

V.C.7 Non-Platinum Cathode Catalysts

Piotr Zelenay (Primary Contact),
Rajesh Bashyam, Eric Brosha, Jong-Ho Choi,
Steven Conradson, Fernando Garzon,
Christina Johnston, Rangachary Mukundan,
John Ramsey

Materials Science and Technology Division
Los Alamos National Laboratory
Los Alamos, NM 87545
Phone: (505) 667-0197; Fax: (505) 665-4292
E-mail: zelenay@lanl.gov

DOE Technology Development Manager:
Nancy Garland

Phone: (202) 586-5673; Fax: (202) 586-9811
E-mail: Nancy.Garland@ee.doe.gov

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Projected End Date: Project continuation and
direction determined annually by DOE

Objectives

The main objective of this project is to 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 of this research are as follows:

- Identify and/or synthesize new cathode catalysts.
- Determine various aspects of performance of the catalysts, including ORR kinetics, low-pH stability, performance durability, etc.
- Establish the mechanism of oxygen reduction, in particular, identify active ORR sites.
- Design and optimize the performance of membrane-electrode assemblies (MEAs) operating with new cathode catalysts.
- 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.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Electrode Performance

Technical Targets

Non-platinum cathode catalysis research at Los Alamos National Laboratory (LANL) focuses on DOE's 2010 technical targets specified in Table 3.4.13 (Electrocatalysts for Transportation Applications) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan. The targets most relevant to this research project are:

Characteristics	Units	2010 Target (Stack)
PGM Total Content	g/kW rated	0.5
PGM Total Loading	mg _{PGM} /cm ² electrode area	0.3
Cost	\$/kW	8
Durability with cycling		
At operating temperature of ≤80°C	hours	5,000
At operating temperature of >80°C	hours	2,000
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

Accomplishments

- Demonstrated a new class of non-precious metal/heteroatomic polymer nanocomposite catalysts with promising ORR activity and unique for non-precious metal catalysts performance durability (several hundred hours).
- Identified a dual role of the heteroatomic polymer: (i) participation in the active ORR site and (ii) stabilization of the non-precious metal center via the formation of a bond with the heteroatom.
- Confirmed by x-ray absorption near-edge spectroscopy (XANES)/extended x-ray absorption fine structure (EXAFS) the key role of Co-N (or Co-O).
- Developed two new synthesis paths for fabricating surface chalcogenide catalysts via "decoration" of Ru nanoparticles by Se.
- Demonstrated high fuel cell activity (40-50 A/cm² @ 0.8 V) and respectable performance stability of Se/Ru catalysts.

- In rotating disk electrode (RDE)/rotating ring-disk electrode (RRDE) experiments, determined kinetic parameters for oxygen reduction on nanocomposites and surface chalcogenides.
- 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).

Introduction

In an effort aimed predominantly at lowering the cost of hydrogen-air fuel cells for automotive transportation, non-Pt catalysis research at Los Alamos has concentrated on identifying, developing, testing and understanding the ORR mechanism on electrocatalysts potentially capable of replacing carbon-supported platinum at the PEFC cathode.

The main objective of this research is to develop non-platinum (either non-precious metal or precious metal but low loading) catalysts that will meet fuel cell stack cost targets without incurring a power-density, energy-conversion efficiency or performance durability penalty. Another important part of this effort is design and development of highly oxygen-permeable electrode structures, specifically for catalysts with lower intrinsic ORR activity (activity per real surface area of the catalyst).

Approach

This project has focused on advanced non-platinum cathode catalysts with either minimum precious metal content or entirely precious metal-free. The two groups of electrocatalysts investigated in this work have been:

1. (Non-precious metal)/(heteroatomic polymer) nanocomposites
2. "Chalcogenide-type" ORR catalysts obtained by modification of the metal surface with a chalcogen
 - Organic-solvent route
 - Aqueous route
 - PGM loading reduction via core-shell approach

Understanding of the ORR mechanism and factors impacting catalyst performance is achieved experimentally via fuel cell testing, "half-cell" ORR kinetic studies (*e.g.* RRDE), and *ex situ* analysis (*e.g.* XANES, EXAFS). An important component of this project also involves research targeting improvements in catalyst utilization (PGM-based materials) and

maximization of catalyst loading (non-precious metal catalysts) by designing more oxygen-permeable cathodes.

Results

In the past 12 months, our effort has concentrated on the synthesis, MEA fabrication and extensive electrochemical and non-electrochemical testing of catalysts from the two different groups listed in the Approach section above. The cobalt-polypyrrole-carbon (Co-PPY-C) composite has been in the focus of our research in Group 1, whereas selenium-modified ruthenium blacks (Se/Ru) have been the primary subject of our effort in Group 2. The surface chalcogenide research has been carried out in close collaboration with Professor Andrzej Wieckowski's group at the University of Illinois, Urbana-Champaign (UIUC), where chalcogenide catalysts were synthesized and initially characterized, before being sent to Los Alamos for further characterization and fuel cell testing.

Recently, we achieved a major advancement towards the development of a new class of (non-precious metal)/(heteroatomic polymer) composite catalysts for oxygen reduction in fuel cells. We demonstrated for the first time a Co-PPY-C composite synthesized via a simple chemical method without resorting to pyrolysis, otherwise universally used for inducing ORR activity in non-precious metal catalysts known to date. A schematic representation of the presumed configuration of the Co-PPY catalyst is shown in Figure 1. The proposed structure highlights the importance of an N-Co link between the pyrrole units in the polymer and Co atoms as key to stabilizing base Co centers in the highly acidic environment of the Nafion[®] ionomer. An H_2 - O_2 fuel cell polarization plot recorded with the cathode made of the Co-PPY-C composite exhibits good ORR activity for a non-precious material, reflected by the maximum power density of $\sim 0.14 \text{ W cm}^{-2}$ (Figure 2). Although promising, volumetric activities of the nanocomposite, 5 A cm^{-3} and 24 A cm^{-3} at 0.80 V and 0.70 V, respectively, need to be improved via further increase in the catalyst's ORR activity and introduction of novel, more open electrode structure allowing for much higher catalyst loadings to be used at the PEFC cathode.

The most striking property of the new catalyst – or, more likely, of a new class of catalysts that Co-PPY-C and Fe-PPY-C catalysts represent – is its durability. Uncharacteristically for a non-precious metal catalyst, the performance of the Co-PPY-C composite cathode is very stable, showing no appreciable deterioration for over 100 hours of operation (Figure 3). This possibly represents the first case ever when a non-precious cathode catalyst, at a low loading, shows at the same time very promising activity and remarkable stability in a PEFC.

In parallel to the effort in catalysis based on (non-precious metal)/(heteroatomic polymer) nanocomposites, we have continued research of surface chalcogenides, identified last year as very promising materials with significant potential for replacing platinum at the PEFC cathode. Together with the University of Illinois, Urbana-Champaign and, in the initial phase of the project, with the University of

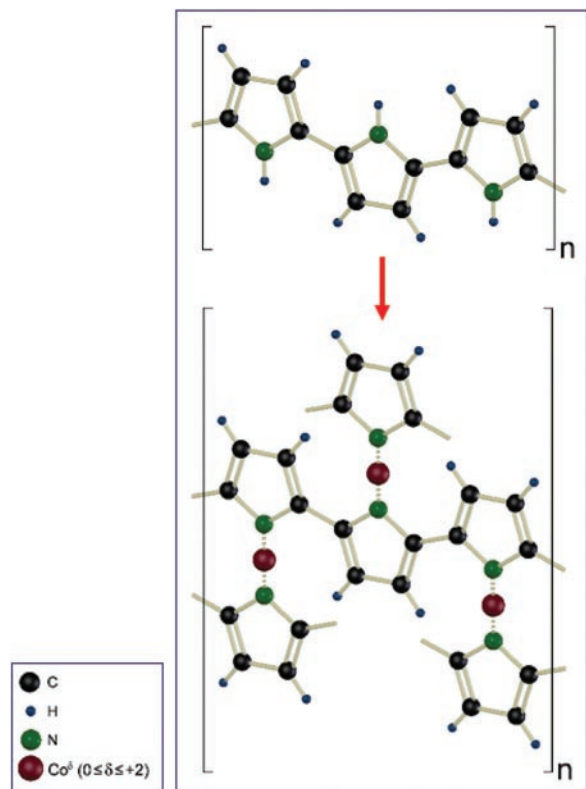


FIGURE 1. Presumed Structure of the Co-PPY Catalyst

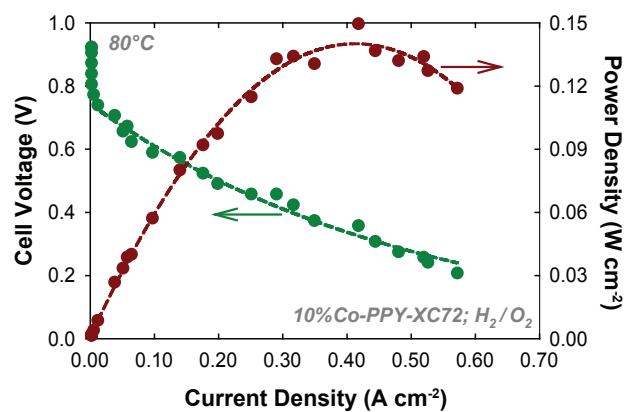


FIGURE 2. O₂-H₂ Fuel Cell Performance of a 10% Co-PPY-C Catalyst at 80°C

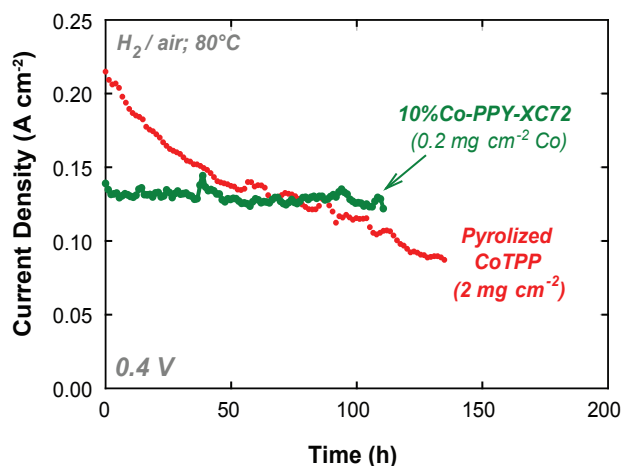


FIGURE 3. Life test of an H₂-air fuel cell operating with a 10% Co-PPY-C cathode. Life test data for a cell with a cobalt tetraphenyl porphyrin (CoTPP) cathode (the most active pyrolyzed-porphyrin cathode catalyst) are shown for comparison. Cell temperature: 80°C.

Poitiers, Poitiers, France, we have developed a new fabrication technique for chalcogenide catalysts, which involves surface modification of metal (ruthenium) black particles rather than synthesis of a bulk metal-chalcogen compound. Se/Ru catalysts have been obtained in this project by depositing Se from either organic solvents (xylenes) or, most recently, directly from aqueous media. As revealed by x-ray diffraction (XRD) data (Figure 4), Ru and Se do not combine in the bulk of the catalyst particles. In the present approach, selenium acts only as a surface modifier, preventing active ruthenium sites from oxidation over long times of fuel cell operation.

Although the “aqueous” path is simpler and possibly leads to slightly better performing catalysts, both methods have resulted in materials with high ORR activity (Figure 5). Even without any advanced optimization of the electrode structure, Se/Ru cathodes yield volumetric ORR activities approaching a respectable 50 A cm⁻³. Similar to the nanocomposites, surface chalcogenides exhibit very good stability in PEFCs operating for hundreds of hours in the temperature range 70-80°C. RRDE data also indicate very low contribution from the 2e⁻ process, thus attesting to minimal H₂O₂ generation.

Further research will concentrate on reducing the ruthenium loading, which is required for making surface chalcogenides viable for high-power fuel cell applications, automotive transportation in particular. Preliminary experiments involving catalysts with ruthenium partially replaced by iron have shown similar ORR performance to that observed with Fe-free catalysts.

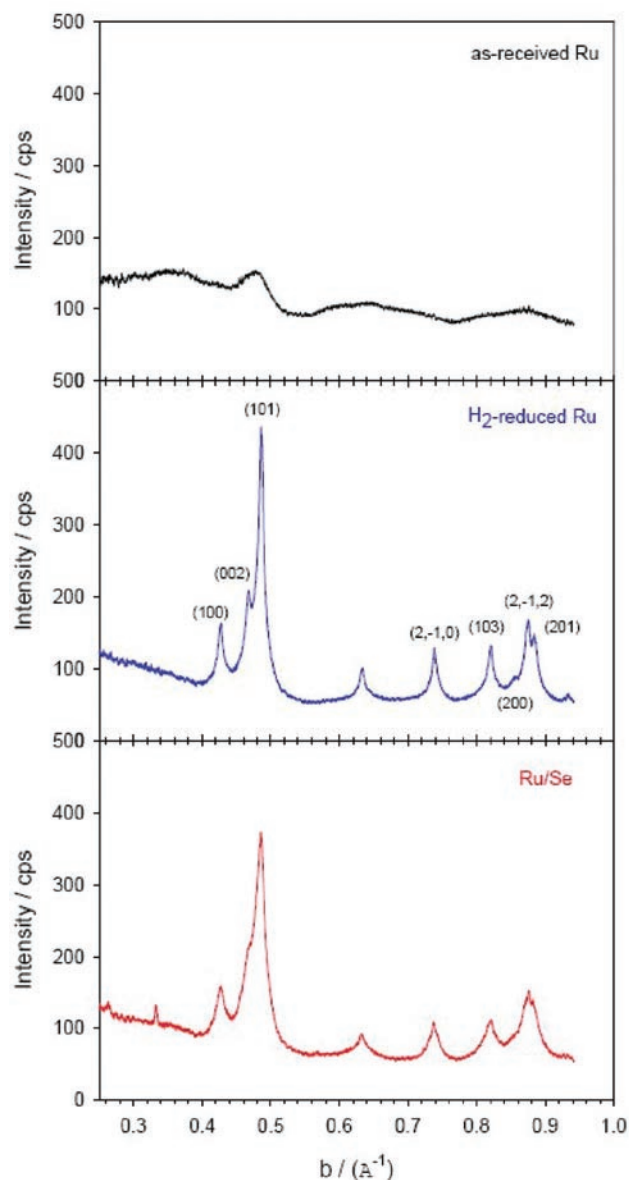


FIGURE 4. XRD data recorded with as-received Ru black (top), reduced Ru black (middle) and Se-modified Ru (bottom) that show no change in the chemical state of bulk ruthenium.

Conclusions

The main conclusions from non-platinum cathode catalysis research at LANL in the past year can be summarized as follows:

1. (Non-precious metal)/(heteroatomic polymer) nanocomposites, *e.g.* Co-PPY-C and Fe-PPY-C, represent a new interesting class of oxygen-reduction catalysts.
2. ORR activity of the composites appears to be directly linked to the presence of a Co-N site resulting from metal-heteroatom interaction.

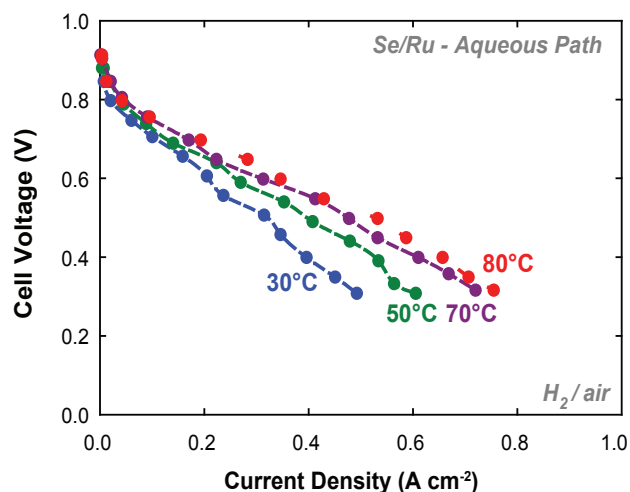


FIGURE 5. H_2 -air polarization plots recorded with a Se/Ru cathode at four different operating temperatures of the fuel cell; Se/Ru catalyst obtained on the aqueous path.

3. The Co-PPY-C composite shows good ORR activity and unique performance durability for a non-precious metal catalyst operating at low pH.
4. Structure characterization of Co-PPY-C catalyst by XANES and EXAFS reveals that during the initial catalyst activation for ~ 30 hours most Co(0), which is present in as-synthesized catalyst, transforms to Co(II) (but not cobalt oxide).
5. Se/Ru catalysts can be fabricated via modification of Ru nanoparticles by Se.
6. Selenium-modified ruthenium catalysts (“surface chalcogenides”), obtained on either non-aqueous or aqueous paths, exhibit higher activity than the corresponding bulk chalcogenides (currently up to 50 A cm^{-3}).
7. In addition to high ORR activity, surface chalcogenides show very good long-term stability under the conditions of PEFC cathode operation.
8. The rates of peroxide generation on Se/Ru at operating potentials of the PEFC cathode are low (less than 0.5%).

Future Directions

- Complete detailed characterization of oxygen reduction on Co nanocomposite.
- Finish RDE/RRDE study of ORR kinetics on the cobalt nanocomposite and two surface chalcogenides.
- 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 utilization (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 catalytic activity (“ORR activators”).
- Perform structure-mechanism correlations; propose approaches to lowering ORR overpotential on non-Pt catalysts.

Special Recognitions & Awards/Patents Issued

1. 2006 Los Alamos National Laboratory Patent & Licensing Award (February 2006; for year 2005).
2. U.S. Patent No. 7,014,93 B1, issued March 21, 2006.

FY 2006 Publications/Presentations

1. “A class of non-precious metal composite catalysts for fuel cells,” R. Bashyam and P. Zelenay, *Nature*, **443** 63-66 (2006).
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,” R. Bashyam* and P. Zelenay.
4. 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).
5. 2006 Materials Science and Technology Division Review, Los Alamos National Laboratory, Los Alamos, New Mexico, April 4-6, 2006. Title: “New Class of Non-precious Metal Nanocomposite Electrocatalysts for Fuel Cells,” R. Bashyam,* R. Mukundan, E. Brosha, F. Garzon, S. Conradson, and P. Zelenay.
6. Hydrogen, Fuel Cells & Infrastructure Technologies Program, 2006 Merit Review and Peer Evaluation Meeting, U.S. Department of Energy, Energy Efficiency and Renewable Energy, Arlington, Virginia, May 16-19, 2006. Title: “Non-Platinum Cathode Catalysts,” P. Zelenay.
7. 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).