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Non-Platinum Cathode Catalysts

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Project ID
FC14

Project Overview

Timeline

- **Start date** – Jan 2004
- **End date** – *TBD*

Budget

- **FY05 Funding** – $350K
- **FY06 Funding** – $500K

Technical Barriers

- **A. Durability**
  - catalyst
  - electrode layer
- **B. Cost**
  - catalyst
  - MEA
- **C. Electrode Performance**
  - ORR overpotential
  - O_2 mass transport

Partners

- **University of Illinois, Urbana-Champaign** (Andrzej Wieckowski)
- **Université de Poitiers, Poitiers, France** (Nicolas Alonso-Vante)
- **University of New Mexico, Albuquerque** (Plamen Atanassov)
- **University of California, Riverside** (Yushan Yan)
- **Mesoscopic Devices LLC, Denver** (Jerry Martin)

Targets

DOE Targets: Electrocatalysts for Transportation Applications (Stack)			
Characteristics (Units)	**2004 Status**	**2010**	**2015**
PGM Total Content (g/kW)	**1.3**	**0.5**	**0.4**
PGM Total Loading (mg/cm^2)	**0.8**	**0.3**	**0.2**
Cost ($\$/kW_e$)	**20**	**8**	**8**
Durability with cycling @ T ≤ 80°C (h)	**1,000**	**5,000**	**5,000**
Activity ($\mu A/cm^2$ @ 0.9 $V_{iR\text{-}free}$)	**180**	**720**	**720**
Non-Pt Catalyst Activity (A/cm^3 @ 0.8 $V_{iR\text{-}free}$)	**< 8**	**> 130**	**300**

Objectives

Primary Objective:

Develop low-cost non-platinum oxygen reduction reaction (ORR) catalysts for the polymer electrolyte fuel cell (PEFC) cathode, with similar activity and performance durability to the currently used Pt-based cathode catalysts

Individual Objectives:

- Identify and/or synthesize new cathode catalysts
- Determine performance of these catalysts, including ORR kinetics, low-pH stability, performance durability, etc.
- Establish the ORR mechanism, in particular, identify ORR active sites
- Design and optimize the performance of membrane-electrode assemblies (MEAs) with new catalyst used at the cathode
- Test and optimize catalyst performance durability
- Collaborate with the fuel cell industry on efficient integration of new catalysts into MEAs and facilitate catalyst technology transfer

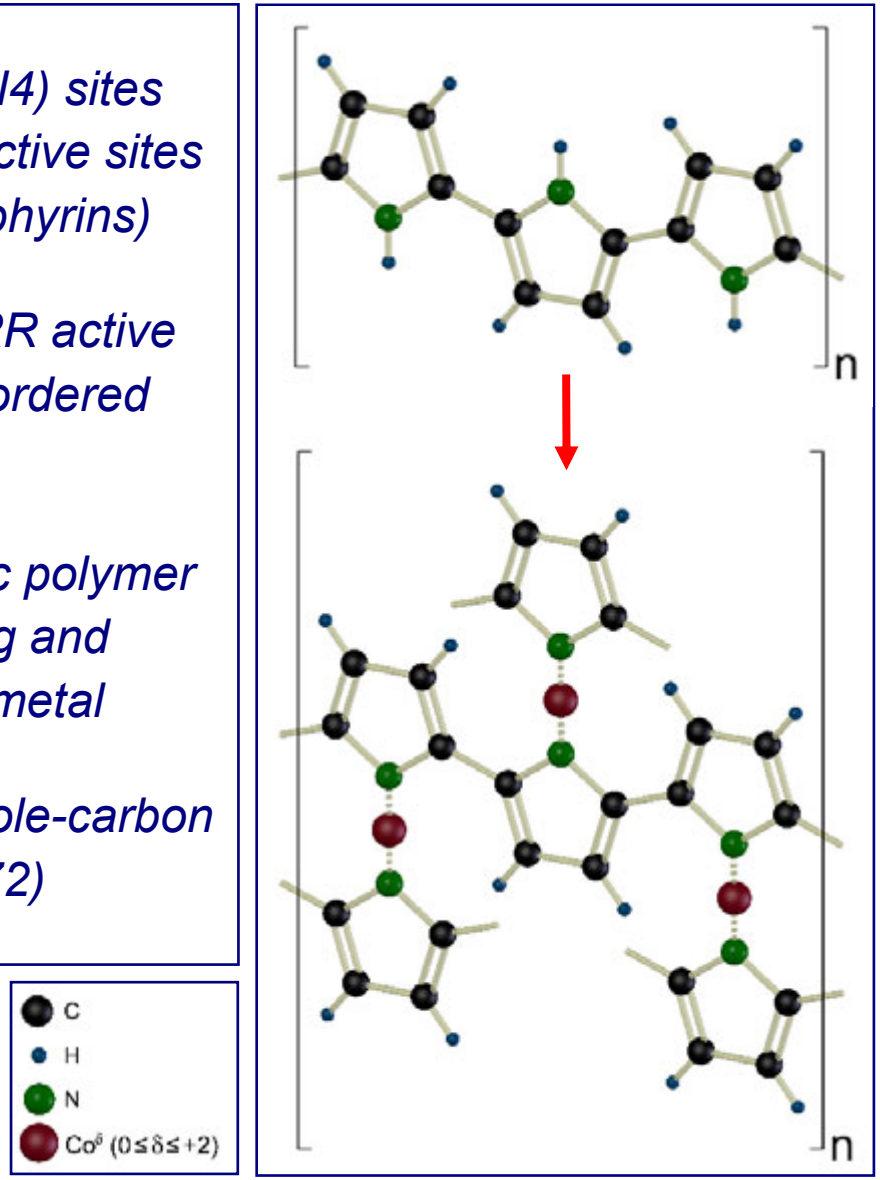
Approach

- **Develop advanced non-platinum cathode catalysts with either minimum precious metal content or entirely free of precious metals**
  - ***Non-precious metal / heteroatomic polymer nanocomposites***
  - ***"Chalcogenide-type" ORR catalysts by surface modification***

    a. *Organic solvent route*
    b. *Aqueous route*
    c. *PGM loading reduction via core-shell approach*
- **Through experimentation develop understanding of the ORR mechanism and factors impacting catalyst performance and durability**
- **Maximize performance, utilization of PGM-based catalysts and achievable loading of non-precious metal catalysts by designing novel ("open frame") cathodes**

Non-Precious Metal/Heteroatomic Polymer Nanocomposites

- ***Hypothesis:*** *CoN2 (CoN4) sites claimed to act as ORR active sites (e.g. in pyrolized Co porphyrins)*
- ***Objective:*** *Generate ORR active sites without destroying ordered structure of the catalyst*
- ***Approach:*** *Heteroatomic polymer as a matrix for entrapping and stabilizing non-precious metal*
- ***Choice:*** *Cobalt-polypyrrole-carbon composite (Co-PPY-XC72)*



Synthesis & Basic Properties of the Co-PPY-XC72 Nanocomposite

Pyrrole + XC72

↓

PPY-XC72

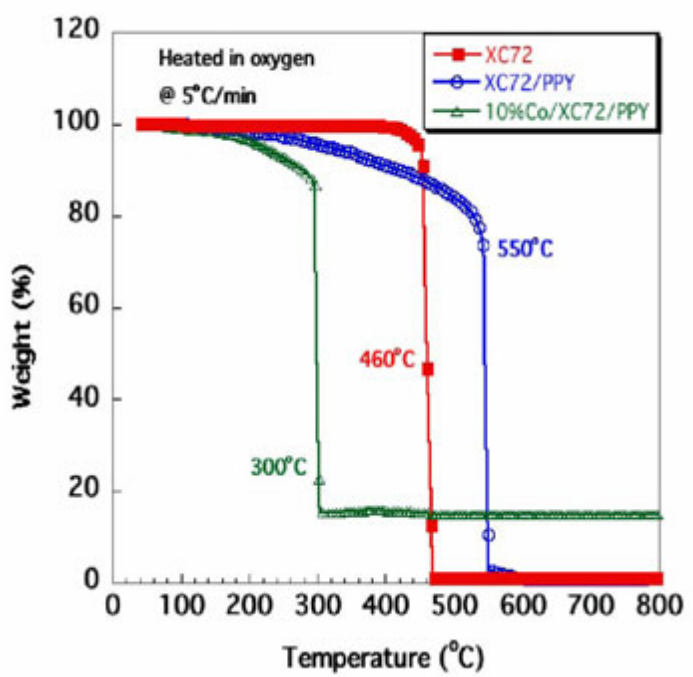
↓ ***(i) Co precursor***

(ii) Reduction

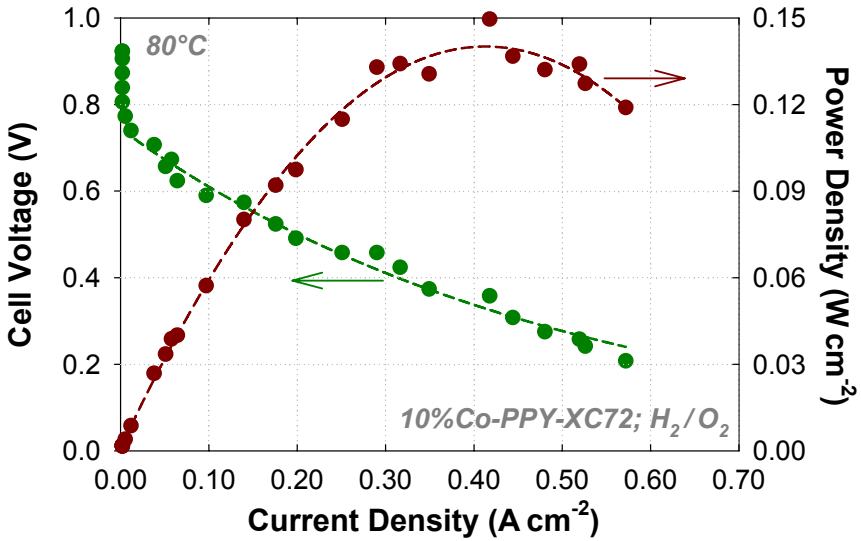
Co-PPY-XC72

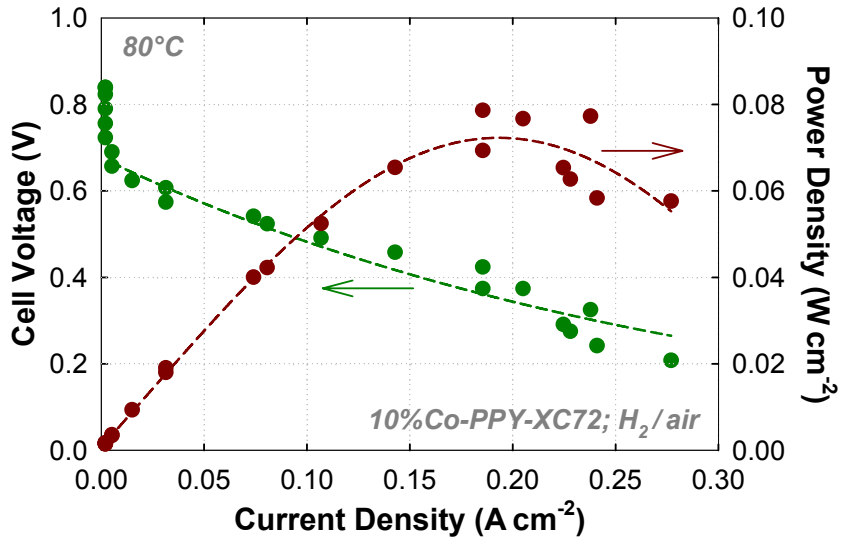
Composite	Surface Area (m^2/g)
XC72	240
PPY-XC72 PPY-XC72 *(reduced)*	100 100
Co-PPY-XC72	124
Co-PPY-XC72 *(pyrolized)*	140

Co-activated thermal decomposition of the catalyst occurring much above temperatures of the PEFC operation



Fuel Cell Testing of the Co-PPY-XC72 Nanocomposite



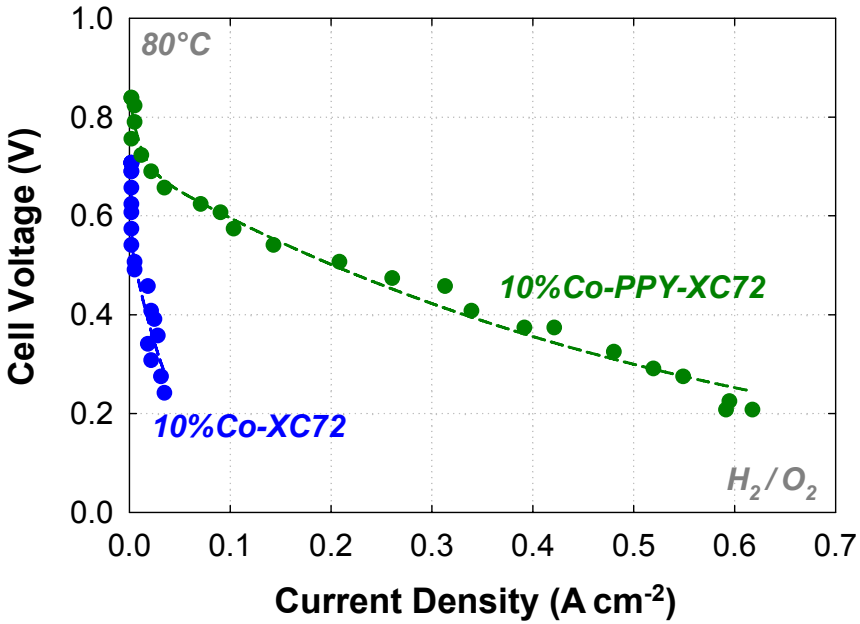


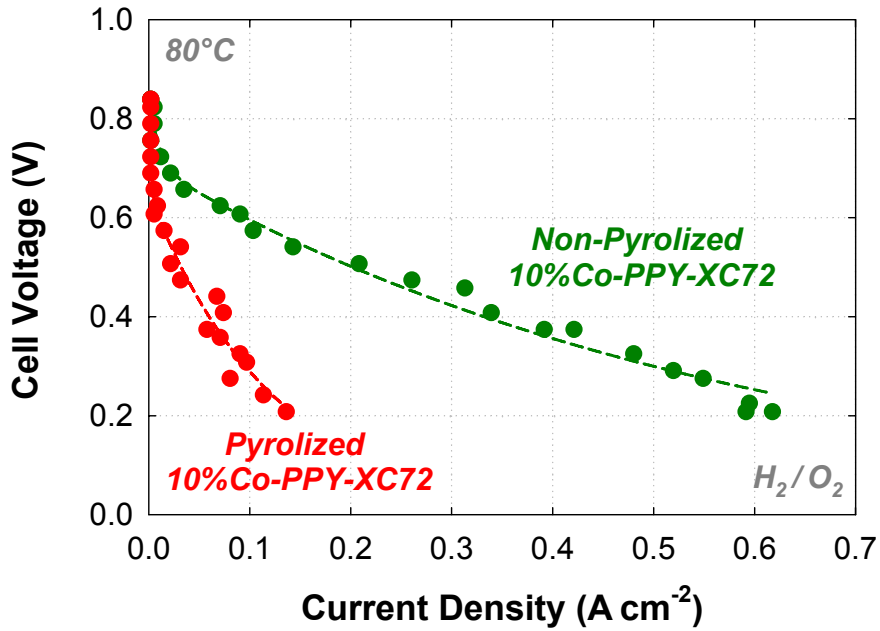
- *OCV in excess of 0.85 V in both O_2 and air operation*
- *PEFC cathode performance of the Co-PPY-XC72 nanocomposite close to that of the best performing pyrolized porphyrin catalysts*

A new class of non-precious metal ORR catalysts identified!

Does the "By-Design" Structure Matter?

***Pyrolysis*: 2 h @ 800°C; N_2 (T-change: 10°C / min)**

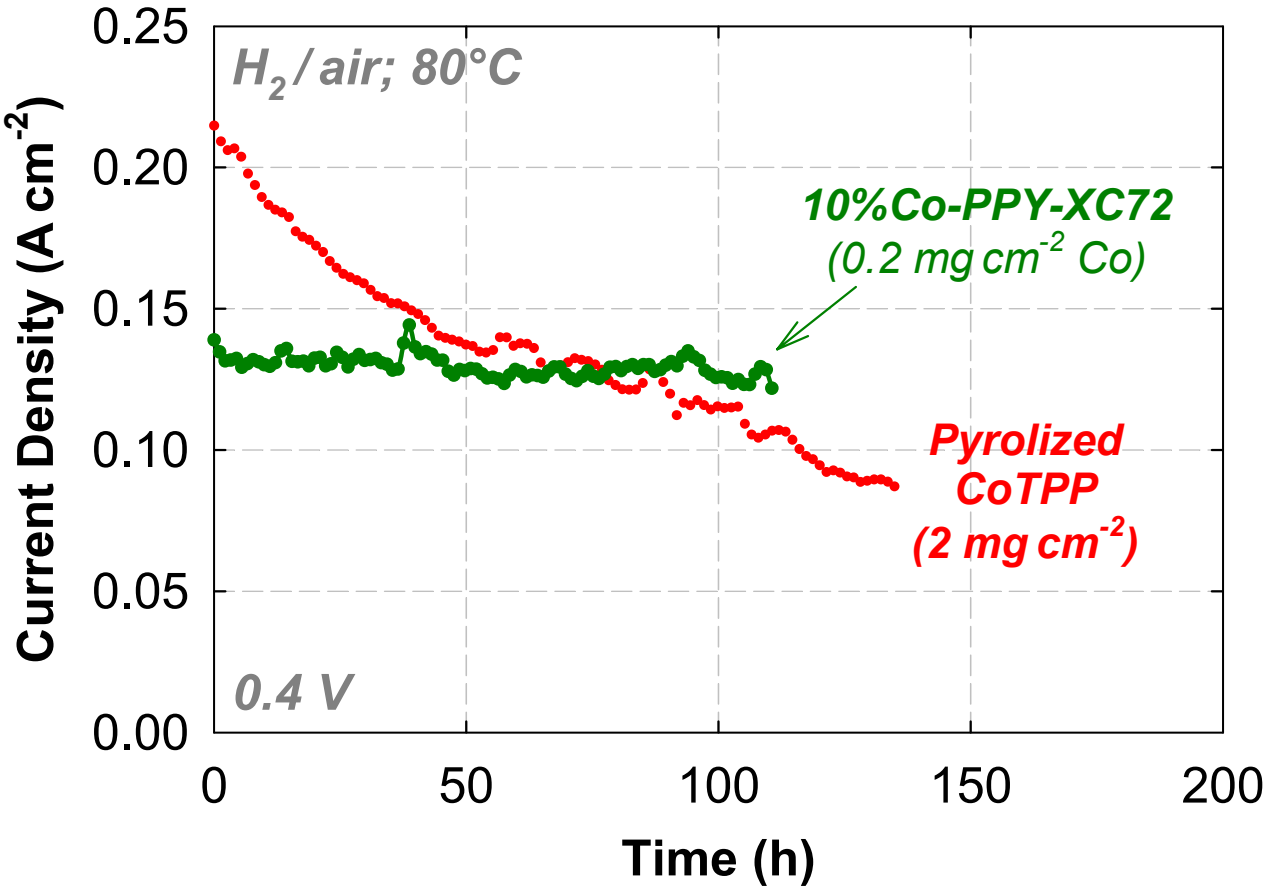




- ***Cell performance of Co-PPY-XC72 composite ~10× better at 0.4 V than that of carbon-supported Co catalyst***
- ***Cell performance of non-pyrolized Co composite ~7× better at 0.4 V than that of pyrolized Co-composite***

Co-N site crucial to ORR activity

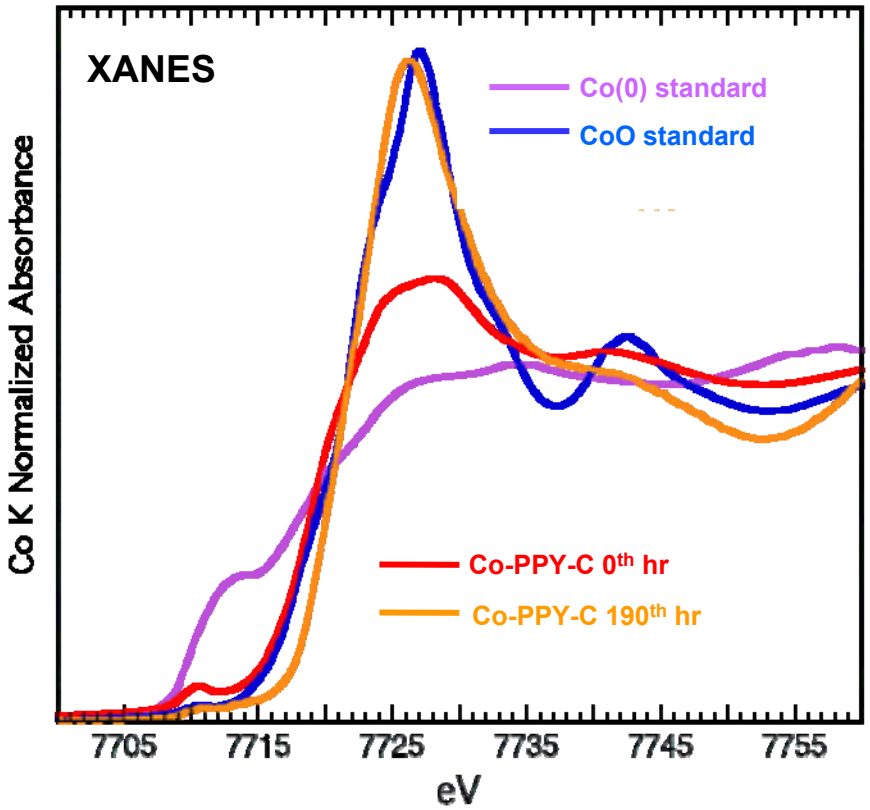
Co-PPY-XC72 Nanocomposite: Performance Durability

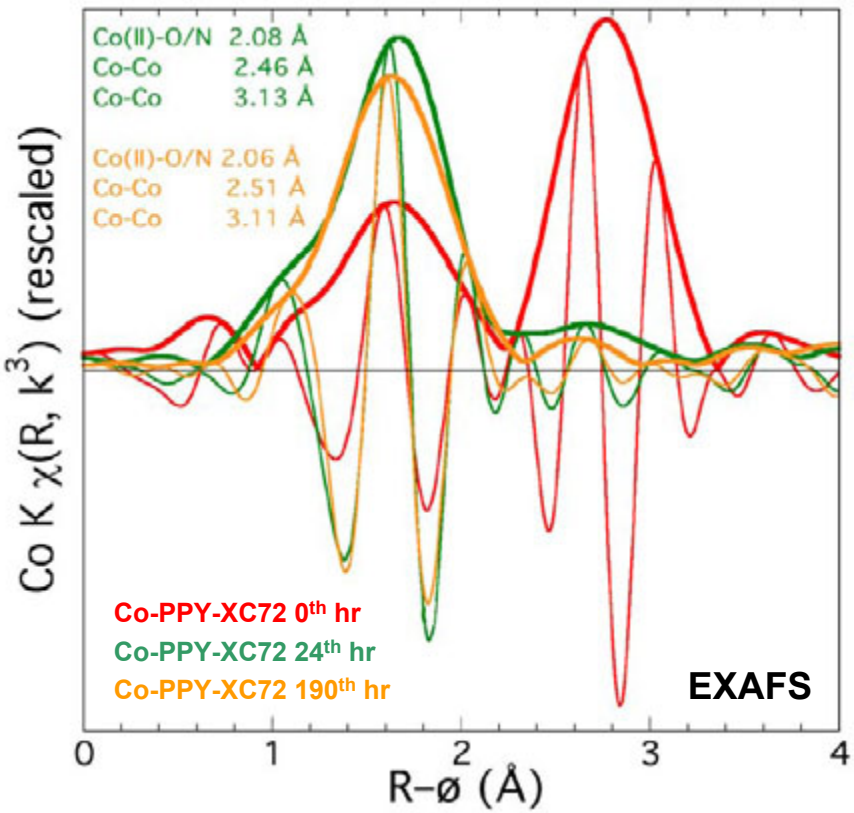


- *Stable operation of the Co nanocomposite catalyst for 110 hours*
- *Major improvement in stability over pyrolized-porphyrin catalysts*

Unique performance durability
for a non-precious metal catalyst at low pH

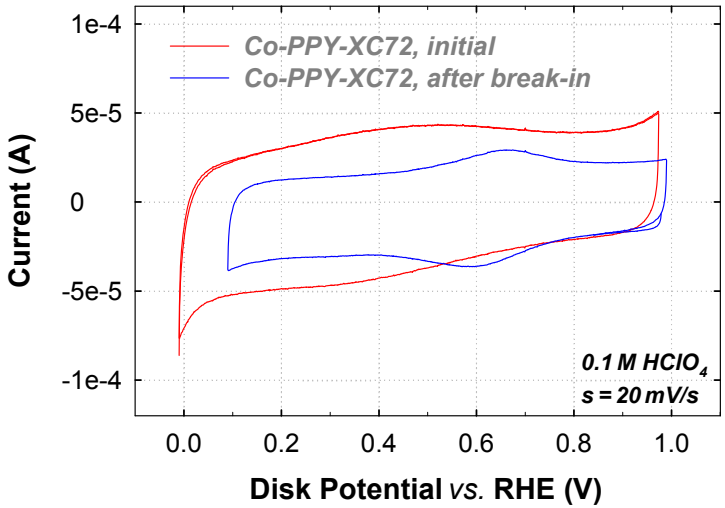
Structural Characterization by XANES and EXAFS

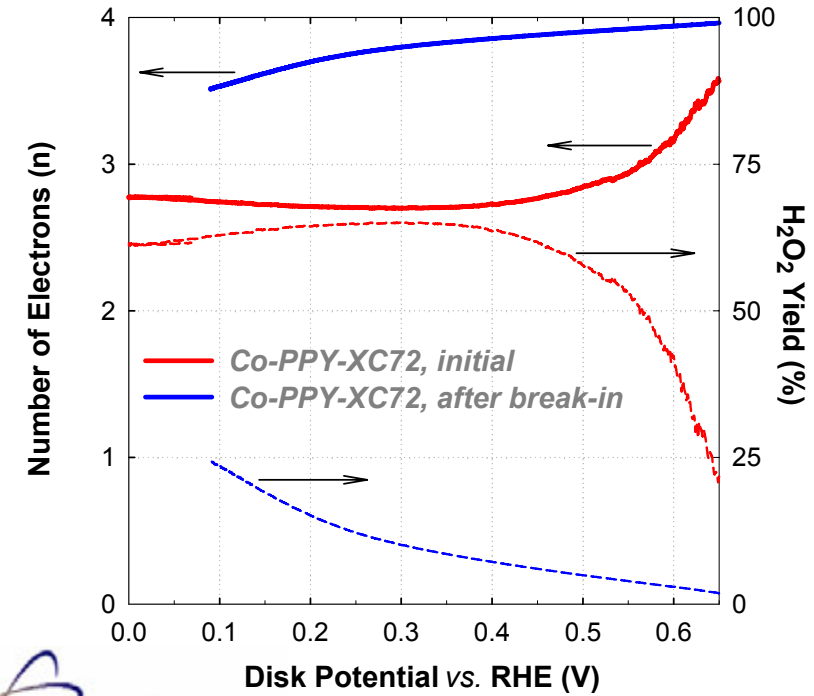


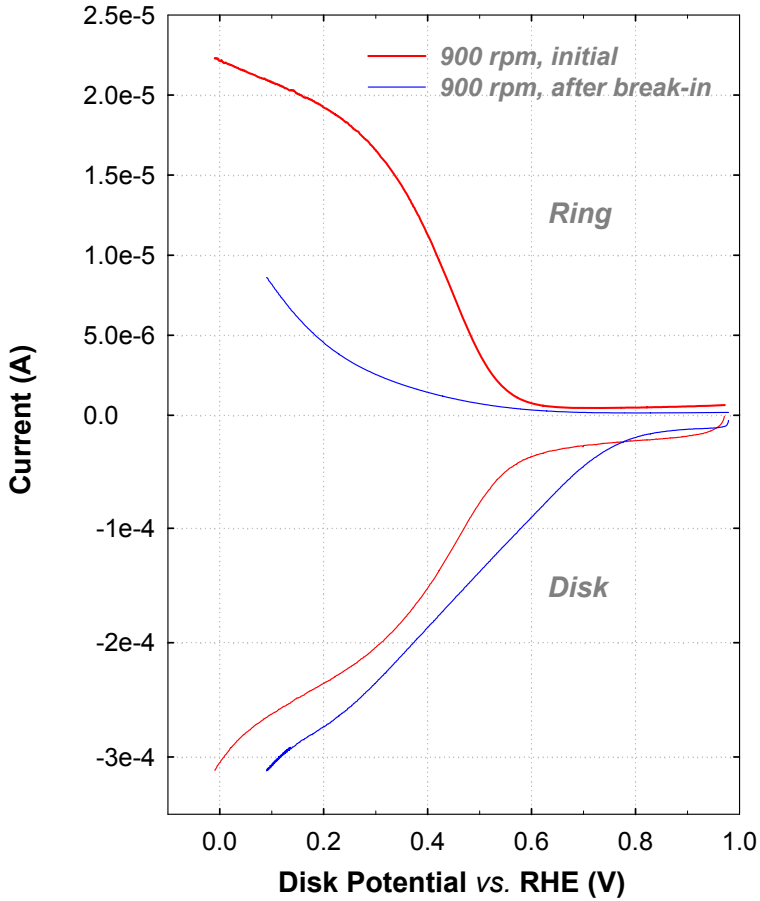


- ***XANES**: Both Co(0) present in as-synthesized catalyst; Co(II)-to-Co(0) ratio increasing during catalyst break-in*
- ***EXAFS**: Most of Co(0) transforming to Co(II)-O/N (i.e. O or N) states (not CoO)*
- ***EXAFS**: Good stability in time-resolved experiments (0^{th}, 24^{th}, and 190^{th} hour)*

Co-PPY-XC72 Nanocomposite: 4e⁻ *vs.* 2e⁻ Process (RRDE Study)

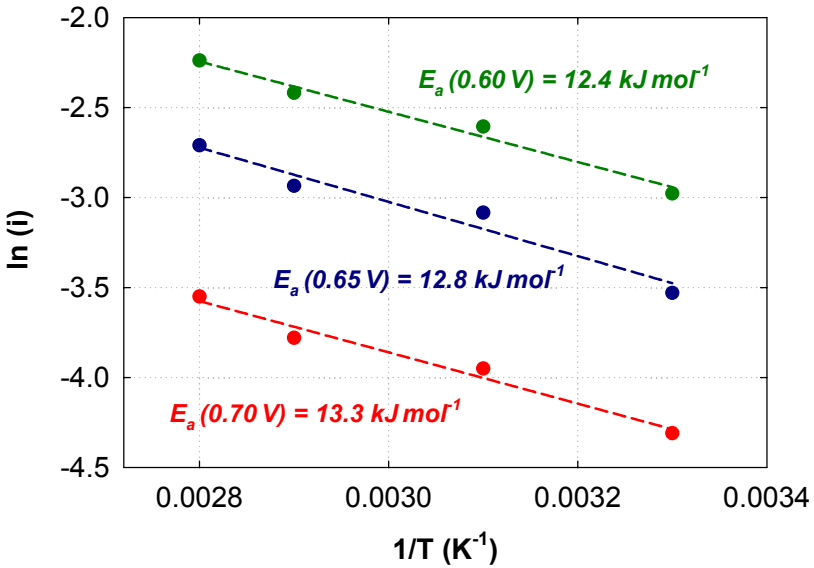






- ***Major reduction in the 2e⁻ process during 24-hour break-in***
- ***Negligible H_2O_2 generation at "practical" cathode potentials***

Co-PPY-XC72 Nanocomposite: ORR Kinetics



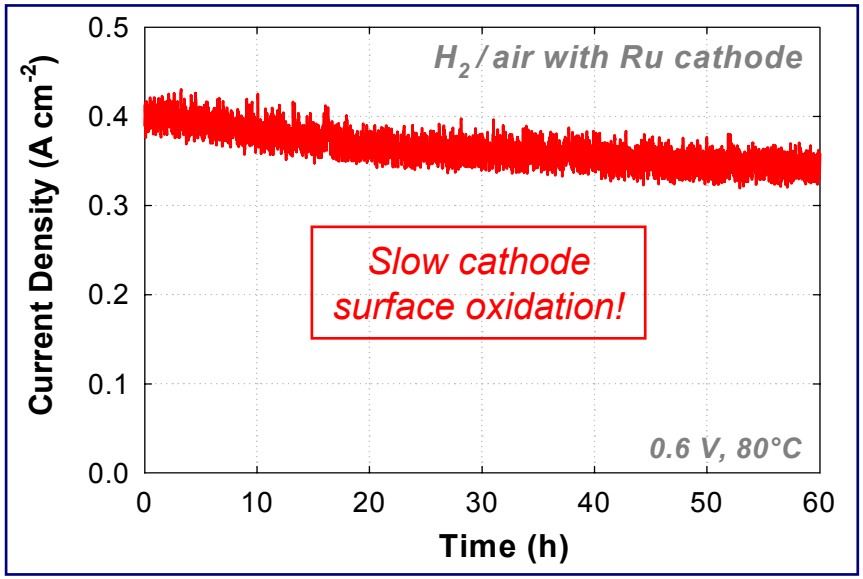
High performance, matching or exceeding that of 'state-of-the-art' non-precious catalysts, achieved in the first year of nanocomposite research!

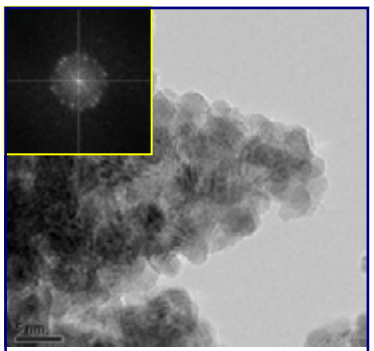
Performance milestone for non-precious metal catalysts achieved

(cf. Supporting Information)

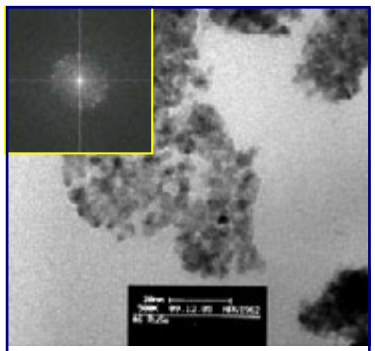
Characteristics (Units)	**Value**	
ORR activation energy, $E_a°$ (kJ mol^{-1})	**40.6**	
ORR activity in H_2-O_2 fuel cell at specified voltage, 80°C (A cm^{-3})	**0.80 V**	**4.9**
	0.70 V	**24.3**
O_2 turnover at RDE, specified potential *vs.* NHE, 25°C (10^{-5} site^{-1} s^{-1})	**0.80 V**	**5.5**
	0.70 V	**25.0**
O_2 turnover in H_2-O_2 fuel cell at specified voltage, 80°C (10^{-3} site^{-1} s^{-1})	**0.80 V**	**3.2**
	0.70 V	**14.0**

"Decorated" Ru Nanoparticles for Oxygen Reduction





Ru (H_2-reduced)



$Se_{0.20}$/Ru

Ru black in powder form

↓

Reduction in H_2

↓

Mixing with Se precursor in (i) organic or (ii) aqueous solvent

↓

Refluxing

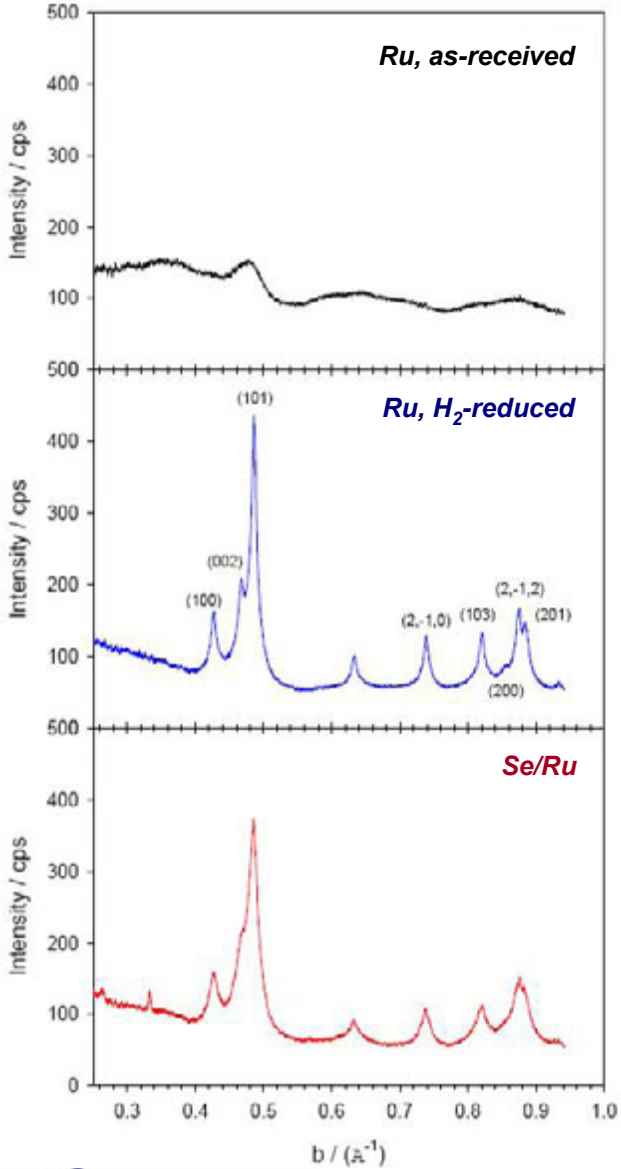
- ***Reduced Ru – a very good ORR catalyst but prone to oxidation***
- ***Ru decoration with selenium:***

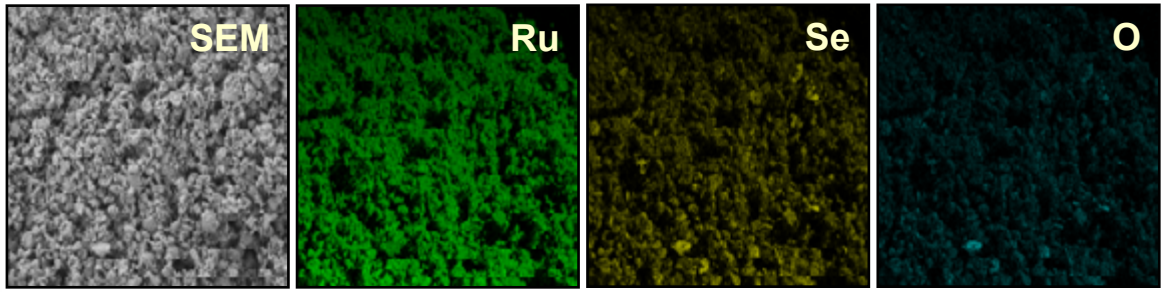
  Se + Ru → Se/Ru
- ***New, and different than Ru, chalcogenide-type, oxidation-resistant catalyst synthesized***

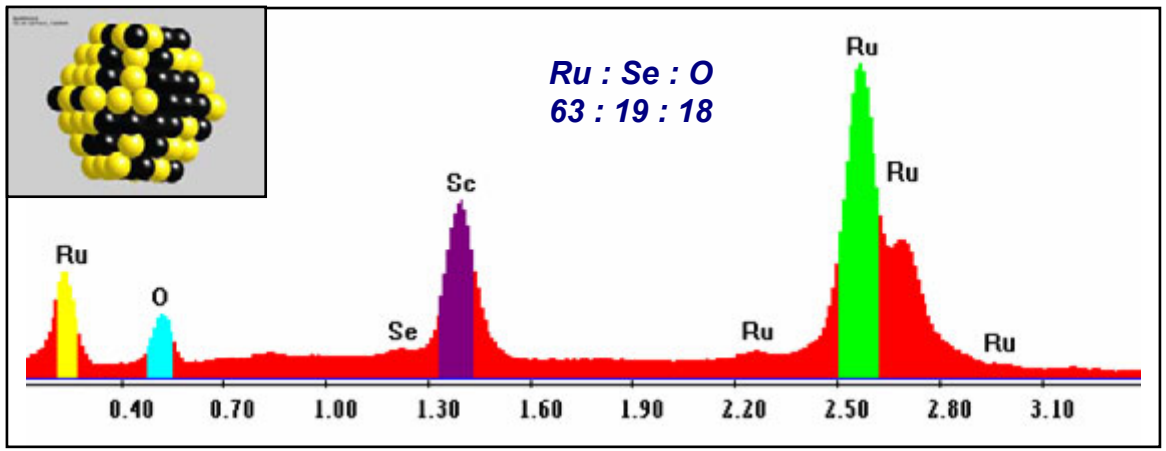
Project in close collaboration with

- ***University of Illinois, Urbana-Champaign***
- ***Université de Poitiers, France***

Se/Ru Catalyst: Structure by XRD and EDX

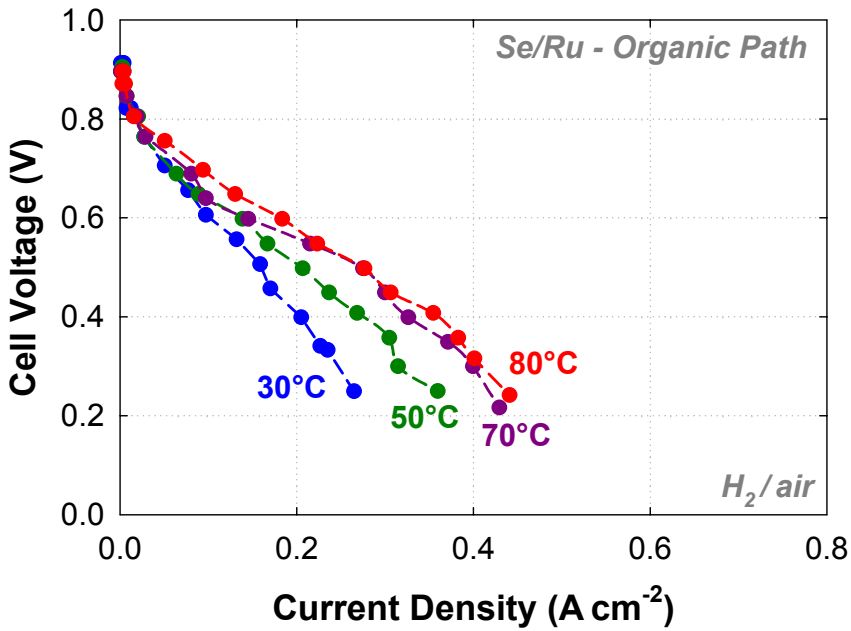


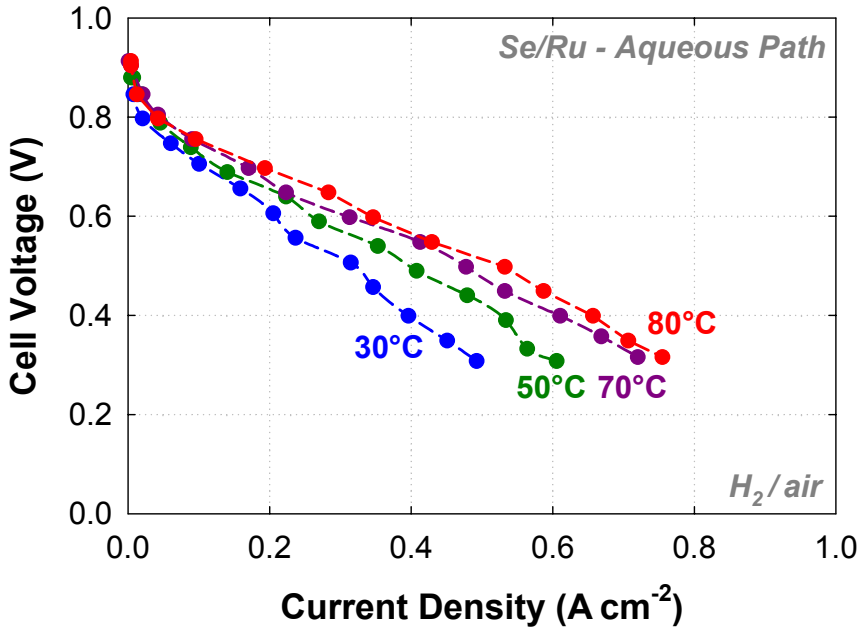




- ***Ru and Se not combining in the bulk***
- ***Ru remaining in Ru(0) form after refluxing with selenium***
- ***Oxygen well-correlated with selenium indicating presence of Se oxides***

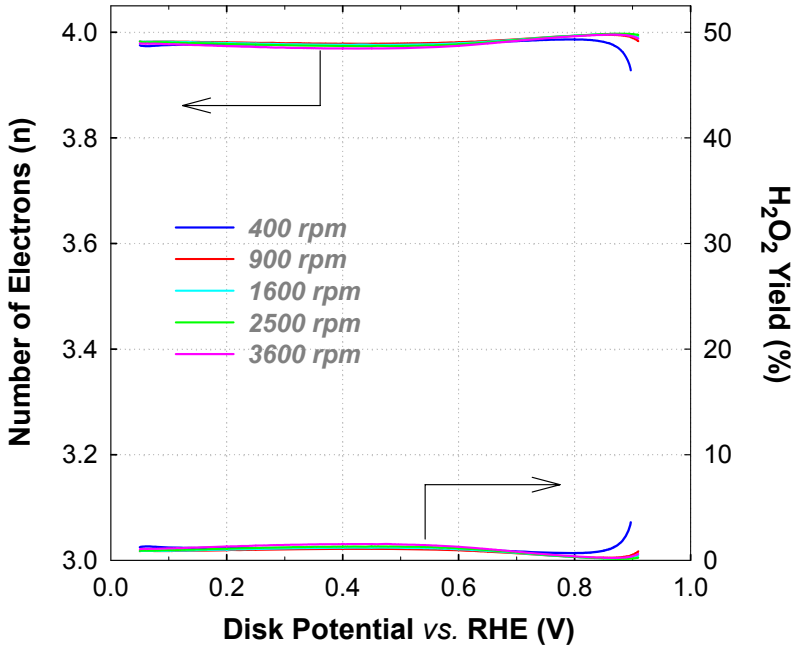
Se/Ru Catalyst: Fuel-Cell Evaluation of Performance

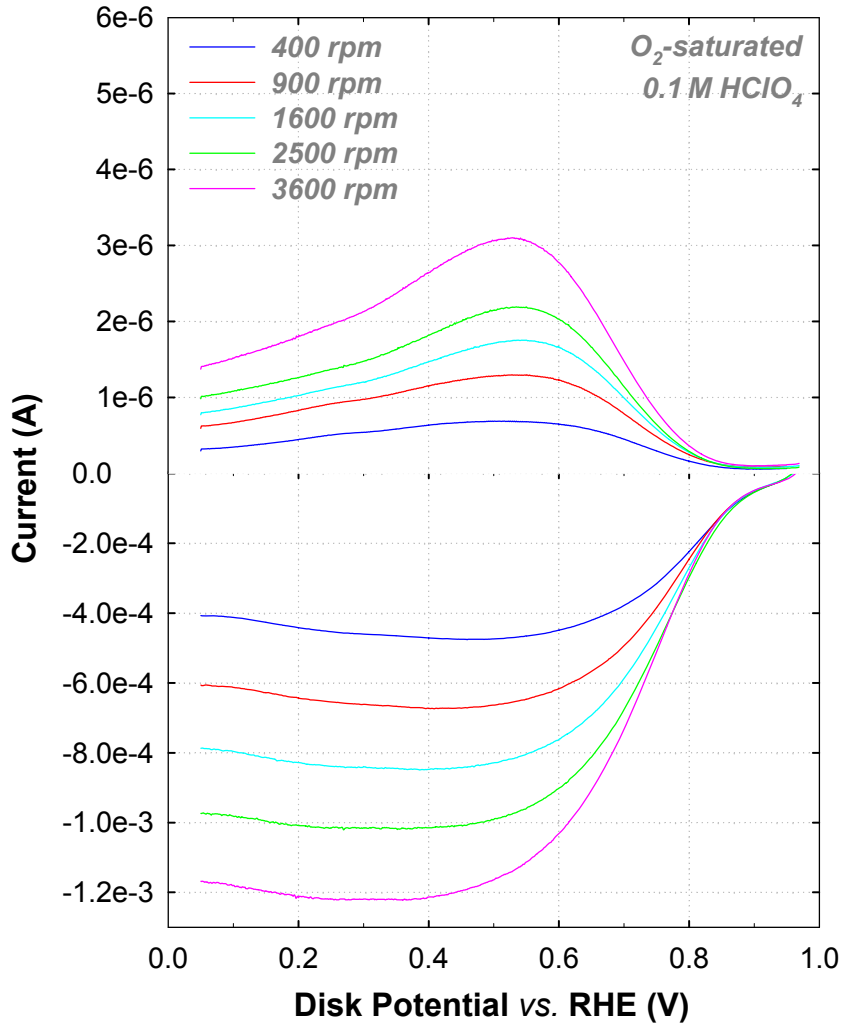




Electrocatalysts for Transportation Applications (Stack)			
Characteristics (Units)	**Se/Ru Organic Path**	**Se/Ru Aqueous Path**	**2010 target**
Non-Pt Catalyst Activity (A/cm^3 @ 0.8 $V_{iR\text{-}free}$)	**19**	**43**	**> 130**

Se/Ru Catalysts: 4e⁻ *vs.* 2e⁻ Process (RRDE Study)





Very little contribution from the 2e⁻ process in ORR at both Se/Ru catalysts obtained via organic and aqueous path (shown)

$n_{aqueous}$ **= 3.98** *(average)*

Number of electrons: $n = (4\, j_{disk}) / (j_{disk} + j_{ring}/\varepsilon)$ (ε - ring collection efficiency)

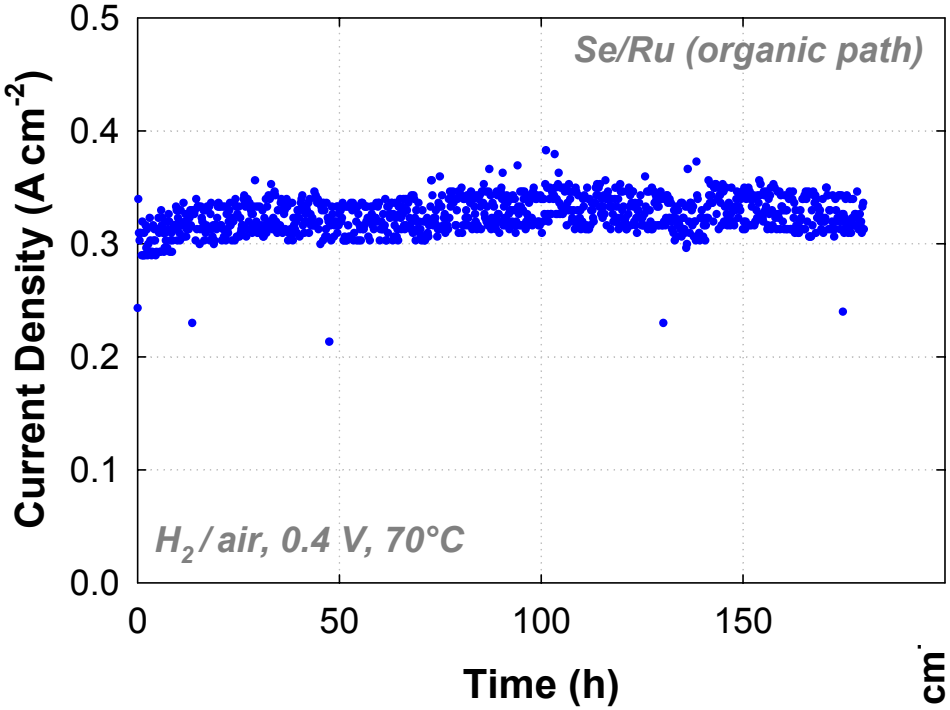
Peroxide yield: $\% H_2O_2 = 100\,(4 - n) / 2$

Se/Ru Catalysts: RRDE Evaluation of ORR Kinetics

RRDE Kinetic Evaluation of Se/Ru Catalysts		
Characteristics (Units)	**Value**	
Kinetic current at RDE, specified potential *vs.* **NHE, 25°C** (10^{-5} A cm^{-2}) *(Surface area estimated by spheres)*	**0.75 V**	**0.8**
	0.70 V	**2.0**
	0.65 V	**4.0**
Apparent rate constant at RDE, specified potential *vs.* **NHE, 25°C** (cm^4 mol^{-1} s^{-1})	**0.75 V**	**0.1**
	0.70 V	**0.3**
	0.65 V	**0.6**
O_2 turnover at RDE, specified potential *vs.* **NHE, 25°C** (10^{-3} site^{-1} s^{-1})	**0.75 V**	**9**
	0.70 V	**20**
	0.65 V	**40**

- ***RRDE*: Significantly higher O_2 turnovers for Se/Ru than nanocomposites**
- ***RRDE & fuel cells*: Mass transport limitations much less pronounced at surface chalcogenides than nanocomposites**
- ***Fuel cells*: Aqueous path yielding Se/Ru with higher activity than organic path**
- ***Fuel cells*: "Volumetric" activity of Se/Ru at ~ *30%* of the DOE 2010 target**

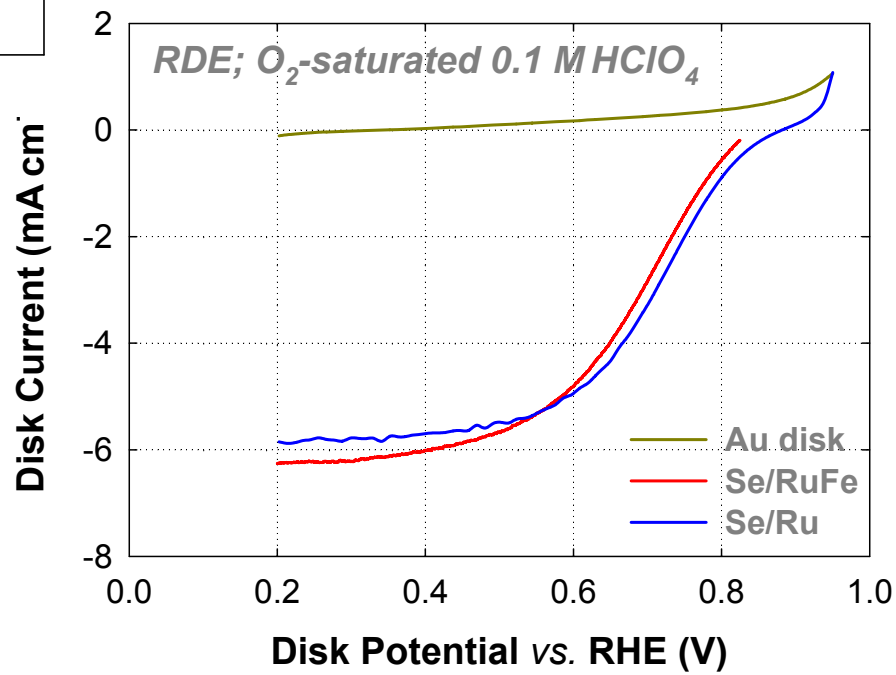
Surface Chalcogenide Catalysts: Durability and Lowering Ru Content



Se/Ru catalysts, obtained on either organic or aqueous synthesis paths by "decorating" Ru nanoparticles with Se, exhibit excellent in-fuel-cell performance stability for hundreds of hours!

Se-decorated bimetallic FeRu synthesized and tested for ORR activity, comparable to that of the Se/Ru catalyst

Pathway to lowering Ru loading



Summary

- ***Demonstrated a new class of non-precious metal/heteroatomic polymer nanocomposite catalysts, such as Co and Fe composites, with promising ORR activity and unique for non-precious metal catalysts performance durability***
- ***Identified a dual role of the heteroatomic polymer: (i) formation of the active ORR site and (ii) stabilization of the non-precious metal center via the formation of a bond with the heteroatom***
- ***Confirmed by XANES / EXAFS the key role of the Co-N (or Co-O)***
- ***Developed two new synthesis paths for fabricating surface chalcogenide Se/Ru catalysts via "decoration" of Ru nanoparticles by Se***
- ***Demonstrated very high fuel cell activity (30% of the DOE's 2010 activity target) and respectable performance stability of Se/Ru catalysts***
- ***In RDE/RRDE experiments, determined ORR kinetic parameters on nanocomposites and chalcogenides and identified inefficient O_2 mass-transport in the catalyst layer as a limiting factor for the scale-up of the nanocomposite performance with catalyst loading***
- ***Experimentally verified validity of the core-shell approach for reducing Ru loading via addition of a non-precious metal (Fe)***

Future Work

Remainder of FY06:

- ***Complete detailed characterization of oxygen reduction on Co nanocomposite***
- ***Finish, already advanced, RDE/RRDE study of ORR kinetics on the cobalt nanocomposite and two surface chalcogenides***
- ***Initiate development of methods for reducing O_2 concentration overpotential in the PEFC cathode***

FY07:

- ***Develop novel mesoporous "open-frame" structures for improved mass transport of O_2 in catalyst layers to (i) maximize catalyst utilization (surface chalcogenide) and (ii) allow for higher catalyst loading (nanocomposites)***
- ***Synthesize and characterize composites based on other heteroatomic polymers, e.g. polyaniline, poly(vinyl) pyridine, poly(ethylene dioxy) thiophene, and non-precious metals other than cobalt, e.g. Ni, Fe, W, Mo, and their alloys***
- ***Establish collaborative effort with the university partners for lowering Ru content in surface chalcogenides (alloying with non-precious metals; "core-shell" catalysts) and further increasing activity ("ORR activators")***
- ***Perform structure-mechanism correlations; propose approaches to lowering ORR overpotential on non-Pt catalysts***

Non-Platinum Cathode Catalysts

Supporting Information

Responses to Reviewers' Comments

"CoTPP types of catalyst are just not sufficiently stable for consideration."

Based on the durability data acquired in the first year of the project (2004-2005), metalloporphyrins have been deleted from the scope and replaced by much more stable non-precious metal/heteroatomic polymer nanocomposites.

"Further emphasis on understanding mechanisms rather than demonstrating the highest fuel cell performance should be considered."

Catalysts in both studied groups have become subject of a detailed mechanistic analysis. The focus of that analysis has been on the identification of the active reaction site and ORR kinetics. XANES/EXAFS, SEM EDX, and XRD/RRDE have been used extensively as complementary techniques to fuel cell testing.

"Unclear if on track to meeting key DOE technical barriers/targets."

Performance of all catalysts has been referred to the DOE targets for non-Pt electrocatalysts, in particular to the 2010 "volumetric" activity target (130 A/cm^3 at 0.8 V, iR-corrected). Se/Ru catalyst has already shown activity greater than 30% of that target.

"Program requires reliable, reproducible catalyst sources."

This project focuses on entirely new materials, none of them available commercially. Catalysts from external sources as well as synthesized at LANL have been carefully evaluated for purity, noble-metal contamination, and reproducibility (cf. batch-to-batch consistency data for the Co nanocomposite in "Supporting Information").

Selected Project-Relevant Publications and Presentations

1. *"New Class of Non-precious Metal Composite Catalysts for Fuel Cells," B. Rajesh, P. Zelenay, Nature, submitted*
2. *University of California – Riverside, Department of Chemical and Environmental Engineering, Riverside, California, October 14, 2005. Title: "Polymer Electrolyte Fuel Cells: Highlights from the Fundamental and Applied Research at Los Alamos," P. Zelenay (invited lecture)*
3. *207th Meeting of the Electrochemical Society, Los Angeles, California, October 16-21, 2005. Title: "A New Non-Precious Metal Catalyst for Oxygen reduction," B. Rajesh,* P. Zelenay*
4. *NANO Commerce – SEMI NanoForum, Chicago, Illinois, November 1-3, 2005. Distributed Energy Systems–Panel; moderated by David Forman, Small Times Magazine, P. Zelenay* (invited panelist)*
5. *2005 Fuel Cell Seminar, Palm Springs, California, November 14-18, 2005. Title: "Compact, Portable, and Robust DMFC System Using Mixed-reactants" P. Zelenay, V. Hovland, A. Kulprathipanja,* J. Martin*
6. *International Battery Association & Hawaii Battery Conference, Waikoloa, Hawaii, January 9-12, 2006. Title: "Non-Platinum Electrocatalysis – A Major Challenge for Polymer Electrolyte Fuel Cells," R. Bashyam, J.-H. Choi and P. Zelenay* (invited lecture)*
7. *LANL Materials Science and Technology Division Review Meeting, April 4-6, 2006. Title: "New class of non-precious metal nanocomposite electrocatalysts for fuel cells," B. Rajesh,* R. Mukundan, E. Brosha, F. Garzon, S. Conradson, P. Zelenay*

Critical Assumptions and Issues

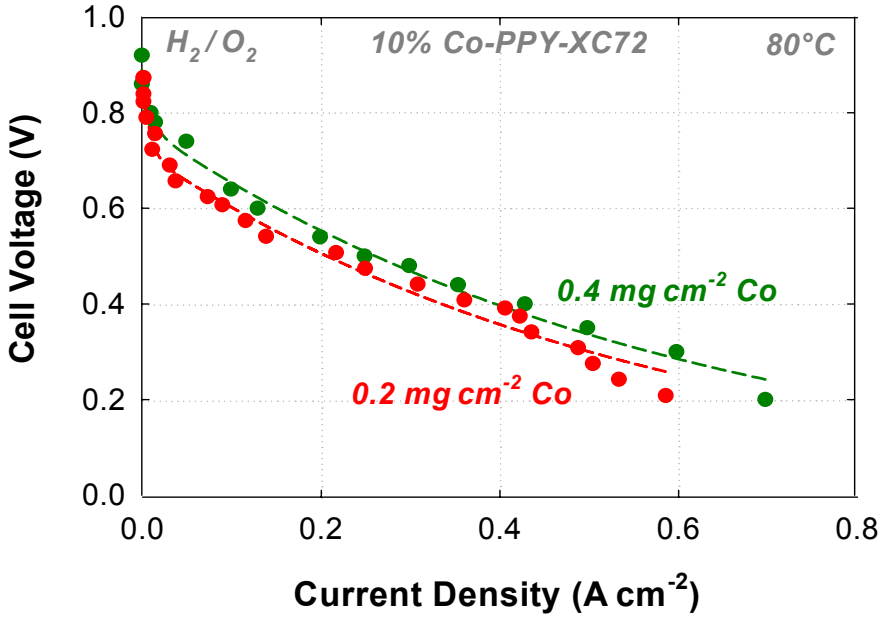
- ***Nanocomposite-type catalysts:*** ***Development of an open-frame, highly O_2-permeable cathode structure allowing for a significant increase in the catalyst loading without introducing a mass-transfer hindrance***
- ***Surface chalcogenides:*** ***Reduction in the Ru content through partial replacement by a non-precious metal, such as Fe ("core-shell" approach); also, further enhancement in the O_2 turnover, for example, via an introduction of ORR activators***
- ***All non-platinum catalysts:*** ***Sufficient stability in the very acidic, high-temperature and oxidizing environment of the polymer electrolyte fuel cell cathode***

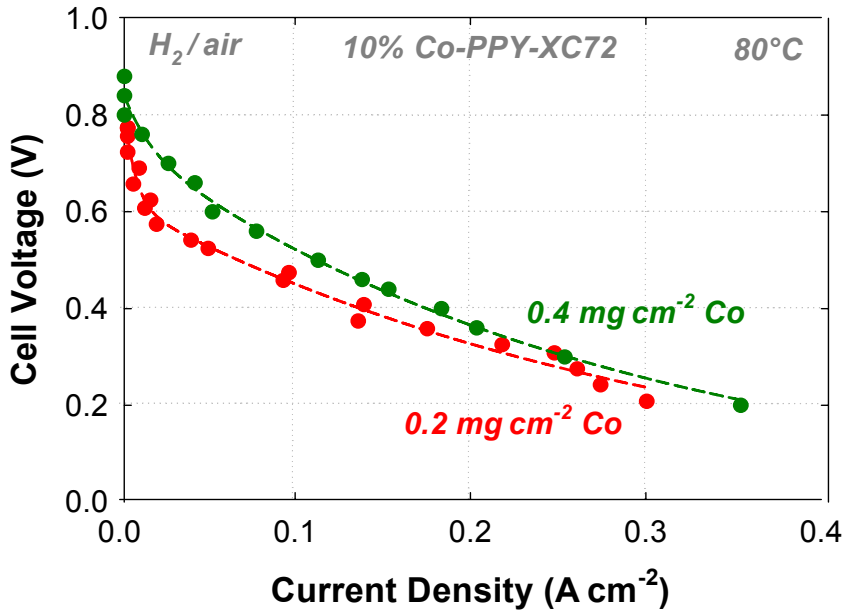
Non-Platinum Catalysts: Progress Towards 2006 Milestones

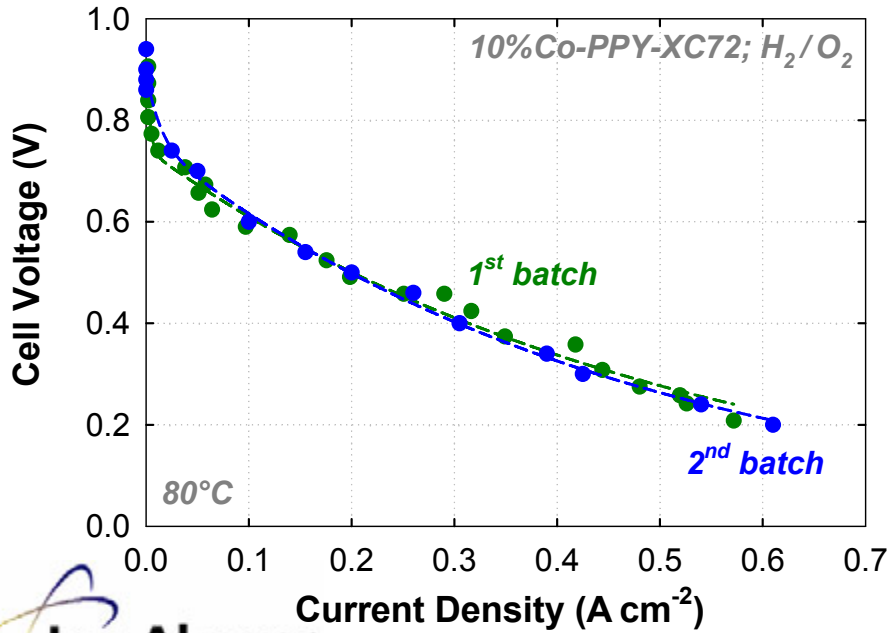
- ***Identify the active ORR site of a selected well-performing nanocomposite*. – Close to completion***
- ***Determine the kinetic parameters and turnover rates on nanocomposite and surface chalcogenide catalysts. – Close to completion***
- ***Demonstrate a Co-composite catalyst with performance and performance stability comparable to the state-of-the-art non-precious metal cathode catalysts. – Achieved (with developed in-house a new class of catalysts)***

** Non-precious metal/heteroatomic polymer composites replace less promising metalloporphyrins*

Loading Effect and Batch-to-Batch Consistency

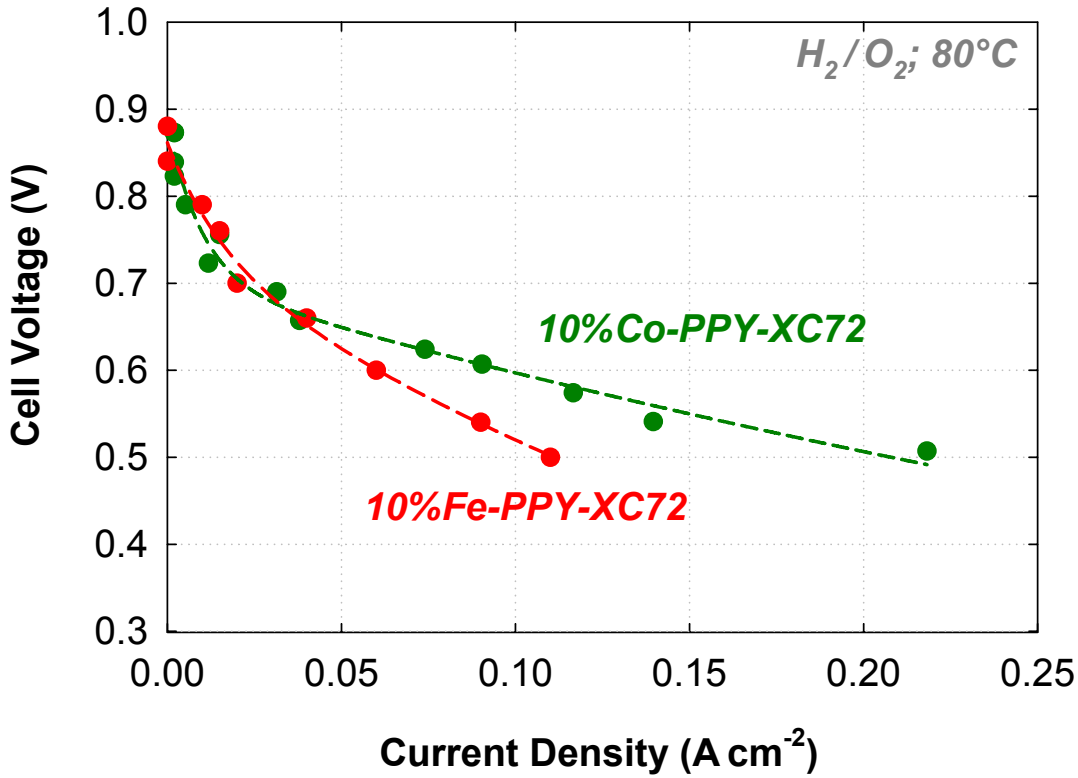






- *Only small performance enhancement upon doubling the loading*
- *O_2 transport in the catalyst layer needs improvement*
- *Excellent batch-to-batch consistency of the catalyst synthesis process*

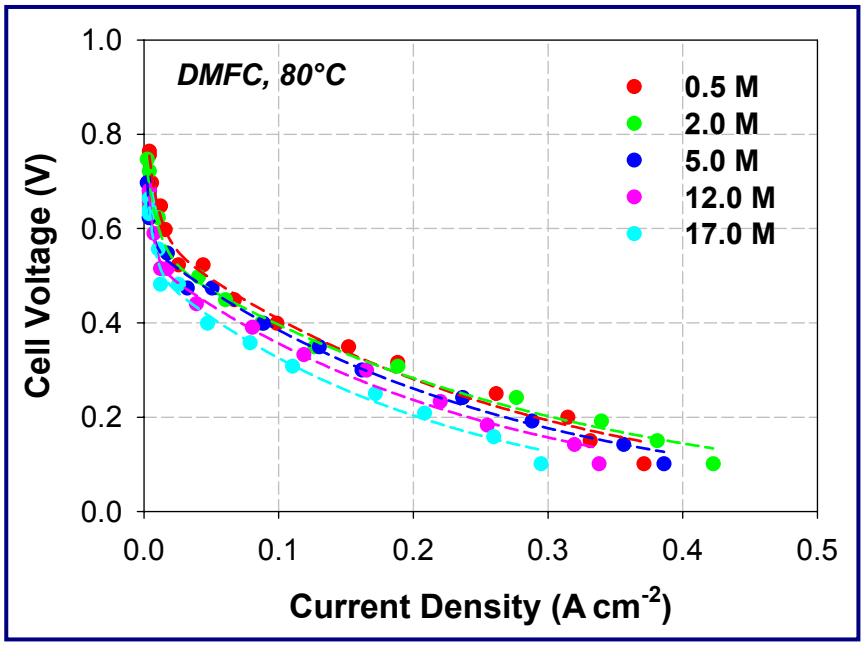
Fe-based Nanocomposite

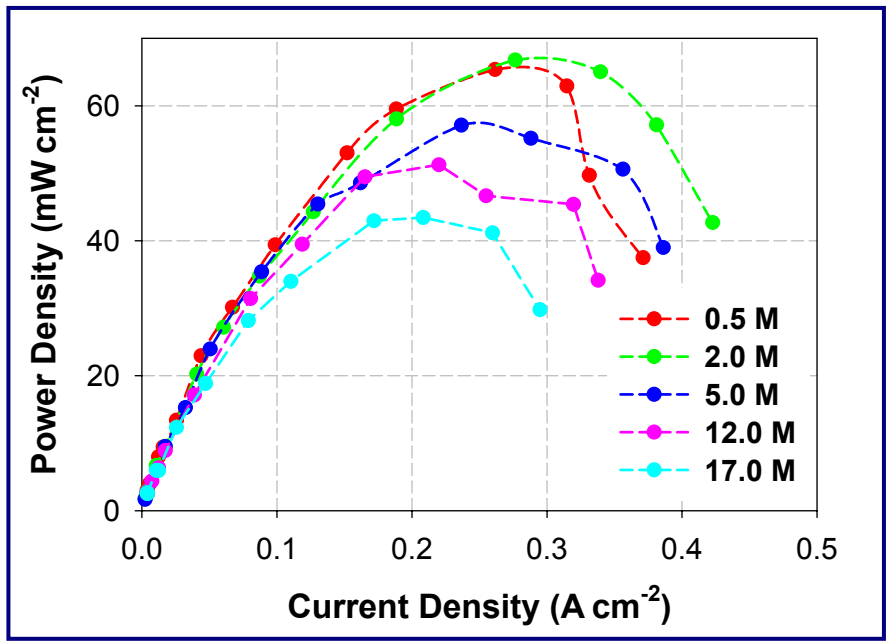


- *Similar performance of Fe and Co nanocomposites at low current densities*
- *Significant mass-transfer limitations observed with Fe-PPY-XC72 below 0.65 V*

A class of non-precious metal/heteroatomic polymer composites demonstrated

"Aqueous" Se/Ru Catalyst: DMFC Performance





- *Very good methanol tolerance of the "aqueous-path" Se/Ru catalyst in cells with up to ~ 17 M methanol concentration in the anode feed stream*
- *Delivered maximum power of 65 mW cm^{-2} and 43 mW cm^{-2} with 0.5 M and 17.0 M methanol, respectively, ~2× better than cells with "organic-path" Se/Ru catalyst*