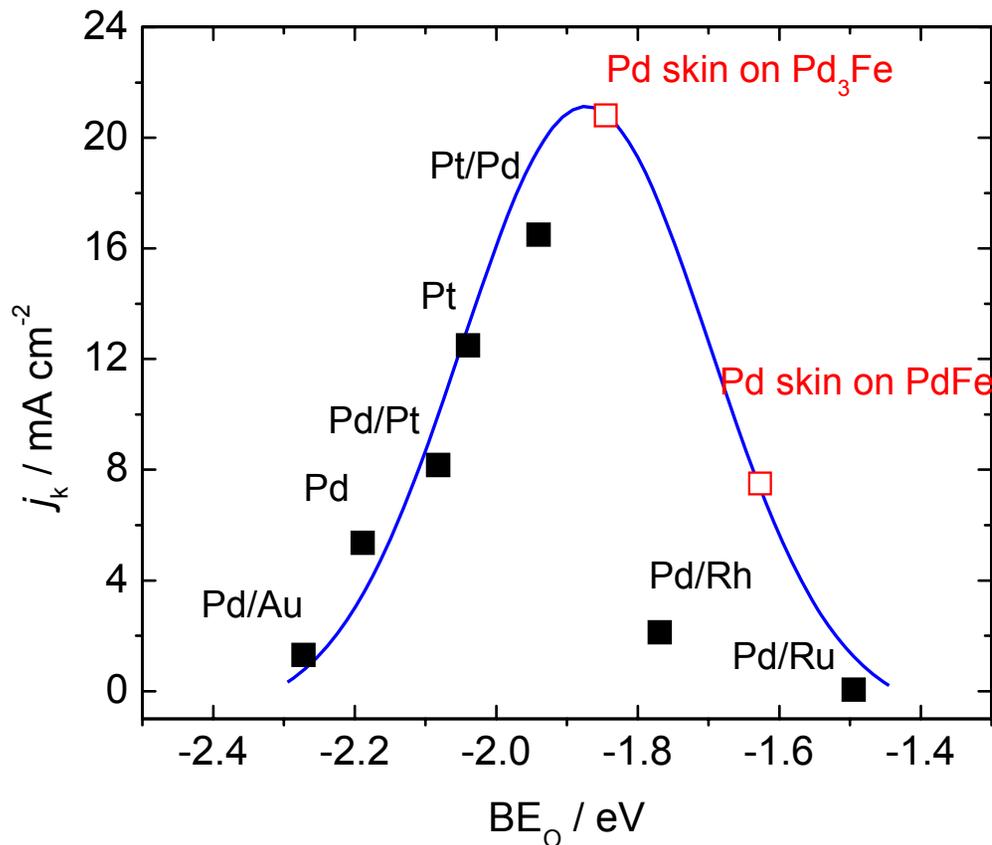


1060  $\mu\text{A cm}^{-2}$  @ 0.90 V  
1.5  $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$  & 2.3  $\mu\text{g}_{\text{Au}} \text{cm}^{-2}$



**Notable electrocatalytic effect with a core-shell  $\text{Pt}/\text{Au}/\text{Ni}/\text{C}$  catalyst relative to “regular” carbon-supported Pt catalyst**

# Catalysts with Ultra-low Pt Content: Experiment & Prediction



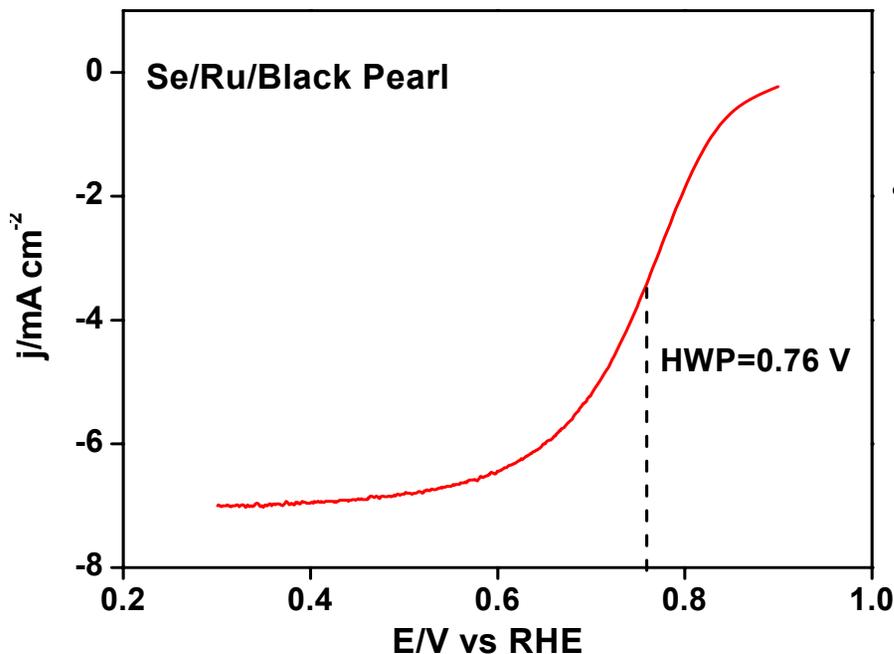
**Experimental RDE oxygen reduction data (solid squares) and predicted ORR current densities for Pd overlayer on Pd<sub>3</sub>Fe(111) and PdFe(111) (open squares) as a function of the calculated oxygen-binding energy.**

*$j_k$  – kinetic current density at 0.8 V vs. RHE; rotation rate 1600 rpm; room temperature*

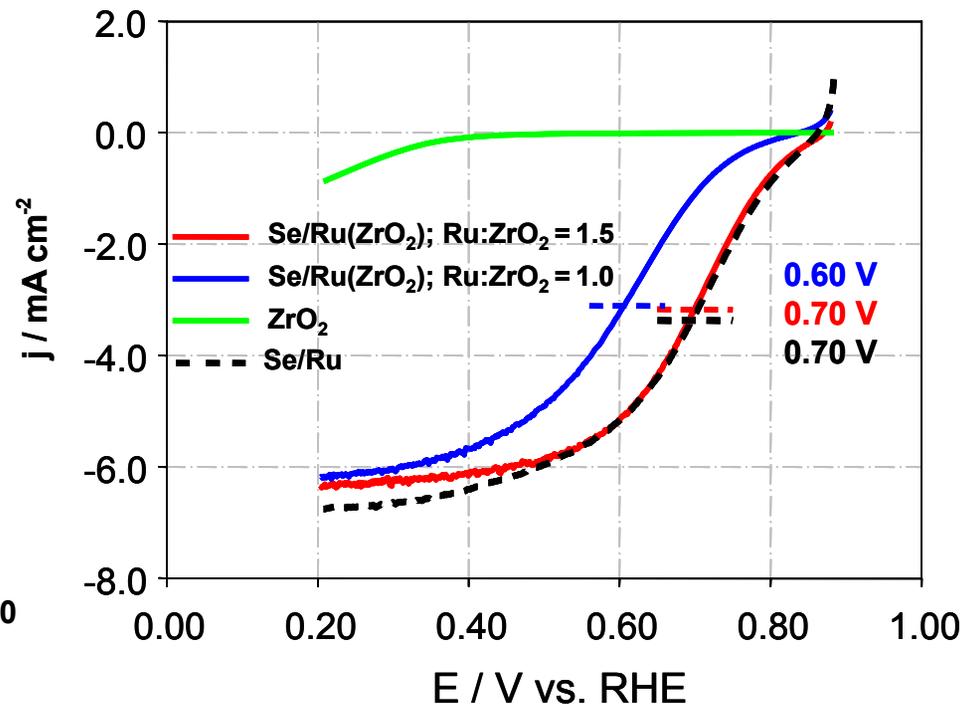
# New-generation Chalcogenides

- Modification of electronic properties of Ru by homogeneous mixing with Fe-group metals; protection of the nanoparticle interior by Ru skin
- Se/Ru/C prepared *via* chemical reduction showing highest ORR activity
- ZrO<sub>2</sub> matrix for high dispersion and possible increase in Se durability

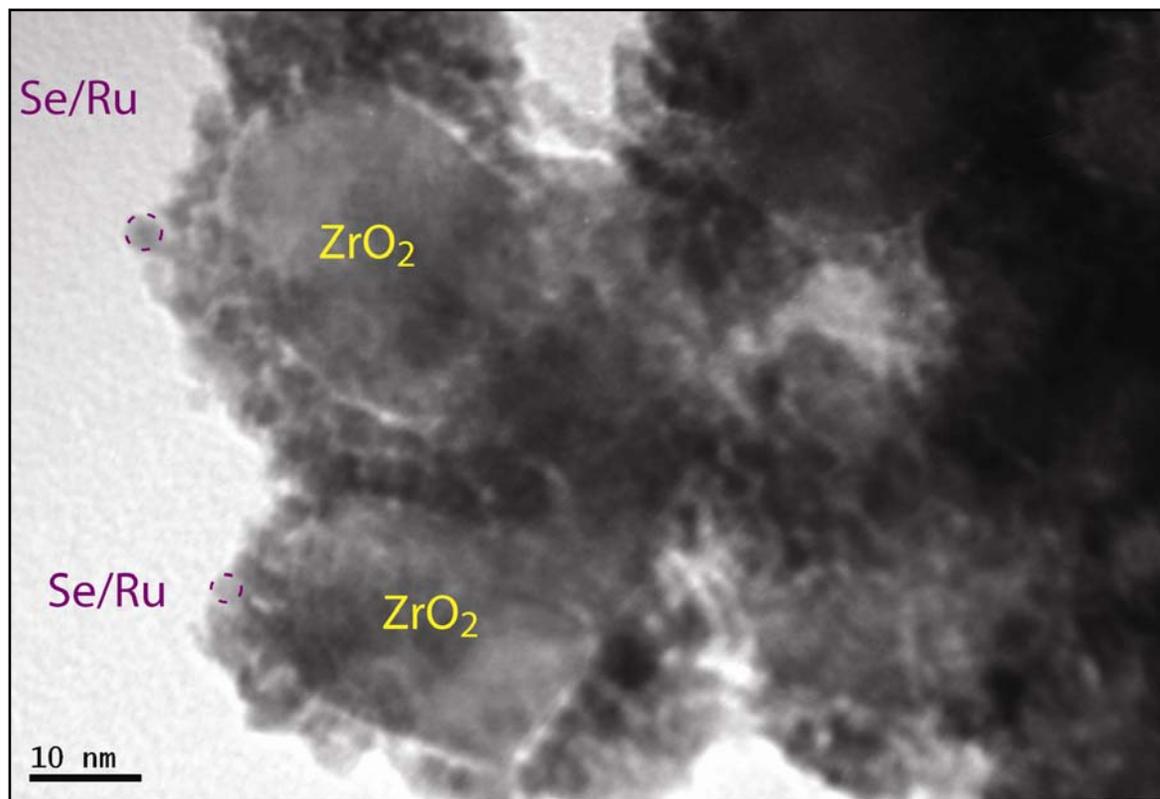
RDE: Au disk at 1600 rpm; 0.1 M H<sub>2</sub>SO<sub>4</sub>, 20 mV s<sup>-1</sup>  
Se-decorated Ru dispersed in Black Pearl



RRDE: Au disk at 1600 rpm; 0.1 M H<sub>2</sub>SO<sub>4</sub>, 20 mV s<sup>-1</sup>  
2-3 nm Se/Ru decorating ZrO<sub>2</sub> solid matrix



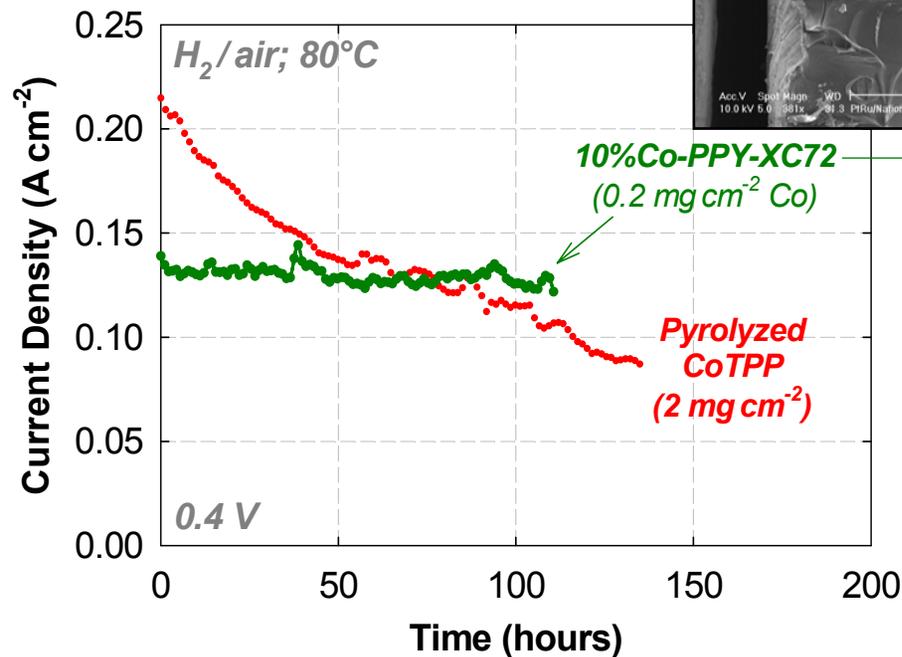
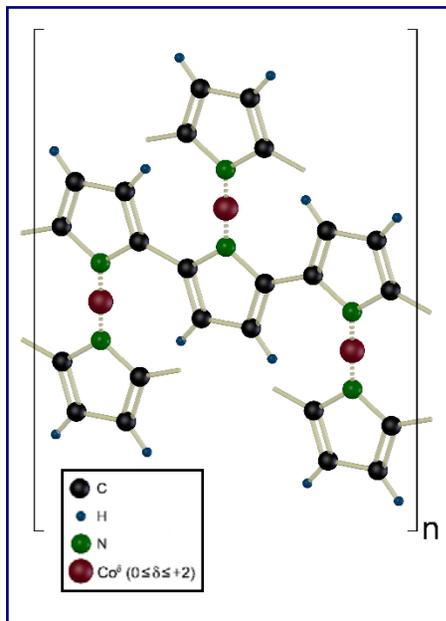
# New-generation Chalcogenides: Se/Ru Particles in ZrO<sub>2</sub> Matrix



*TEM image of 2-3 nm nanoparticles of Se/Ru anchored to ~ 20 nm ZrO<sub>2</sub> support*

# Non-precious Metal Composites

- Development of a family of catalysts based non-precious-metal incorporation into a heteroatomic polymer matrix
- Activity enhancement via effective active-site entrapment and major cathode-structure re-design
- Active-site and ORR-mechanism determination
- Modeling



## Purpose:

- Use semi-empirical methods, e.g. PM3, capable of handling large systems
- Model complexes of transitional metals with organic ligands imitating long polymer chains
- Quantify interaction of molecular oxygen with metal center
- Elucidate possible oxygen reduction mechanisms
- Predict molecular properties and correlate with experimental data for real catalysts
- Determine effects of molecular structure on ORR catalysis
- Define ways to improve catalyst performance

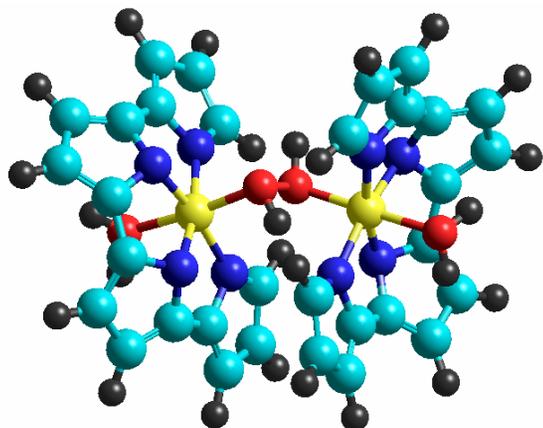
## Example:

- Effect of complex Co-O<sub>2</sub>-Co complex formation and two-electron reduction on the length of O-O bond ( $D_{O-O}$ )
- Method: PM3 (Parametric Method 3)

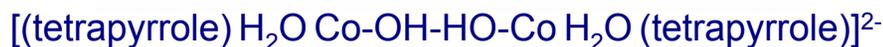
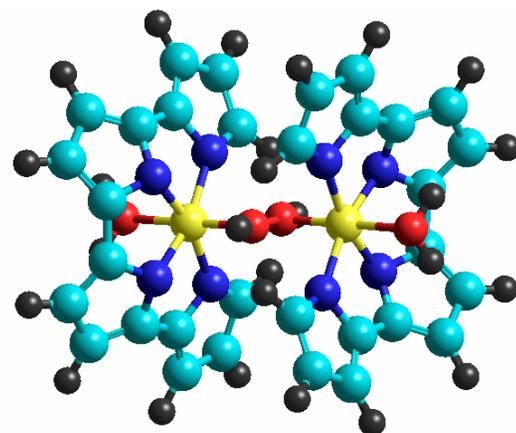
J. J. P. Stewart, *J. Comput. Chem.* **10** (1989) 209; **10** (1989) 221

# Non-precious Metal Composites: Molecular Modeling

$$D_{O-O} = 1.56 \text{ \AA}$$



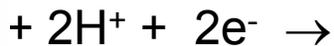
$$D_{O-O} = 1.99 \text{ \AA}$$



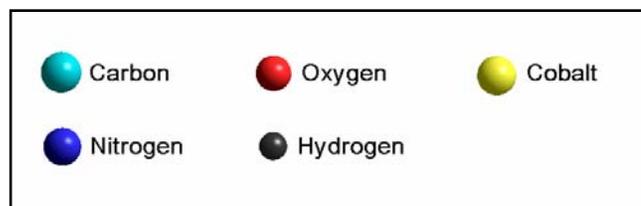
$$D_{O-O} = 1.17 \text{ \AA}$$



dioxygen



$$D_{O-O} = 1.40 \text{ \AA}$$



***Dioxygen interaction with two Co centers significantly weakening O-O bond relative to the O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> reference system***

# Non-precious Metal Composites: Elemental Analysis of Co/PPY/XC72

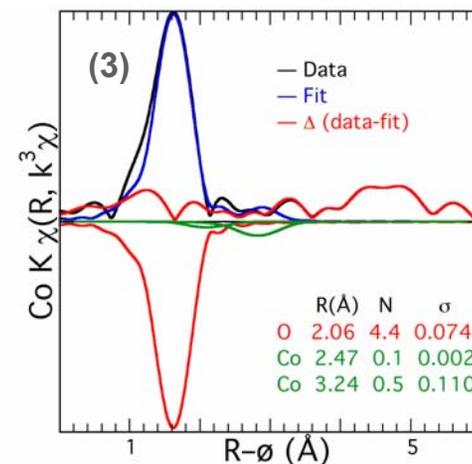
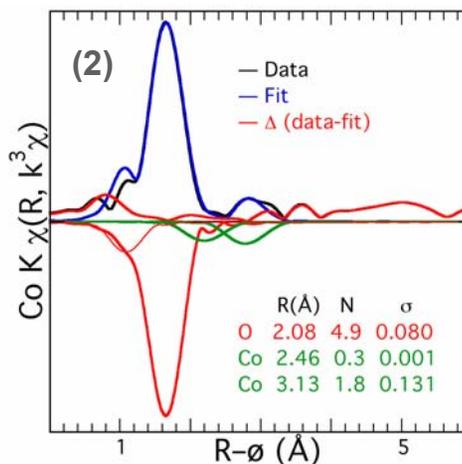
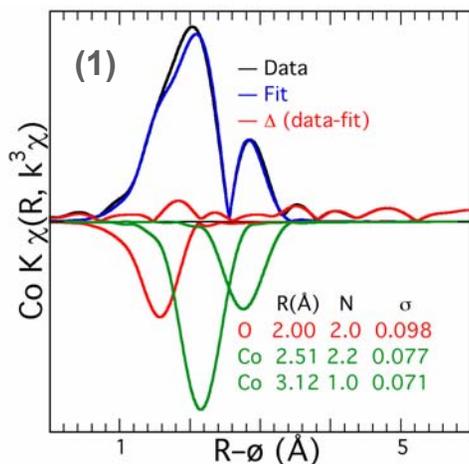
**Methods:** C, N, S - combustion method, except for N in XC72 (by Kjeldahl method);  
O - pyrolysis; B, Co - ICP; H - not determined

| Sample   | Elements (Weight %)                                     | Elements (Atomic %)                                     |
|--|---|---|
| <b>Carbon (Vulcan XC72)</b>  | C (97.1), N (0.1), S (1.2)<br>O - <i>not determined</i> | C (99.4), N (0.1), S (0.5)<br>O - <i>not determined</i> |
| <b>PPY/XC72</b><br>PPY 1-hour polymerized  | C (95.3), N (2.2), S(1.1),<br>O (1.6)                   | C (96.5), N (1.9), S (0.4),<br>O (1.2)                  |
| <b>PPY/XC72</b><br>PPY 24-hour polymerized   | C (92.7), N (2.2), S (1.1),<br>O (3.1)                  | C (95.2), N (2.0), S (0.4),<br>O (2.4)                  |
| <b>PPY/XC72</b><br>PPY 1-hour polymerized;<br>then PPY/XC72 reduced<br>using NaBH <sub>4</sub>       | C (93.9), N (2.0), S(1.2),<br>O (2.6), B (<93 ppm)      | C (96.0), N (1.7), S (0.4),<br>O (2.0)                  |
| <b>Co/PPY/XC72</b><br>PPY 1-hour polymerized;<br>then Co/PPY/XC72<br>reduced using NaBH <sub>4</sub> | C (78.2), N (1.6), S (1.0),<br>O (3.1), Co (9.6)        | C (85.3), N (1.7), S (0.4),<br>O (2.8), Co (2.4)        |

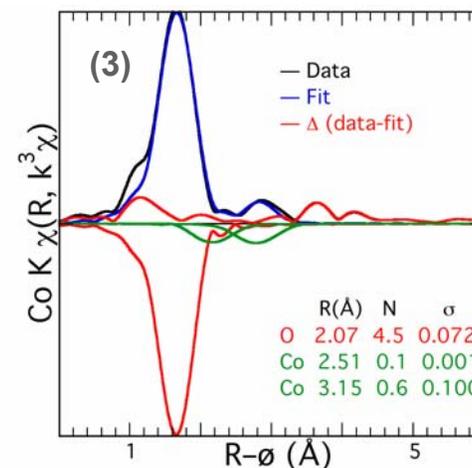
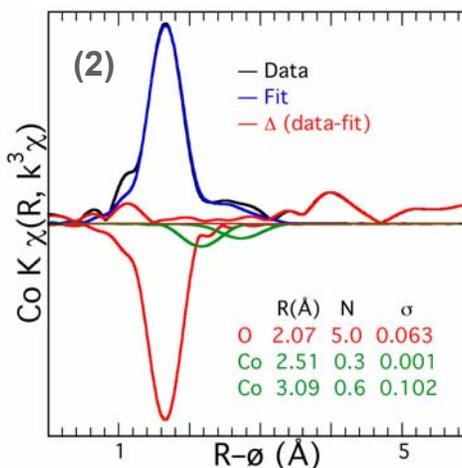
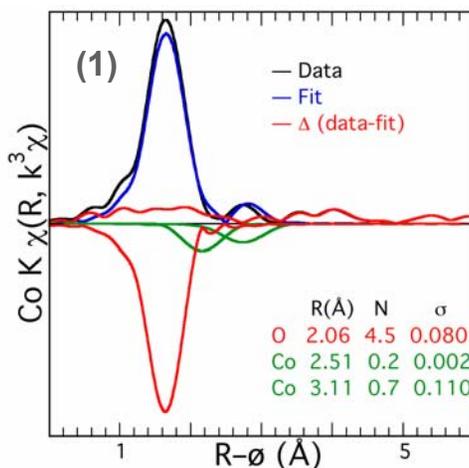
**Co-to-N ratio in the Co/PPY/XC72 possibly too high**

# Non-precious Metal Composites: XAFS of Co/PPY/XC72 – Species I

as-synthesized



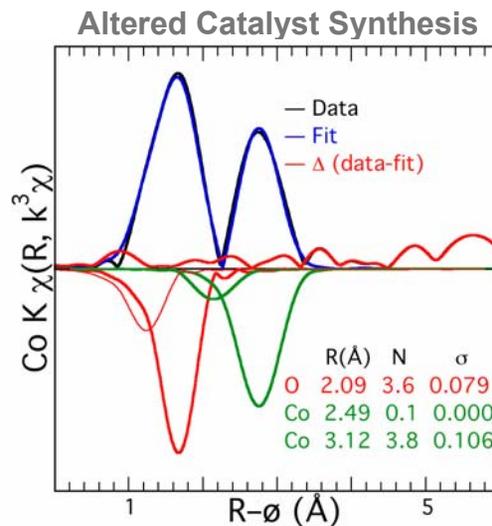
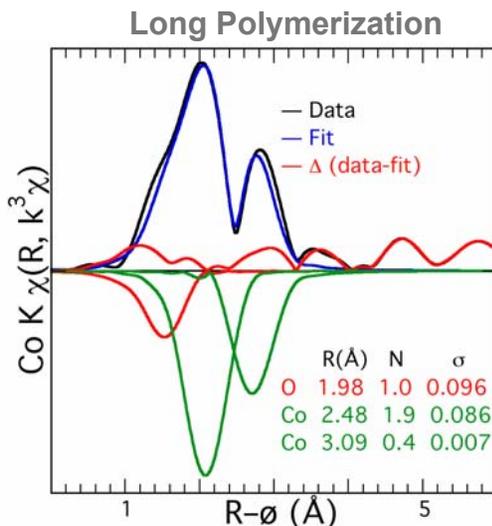
after fuel cell operation



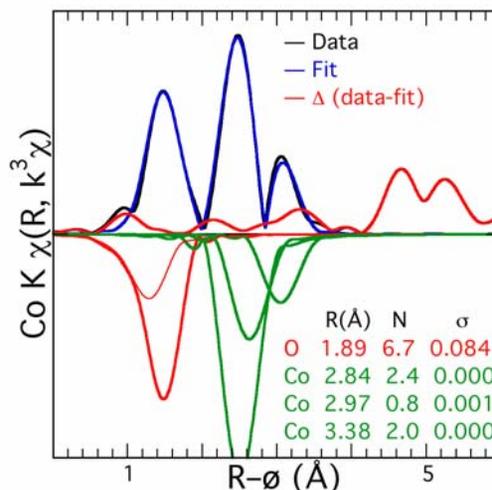
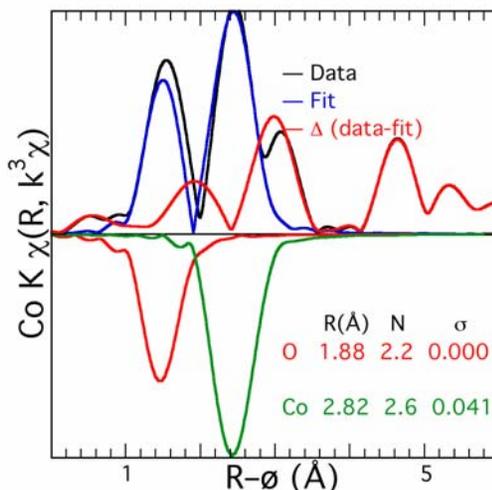
**Despite varying fractions of three components in as-synthesized catalyst, Co speciation after fuel cell operation remains similar (O shell near 2.07 Å and Co shells near 2.51 and 3.11 Å) – mononuclear; only traces of Co metal and oxide.**

# Non-precious Metal Composites: XAFS of Co/PPY/XC72 – Species II

As-synthesized

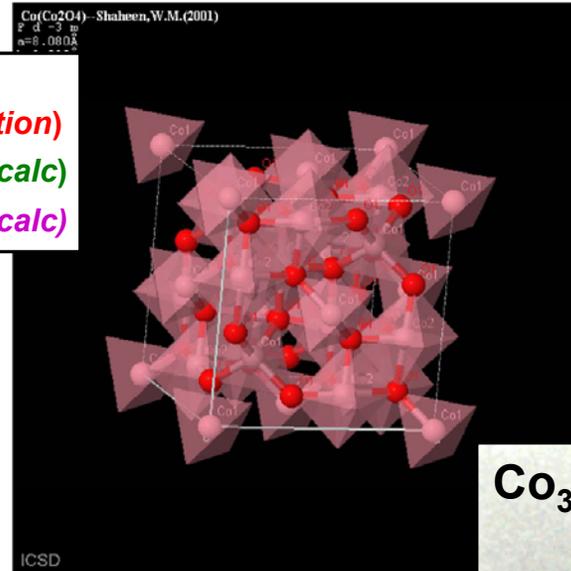
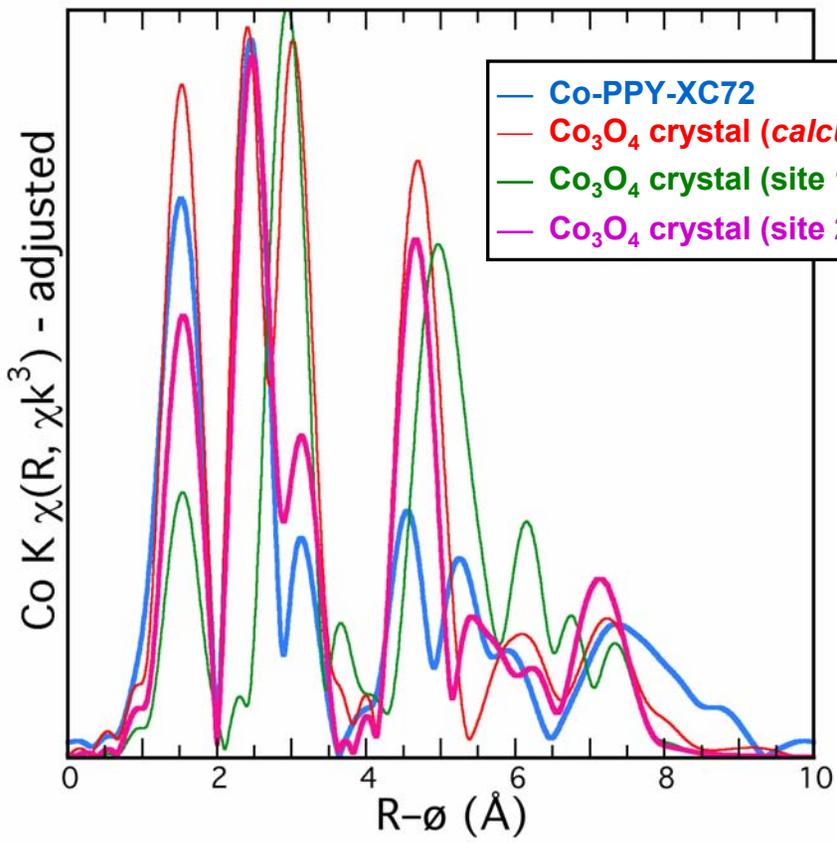


After fuel cell operation

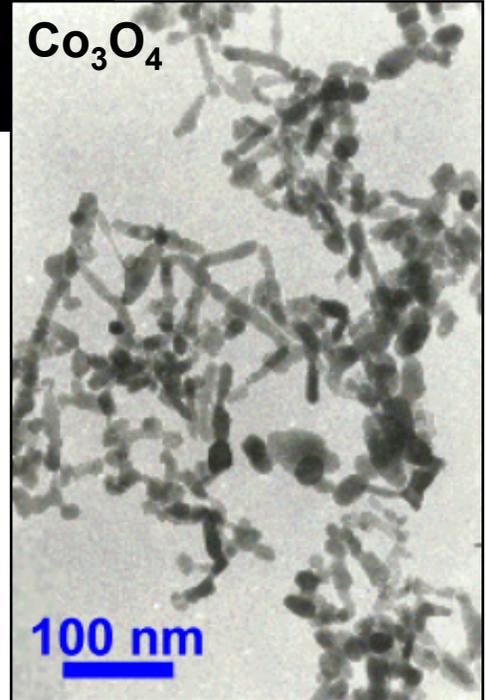


**Two different paths yielding a highly and consistently ordered nanocluster or nanocrystallite. Nearest neighbor Co-O bond length ( $\sim 1.89 \text{ \AA}$ ) much shorter than in "mononuclear" species.**

# Non-precious Metal Composites: XAFS of Co/PPY/XC72 – Species II



Inorganic Crystal Structure Data Base FIZ Karlsruhe, Germany



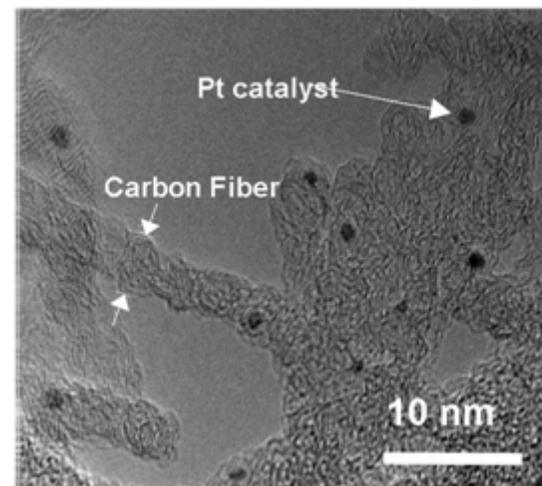
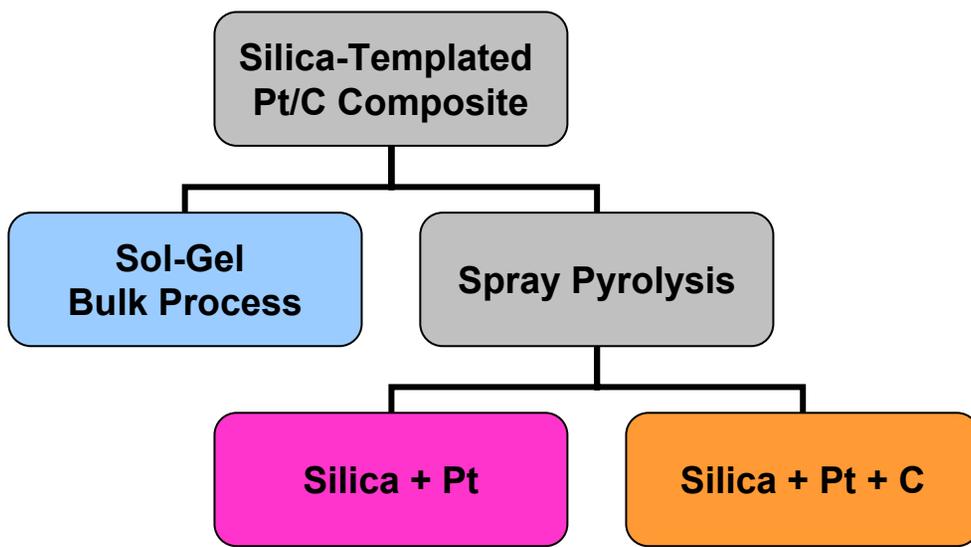
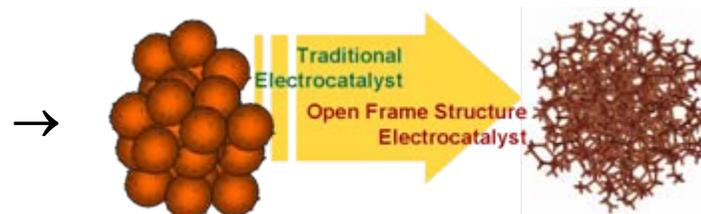
*Although sharing many spectral features with calculated  $\text{Co}_3\text{O}_4$  crystal structure, the “ordered oxide” structure is different. Based on high-R structure, the differences may be caused by different order, possibly rod-like morphology.*

Nanostructured & Amorphous Materials, Inc. ([www.nanoamor.com](http://www.nanoamor.com))

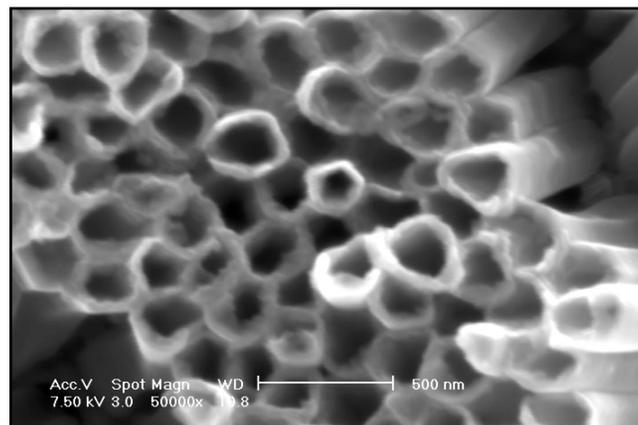
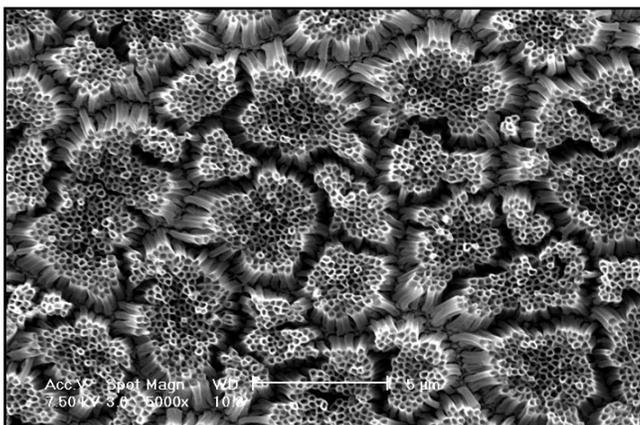
# Novel Electrode Structures

- Improved oxygen transport and precious-metal catalyst utilization
- Increased non-precious catalyst loading
- Tunable hydrophobicity/hydrophilicity
- Enhanced stability
- Efficient H<sub>2</sub>O management

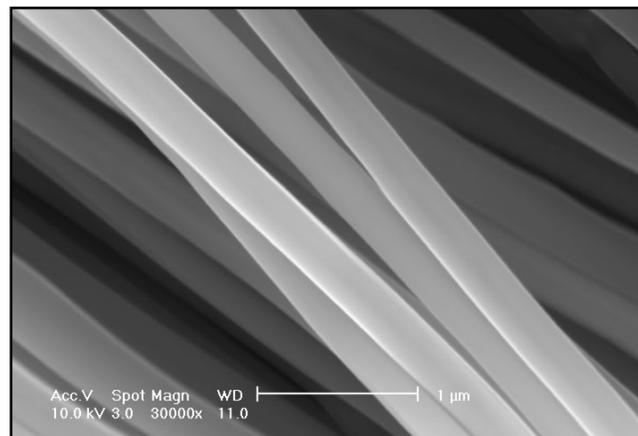
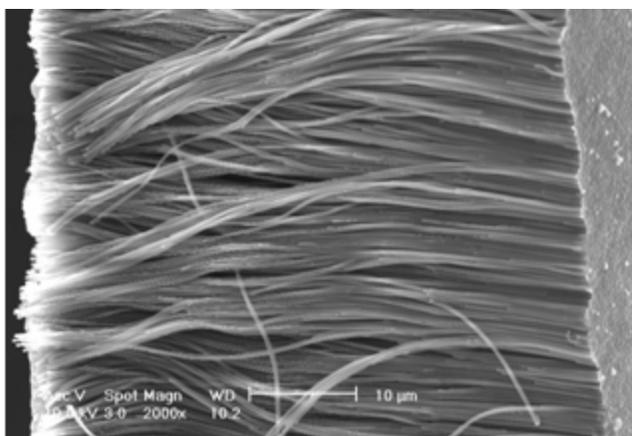
From Decorated Particles to Open-frame Networks



# Novel Electrode Structures: Conductive Nanostructures



*PPY nanotubes by electrochemical polymerization*

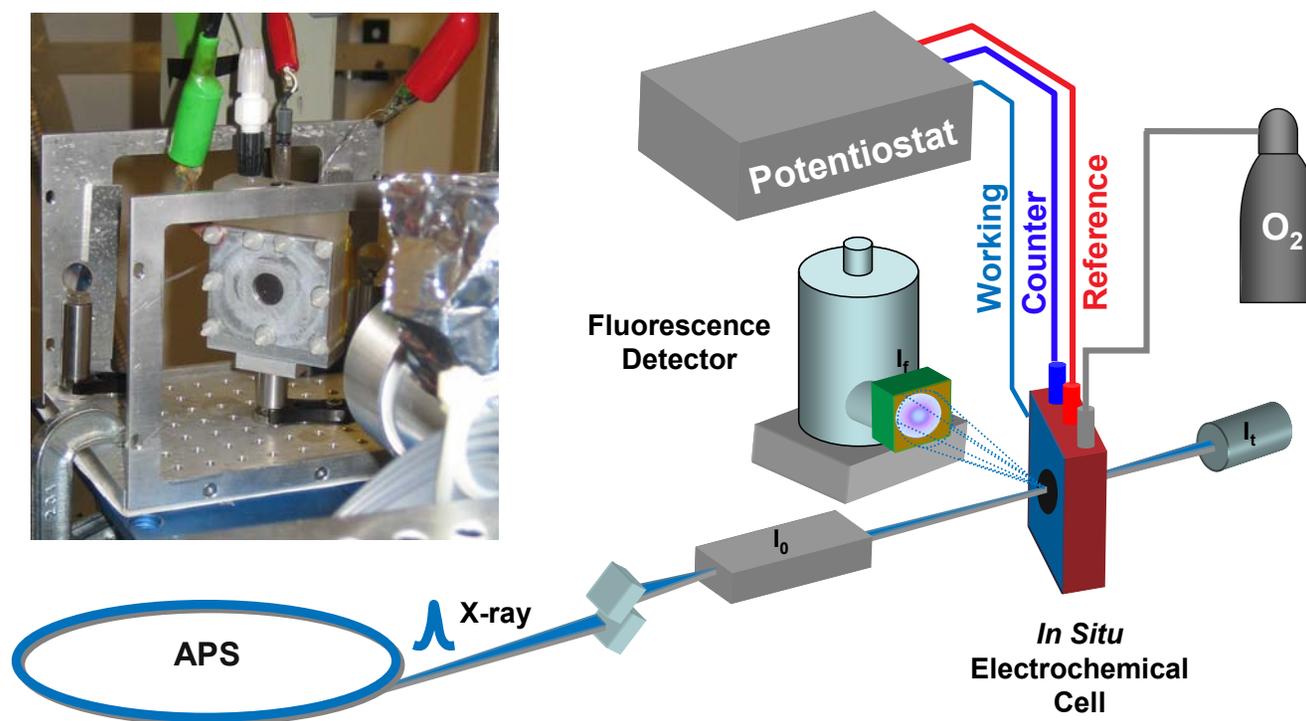


*PPY nanowires by chemical polymerization*

***Electrochemically- and chemically-synthesized polymeric nanostructures as catalyst supports with tunable hydrophilic/hydrophobic properties***

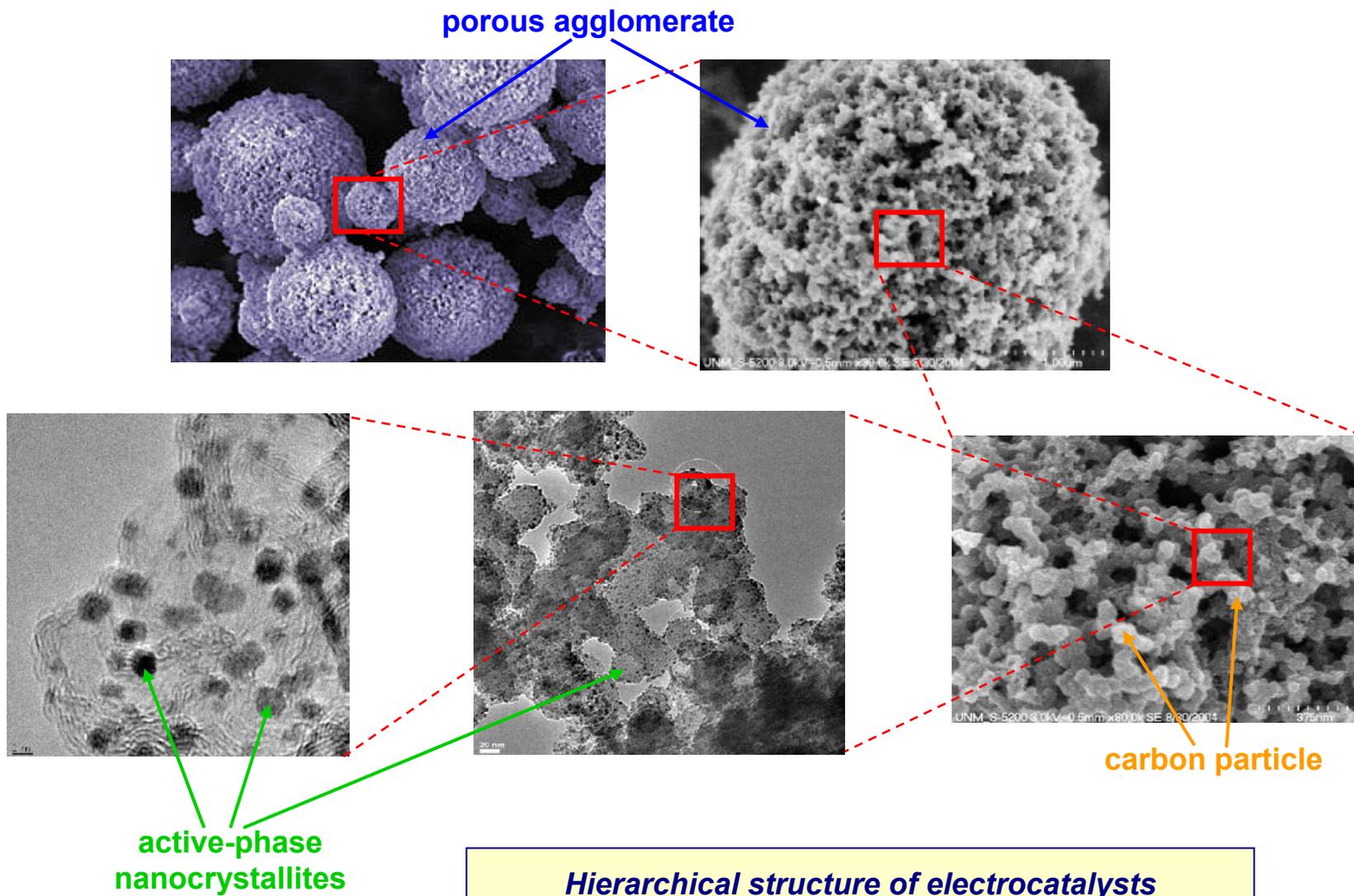
# Extensive Catalyst Characterization

- Stability characterization of advanced cathode electrocatalysts using catalyst dissolution measurements
- Determination of the rates and mechanisms of catalyst degradation
- Pre- and post-polarization *ex situ* spectroscopic and microscopic analyses of the catalyst materials; *in situ* x-ray spectroscopic and scattering studies

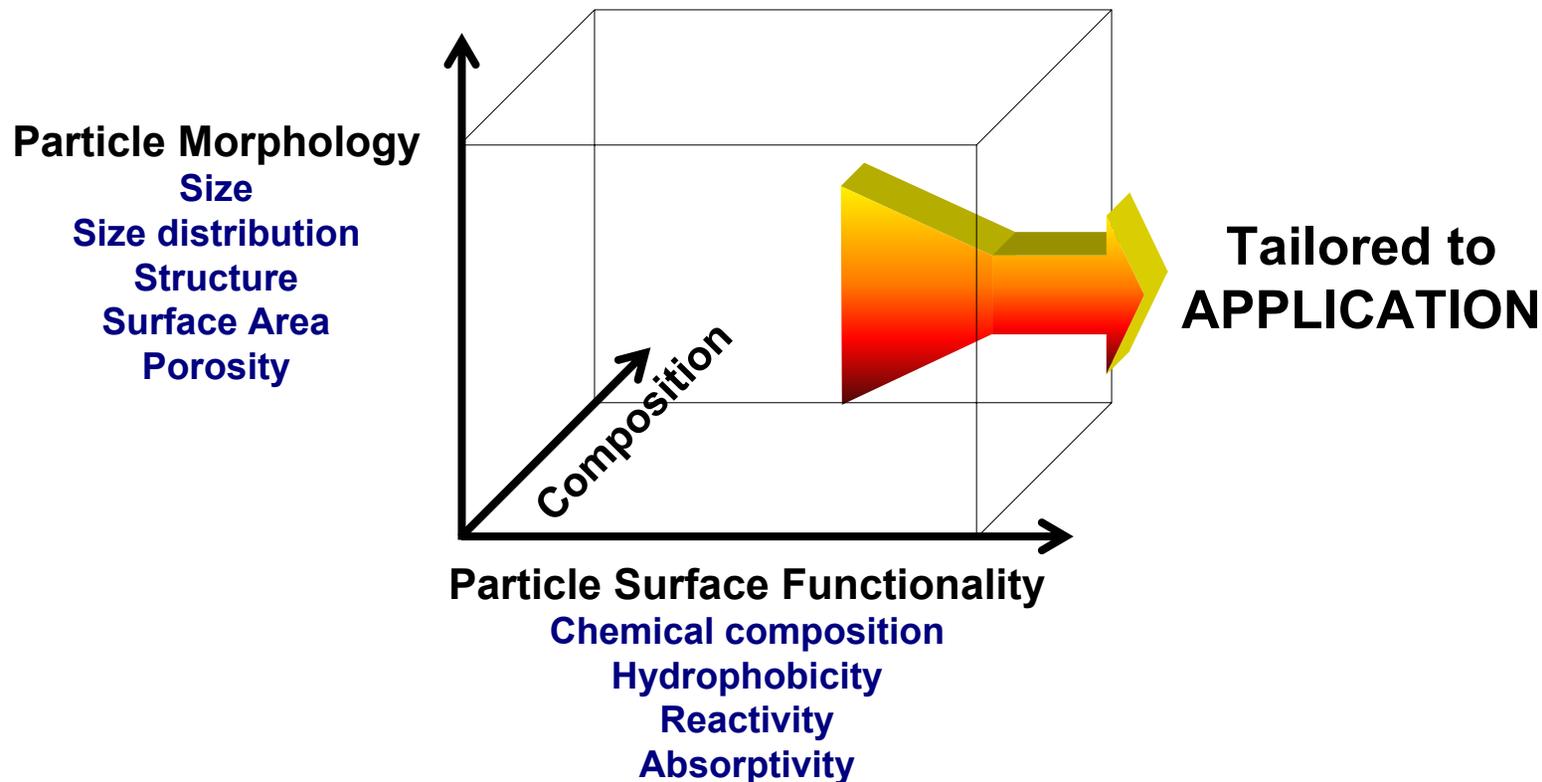


*In situ* X-ray absorption spectroscopy for probing ORR active-site identity

# Scale-up and Fabrication of Practically Viable Catalysts



# Scale-up and Fabrication of Practically Viable Catalysts



*Controlling particle (i) morphology, (ii) composition, and (iii) surface functionality through spray-based powder manufacturing*

## **Task 1: Nanoparticle Catalysts with Ultra-low Platinum Content**

- Synthesis of Pt-metal monolayer catalyst(s)
- Synthesis of core-shell nanoparticle catalyst(s)
- Synthesis of Au-modified Pt nanoparticle catalyst
- Synthesis of Pd alloy nanoparticle catalyst(s)

## **Task 2: New-Generation Chalcogenides**

- Synthesis of Te/Ru nanoparticle catalysts
- Synthesis of Se/Me/Ru and Te/Me/Ru nanoparticle catalysts
- Advanced synthesis development

## **Task 3: Non-precious Metal/Heteroatomic Polymer Nanocomposites**

- Synthesis of heteroatomic polymer with mesoporous carbon structure  
(G - surface area, morphology, and catalyst activity)
- Synthesis of heteroatomic polymer(s) on carbon nanotube structure  
(G - conductivity and hydrophobicity)

## FY07 Milestones & Go/No-Go Decisions

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- Introduction of novel approaches synthesis method to (i) vary the type and composition of polymer coordination centers, (ii) facilitate water management, and (iii) improve catalyst activity and durability by heat treatment and other methods (G - material properties)
- Integration of non-precious metals and alloys into heteroatomic polymer (G - material properties)

### **Task 4: Novel Electrode Structures for Cathode Catalysts**

- Synthesis of Pt and PGM alloy nanoparticle catalysts with open frame structures
- Synthesis of polypyrrole nanotubes/nanofibers using both chemical and electrochemical oxidation with template approach and deposit non-precious metal catalyst into polymer matrix (G - conductivity)

### **Task 5: Catalyst Performance Durability – *ongoing, no milestones***

### **Task 6: Fabrication and Scale-up of Practically Viable Cathode Catalysts**

- Evaluate powder synthesis approach for catalyst material(s) and report results (G - catalyst morphology, performance)

## Future Work: Remainder of FY07

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- **Synthesis of Pt monolayer on core-shell nanoparticles using a direct reaction of noble-metal cations with a non-noble particle controlled by strong surfactants**
- **Stability and fuel cell tests of Pt/AuNi/C, Pt/PdCo<sub>5</sub>/C and PtML/Pd<sub>3</sub>Fe and Au clusters-stabilized Pt/PdCo<sub>5</sub>/C and PtML/Pd<sub>3</sub>Fe electrocatalysts**
- **Development of Fe, Co- and Ni-rich chalcogenide catalysts with high ORR activity**
- **Synthesis, fuel cell & RRDE testing of composites based on polypyrrole and transition metals: Cu, Ni and Fe**
- **Demonstration of uncatalyzed and Pt-catalyzed artificial carbon network in a sol-gel derived mesoporous silica matrix**
- **Synthesis and characterization of PPY on carbon nanotubes and provide the sample to LANL for catalyst deposition and MEA testing**
- **Evaluation of large-scale powder synthesis approach most suitable for one or two selected catalysts**

## Future Work: FY08

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- Segregation of Au in AuNi alloy using a micro-powder x-ray diffraction technique
- Method for describing the kinetic current of the hydrogen oxidation reaction on Pt using free energies of activation and the intermediates adsorption
- Reduction in the amount of Ru present in chalcogenide catalysts with maintained high ORR activity
- Complete characterization of oxygen reduction on selected non-precious metal nanocomposites
- Development of non-precious metal catalysts based on heteroatomic polymers other than polypyrrole, e.g. polyaniline, poly(vinyl) pyridine, poly(ethylene dioxy) thiophene
- Demonstrate uncatalyzed and precious metal/non-precious metal catalyzed artificial carbon network formed in a spray pyrolysis sol-gel derived mesoporous silica matrix
- Synthesis of PPY nanofibers that are electronically conducting and provide the samples for LANL for catalyst deposition and MEA testing
- Optimization of large-scale powder synthesis approach most suitable for selected catalysts; physical characterization and fuel cell testing of performance

## Summary

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- This is a new research project focusing on oxygen reduction catalysts in three different classes of materials: (i) catalysts with ultra-low platinum content, (ii) novel chalcogenides, and (iii) non-precious metal/heteroatomic polymer composites
- Development of new catalyst supports (open-frame catalysts, polymeric nanostructures) is an integral part of this effort; such supports are needed for effective use of catalysts in practical fuel cell systems by, for example, allowing significant loadings of catalysts with intrinsically lower ORR activity than Pt
- The project success largely depends on gaining fundamental understanding of oxygen reduction electrocatalysis on relatively little known or unknown catalysts; this makes advanced characterization by electrochemical and non-electrochemical methods, both *in situ* and *ex situ*, absolutely crucial
- Partnership with the industry will assure scale-up of the fabrication process for the most promising catalysts