Hydrogen, Fuel Cells & Infrastructure Technologies Program, 2007 Annual Review
Arlington, Virginia – May 15-18, 2007

Advanced Cathode Catalysts

PI - Organization

Radoslav Adzic - **Brookhaven National Laboratory**
Paolina Atanassova - **Cabot Superior MicroPowders**
Plamen Atanassov - **University of New Mexico**
Karren More - **Oak Ridge National Laboratory**
Debbie Myers - **Argonne National Laboratory**
Andrzej Wieckowski - **University of Illinois Urbana-Champaign**
Yushan Yan - **University of California – Riverside**
Piotr Zelenay (presenter) - **Los Alamos National Laboratory**

Project ID: FCP 27

Timeline

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

Budget

Period	Amount, $		
	DOE Share	Contractor Share	Total Funding
FY06	*New project started in FY07*		
FY07	**1,980,000** (96%)	**80,000** (4%)	**2,060,000** (100%)

DOE Technical Targets

- Precious metal loading: **~ 0.25 mg/cm^2**
  (with ~ 0.05 mg/cm^2 anode)
- Cost: **< 5 $/kW**
- Activity (precious-metal based catalysts): **0.44 A/mg$_{Pt}$ at 0.90 V$_{iR\text{-}free}$**
  720 μA/cm^2 at 0.90 V$_{iR\text{-}free}$
- Activity (precious-metal free catalysts): **> 130 A/cm^3 at 0.80 V$_{iR\text{-}free}$**
- 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_2 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

– 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)

– fabrication & scale-up

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

Objectives

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**

Overall Technical Approach

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

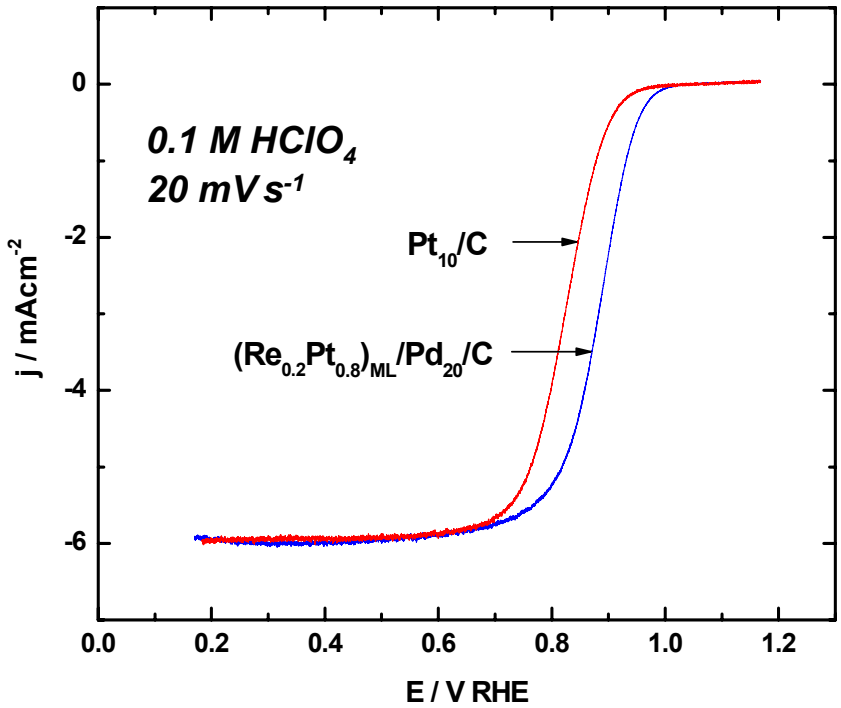
- Fuel cell performance durability
- Catalyst dissolution rates and mechanisms

Fabrication & scale-up of practically viable cathode catalysts

Catalysts with Ultra-low Pt Content

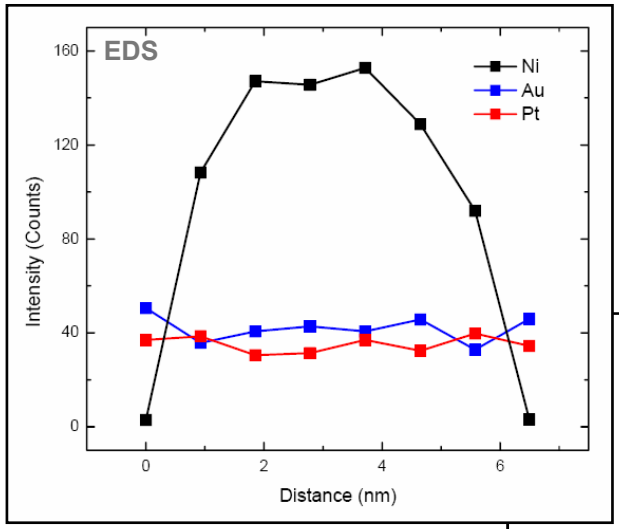
Stabilization of Pt_{ML}/Me/C and Pt/C, and reduction of precious metal content in Pt_{ML} catalysts using:

- **mixed Pt-metal monolayer catalysts,**
- **non-precious-metal core/precious-metal shell nanoparticle catalysts**
- **stabilization of Pt/C by Au clusters**
- **Pd alloy catalysts**



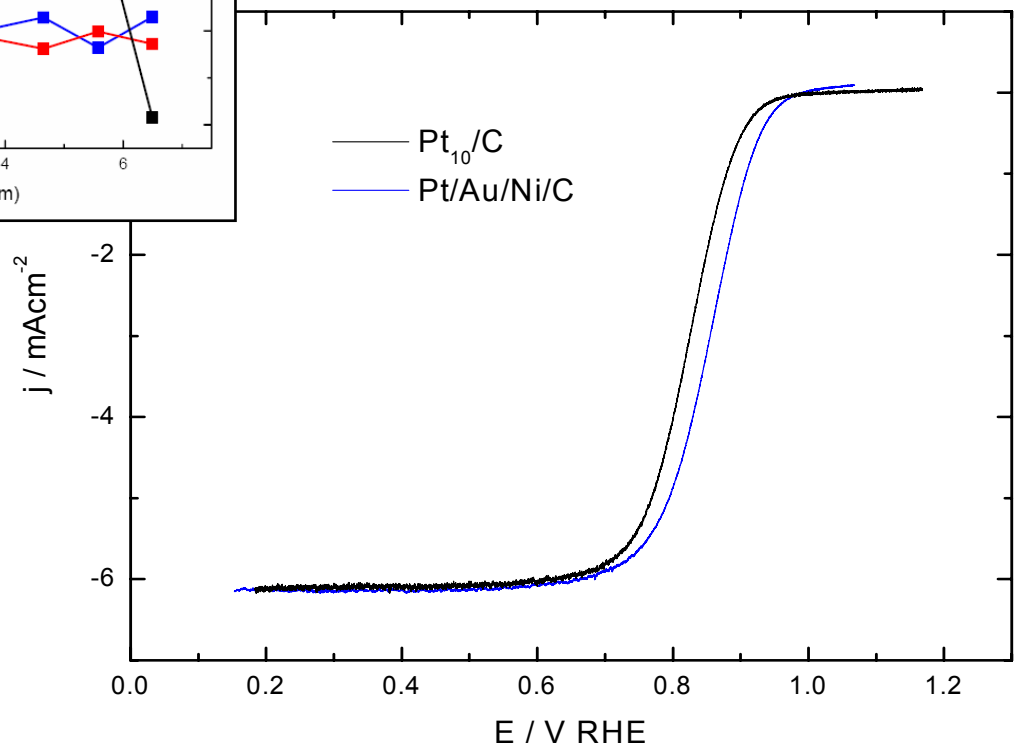
Pt mass-activity of a mixed $Pt_{0.8}Re_{0.2}$/Pd/C catalyst ~20× that of Pt/C

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



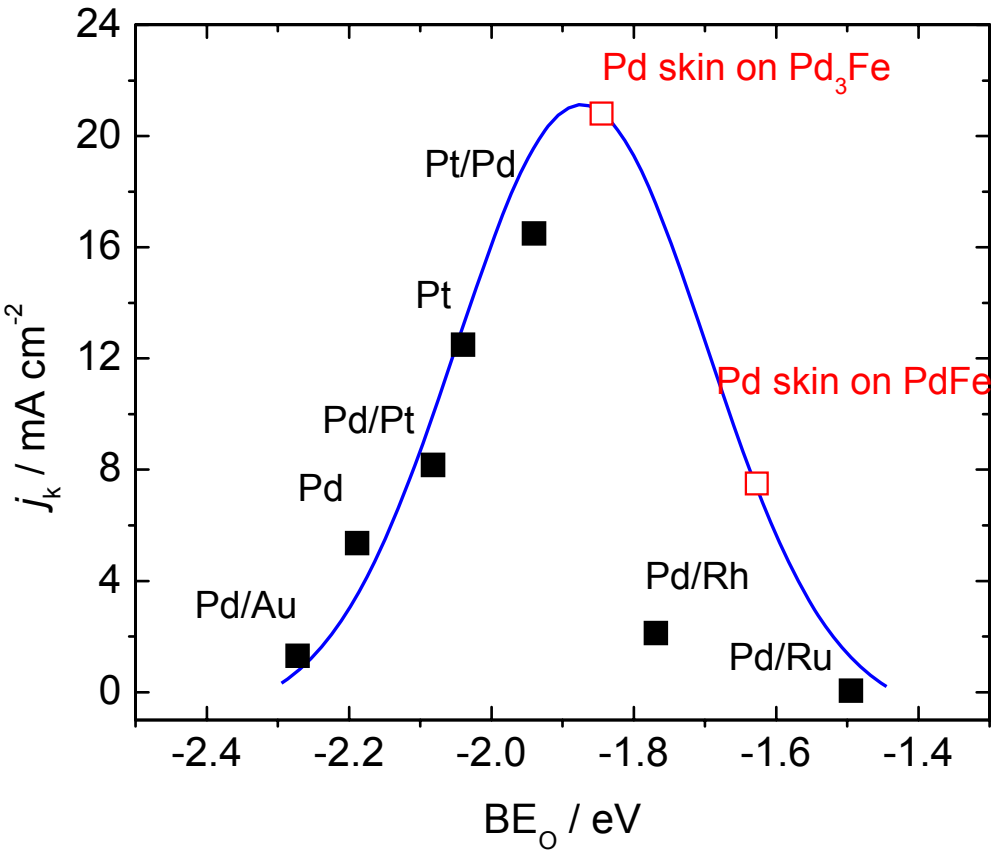
1060 μA cm^{-2} @ 0.90 V

1.5 μg$_{Pt}$ cm^{-2} & 2.3 μg$_{Au}$ cm^{-2}



Notable electrocatalytic effect with a core-shell Pt/Au/Ni/C catalyst relative to "regular" carbon-supported Pt catalyst

Catalysts with Ultra-low Pt Content: Experiment & Prediction



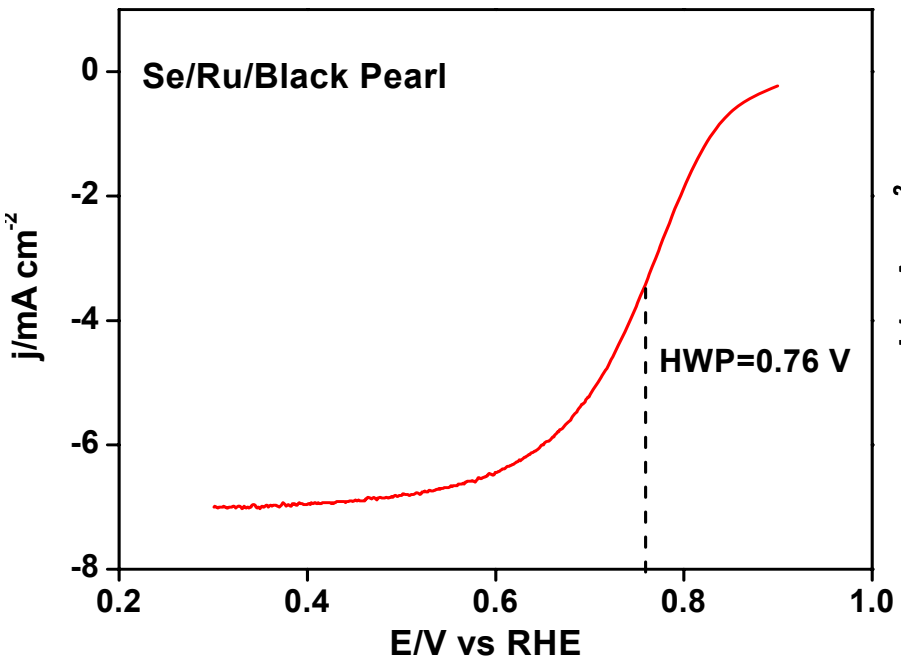
Experimental RDE oxygen reduction data (solid squares) and predicted ORR current densities for Pd overlayer on $Pd_3Fe(111)$ and PdFe(111) (open squares) as a function of the calculated oxygen-binding energy.

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

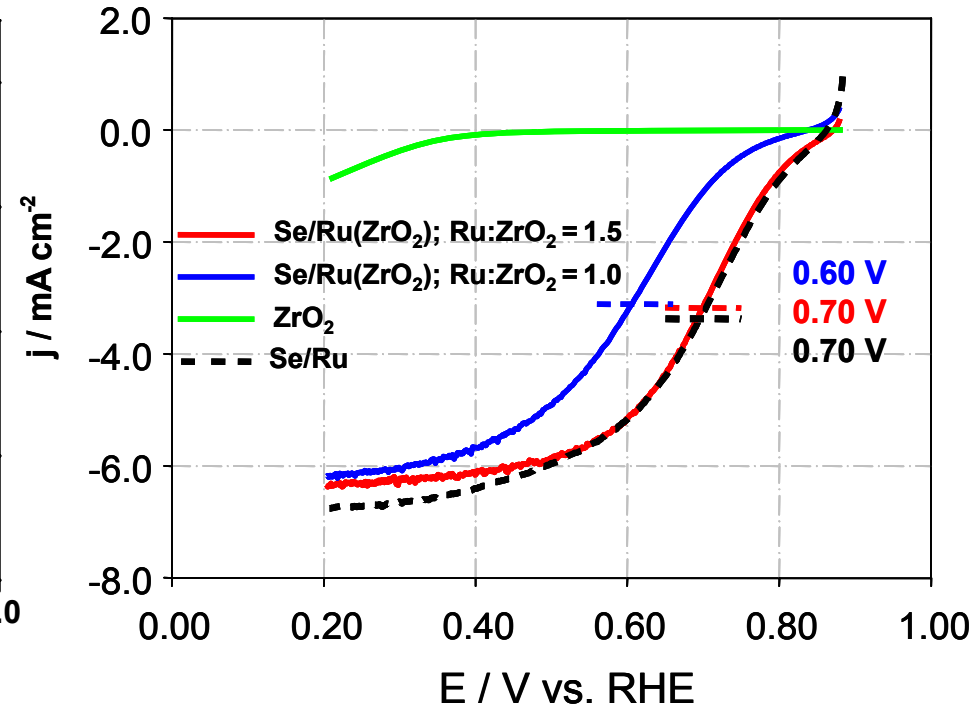
New-generation Chalcogenides

- 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_2 matrix for high dispersion and possible increase in Se durability

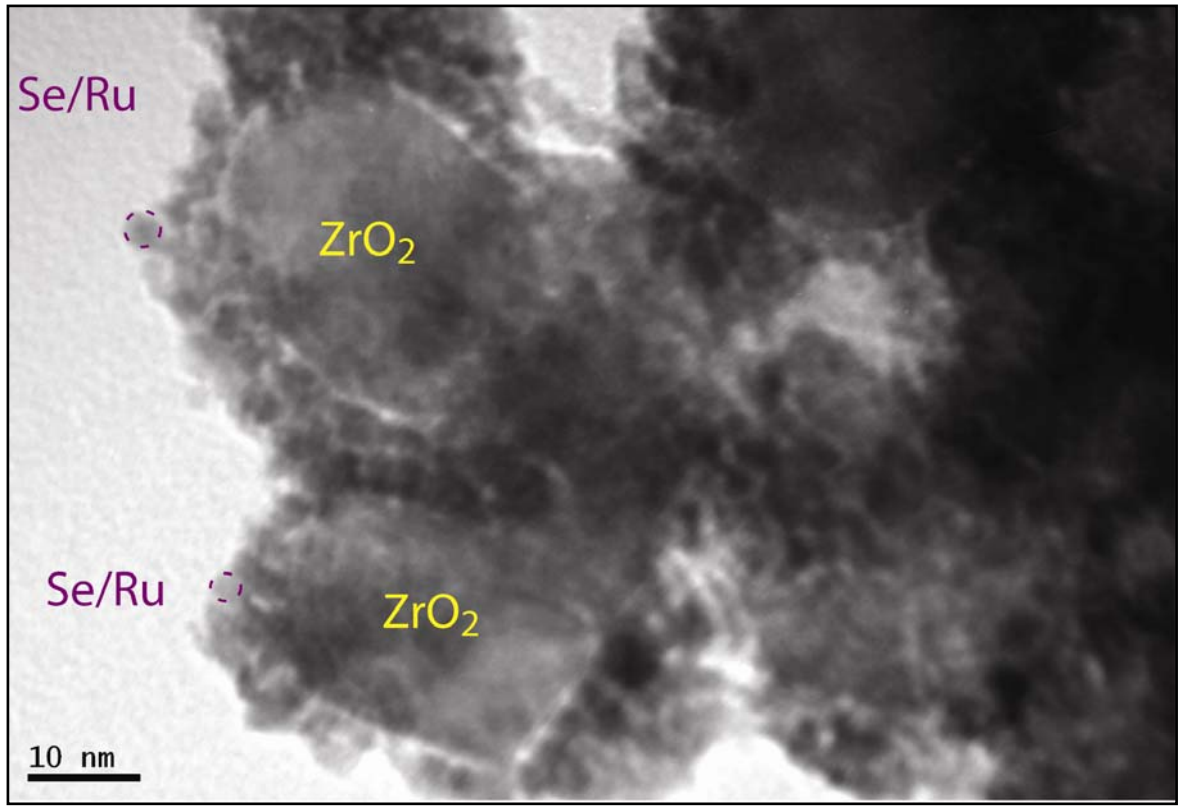
RDE: Au disk at 1600 rpm; 0.1 M H_2SO_4, 20 mV s^{-1}
Se-decorated Ru dispersed in Black Pearl



RRDE: Au disk at 1600 rpm; 0.1 M H_2SO_4, 20 mV s^{-1}
2-3 nm Se/Ru decorating ZrO_2 solid matrix



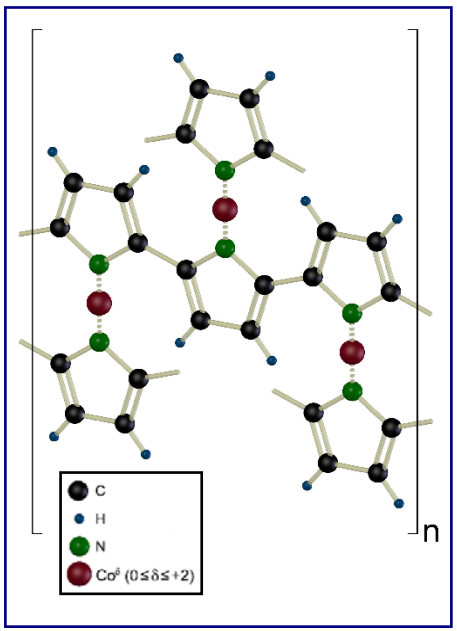
New-generation Chalcogenides: Se/Ru Particles in ZrO_2 Matrix

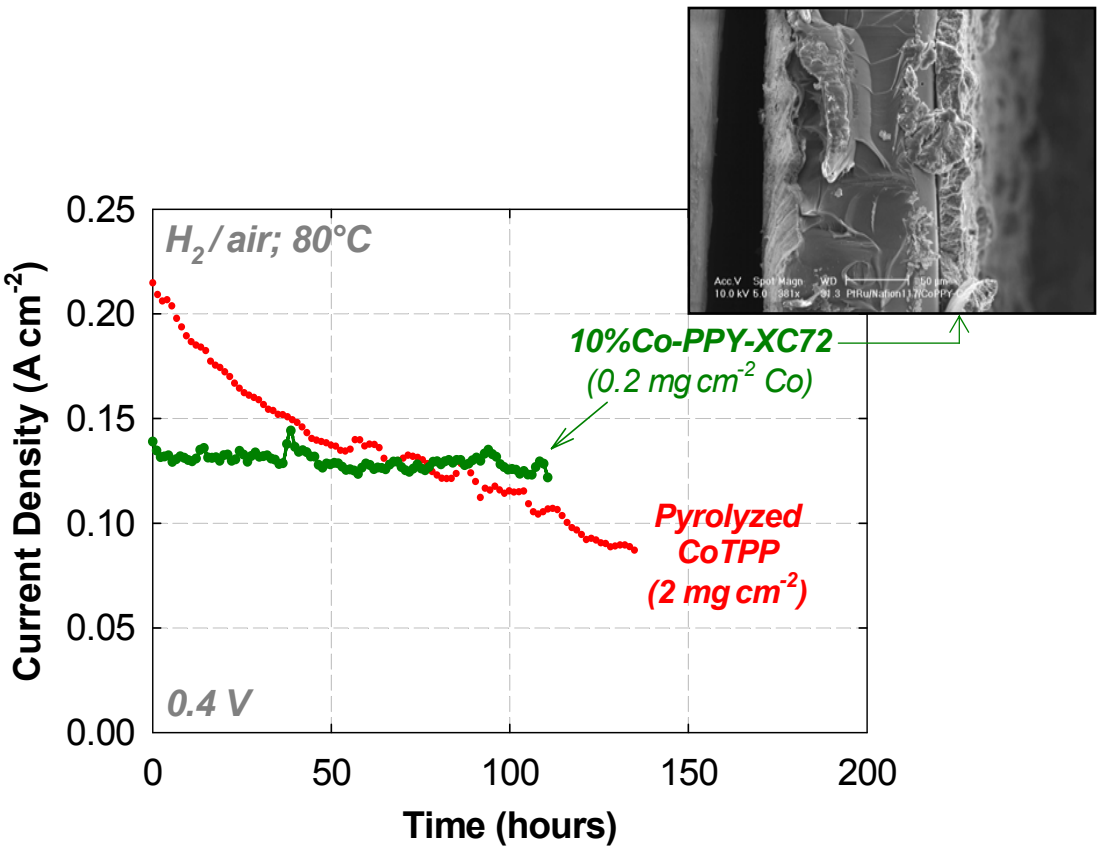


TEM image of 2-3 nm nanoparticles of Se/Ru anchored to ~ 20 nm ZrO_2 support

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





Non-precious Metal Composites: Molecular 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**

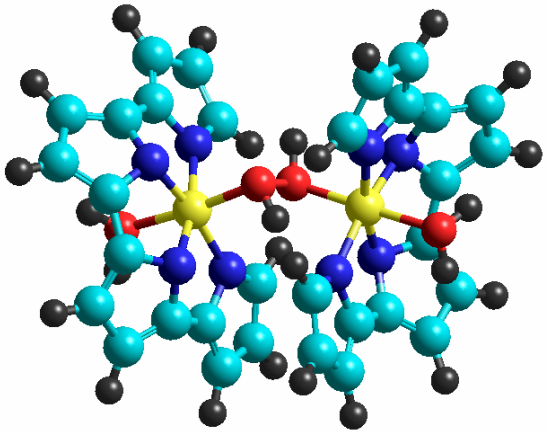
Example:

- **Effect of complex Co-O_2-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

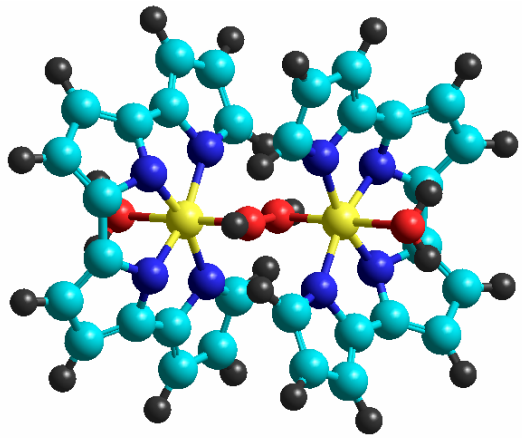
Non-precious Metal Composites: Molecular Modeling

$D_{O-O} = 1.56$ Å



+ $2e^-$ →

$D_{O-O} = 1.99$ Å



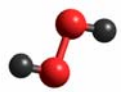
[(tetrapyrrole) H_2O Co-OH-HO-Co H_2O (tetrapyrrole)]$^{2-}$

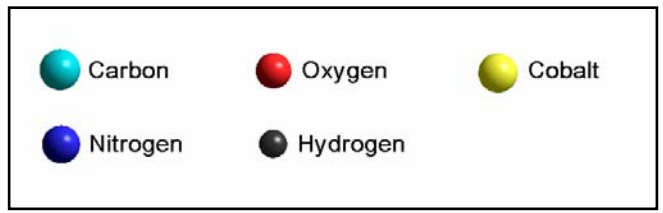
$D_{O-O} = 1.17$ Å

dioxygen

+ $2H^+$ + $2e^-$ →

$D_{O-O} = 1.40$ Å





Dioxygen interaction with two Co centers significantly weakening O-O bond relative to the O_2/H_2O_2 reference system

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

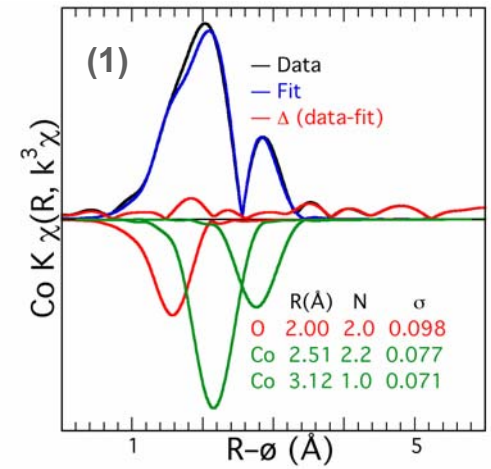
Methods: C, N, S - combustion method, except for N in XC72 (by Kjeldahl method); O - pyrolysis; B, Co - ICP; H - not determined

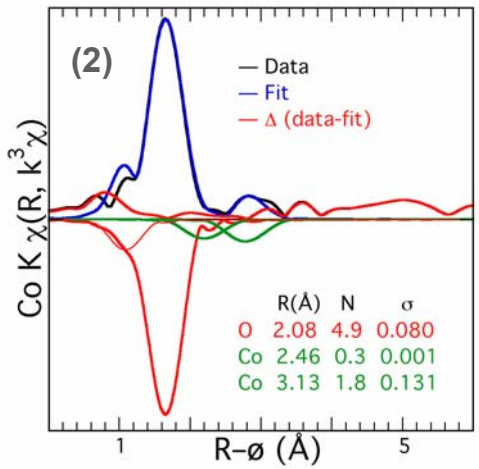
Sample	Elements (Weight %)	Elements (Atomic %)
Carbon (Vulcan XC72)	C (97.1), N (0.1), S (1.2) O - *not determined*	C (99.4), N (0.1), S (0.5) O - *not determined*
PPY/XC72 PPY 1-hour polymerized	C (95.3), N (2.2), S(1.1), O (1.6)	C (96.5), N (1.9), S (0.4), O (1.2)
PPY/XC72 PPY 24-hour polymerized	C (92.7), N (2.2), S (1.1), O (3.1)	C (95.2), N (2.0), S (0.4), O (2.4)
PPY/XC72 PPY 1-hour polymerized; then PPY/XC72 reduced using $NaBH_4$	C (93.9), N (2.0), S(1.2), O (2.6), B (<93 ppm)	C (96.0), N (1.7), S (0.4), O (2.0)
Co/PPY/XC72 PPY 1-hour polymerized; then Co/PPY/XC72 reduced using $NaBH_4$	C (78.2), N (1.6), S (1.0), O (3.1), Co (9.6)	C (85.3), N (1.7), S (0.4), O (2.8), Co (2.4)

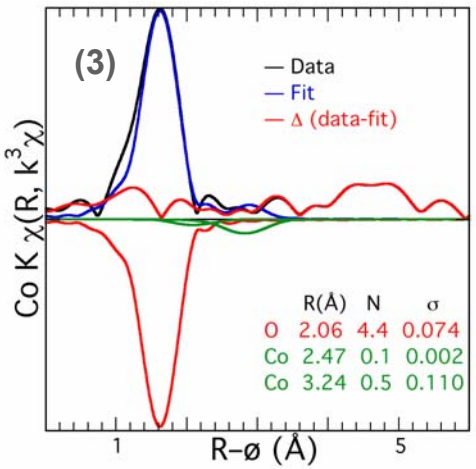
Co-to-N ratio in the Co/PPY/XC72 possibly too high

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

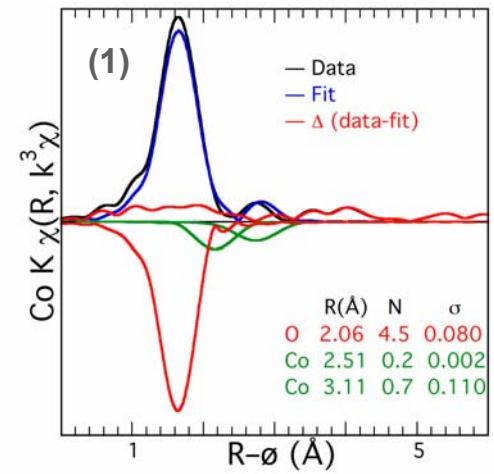
as-synthesized

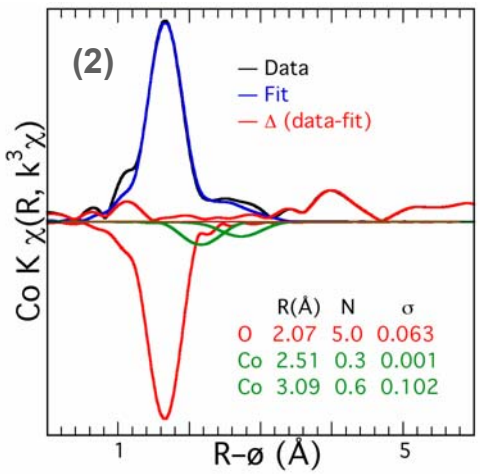


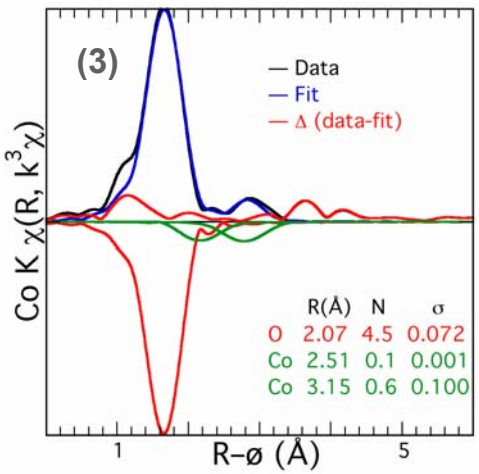




after fuel cell operation







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.

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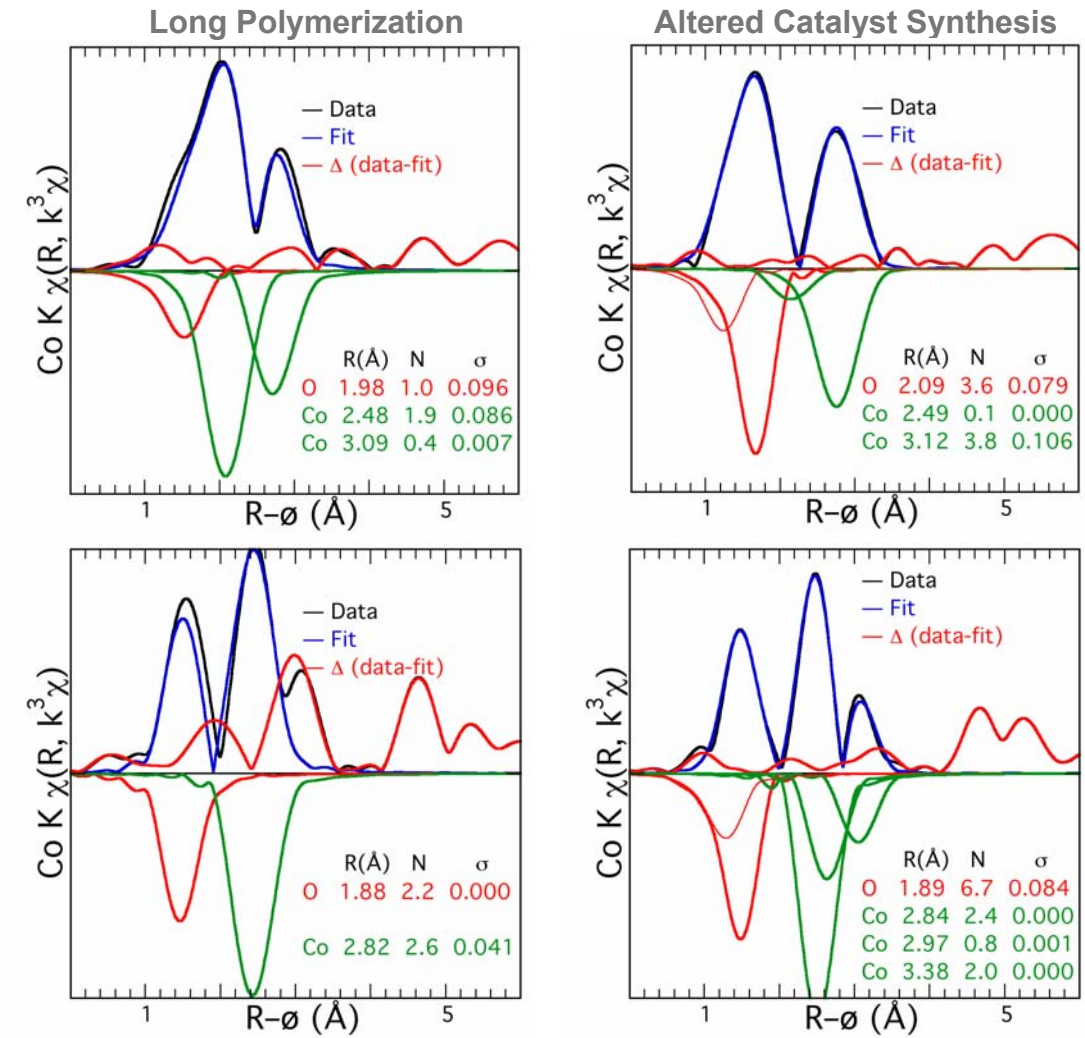
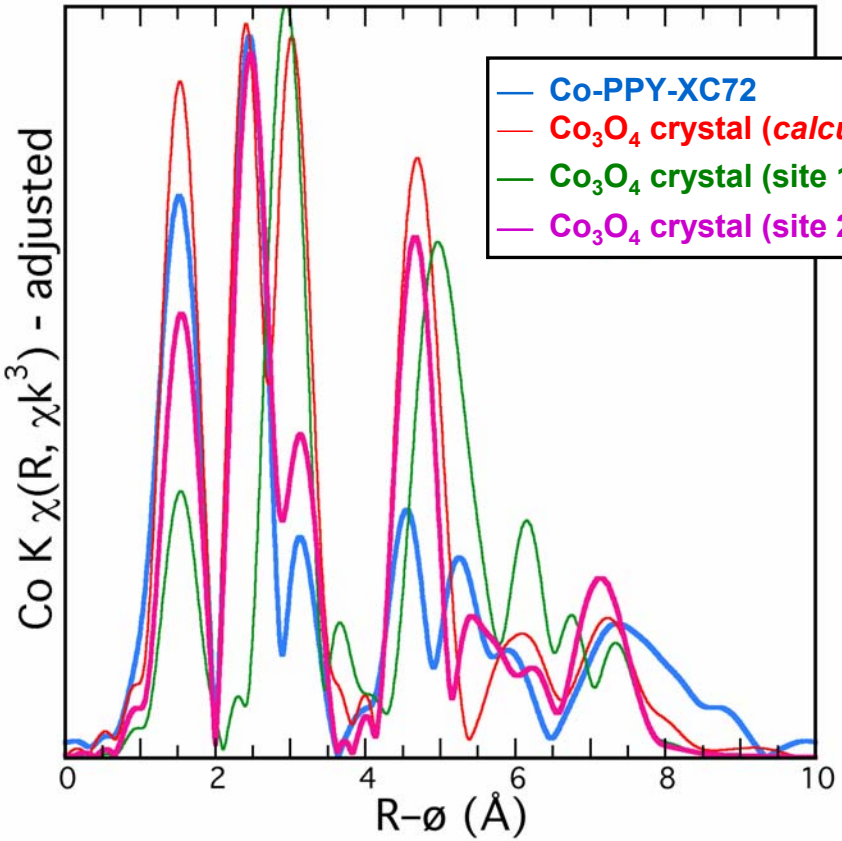
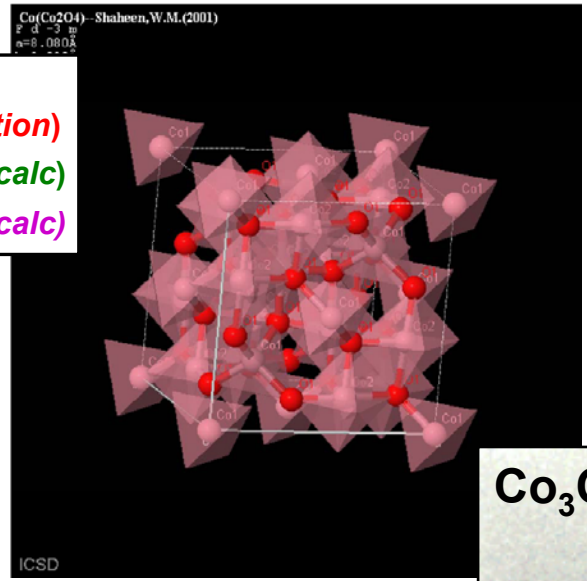
Non-precious Metal Composites: XAFS of Co/PPY/XC72 – Species II



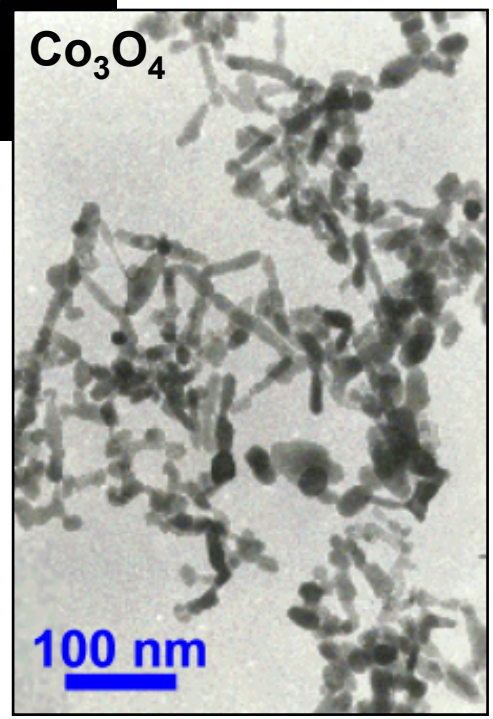
Two different paths yielding a highly and consistently ordered nanocluster or nanocrystallite. Nearest neighbor Co-O bond length (~ 1.89 Å) much shorter than in "mononuclear" species.

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





Inorganic Crystal Structure Data Base FIZ Karlsruhe, Germany



Nanostructured & Amorphous Materials, Inc. (www.nanoamor.com)

Although sharing many spectral features with calculated Co_3O_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.

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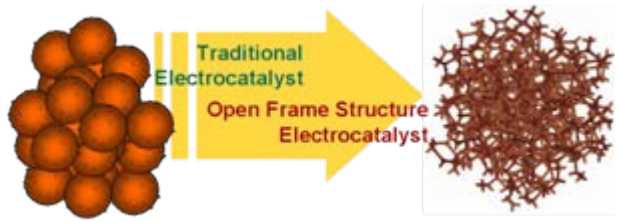
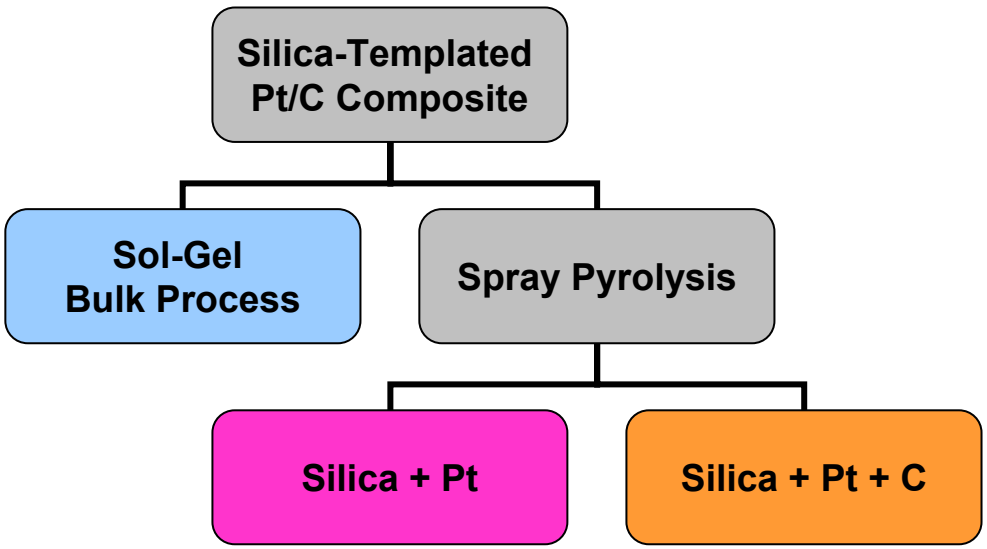
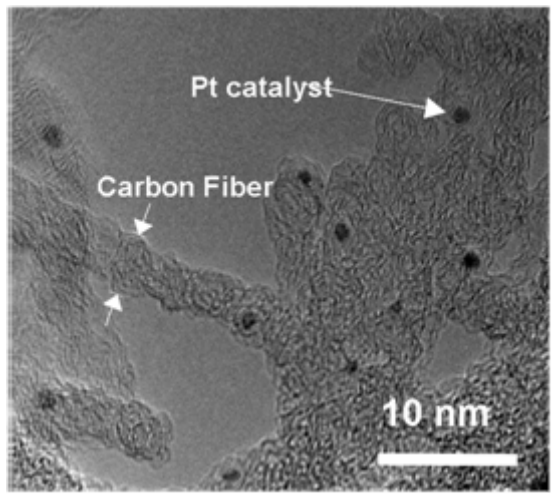
Novel Electrode Structures

- Improved oxygen transport and precious-metal catalyst utilization
- Increased non-precious catalyst loading
- Tunable hydrophobicity/hydrophilicity
- Enhanced stability
- Efficient H_2O management

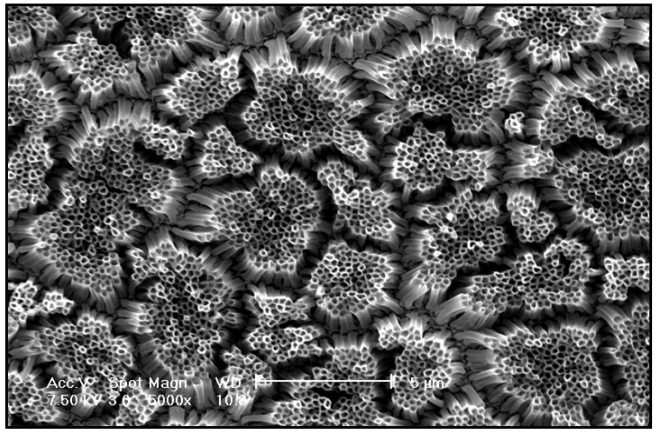
From Decorated Particles to Open-frame Networks →

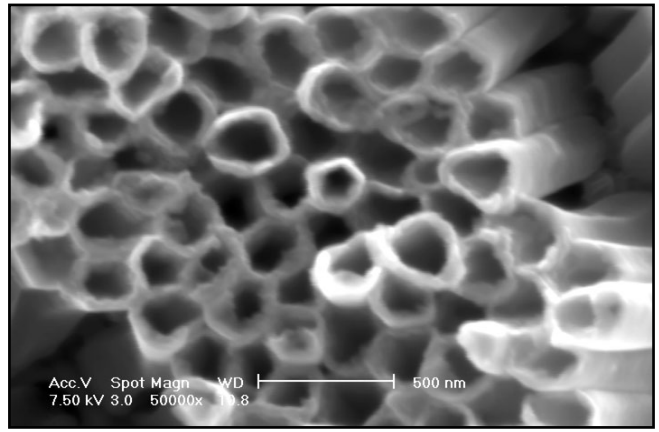




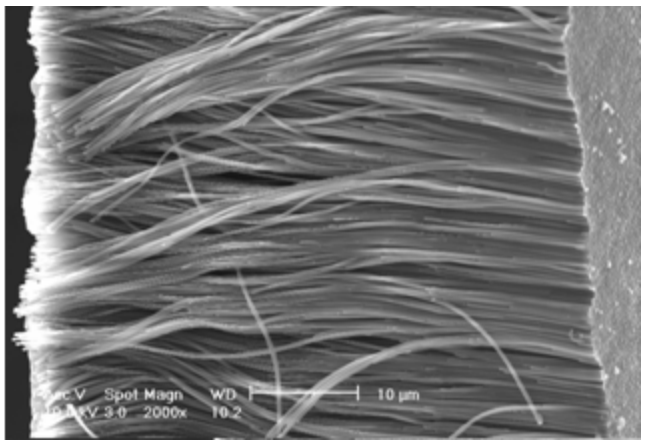


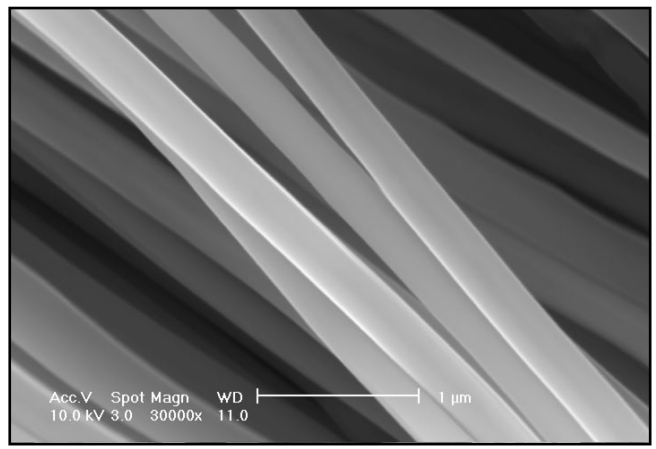
Novel Electrode Structures: Conductive Nanostructures





PPY nanotubes by electrochemical polymerization



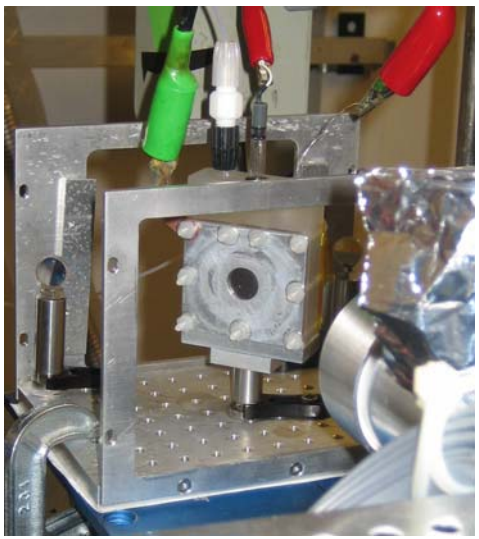


PPY nanowires by chemical polymerization

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

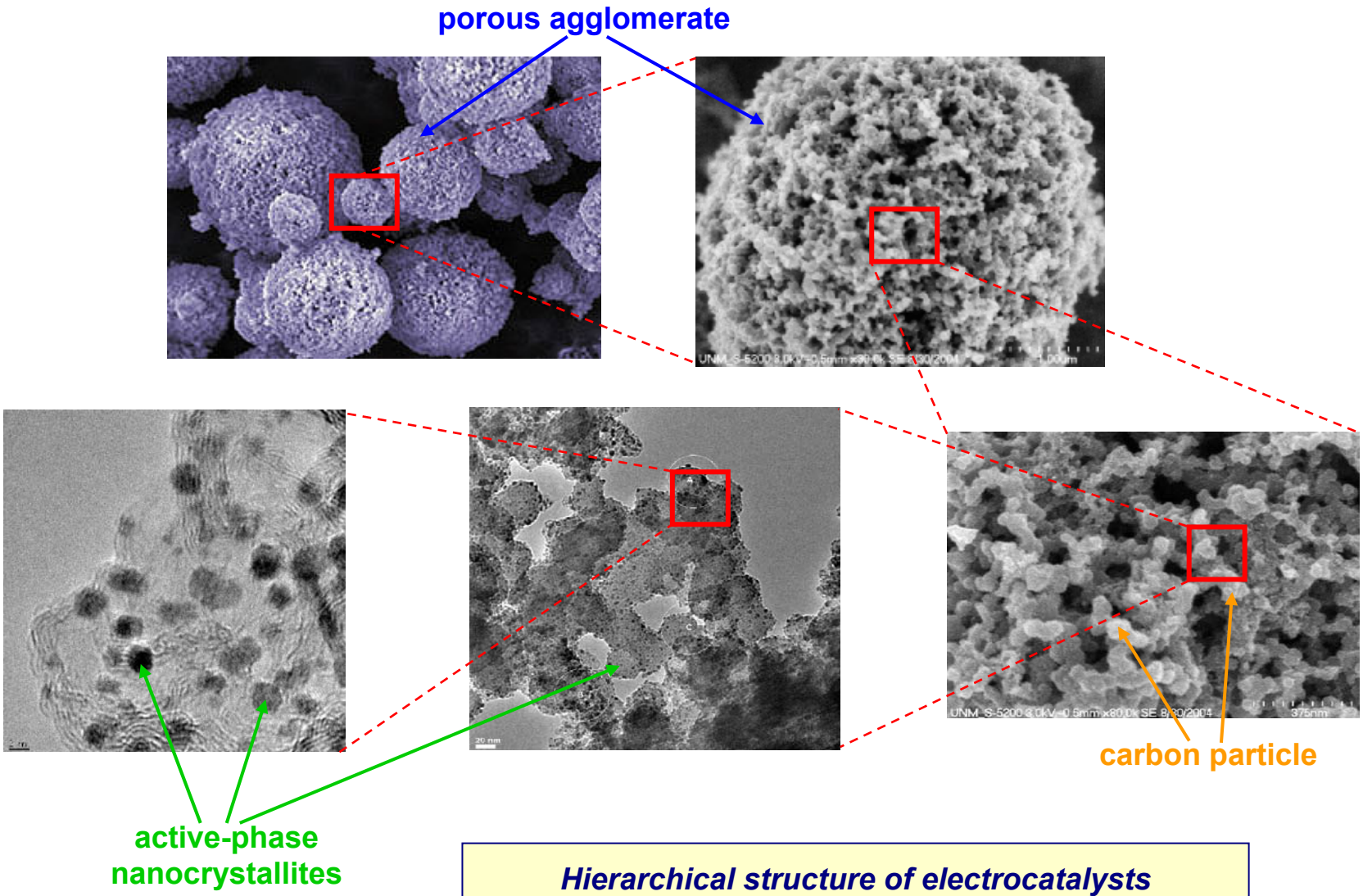
Extensive Catalyst Characterization

- 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

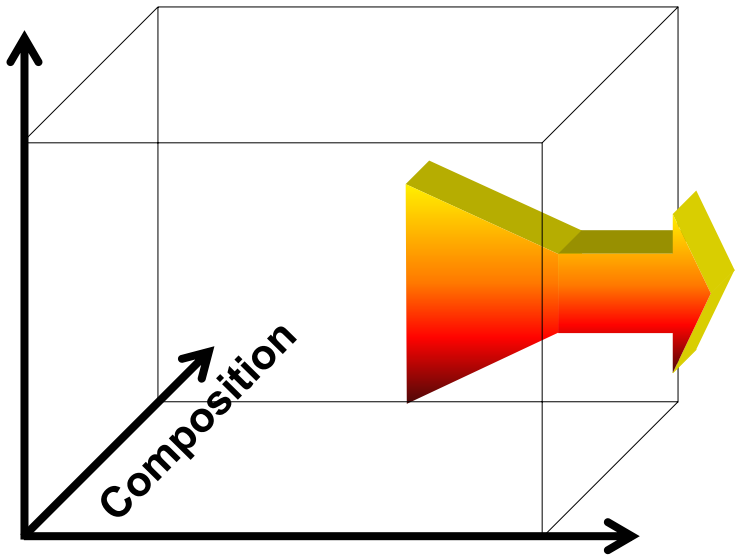
Scale-up and Fabrication of Practically Viable Catalysts



Hierarchical structure of electrocatalysts

Scale-up and Fabrication of Practically Viable Catalysts

Particle Morphology
- Size
- Size distribution
- Structure
- Surface Area
- Porosity



Tailored to APPLICATION

Particle Surface Functionality
- Chemical composition
- Hydrophobicity
- Reactivity
- Absorptivity

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

FY07 Milestones & Go/No-Go Decisions

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

- 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

- 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/$PdCo_5$/C and PtML/Pd_3Fe and Au clusters-stabilized Pt/$PdCo_5$/C and PtML/Pd_3Fe 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

- 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 pyrolyis 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

- 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