Hydrogen, Fuel Cells & Infrastructure Technologies Program, 2008 Annual Review
Arlington, Virginia – June 9-13, 2008

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 (Project Lead) - **Los Alamos National Laboratory**

Project ID: FC3

Project Overview

Timeline

- **Start date:** January 2007
- **End date:** Four-year duration

Budget

- **Total funding estimate:**
  - DOE share: $10,000K
  - Contractor share: $445K
- **FY07 funding received:** $2,046K
- **FY08 funding estimate:** $2,800K

Barriers

- **A. Durability** (catalyst; electrode)
- **B. Cost** (catalyst; MEA)
- **C. Electrode Performance** (ORR kinetics; O_2 mass transport)

2010 Technical Targets

(from DOE's MYPP Table 3.4.12)

- **Platinum group metal loading:** 0.3 mg_{PGM}/cm^2 (both electrodes)
- **Cost:** < 5 $/kW
- **Activity** (PGM catalysts): 0.44 A/mg_{Pt} at 0.90 $V_{iR\text{-}free}$; 720 $\mu A/cm^2$ at 0.90 $V_{iR\text{-}free}$
- **Activity** (non-PGM catalysts): > 130 A/cm^3 at 0.80 $V_{iR\text{-}free}$
- **Durability with cycling:** 5,000 hours at $T \leq 80°C$; 2,000 hours at $T > 80°C$
- **ESA loss:** < 40%

Participating Organizations, Roles, Key Personnel

BROOKHAVEN NATIONAL LABORATORY – **catalysts with ultra-low Pt content**

R. R. Adzic (PI), W-P. Chen, K. Sasaki, M. Vukmirovic, J. Wang, W-P. Zhou

ILLINOIS UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN – **chalcogenide-based catalysts**

A. Wieckowski (PI), P. K. Babu, A. Bonakdarpour, C. Delacôte, H. T. Duong

Los Alamos NATIONAL LABORATORY – **precious metal-free catalysts; characterization**

P. Zelenay (PI), Z. Chen, J. Chlistunoff, H. Chung, S. Conradson, F. Garzon, C. Johnston, G. Purdy, T. Rockward, J. Valerio, G. Wu

The University of New Mexico – **open-frame catalyst structures**

P. Atanassov (PI), K. Artyushkova, D. Konopka, S. Pylypenko

UNIVERSITY OF CALIFORNIA **UC RIVERSIDE** – **nanostructure catalyst structures**

Y. Yan (PI), S. Alia, Z. Chen, P. Larsen, L. Xu,

Argonne NATIONAL LABORATORY – **characterization & durability**

D. Myers (PI), A. J. Kropf, M. Smith, X. Wang

ornl - **characterization**

K. More (PI)

CABOT – **fabrication & scale-up**

P. Atanassova (PI), B. Blizanac, G. Rice, 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:

- **Design, synthesize and characterize new catalyst supports and electrode structures for new-generation ORR catalysts**
- **Determine ORR mechanism on newly developed catalysts via extensive physicochemical characterization, electrochemical and fuel cell testing**
- **Optimize electrode with new catalysts and structures for maximum performance and catalyst utilization**
- **Evaluate catalyst stability; minimize performance loss over time**
- **Assure path forward for fabrication and scale-up of viable catalysts**

Technical Approach

Three classes of ORR catalysts

- Catalysts with ultra-low platinum content (stable metals or alloys as cores; non-precious-metal core catalysts; mixed metal shells for higher ORR activity)
- Chalcogenide-based catalysts (surface chalcogenides; chalcogenides with non-precious metal core)
- Precious metal-free catalysts (low- and high-temperature catalysts based on transition metals precursors)

Novel electrode structures for cathode catalysts

- Open-frame catalyst structures (microemulsion and other techniques)
- Nanostructures for maximum catalyst utilization and effective mass transport

Characterization, active-site and ORR mechanism determination, modeling

Performance durability

- Long-term fuel cell performance
- Performance degradation mechanism

Fabrication & scale-up of selected, practically viable cathode catalysts

Milestones

- **Dec 07: Scale up synthesis of core-shell Se/Ru-Fe/C catalyst for fuel cell testing – achieved**
- **Mar 08: Achieve 1.5 A/mg$_{Pt}$ (or 0.40 A/mg$_{Pt+Pd}$) with a Pt$_{ML}$/Pd$_3$Fe/C catalyst – ongoing; complete electrochemical characterization of composite catalysts based on different transition metals – achieved**
- **Apr 08: Demonstrate nanotubes/nanofibers support with electronic conductivity comparable with carbon – achieved**
- **Jun 08: Demonstrate (i) uncatalyzed and (ii) precious metal/non-precious metal catalyzed carbon network formed in a spray pyrolysis sol-gel derived mesoporous silica matrix – modified (a more promising approach developed & demonstrated)**
- **Aug 08: Complete characterization of the oxygen reduction active site on selected non-precious metal nanocomposite catalyst – ongoing**
- **Sep 08: Achieve stability of Au-clusters-stabilized Pt/Pd/C with a $E_{½}$ loss < 10 mV in 100,000 potential cycles – ongoing; optimize heat-treatment procedure to remove surface Se from Se/Ru/C catalysts – ongoing; determine oxidation state, chemical composition, and stability of catalysts in advanced cathode catalyst classes as a function of potential and time using *in situ* and *ex situ* X-ray absorption spectroscopy and electrochemical measurements – ongoing (six catalysts characterized)**

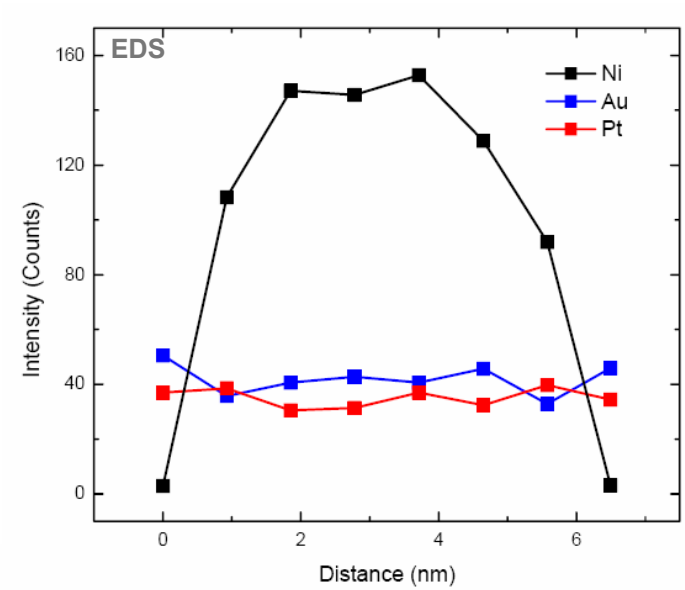
- **Go/no-go: Research on Te/RuFe/C stopped (poor fuel cell performance)**

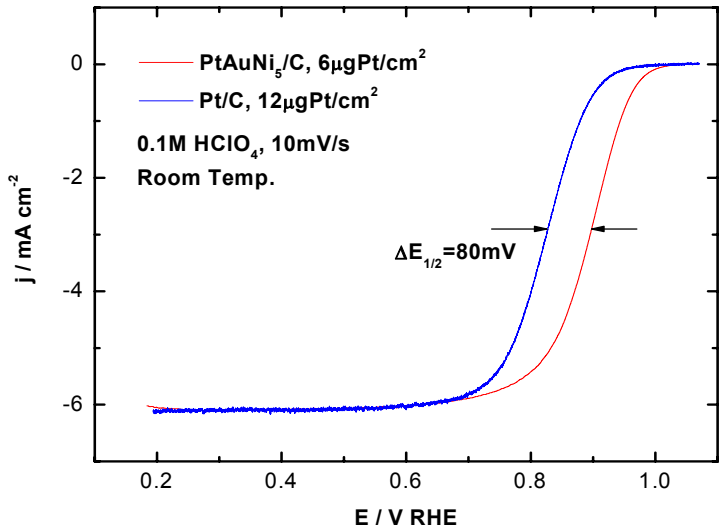
Ultra-low Pt Content Catalysts: Overview; $PtAuNi_5/C$ Catalyst

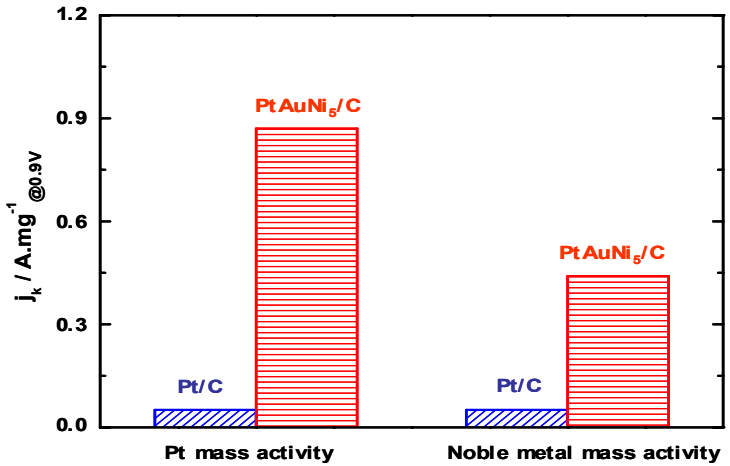
- Mixed Pt-metal monolayer catalysts (e.g. $PtAuNi_5/C$)
- Transition-metal core/precious-metal shell catalysts (e.g. $PtAuNi_5/C$; $Pt_{ML}Pd_3Fe/C$)
- Stable-metal core/precious-metal shell catalysts (Pt/Pd/C; Pt/Pd/Ru/C; Pt/Re/C)

$PtAuNi_5/C$ catalyst:

- ~80 mV ORR half-wave potential advantage relative to Pt/C in RDE testing
- Pt mass activity improvement: ~16×
- Total noble-metal activity improvement: ~8×



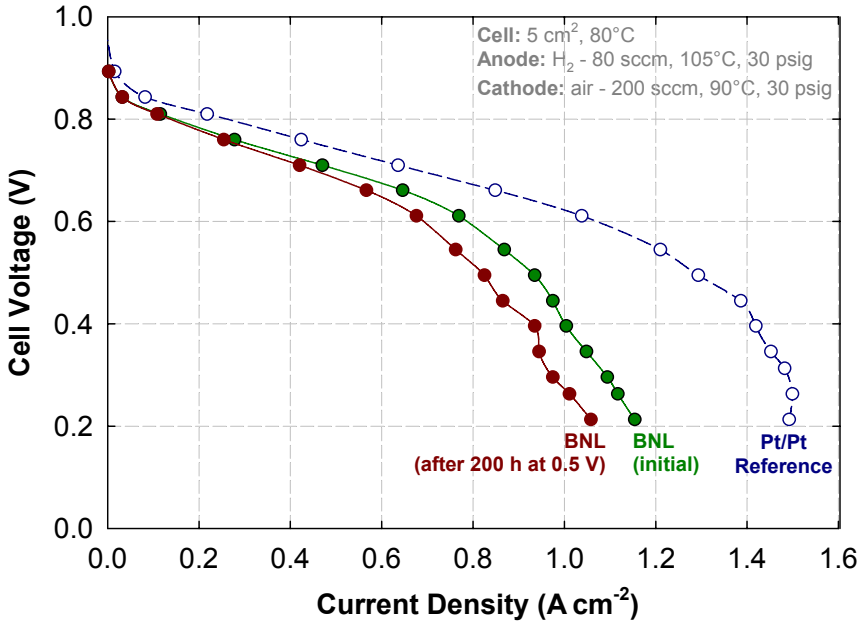




$PtAuNi_5$/C Catalyst: Fuel Cell Testing

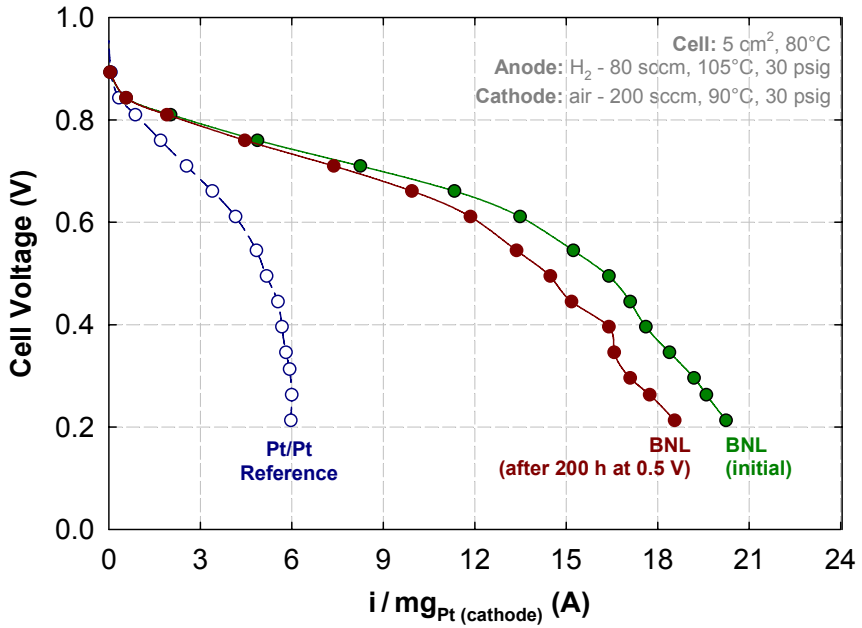
Current-based Comparison

BNL: 20 wt% Pt / C anode - 0.21 $mg_{Pt}\,cm^{-2}$; 20 wt% **$PtAuNi_5$ / C cathode** - 0.21 mg cm^{-2}
Reference: 20 wt% Pt / C anode - 0.21 $mg_{Pt}\,cm^{-2}$; 20 wt% **Pt / C cathode** - 0.25 $mg_{Pt}\,cm^{-2}$



Pt-mass-based Comparison

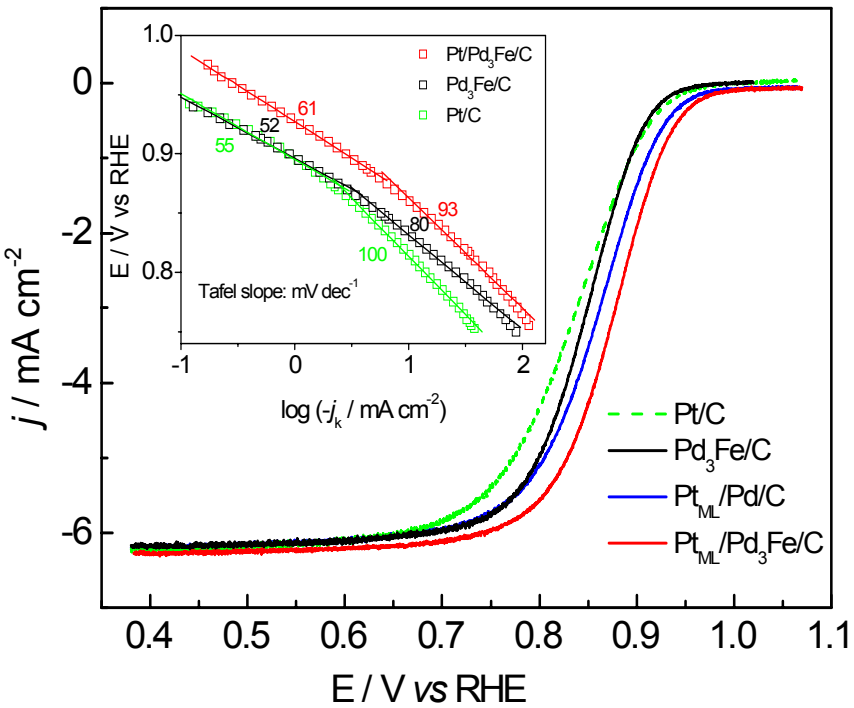
BNL: 20 wt% Pt / C anode - 0.21 $mg_{Pt}\,cm^{-2}$; 20 wt% **$PtAuNi_5$ / C cathode** - 0.21 mg cm^{-2}
Reference: 20 wt% Pt / C anode - 0.21 $mg_{Pt}\,cm^{-2}$; 20 wt% **Pt / C cathode** - 0.25 $mg_{Pt}\,cm^{-2}$

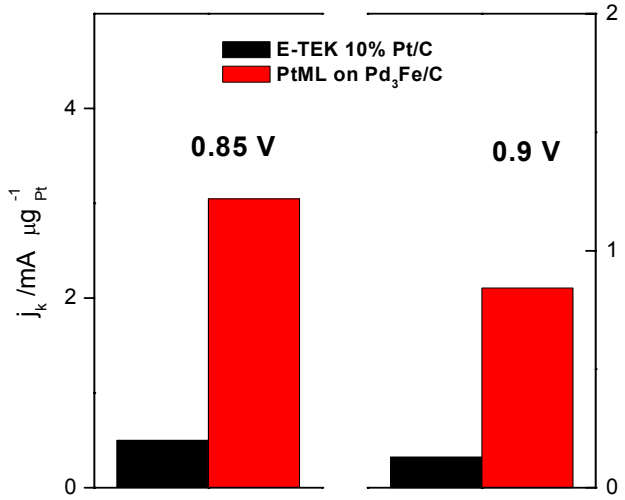


- **$PtAuNi_5$ catalyst (not optimized) showing ~ 3.3× Pt-mass performance advantage over a reference Pt catalyst performance in the entire range of fuel cell voltage**
- **Challenges: (i) performance stability of the alloy catalyst; (ii) uniformity of the Au layer on top of Ni core; (iii) formation of separate Au particles (XRD data)**

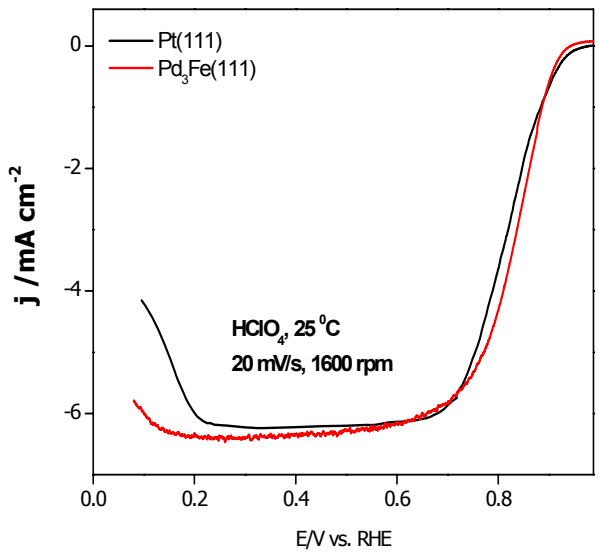
Ultra-low Pt Content Catalysts: Pd_3Fe-based Systems

Pt/C: 10 μg_{Pt} cm^{-2}; Pd_3Fe/C: 10 μg_{Pd} cm^{-2}; 0.1 M $HClO_4$; 10 mV s^{-1}





ORR on Pd_3Fe(111) vs. Pt(111)



- **Pt mass activity in Pt_{ML}/Pd_3Fe/C enhanced by ~ 6× at 0.85 V and 0.90 V relative to Pt/C**
- **"Intrinsic" ORR activity of Pd_3Fe(111) comparable to that of Pt(111)**
- **Challenge: Preventing Fe dissolution**

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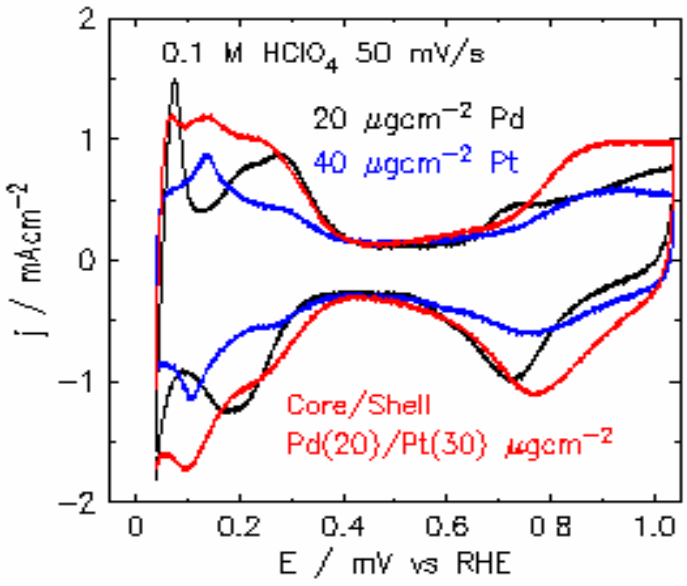
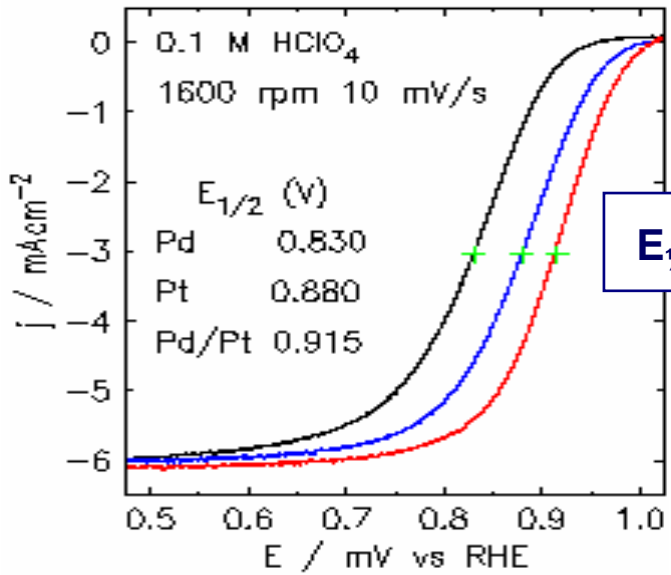
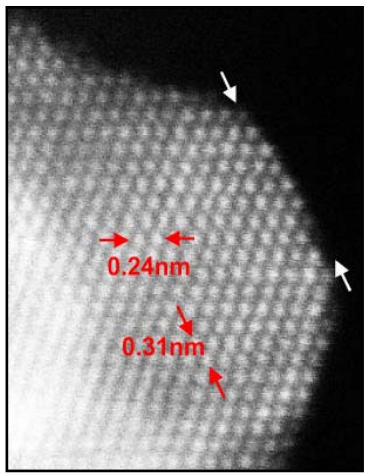
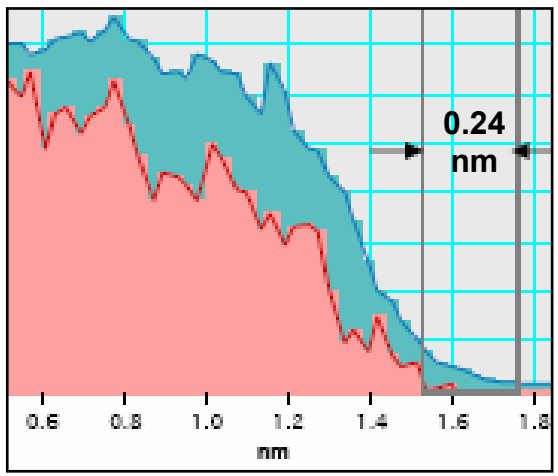
Ultra-low Pt Content Catalysts: Pd/Pt/C System & Layer-by Layer Growth





$E_{½}$ (Pd/Pt) = 0.915 V

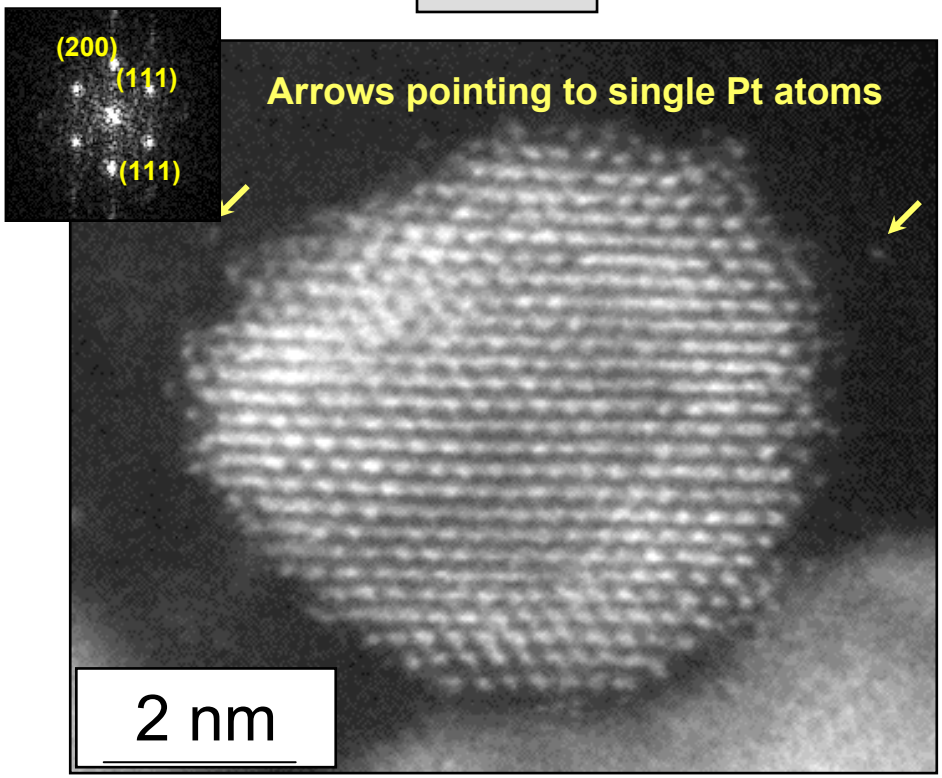




- Pd_{core}–Pt_{shell} catalysts, 1-4 ML-thick by Z-contrast TEM imaging and EELS chemical mapping
- 5-nm Pd core with 4-ML Pt shell, with Pt and Pd loading of 30 and 20 μg cm^{-2}, respectively, exhibiting activity equivalent to **2.5×** that of reference Pt catalyst (8 nm, 40 μg cm^{-2})

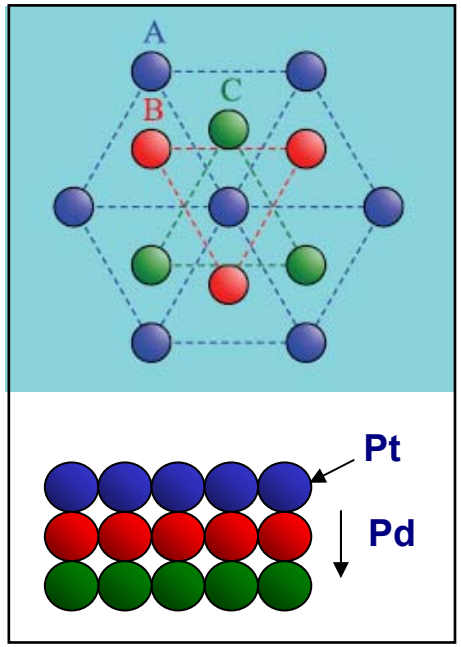
Ultra-low Pt Content Catalysts: Pd/Pt/C – An Ideal Core-Shell Particle

TEM



- **Complete core-shell particle: ~ 1-nm Pt shell** uniformly covering ~ **2-nm Pd core**
- Pd-core showing primary faceting of (111) planes (particle oriented with Pd-ZA=[011])

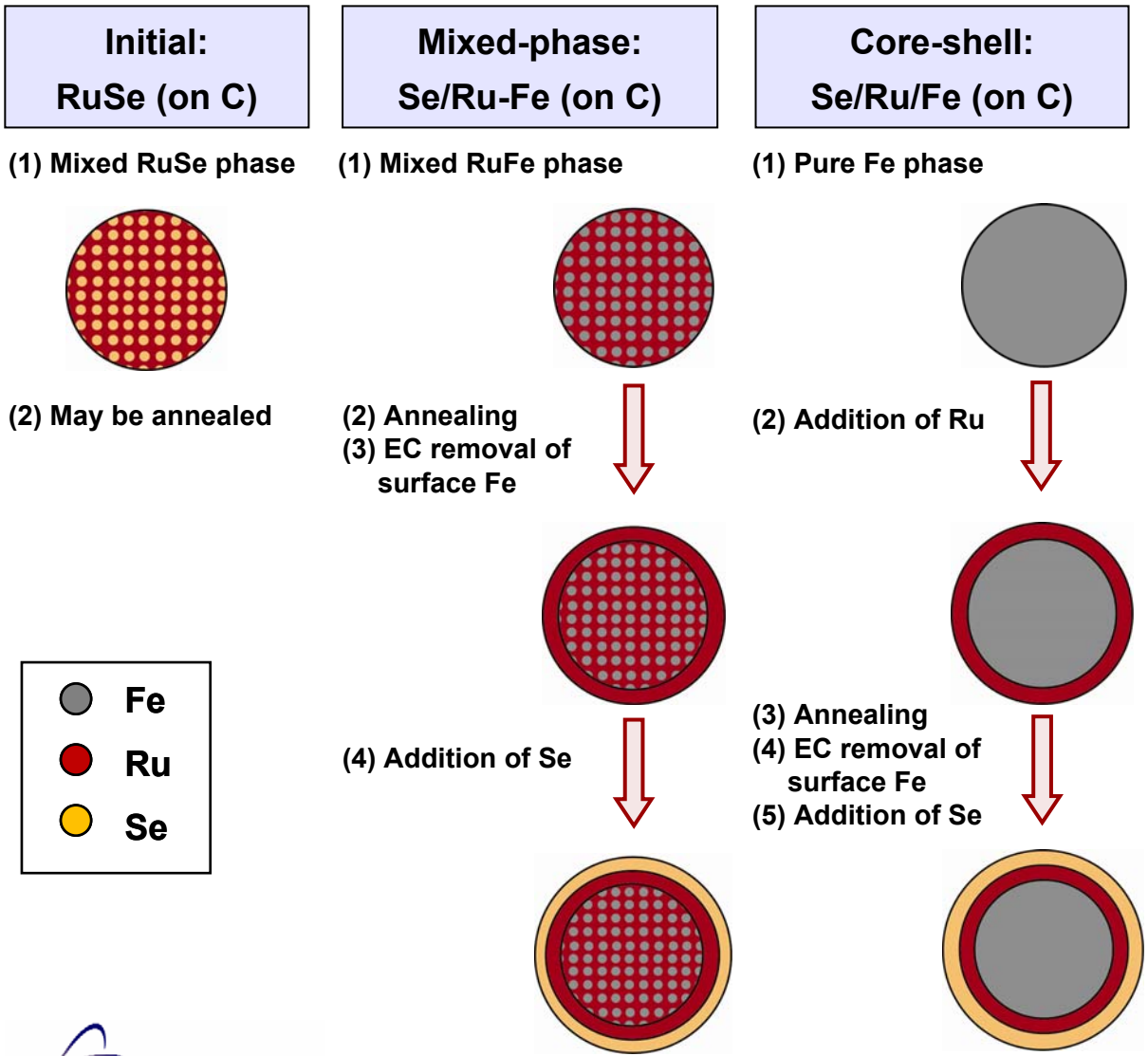
EXAFS & ICP Analysis



- Coordination numbers (EXAFS): Pt-Pt : 6.5; Pt-Pd : 3.3
- ICP: 26 at% Pt (as expected for 4 nm nanoparticles
- **EXAFS/ICP → Pt monolayer on Pd core; 4.2 nm nanoparticles**

Chalcogenide-Based Catalysts: Approach and Synthesis

Three Different Synthesis Paths

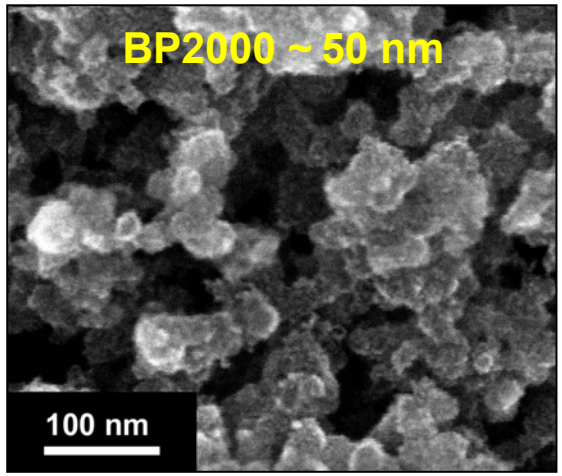


Approach

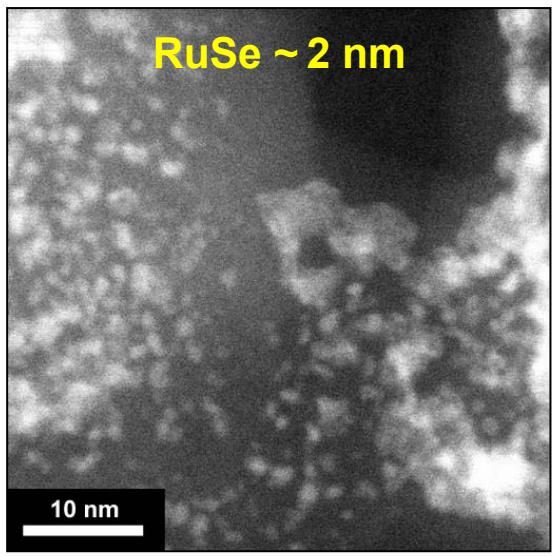
- Replace Pt (shell) with less expensive Ru
- Optimize performance of carbon-supported RuSe
- Replace most of Ru with Fe using mixed-phase or core-shell structure
- Additional bonus: Ru more tolerant than Pt to cathode feed stream poisons, such as CO and NO_x

Chalcogenide-Based Catalysts: 10 wt% RuSe/C

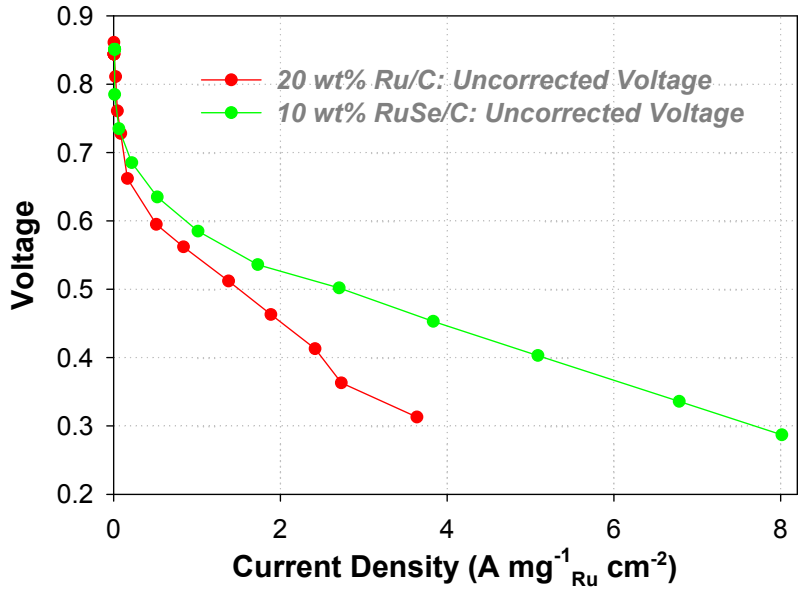
SEM image of RuSe/C (as-prepared)



TEM image of RuSe/C (as-prepared)



Voltage-current plots vs. mass of Ru



Anodes: 0.25 mg_{Pt} cm^{-2} (ELAT); H_2 300 sccm 30 psig; **Cell:** 80°C
Cathode: 0.067 mg_{Ru} cm^{-2} (RuSe/C); 0.16_5 mg_{Ru} cm^{-2} (Ru/C); air - 500 sccm, 30 psig

- High dispersion of RuSe catalyst achieved
- Cell performance of 10 wt% RuSe/C comparable to that of 20 wt% Ru/C (wt% refers to Ru + Se; actually 7 wt% Ru)
- Per Ru mass, performance of 10 wt% RuSe/C superior to 20 that of wt% Ru/C

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Chalcogenide-Based Catalysts: Ru Replacement by Fe in Se/Ru/Fe/C

Synthesis Steps

(1) Form Fe core (reduce $FeCl_3$)
Add Ru shell (reduce $RuCl_3$)

(2) Anneal

(3) Remove Fe from surface (electrochemically)

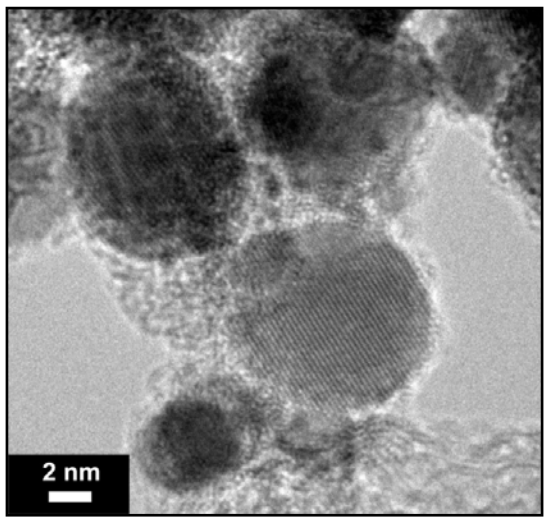
(4) Add Se (reduce SeO_2)

Catalyst Composition After Successive Steps

Sample	EDAX		
	Ru content (at%)	Fe content (at%)	Se content (at%)
Step (1)	47	53	-
Step (3)	67	33	-
Step (4)	64	28	8

TEM Image

- After Step 3
- Ru/Fe: ~8 nm
- Evident lattice structure



- Fe content retained at 33 at% after Step 3
- Improvement over Se/RuFe/C "mixed-phase" catalyst (20 at% Fe)
- Indication of "core-shell" structure with new synthetic approach

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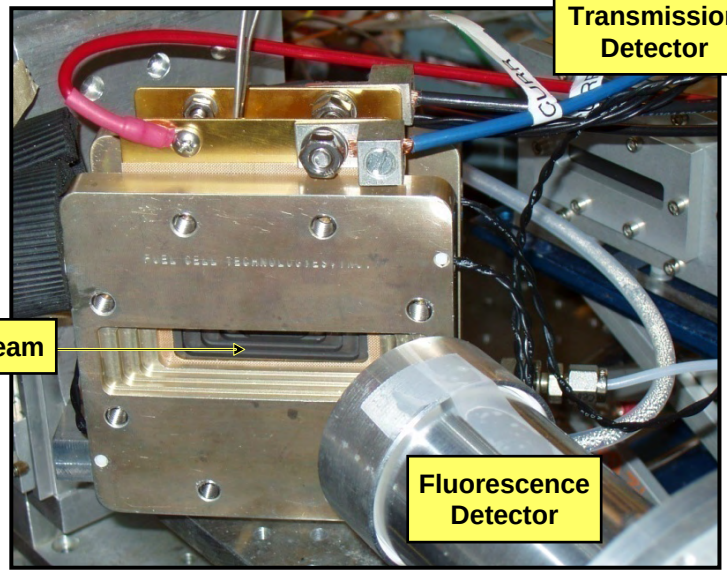
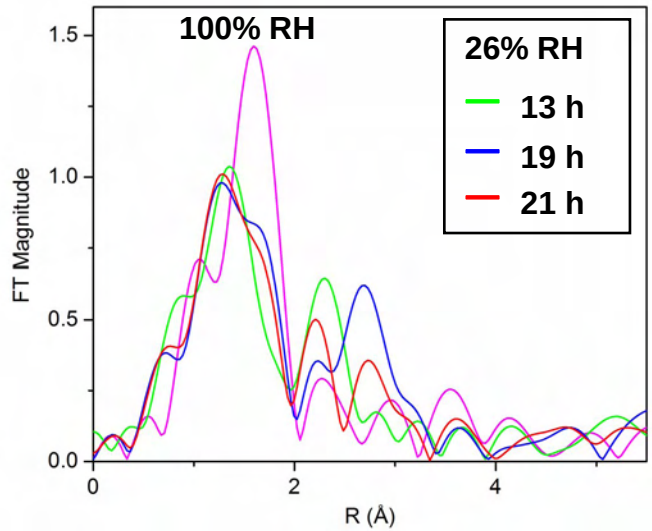
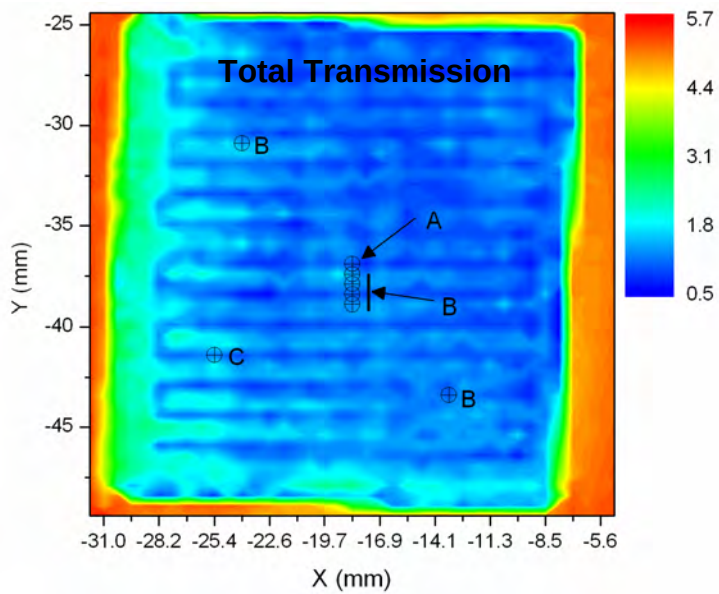
Co-PPy-XC72: *In situ* X-ray Absorption



Co-PPy-XC72 Activation for 21 h (0.1 V)





- A cell designed and fabricated at ANL for ***in situ*** EXAFS and XANES studies of low-Z metals
- Fluorescence mapping revealing (i) higher Co concentration in channels than below lands (not shown); (ii) loss of Co during activation
- Catalyst structure at 0.1 V, 100% RH and > 0.4 V, 26% RH: six Co-O/N bonds at 2.06-2.08 Å
- Two phases at < 0.3 V, 26% RH:
  - Co-Co at 2.83 Å; Co-O at 2.11 Å (H_2O) and 1.92 Å (OH)
  - Co-Co bond at 3.10 Å; Co-O bond at 2.05 Å, a single OH bridge between Co centers

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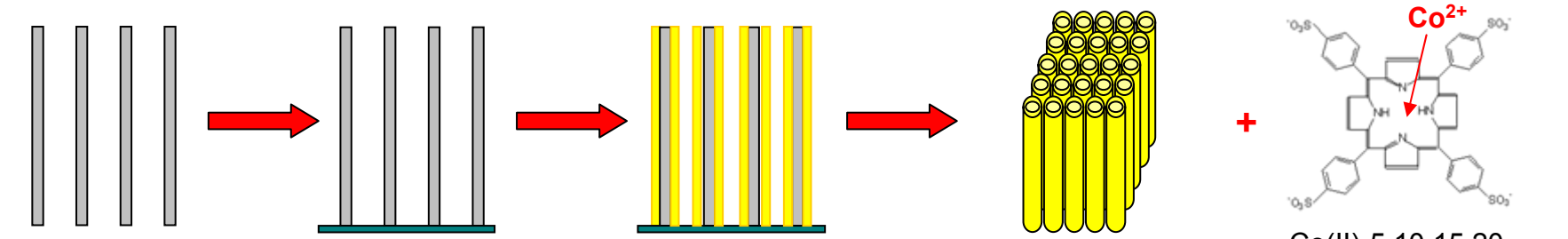
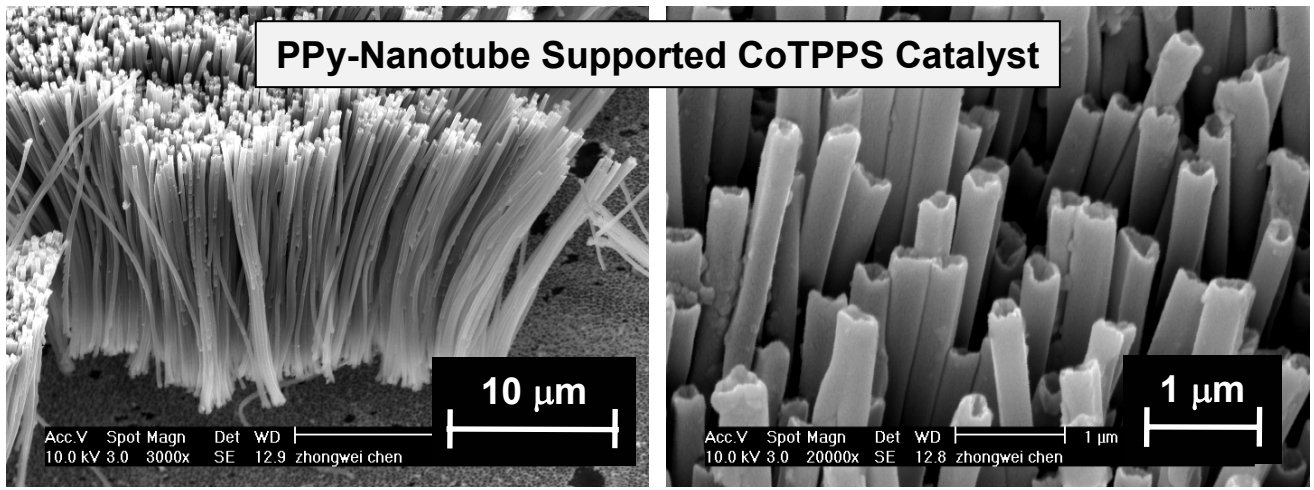
Precious Metal-Free Catalysts: Overview; CoTPPS (NT) System

- **Thermally-untreated ORR catalysts, e.g. Co-PPy-XC72, Co-TPPS-NT**
- **Heat-treated (pyrolyzed) catalysts, e.g. PPy-, PANI-based, N-free catalysts**



Porous AAO template → Metal-film added → Polymer electrodeposited → Template removed

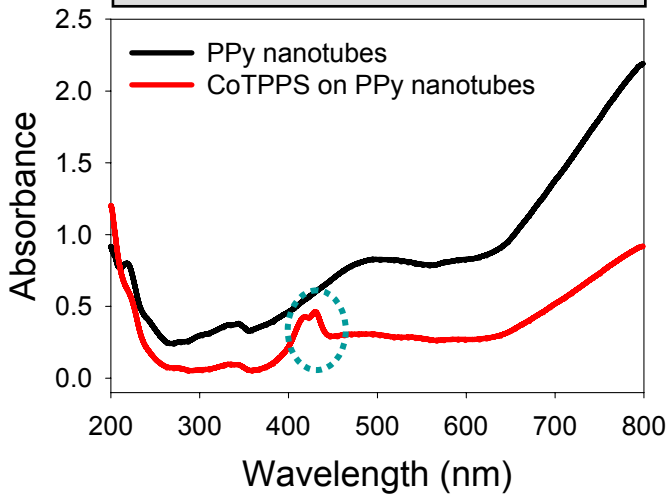
Co(II)-5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin (CoTPPS)



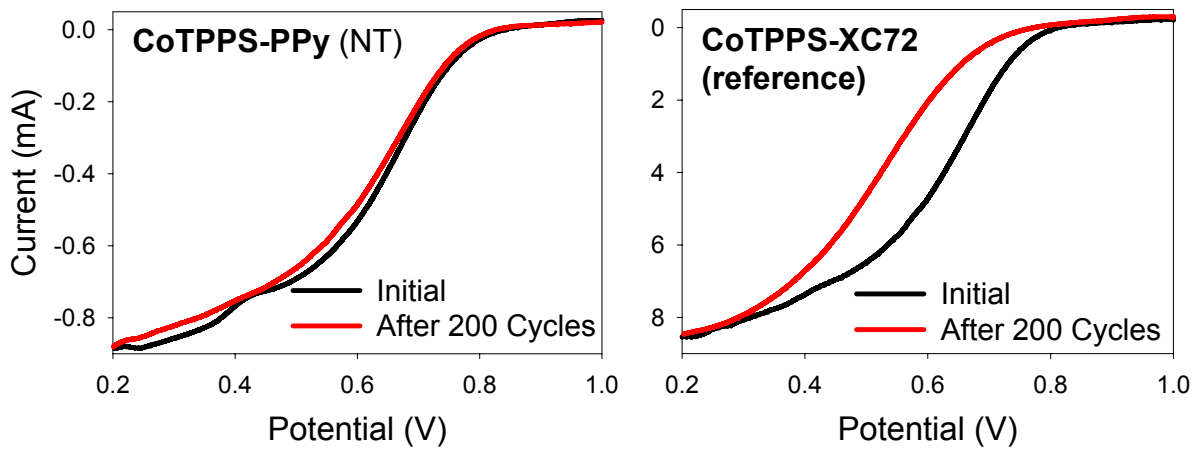
- **CoTPPS – active ORR catalyst**
- **PPy – catalyst anchor for better mass transport, durability, and activity**

Thermally-untreated CoTPPS-PPy (NT) Catalyst: Characterization & Durability

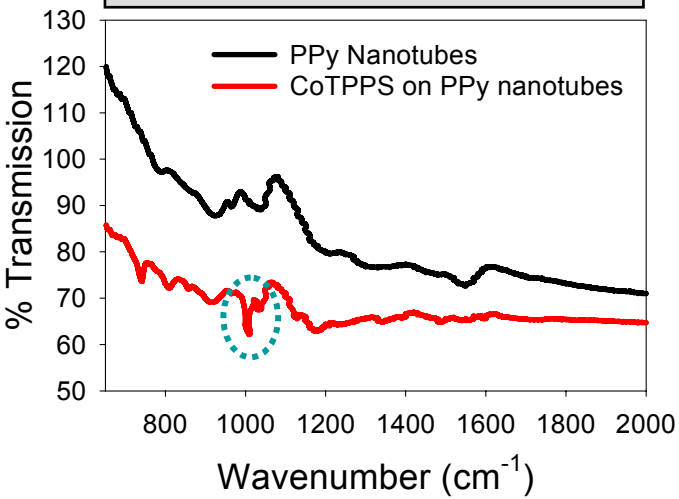
UV-vis Spectroscopy



Oxygen Reduction Activity Under CV Conditions



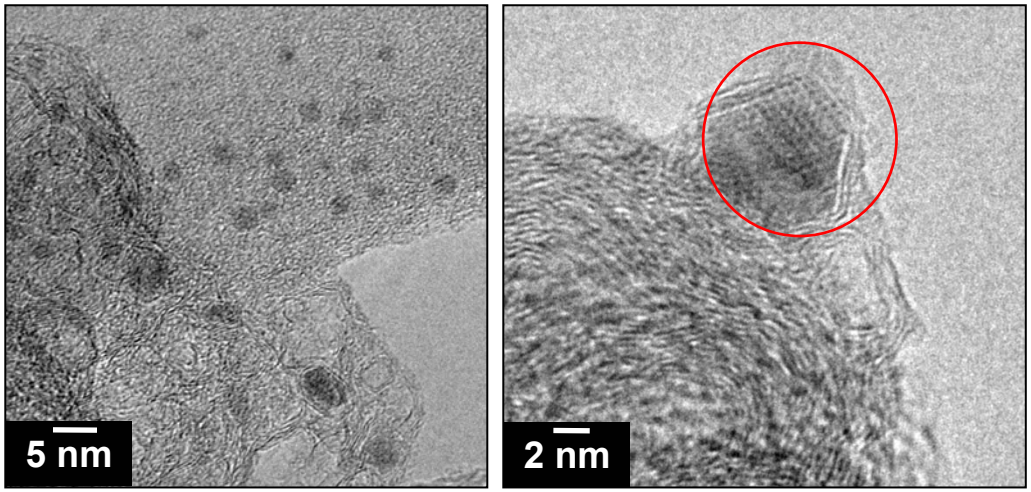
FTIR Spectroscopy



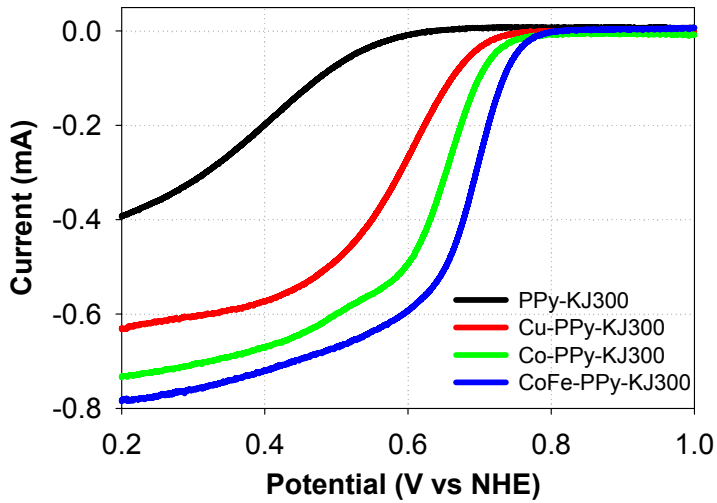
- **New thermally-untreated catalyst demonstrated**
- **Spectroscopy showing good anchoring of CoTPPS to the PPy nanotubes**
- **After 200 cycles:**
  - **CoTPPS-XC72** $\Delta E_{1/2}$ **~100 mV**
  - **CoTPPS-PPy (NT)** $\Delta E_{1/2}$ **~15 mV**
- **Catalyst durability much improved relative to that of CoTPPS supported on carbon (XC72)**

Heat-treated Catalysts: *Metal*-PPy-KJ300 System

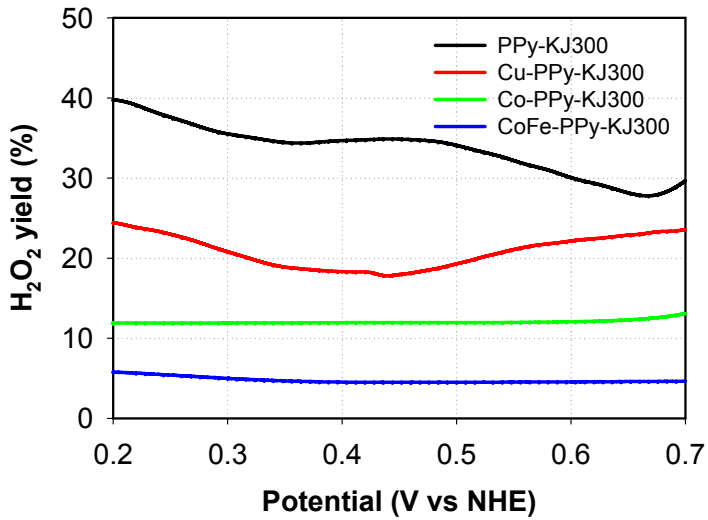
TEM of CoFe-PPY-KJ300



ORR by RRDE



- Heat-treated catalysts: PPy, PANI, and other complexes of Co, Cu, Fe, and Ni used as precursors in synthesis of transition-metal catalyzed nitrogen-doped and nitrogen-free ORR catalysts
- $E_{½}$ of CoFe-PPy-KJ300 reaching 0.7 V
- H_2O_2 yields reduced to about 5% for the best performing catalyst (CoFe-PPy-KJ300)
- Crystalline, metallic, phase detected by TEM and *in situ* XAFS



0.4 mg *Metal-PPy-KJ300* cm^{-2}; 0.5 M H_2SO_4
5 mV s^{-1}; 900 rpm

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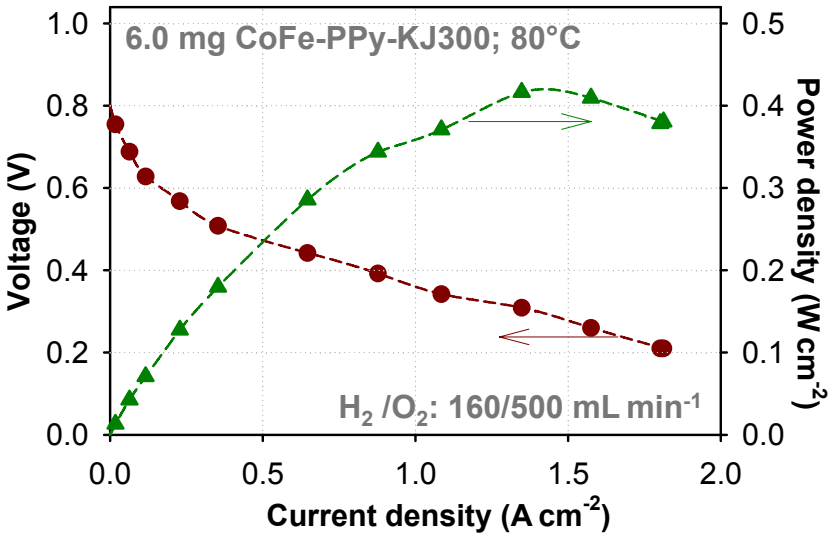
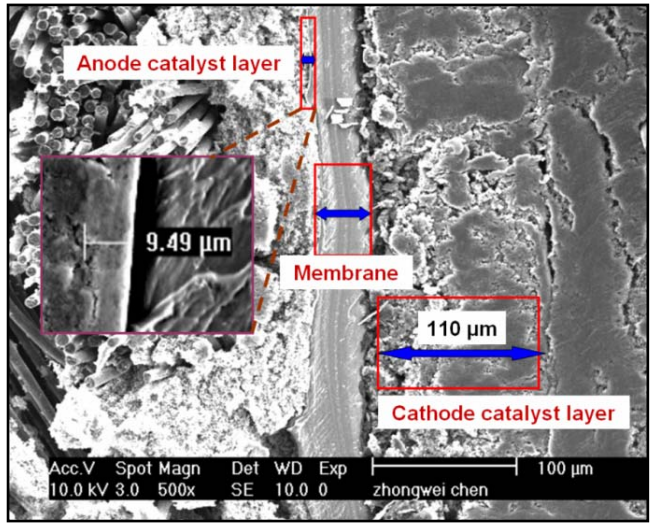
CoFe-PPy-KJ300 Catalyst: Fuel Cell Performance

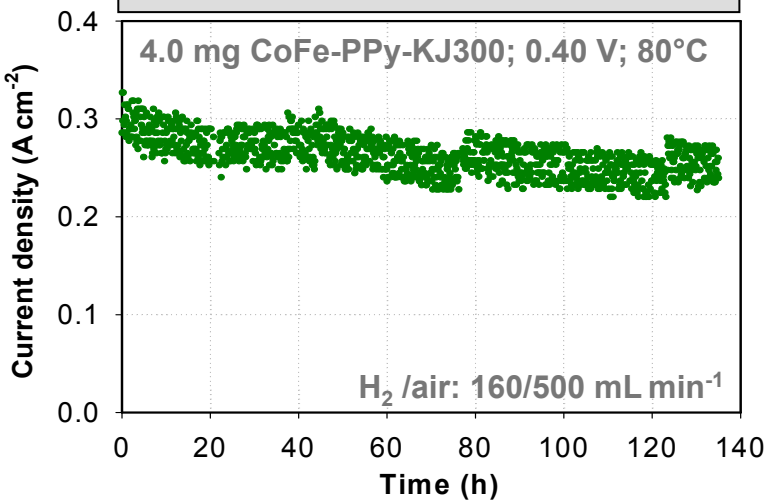
Polarization curve: O_2



Cross-sectional SEM image of MEA



Life test: Air



CoFe-PPy-KJ300 layer thickness:

- *ca.* 100 µm at 6.0 mg cm^{-2}

Volumetric current density (O_2):

- 0.60 V: 3 A cm^{-3}
- 0.40 V: 17 A cm^{-3}
- 0.20 V: 37 A cm^{-3}

Good performance stability at 0.40 V, with less than 10% degradation over 130 hours; flooding the likely cause

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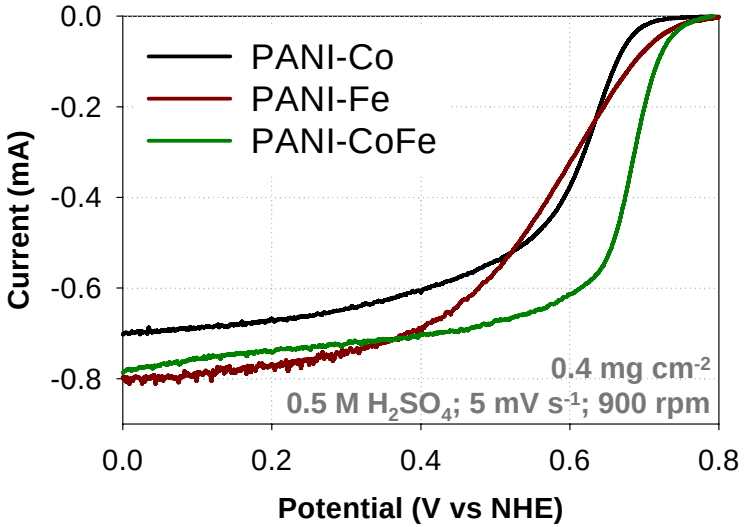
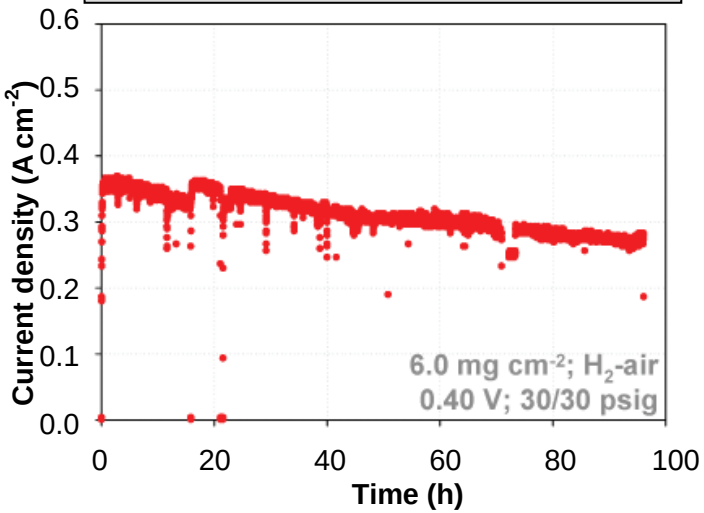
Polyaniline-derived Catalysts: RRDE & Fuel Cell Testing

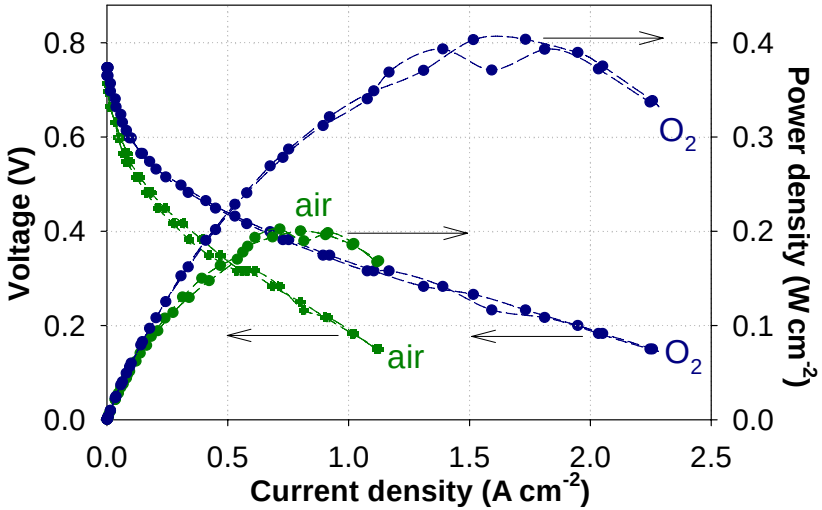
ORR by RRDE



Fuel cell life test



Fuel cell performance

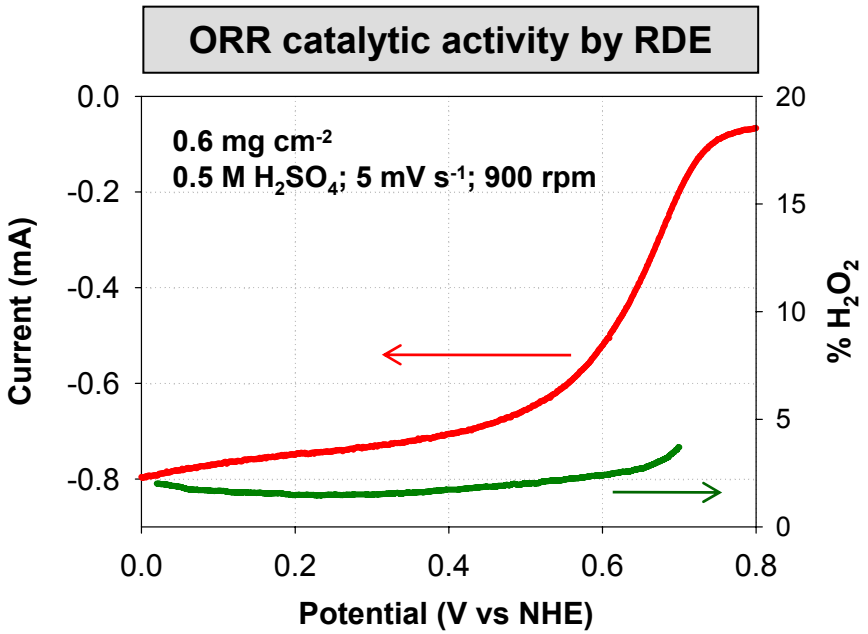


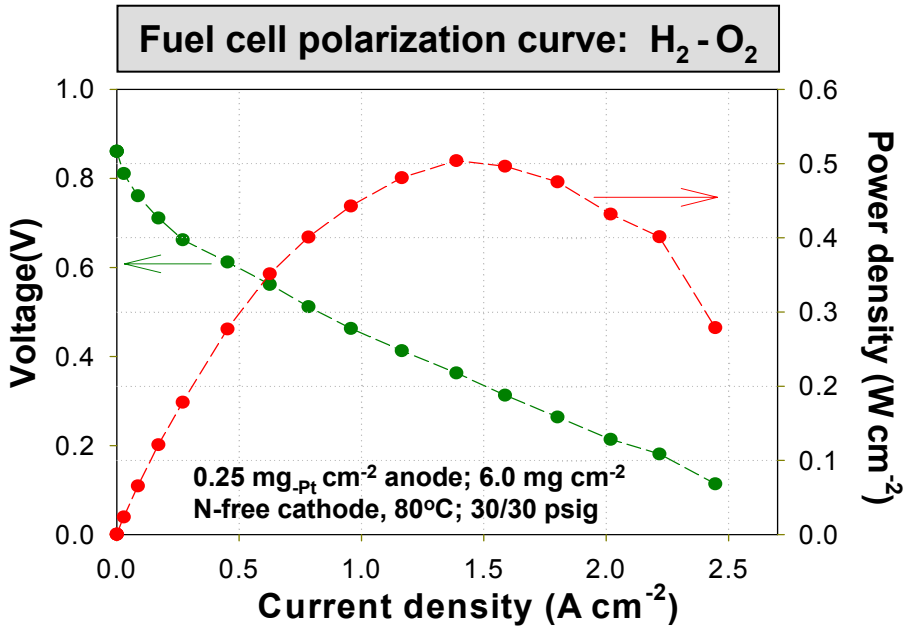
- **Combining Co and Fe produces the best catalytic activity and less than 4% H_2O_2 yield (ring data not shown)**
- **Overall performance similar to that of CoFe-PPy-KJ300 catalyst**

O_2 (volumetric):		**Air (volumetric):**	
0.60 V:	**2 A cm^{-3}**	**0.60 V:**	**1 A cm^{-3}**
0.40 V:	**13 A cm^{-3}**	**0.40 V:**	**6 A cm^{-3}**
0.20 V:	**39 A cm^{-3}**	**0.20 V:**	**19 A cm^{-3}**

0.25 mg_{-Pt} cm^{-2} anode (ELAT); 6.0 $mgcm^{-2}$
FeCo-PANI-KJ300 cathode, 80°C

New Nitrogen-free Fe-based Catalyst (Heat-treated)





- High ORR half-wave potential: ~ 0.7 V
- H_2O_2 yield reduced to ca. 2% between 0.1 and 0.6 V
- Catalyst showing good performance stability for more than 100 hours
- Volumetric current density (O_2):

0.60 V:	8 A cm^{-3}
0.40 V:	22 A cm^{-3}
0.20 V:	40 A cm^{-3}

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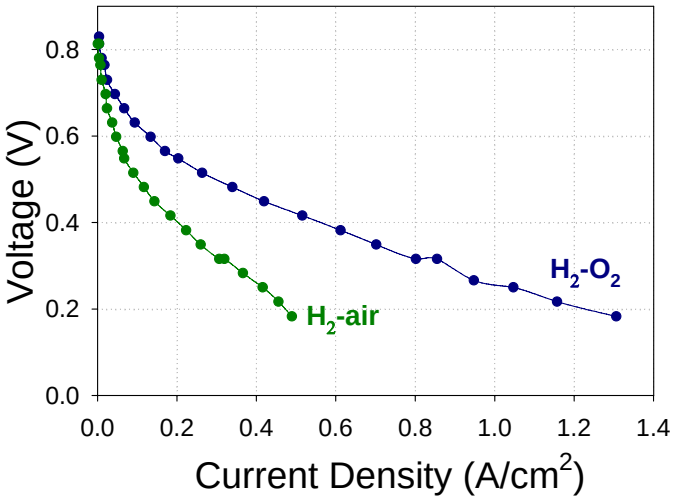
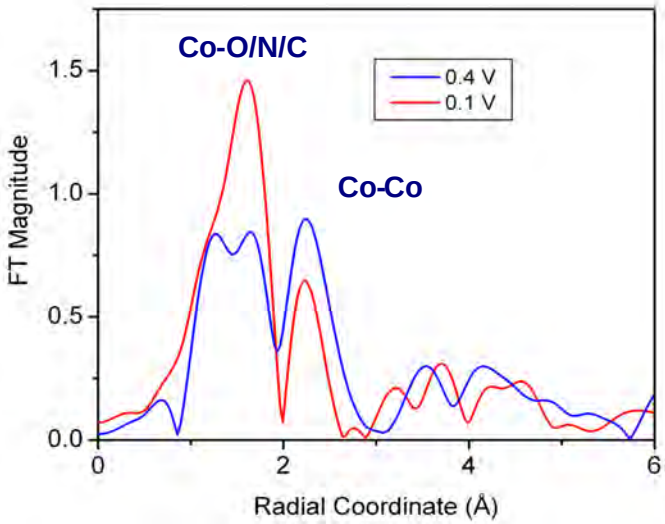
EDA-derived Catalyst: FeCo-EDA-KJ300

Fuel cell polarization data

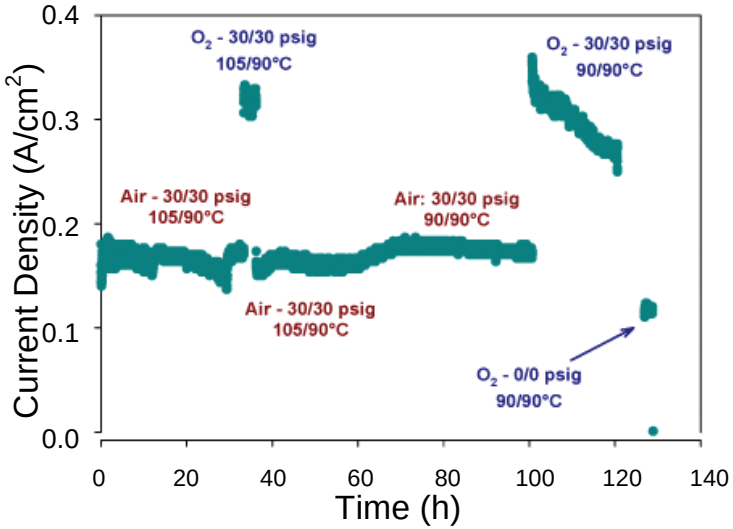


XAFS



Fuel cell life test

Anode: 0.2 mg cm^{-2} 20% Pt/C (E-TEK); Cathode: 2 mg cm^{-2} (V-i curves) or 4 mg cm^{-2} (life test) ***FeCo-EDA-KJ300;*** *Membrane: Nafion®115 Cell: 80°C; H_2/air (O_2)*



- **Catalyst derived from ethylenediamine (EDA) complexes of Fe and Co**
- ***In situ* XAFS showing metallic Co not affected by potential and mobile Co-N/C/O species**
- **Respectable current density of 0.52 and 0.22 A cm^{-2} generated at 0.40 V using oxygen and air**
- **Water accumulation affecting MEA performance**
- **Novel electrode structures needed**

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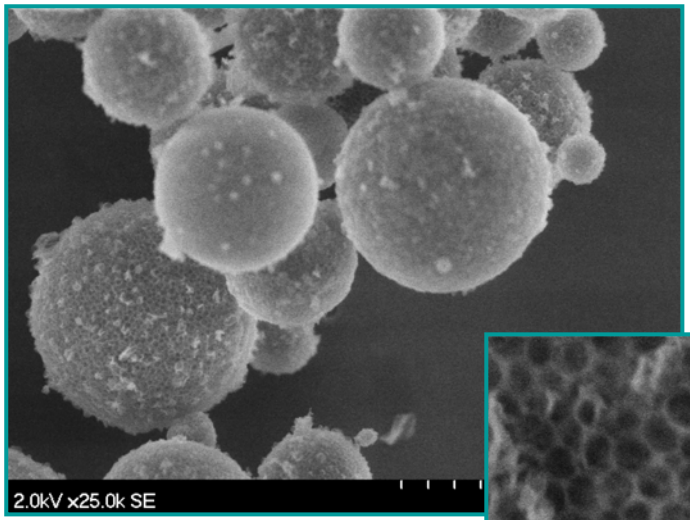
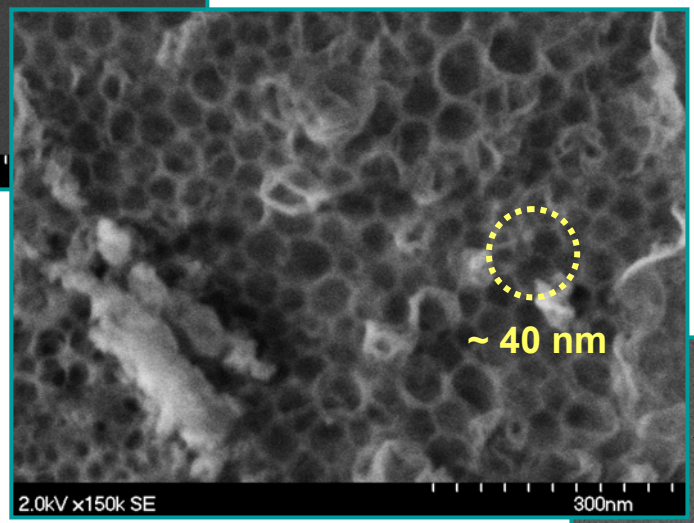
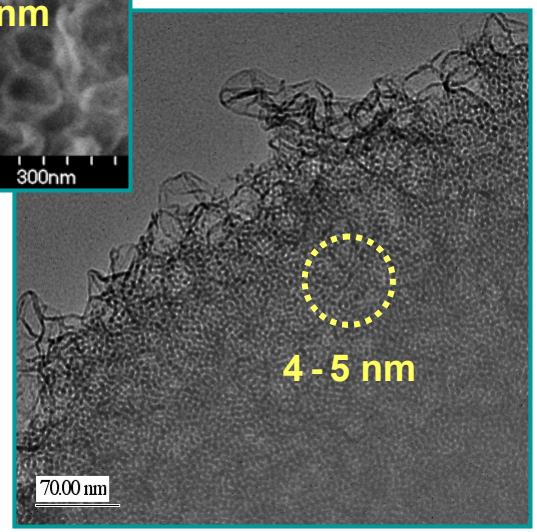
New Silica-templated Electrode Structures with Hierarchical Porosity



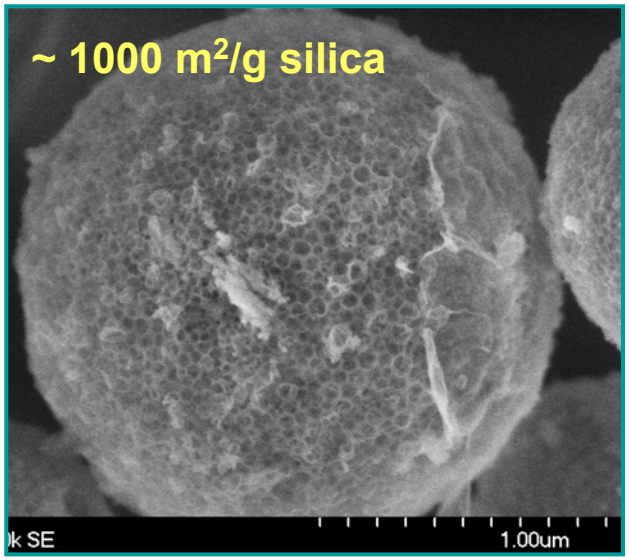
BET surface area ~ 1000 m^2/g



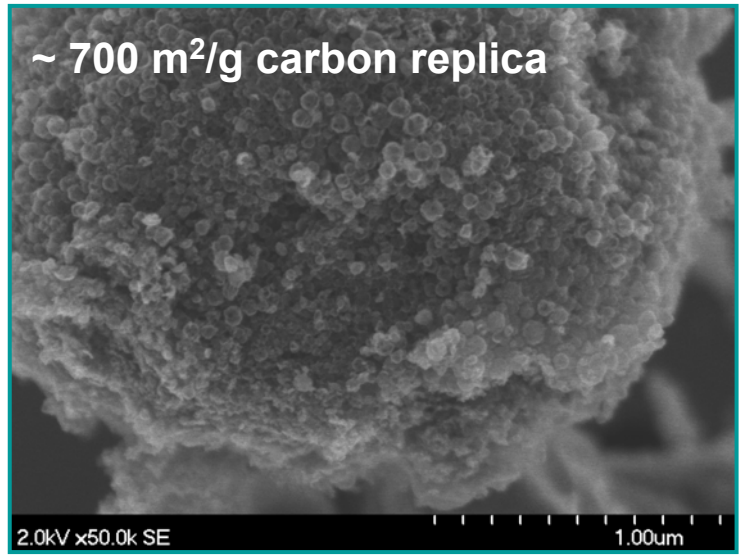


- Droplets of oil emulsion in an aqueous phase defining the mesopore size
- Droplets of water oil phase (reverse emulsion) dictating the micropore size

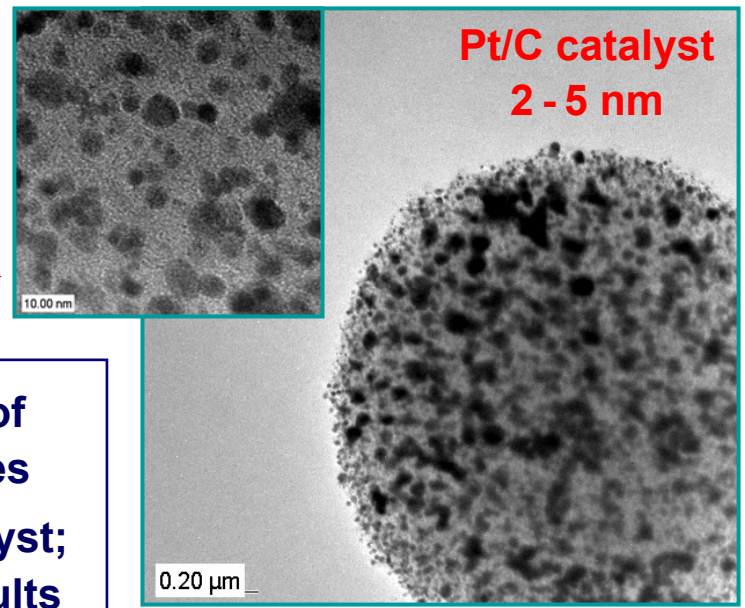
New Silica-templated Electrode Structures: Catalyzation



1. *Carbon precursor*
2. *Pyrolysis (900 ℃)*
3. *Silica removal*



1. *Impregnation with carbon- and Pt-precursors*
2. *Pyrolysis (900 ℃)*
3. *Silica removal (KOH leach)*



- **Developed a new microemulsion method of making hierarchically structured electrodes**
- **Approach used to make 30 wt% Pt/C catalyst; catalyst tested at RDE with promising results**

Future Work

Remainder of FY08:

- Synthesize sufficient amount of three most promising core-shell catalysts for fuel cell testing (ultra-low Pt content catalysts); perform fuel cell testing of core-shell catalysts at LANL
- Finish synthesis and performance testing, including fuel cell test, of Se/Ru-Fe/C catalyst
- Optimize synthesis and performance of heat-treated PANI-based and new N-free catalysts
- Develop system for direct electrochemical detection of H_2O_2 in polymer electrolytes
- Characterize oxidation state and chemical composition of (i) non-precious metal catalysts during the heat-treatment step of the preparation and (ii) ultra-low Pt and chalcogenide catalysts
- Demonstrate control of porosity and metal particle-size in silica-templated hierarchical catalysts

FY09:

- Develop core-shell catalysts with acid-stable, well-protected cores as support for a Pt monolayer; initiate synthesis of nanoparticles with controlled shapes as substrates for Pt
- Increase non-precious metal content in chalcogenide catalysts to at least 50%; improve fuel cell performance of chalcogenide catalysts to the level expected based on the RDE testing
- Improve volumetric activity of catalysts based on heat-treated and untreated heteroatomic polymer nanostructures (nanofibers, nanotubes)
- Improve volumetric activity of thermally-treated nanostructured carbon-on-carbon catalysts
- Determine oxidation state and chemical composition of three selected advanced cathode catalysts as a function of potential and time using in-situ X-ray absorption and electrochemistry
- Investigate tri-phase interface in catalysts with hierarchically porous carbonaceous structure
- Optimize polymer nanostructure for oxygen transport in selected non-precious catalyst system

Summary

- Several "core-shell" catalysts offer more than threefold fuel-cell performance advantage per mass of Pt than a reference Pt/C catalyst in the entire range of the cell voltage and meet 2010 DOE performance targets
- Partial replacement of Ru by Fe in chalcogenide catalysts is possible without a significant drop in the ORR activity (half-wave potential of maximizing at ~ 0.75 vs. RHE)
- Thermally-untreated CoTPPS-PPy catalyst, supported on polypyrrole and synthesized electrochemically using an AAO template, exhibits good activity and greatly improved durability compared to the carbon-supported CoTPPS reference catalyst
- Several novel non-precious catalysts, derived from transition-metal complexes of PPy, PANI, and EDA using heat treatment, show high activity and selectivity in aqueous electrolytes as well as at the fuel cell cathode
- Susceptibility of carbon-rich non-precious catalysts to flooding, especially at high current densities, appears to be a major performance issue for non-precious catalysts
- Novel electrode structures, either polymer- or carbon-based (including AAO- and silica-templated structures) have been developed for ORR catalysts, with very promising performance in preliminary testing