Advanced Cathode Catalysts

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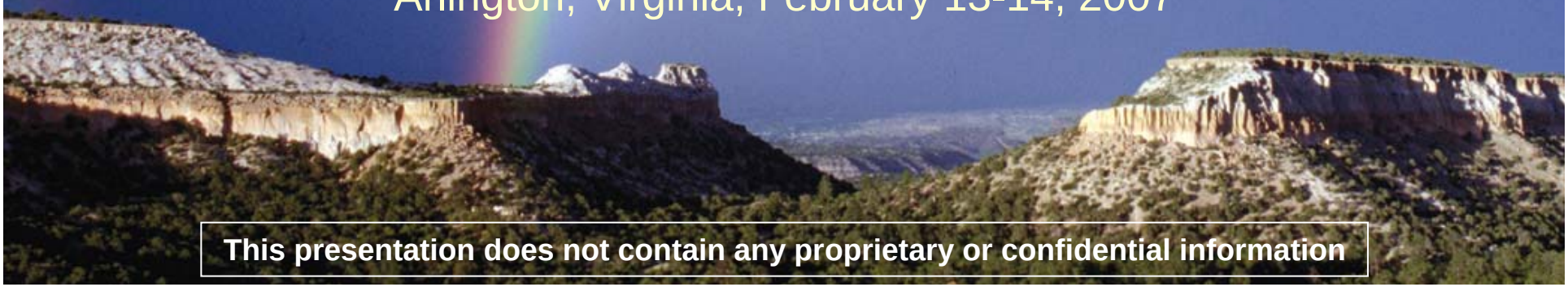
Hydrogen, Fuel Cells and Infrastructure Technologies
Program Kick-off Meeting
Arlington, Virginia, February 13-14, 2007



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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**

Technical Targets & Barriers

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)

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

Participating Organizations

– catalysts with ultra-low Pt content; Radoslav Adzic (PI)

– new-generation chalcogenides; Andrzej Wieckowski (PI)

– non-precious metal composites; Piotr Zelenay (lead-PI)

– open-frame catalyst structures; Plamen Atanassov (PI)

– nanostructure catalyst supports; Yushan Yan (PI)

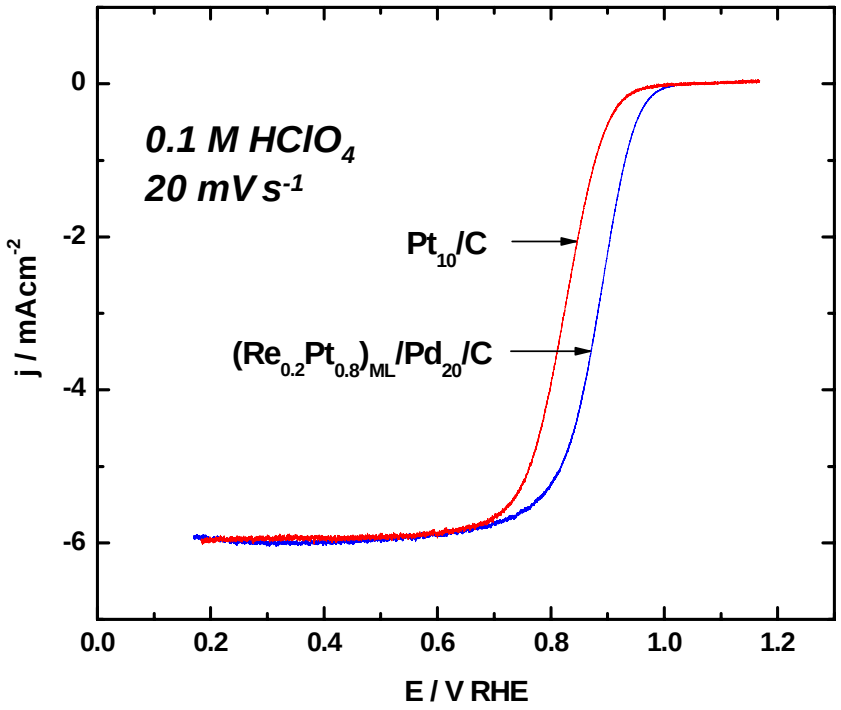
– characterization & durability; Debbie Myers (PI)

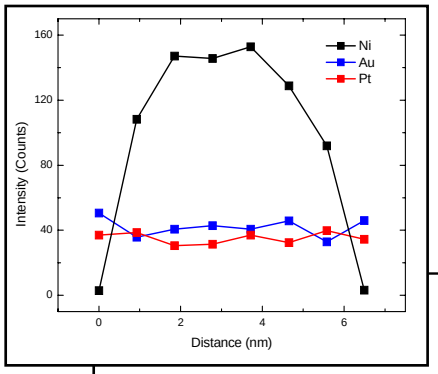
– characterization; Karren More (PI) - *planned start in FY08*

– fabrication & scale-up; Paolina Atanassova (PI)

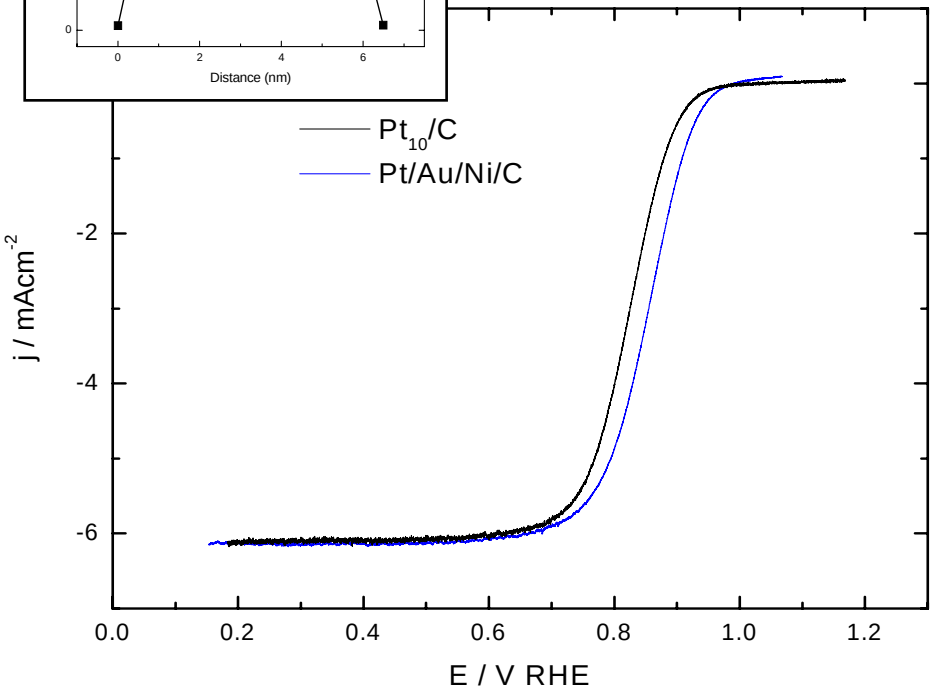
Catalysts: Materials with Ultra-low Pt Content

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





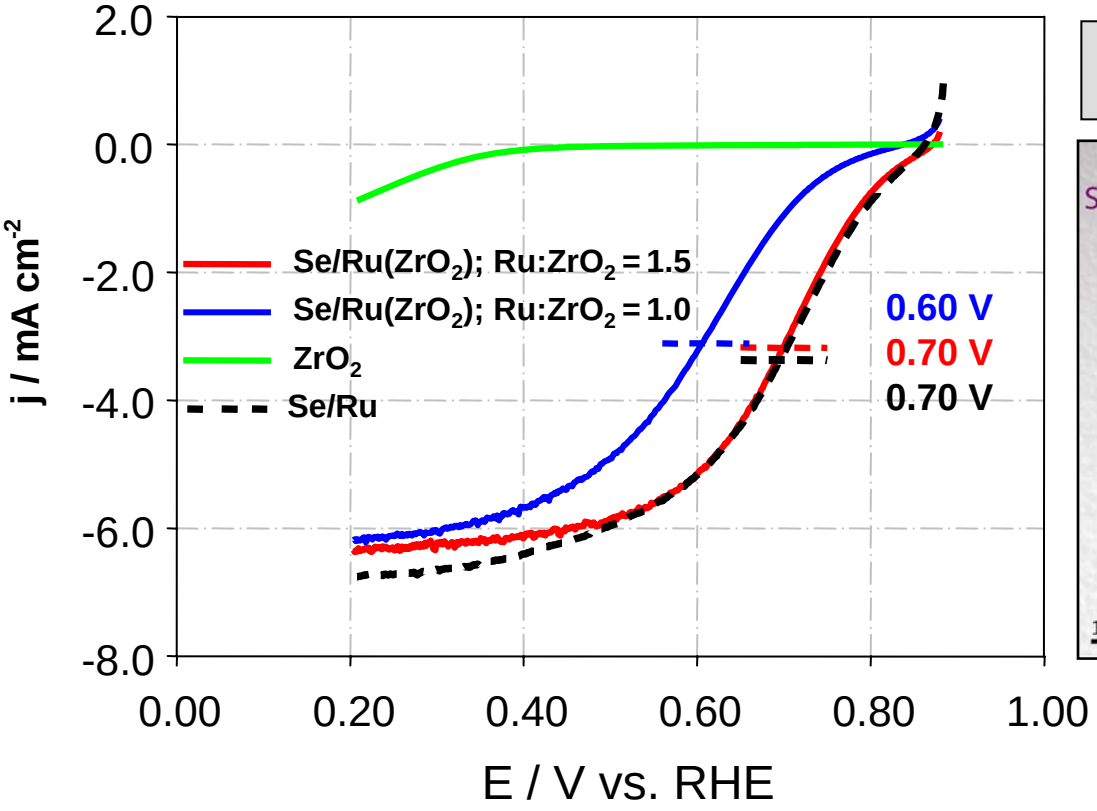
1060 μA cm^{-2} @ 0.90 V
1.5 μg$_{Pt}$ cm^{-2} & 2.3 μg$_{Au}$ cm^{-2}



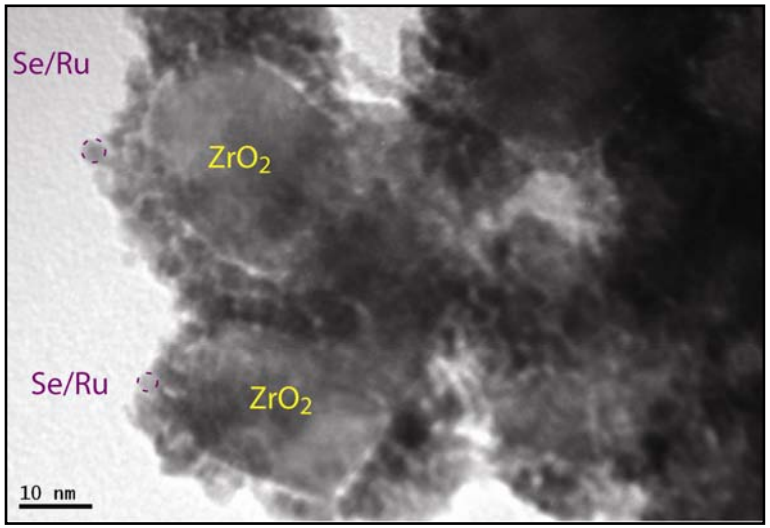
Stabilization of Pt_{ML}/Me/C and Pt/C, and reduction of noble metal content in Pt_{ML} catalysts using (i) mixed Pt-metal monolayer catalysts, (ii) non-precious-metal core/precious-metal shell nanoparticle catalysts, (iii) stabilization of Pt/C by Au clusters, (iv) Pd alloy catalysts

Catalysts: New-generation Chalcogenides

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

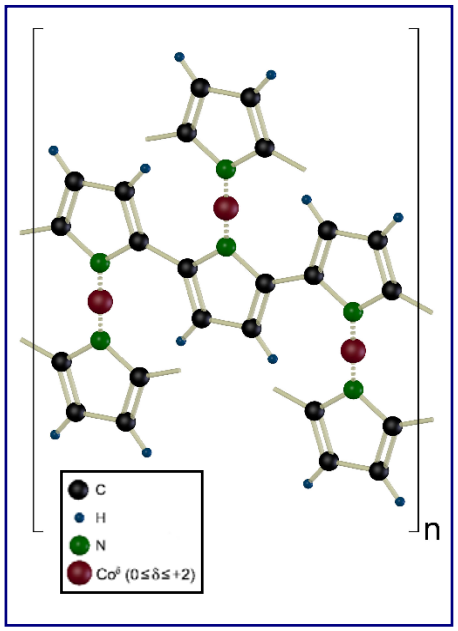


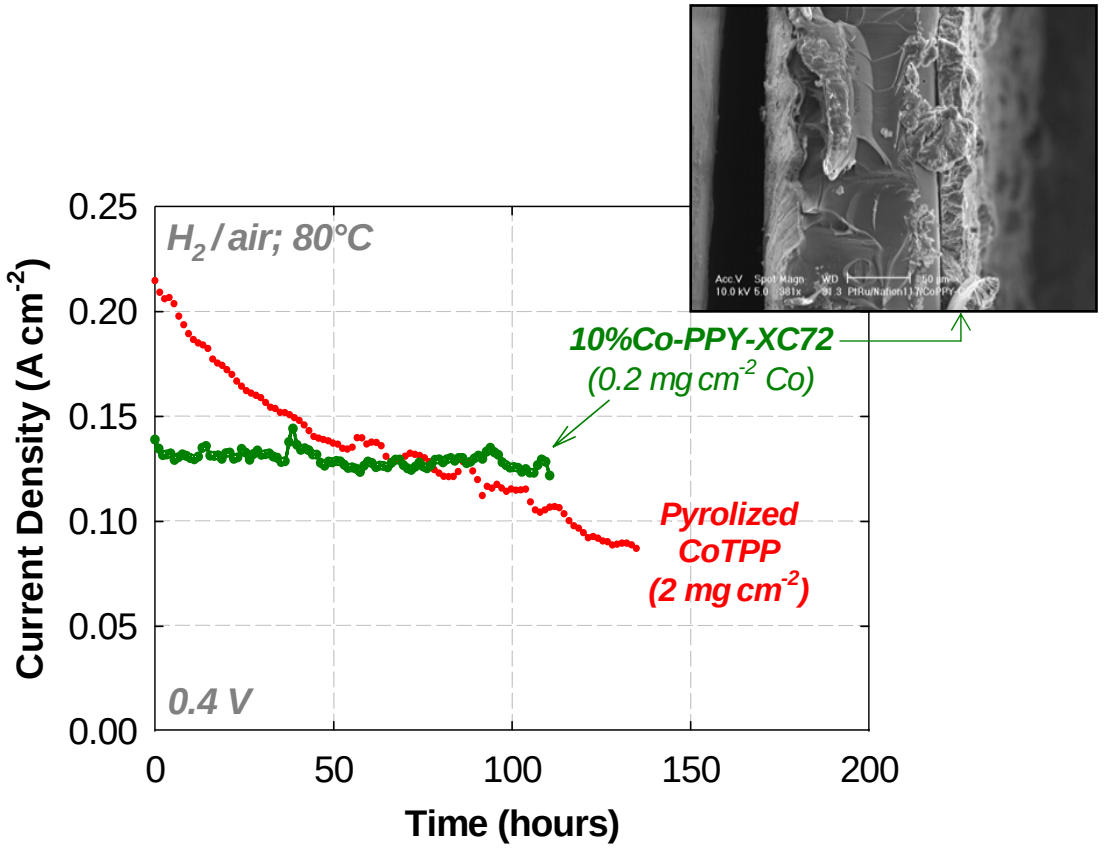
Transmission Electron Microscopy:
Se/Ru(ZrO_2) (~ 20 nm ZrO_2 particle size)



- ***Modification of electronic properties of Ru by homogeneous mixing with Fe-group metals; protection of the nanoparticle interior by Ru skin***
- ***ZrO_2 matrix for high dispersion and possible increase in Se durability***

Catalysts: Non-precious Metal Composites

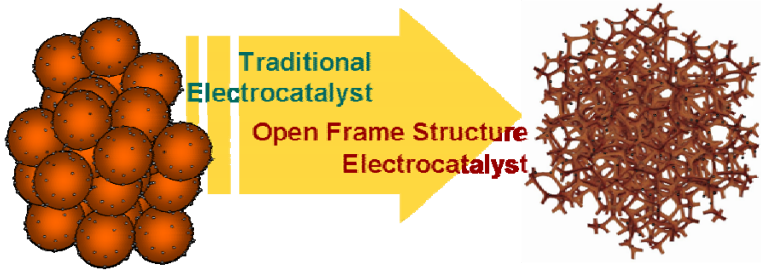


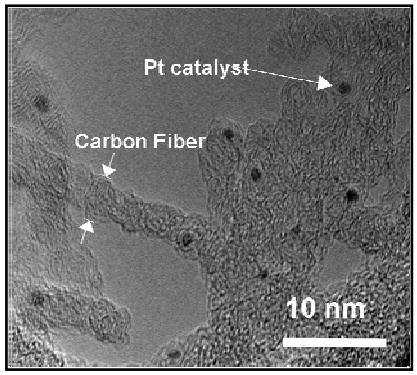


- ***Novel strategies for the preparation of nanoporous heteroatomic polymers and non-precious-metal incorporation into polymer matrix***
- ***Activity enhancement: (i) ORR mechanism understanding, (ii) effective active-site entrapment, (iii) major cathode-structure re-design***

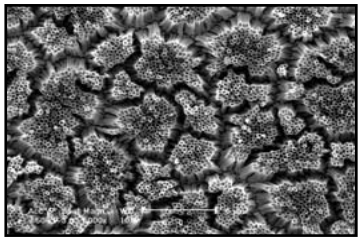
Novel Electrode Structures

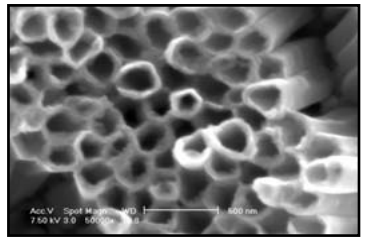
Open-frame Catalyst Structures



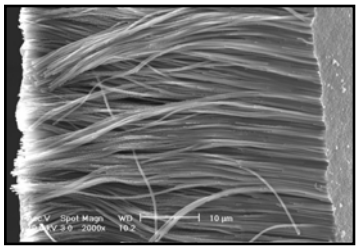


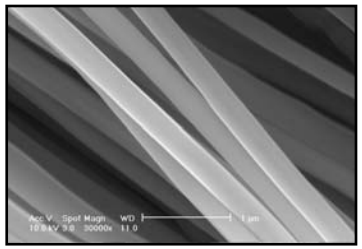
Conductive Nanostructures





PPY nanotubes by electrochemical polymerization

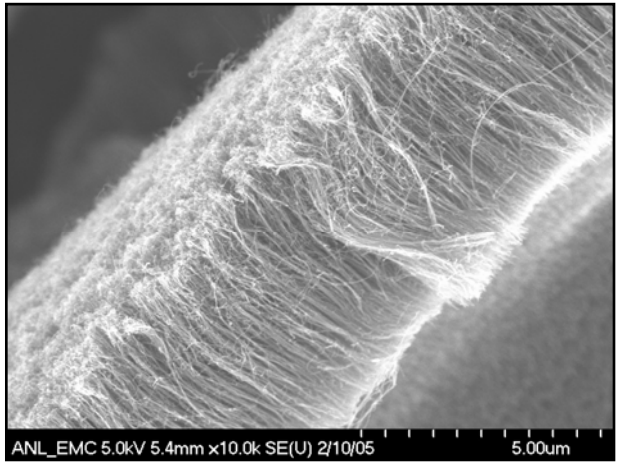




PPY nanowires by chemical polymerization

Electrode structures for (i) improved oxygen transport and precious-metal catalyst utilization, (ii) increased non-precious catalyst loading, (iii) tunable hydrophobicity/hydrophilicity, (iv) enhanced stability, (v) efficient H_2O management

Extensive Catalyst Characterization



X-ray Absorption Spectroscopy for Determining Atomic Structure (Example: ANL)

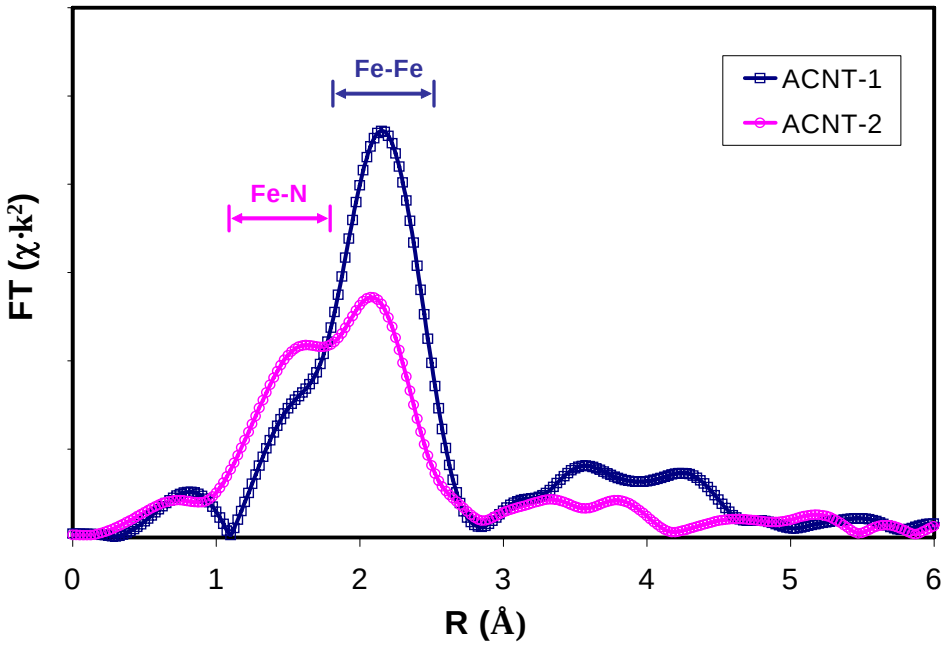
ACNT - iron-aligned carbon nanotube catalyst
ACNT-1 - ACNT without nitrogen during synthesis
ACNT-2 - nitrogen-incorporated ACNT

EXAFS Analysis of ACNT-1

Shell	CN	R (Å)	σ^2
Fe-Fe	4.5	2.56	0.0005

EXAFS Analysis of ACNT-2

Shell	CN	R (Å)	σ^2
Fe-N	4.2	1.95	0.0005



Task Leads & Schedule

TASKS & LEADS		QUARTER															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
BNL	1.1				M				M G				M G				M
	1.2				M				M G				M G				M
	1.3				M				M G				M G				M
	1.4				M				M G				M G				M
	1.5																M
UIUC	2.1				M				M G				M G				M
	2.2				M				M G				M G				M
	2.3											M		M G	M G		M
LANL	3.1	M G															
	3.2		M G														
	3.3			M G													
	3.4				M G												
	3.5								M G				M G				M
UNM	4.1				M				M G				M G				M
UCR	4.2				M G				M G				M G				M
ANL LANL	5.1																M
	5.2																M
	5.3																M
CSMP	6.1				M G												M
	6.2								M G								M
	6.3								M G								M

M – milestone
G – go/no-go decision

FY 2007 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

Task 3: Non-precious Metal/Heteroatomic Polymer Nanocomposites

- Synthesis of heteroatomic polymer with mesoporous carbon structure (G - material properties)
- Synthesis of heteroatomic polymer(s) on carbon nanotube structure (G - material properties)
- Synthesis of heteroatomic polymer using novel techniques (G - material properties)
- Integration of non-precious metals and alloys into heteroatomic polymer (G - material properties)

FY 2007 Milestones & Go/No-Go Decisions

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)

Note: **Modifications to scope of work may be needed as a result of:**

(a) reduced project funding
(b) delay in contracts

Project Funding Estimate

Source	Period	Amount, $
DOE	2007	1,980,000
	2008	2,150,000
	2009	2,200,000
	2010	2,200,000
	2011	$70,000
	2007-2011	**8,600,000** (96%)
Recipients	**2007-2011**	**360,000** (4%)
TOTAL	**2007-2011**	**8,960,000** (100%)


Thank You & Good Luck!