

V.E.6 Advanced Cathode Catalysts

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Project Start Date: March 2007
 Project End Date: 2011

Objectives

The main objective of this project is to:

- Develop an 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.

Individual objectives of this research are as follows:

- Investigate new catalyst supports and electrode structures for maximum catalyst utilization.

- Determine the 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 Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Durability
- Cost
- Performance

Technical Targets

Non-platinum cathode catalysis research in this project focuses on DOE's 2010 technical targets specified in Table 3.4.12 (Electrocatalysts for Transportation Applications) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan. The targets relevant to this research project are:

Characteristics	Units	2010 Stack Target
PGM total content (both electrodes)	g/kW (rated)	0.3
PGM total loading	mg _{PGM} /cm ² electrode area	0.3
Cost	\$/kW	5
Durability with cycling At operating temperature of ≤80°C At operating temperature of >80°C	hours hours	5,000 2,000
Mass activity	A/mg _{Pt} @ 900 mV _{IR-free}	0.44
Specific activity	μA/cm ² @ 900 mV _{IR-free}	720
Non-Pt Catalyst Activity per Volume of Supported Catalyst	A/cm ³ @ 800 mV _{IR-free}	> 130



Approach

This is a new four-year, multi-partner research project aimed at the development of oxygen-reduction catalysts for the PEFC cathode with either very low precious metal content or entirely precious metal-free. The approach taken involves:

1. Parallel development of ORR catalysts in three classes:
 - Oxygen catalysts with ultra-low platinum content.
 - New-generation chalcogenides.
 - Non-precious metal/heteroatomic polymer nanocomposites.
2. Research and development of electrode structures, specifically designed for the ORR catalysts to maximize catalyst utilization and/or loading:
 - Open-frame catalyst structures.
 - Conductive-polymer nanofibers and nanotubes for non-precious metal cathode structure.
3. Extensive catalyst characterization to understand catalyst structure, ORR mechanism, the nature of the active site, etc. via fuel cell testing, “half-cell” ORR kinetic studies (e.g. rotating ring-disk electrode [RRDE]), and ex-situ analysis (e.g. X-ray absorption near-edge spectroscopy [XANES], X-ray absorption fine structure [XAFS], scanning electron microscopy [SEM], energy dispersive X-ray microanalysis [EDX], X-ray diffraction [XRD])
4. Determination of the performance durability of all catalysts with promising ORR activity:
 - Fuel cell performance durability.
 - Catalyst dissolution rates and mechanisms.
5. Fabrication and scale-up of viable cathode catalysts.

Accomplishments

Although this research project started in the early 2007, several of its research components stem from fuel cell electrocatalysis and electrode-structure research in the partner organizations in previous years. Reported below are selected accomplishments from the early 2007 phase of the project.

Molecular modeling of non-precious metal composite catalysts. Used semi-empirical methods, capable of handling large systems to model complexes of transitional metals (cobalt) with organic ligands (tertrapyrrole) to imitate long polymer chains and possibly quantify interaction of molecular oxygen with such metal centers.

- This modeling effort is intended to elucidate possible oxygen reduction mechanisms, predict molecular properties of (non-precious-metal)/(heteroatomic

polymer) composites, such as Co-PPy-XC72 [1,2], and possibly correlate such properties with experimental data for real catalysts. Ultimately, molecular modeling will be used to determine the effects of molecular structure on ORR catalysis.

- As shown in Figure 1a, molecular modeling of cobalt-tratrapyrrole complexes of dioxygen, before and after the transfer of first two electrons, not only points to the high affinity of molecular oxygen to such catalytic sites but also to significant increase in the O-O bond as a result of the interaction between dioxygen and the site. Dioxygen interaction with two Co centers significantly weakens the O-O bond relative to the O₂/H₂O₂ reference system (Figure 1b).

X-ray absorption studies of cobalt-based composites. Using X-ray absorption spectroscopy (XANES and XAFS) detected the presence of up to two active ORR sites in the Co-PPy-XC72 catalyst.

- As determined by XANES, Co(II) and Co metal are present in as-synthesized catalyst in varying proportions, with Co(II)-to-Co-metal ratio increasing during catalyst break-in in the fuel cell. In turn, XAFS cobalt speciation data indicate the presence of three different Co species in the as-synthesized catalyst occurring in various proportions: (i) Co metal, (ii) a Co(II) oxide, and (iii) a mononuclear Co(II) species with the same Co-O(N) bond length as Co(II) oxide (oxy-hydroxide cannot be excluded). As shown in Figure 2, 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 Å and 3.11 Å). XAFS indicates that mononuclear Co species, surrounded by approximately four to five oxygen atoms are the dominant species in the fully broken-in composite catalyst. Co metal and oxide are present in the catalyst in only trace amounts.
- In two cases, following the use of polymerization time and also after a low-voltage catalyst conditioning, more ordered oxide-type species were also identified in the Co-composite catalyst. These two different synthesis/conditioning paths yielded a highly and consistently ordered nanocluster or nanocrystallite species with the nearest neighbor Co-O bond length of ~1.89 Å, much shorter than in mononuclear” species shown in Figure 2. Although sharing many spectra features with calculated Co₃O₄ crystal structure, the “ordered oxide” structure differs from the pure mixed-oxide phase. Based on the high-R structure, the differences may be caused by altered order in the oxide phase, possibly rod-like morphology (known to form in some cases).
- Regardless of the nature of the ORR site in Co-PPy-XC72, the oxygen turnover frequency (TOF) appears

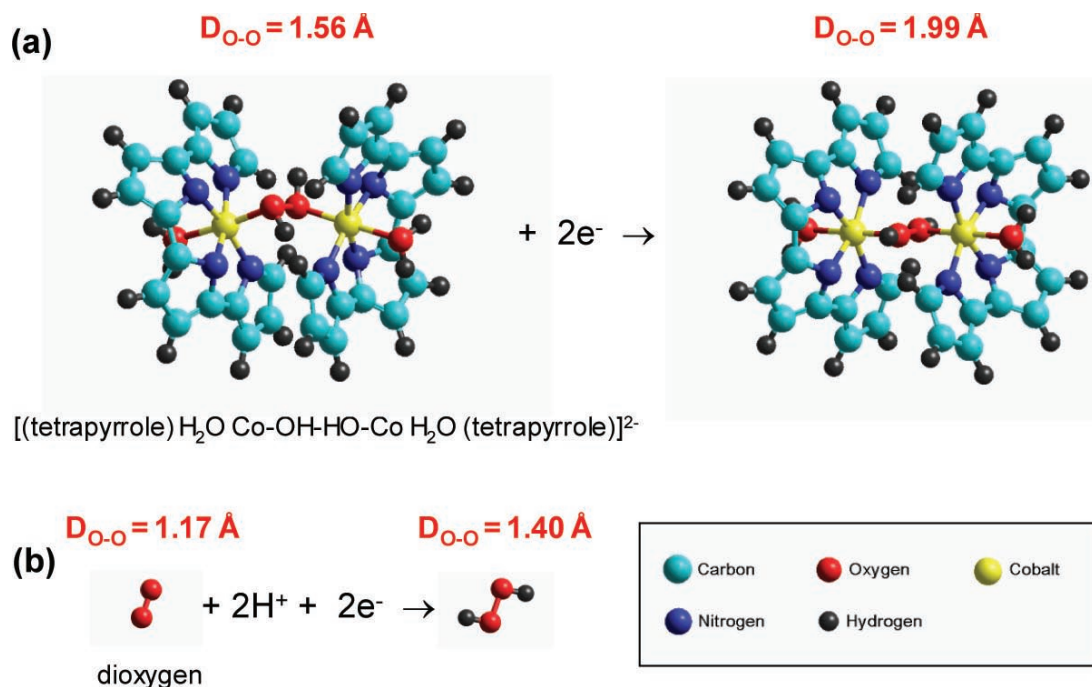


FIGURE 1. Molecular Modeling of (a) $[(\text{Tetrapyrrole})\text{H}_2\text{O Co-OH-HO-Co H}_2\text{O}(\text{Tetrapyrrole})]^{2-}$ Complex and (b) Dioxygen That Shows How Dioxygen Interaction With Two Co Centers is Likely to Significantly Weaken the O-O Bond in the Co-Complex Relative to the $\text{O}_2/\text{H}_2\text{O}_2$ Reference System

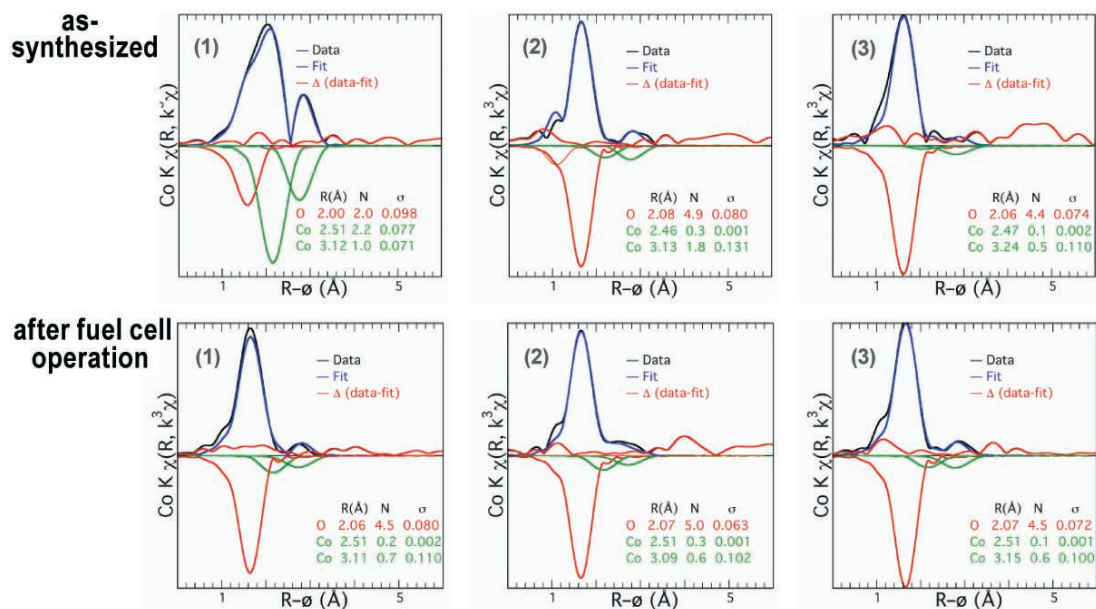


FIGURE 2. XAFS Co Speciation Data Obtained With Three Different Samples of the Co-PPy-XC72 Catalyst Before and After Fuel Cell Operation That Demonstrate the Formation of “Mononuclear” Co-Species in All Three Catalyst Samples as a Result of a Prolonged Fuel Cell Operation

to be significant given limited amount of Co left in the active catalyst after break-in (less than 50 μg per cm^2 of the membrane electrode assembly [MEA], X-ray fluorescence [XRF] data).

New-generation surface chalcogenides. Developed zirconia matrix for high dispersion of the Se/Ru catalysts and possible improvement in Se durability.

- Kinetic ORR data, obtained using a RRDE in a standard electrochemical cell in 0.1 M H_2SO_4 aqueous electrolyte (Figure 3), indicate comparable activity of the Se/Ru (selenium-decorated nanoparticles of Ru) catalyst supported

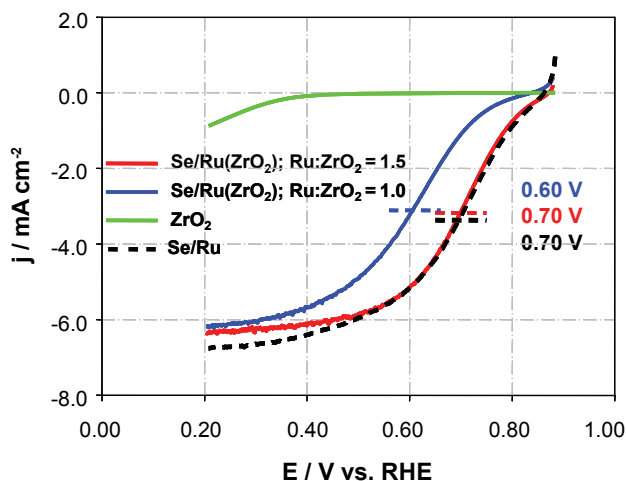
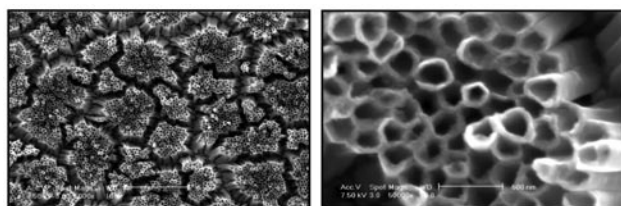
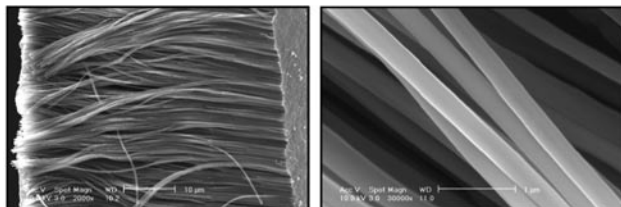


FIGURE 3. RRDE oxygen reduction data collected with ZrO_2 -supported Se/Ru nanoparticle catalysts of two different Ru-to- ZrO_2 ratios. Polarization plots recorded with pure non-catalyzed ZrO_2 and unsupported Se/Ru catalyst are shown for comparison. Au disk at 1,600 rpm; 0.1 M H_2SO_4 aqueous electrolyte; scan rate 20 mV s^{-1} .



PPy nanotubes by electrochemical polymerization



PPy nanowires by chemical polymerization

FIGURE 4. Micrographs of Electrochemically-Generated PPy Nanotubes (Top) and Chemically-Synthesized PPy Nanowires (Bottom)

on $\sim 20\text{-nm}$ ZrO_2 particles and unsupported Se/Ru catalyst. Transmission electron microscopy (TEM) imaging indicates that this approach, alternative to supporting such catalysts on carbon, yields very fine nanoparticles of Se/Ru, between 2-3 nm in particle size.

Electrode structures for maximum catalyst utilization and/or loading. Used both chemical and electrochemical methods to successfully synthesize polypyrrole nanostructures (nanofibers and nanotubes) as supports for non-precious metal catalysts with tunable hydrophilic/hydrophobic properties (Figure 4).

Special Recognitions & Awards/Patents Issued

1. 2007 Los Alamos National Laboratory Patent & Licensing Award (May 2007; for year 2006).
2. R. Bashyam, LANL Postdoctoral Publication Prize in Experimental Sciences for the *Nature* article, June 2007.

Relevant FY 2007 Publications

1. "Performance and Durability of Chalcogenide-Modified Ruthenium Catalysts for Oxygen Reduction: Hydrogen-Air MEA and RRDE Studies;" C. M. Johnston, J.-H. Choi, P. K. Babu, A. Wieckowski, and P. Zelenay; *ECS Trans.*, submitted.
2. "Novel Chalcogenide-Based Materials for Oxygen Reduction Reaction;" C. Delacôte, C. M. Johnston, P. Zelenay, and N. Alonso-Vante; *ECS Trans.*, submitted.
3. "Direct Measurement of iR -Free Individual-Electrode Overpotentials in Polymer Electrolyte Fuel Cells;" P. Piela, T. E. Springer, J. Davey, and P. Zelenay; *J. Phys. Chem. C*, **111**, 6512-6523 (2007).
4. "Oxygen Reduction Electrocatalysis at Chalcogen-modified Ruthenium Cathodes: J.-H. Choi, C. M. Johnston, P. K. Babu, A. Wieckowski, N. Alonso-Vante, and P. Zelenay, *ECS Trans.*, **3**, (1) 171-179 (2006).
5. "Electrochemical Impedance Spectroscopy for Direct Methanol Fuel Cell Diagnostics;" P. Piela, R. Fields, and P. Zelenay; *J. Electrochem. Soc.*, **153**, A1902-A1913 (2006).
6. "A Class of Non-precious Metal Composite Catalysts for Fuel Cells;" R. Bashyam and P. Zelenay, *Nature*, **443**, 63-66 (2006).

Relevant FY 2007 Presentations

1. Hydrogen, Fuel Cells & Infrastructure Technologies Program, 2007 Merit Review and Peer Evaluation Meeting, U.S. Department of Energy, Energy Efficiency and Renewable Energy, Arlington, Virginia, May 15-18, 2007. Title: "Advanced Cathode Catalysts;" P. Zelenay.

2. 211th Meeting of The Electrochemical Society, Chicago, Illinois, May 6-10, 2007. Title: "Novel Chalcogenide-Based Materials for Oxygen Reduction Reaction;" C. Delacôte, C. M. Johnston, P. Zelenay, and N. Alonso-Vante.
3. 211th Meeting of The Electrochemical Society, Chicago, Illinois, May 6-10, 2007. Title: "Performance and Durability of Chalcogenide-Modified Ruthenium Catalysts for Oxygen Reduction: Hydrogen-Air MEA and RRDE Studies;" C. M. Johnston, J.-H. Choi, P. K. Babu, A. Wieckowski, and P. Zelenay.
4. National Research Council of Canada, Institute for Fuel Cell Innovation, Vancouver, Canada, April 17, 2007. Title: "Cathode Electrocatalysis: A Great Challenge of Polymer Electrolyte Fuel Cells;" P. Zelenay (*invited lecture*).
5. 233rd American Chemical Society National Meeting, Chicago, Illinois, USA, March 25-27, 2007. Title: "Oxygen reduction electrocatalysis on non-precious metal nanocomposites;" R. Bashyam, C. M. Johnston, S. D. Conradson, and P. Zelenay (*invited lecture*).
6. 3rd International Hydrogen and Fuel Cell EXPO, Tokyo, Japan, February 7-9, 2007. Title: "Durability of Direct Methanol Fuel Cells;" Piotr Zelenay (*invited keynote lecture*).
7. University of Yamanashi, Kofu, Japan, February 5, 2007 (departmental seminar). Title: "Alternative Oxygen Reduction Catalysts for Polymer Electrolyte Fuel Cells;" P. Zelenay.
8. 2006 Fuel Cell Seminar, Honolulu, Hawaii, November 13-17, 2006. Title: "Pt-free Electrocatalysts for Polymer Electrolyte Fuel Cells;" P. Zelenay, B. Rajesh, J.-H. Choi, S. Conradson, and A. Wieckowski.
9. 210th Meeting of The Electrochemical Society, Cancun, Mexico, October 29 - November 3, 2006. Title: "Oxygen Reduction Electrocatalysis at Chalcogen-modified Ruthenium Cathodes;" J.-H. Choi, C. M. Johnston, P. K. Babu, A. Wieckowski, N. Alonso-Vante, and P. Zelenay.
10. Fuel Cell Catalysis: A Surface Science Approach, Leiden, The Netherlands, October 16-20, 2006. Title: "Surface chalcogenides as catalysts of oxygen reduction at the polymer electrolyte fuel cell cathode;" P. Zelenay (*invited lecture*).
11. 8th Gordon Research Conference on Fuel Cells, Smithfield, Rhode Island, July 23-28, 2006. Title: "Non-precious metal-polymer composite electrocatalysis: Activity and Durability studies;" B. Rajesh, R. Mukundan, S. Conradson, F. Garzon, and P. Zelenay.
12. The 3rd Guangzhou Fuel Cell Conference, Guangzhou, China, June 20-23, 2006. Title: "Ru/Se as Methanol Tolerant Oxygen Reduction Electrocatalyst;" Z. Cao, A. Wieckowski, J.-H. Choi, P. Zelenay.
13. The Electrochemical Society, Local Twin Cities Section, Minneapolis, Minnesota, June 7, 2006. Title: "Selected Highlights from Fundamental and Applied PEFC Research at Los Alamos" P. Zelenay (*invited lecture*).
14. 3M Company, St. Paul, Minnesota, June 7, 2006. Title: "Non-platinum Oxygen Reduction Electrocatalysis;" P. Zelenay (*invited lecture*).

References

1. "A Class of Non-precious Metal Composite Catalysts for Fuel Cells;" R. Bashyam and P. Zelenay, *Nature*, **443**, 63-66 (2006).
2. "Non-platinum Cathode Catalysts;" P. Zelenay, R. Bashyam, E. Brosha, J.-H. Choi, S. Conradson, F. Garzon, C. Johnston, R. Mukundan, J. Ramsey; US Department of Energy, Hydrogen, Fuel Cells & Infrastructure Technologies Program; 2006 Annual Progress Report; pp. 794-798. http://www.hydrogen.energy.gov/pdfs/progress06/v_c_7_zelenay.pdf.