

VII.C.7 Non-Precious Metal Catalysts

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

Objectives

The main research task of the project is to develop non-precious metal oxygen reduction reaction (ORR) catalyst(s) for the polymer electrolyte fuel cell (PEFC) cathode with activity and performance durability similar to the currently used precious-metal based catalysts. Individual objectives are as follows:

- Identify candidate materials with promising catalytic activity in oxygen reduction.
- Synthesize cathode catalysts in the form that allows electrochemical (“half-cell”), non-electrochemical, and fuel cell testing.
- Carry out performance characterization of the catalysts, including kinetic ORR measurements, turnover rates, stability at low pH, performance durability, etc.
- Determine the mechanism of oxygen reduction on different catalysts; in particular, identify the active site of the oxygen reduction process.
- Design and optimize membrane-electrode assemblies (MEAs) with alternative catalyst used at the cathode.
- Find main routes of cell performance degradation and improve performance durability.
- Collaborate with the fuel cell industry on efficient MEA integration of new materials and facilitate technology transfer of non-precious catalysts.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section 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

Research in non-precious metal catalysis is carried out at Los Alamos National Laboratory (LANL) to specifically meet 2010 and 2015 DOE technical targets formulated in Table 3.4.4 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan for transportation fuel cell stacks operating on direct hydrogen. The most relevant targets included in that table are as follows:

Table 1. Relevant DOE Technical Targets for Transportation Fuel Cell Stacks Operating on Direct Hydrogen

Characteristics	Units	2010	2015
Power density	W/L	2,000	2,000
Specific Power	W/kg	2,000	2,000
Efficiency @ 25% rated power	%	65	65
Efficiency @ rated power	%	55	55
Precious metal loading	g/kW	0.3	0.2
Cost	\$/kW _e	30	20
Durability with cycling	hours	5,000	5,000

Approach

- Build, operate and test electrochemical cells and fuel cells with non-precious metal catalysts under the conditions relevant to future stack operation.
- Through experimentation, develop a thorough understanding of the ORR mechanism and key factors impacting catalyst performance and durability.
- Maximize power and energy density delivered by the fuel cell operating with the alternative cathode catalyst through careful optimization of the MEA components and experimental verification of cell performance.

Accomplishments

- Developed techniques for electrochemical characterization of non-precious metal catalysts under conditions relevant to fuel cell operation.
- Demonstrated high ORR activity and, in some cases, respectable performance durability of several pyrolyzed metalloporphyrins.
- Performed initial electrochemical/pH stability experiments with several metalloporphyrins and developed dilute-acid treatment as a method of enhancing catalyst activity.
- Completed the first stage of ORR mechanism study for cobalt metalloporphyrins.
- Identified very promising chalcogenide catalyst for oxygen reduction at the PEFC cathode.
- Demonstrated exceptional methanol tolerance of several non-Pt cathode catalysts.

Future Directions

Remainder of FY 2005

- Identify and characterize the active site (or sites) for oxygen reduction reaction on metalloporphyrin catalysts.

FY 2006 Objectives

- Determine distribution of active ORR sites on metalloporphyrin catalysts as a function of (i) catalyst type, (ii) fabrication technique and conditions, and (iii) catalyst “post-treatment” (including the effect of solution pH).
- Investigate structures potentially leading to the protection of active ORR site(s) in acidic media and improved activity and durability of metalloporphyrin catalysts.
- Lower high-frequency resistance of membrane-electrode assemblies with non-precious metal cathode catalysts.
- Carry out performance study of metal chalcogenides as promising alternatives to metalloporphyrins.

Introduction

In an effort aimed predominantly at lowering the cost of hydrogen-air fuel cells as viable power sources for automotive transportation, the alternative catalysis research at Los Alamos has concentrated on identifying, developing, testing and understanding electrocatalysis with materials that are potentially capable of replacing supported platinum at the PEFC cathode. An important part of this effort has been the selection and optimization of “non-catalytic” components of the MEA that would allow successful implementation of non-precious metal catalyst(s) in fuel cells without an additional “MEA performance penalty”.

In general, the main objective of this research has been to develop non-precious metal catalyst(s) that, while allowing PEFC systems to meet the fuel cell stack cost targets, would not lead to lower performance in terms of power density, energy conversion efficiency and durability.

Approach

At the heart of the LANL approach is to subject advanced alternative cathode catalysts, developed onsite and by our university and industrial partners, to a variety of electrochemical, non-electrochemical and fuel cell testing to identify the most active and durable catalysts, determine the mechanism of oxygen reduction on these catalysts, and design MEAs with optimum performance. Through experimentation, we attempt to develop thorough understanding of the key factors that impact performance of the ORR catalysts and their performance durability. In addition to targeting reduction of the cathode catalyst cost, the effort also focuses on maximizing specific power and fuel conversion efficiency to avoid, or at least minimize, performance degradation caused by replacement of platinum with non-precious catalysts.

Results

In FY 2005, our effort has concentrated on (i) developing techniques for catalyst characterization, (ii) performing initial electrochemical/pH stability experiments with pyrolyzed metalloporphyrins, and (iii) determining the active reaction site for ORR on pyrolyzed

metalloporphyrins. Porphyrin research has been carried out in a very close collaboration with Plamen Atanasov's group at the University of New Mexico (UNM), where porphyrin catalysts were synthesized and partially characterized before being sent to Los Alamos for further characterization and fuel cell testing.

UNM has developed a method of catalyst synthesis based on supporting the precursors on silica, then pyrolyzing at 600-700°C and, finally, etching the silica support to obtain very well dispersed, porous and “self-supported” pyropolymer. This highly innovative fabrication technique resulted in catalysts capable of delivering good fuel cell performance (Figure 1a) and, in some cases, respectable stability (Figure 1b). As shown in Figure 1a, all three cobalt porphyrins, CoTMPP [cobalt tetramethoxyphenyl porphyrin], CoTPP [cobalt tetraphenyl porphyrin] and Co/Fe(1:1)TPP, deliver similar initial cathode

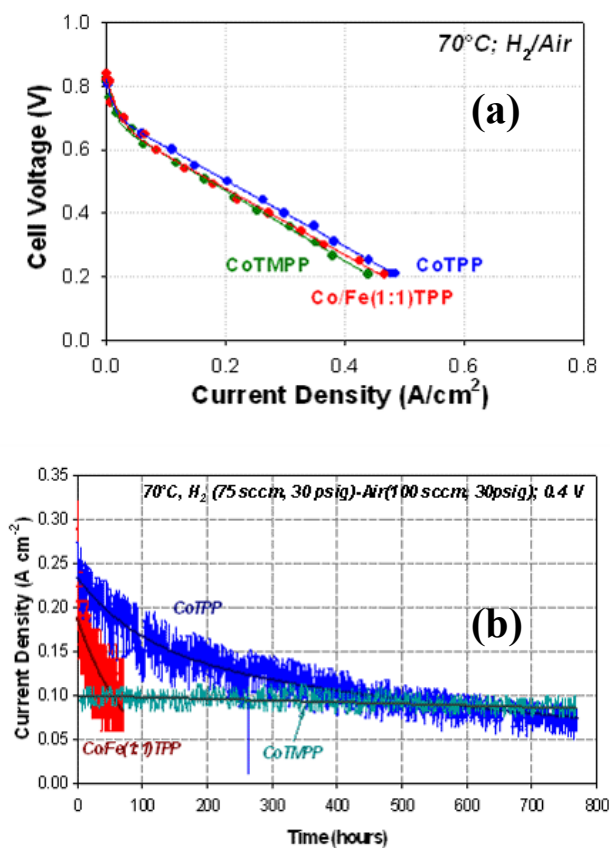


Figure 1. Hydrogen-Air Fuel Cell Performance of Metalloporphyrins: (a) Cell Polarization Plots, (b) Life Test Data

performance. (When operated on oxygen rather than air, the Co/Fe porphyrin has shown lower performance than the other two catalysts, possibly due to an oxidative loss of Fe.) Operation over longer times, close to 800 hours, reveals remarkable differences in the stability of the three catalysts, with CoTPP exhibiting the highest initial activity and CoTMPP assuring the best durability (Figure 1b). Once again, Co/Fe(1:1)TPP turns out to be the poorest performer, quickly losing its initial ORR activity in the first 50 hours of the life test.

A comparative activity study of Co-based catalysts derived from precursors in different chemical form reveals that metal chelates (metal-N₄ type compounds) lead to the most active catalysts. That said, the metal-N₄ geometry of the precursor is largely lost in the pyrolysis process, leaving the question of the active catalyst site quite open. X-ray diffraction studies of pyrolyzed cobalt porphyrins indicate crystalline metallic Co is absent in all these catalysts. In turn, scanning electron microscopy

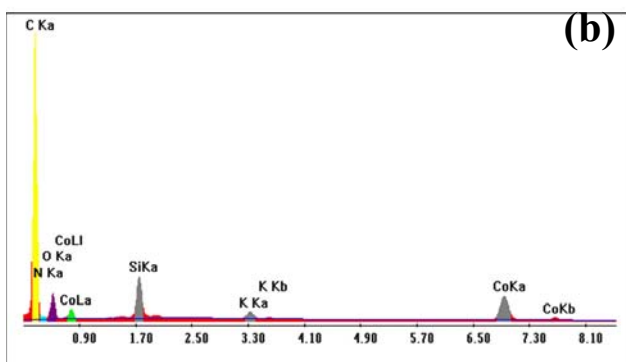
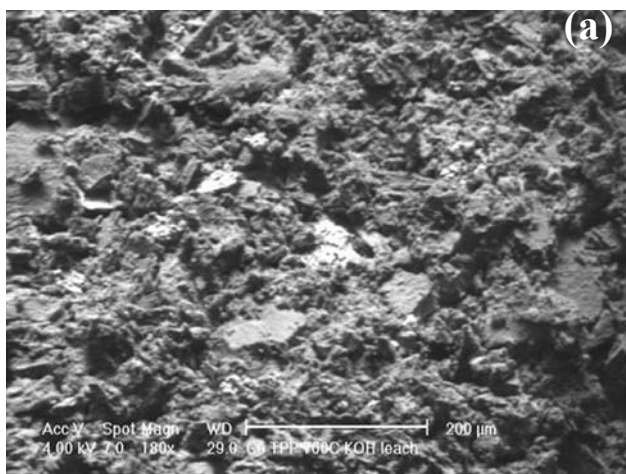


Figure 2. (a) Scanning Electron Microscopy and (b) EDX Spectrum for the CoTPP Catalyst

(SEM) images show highly non-homogeneous catalyst morphology, with both Co-rich (bright) and Co-deficient (dark) particles clearly present in the micrograph (Figure 2a). Energy dispersive X-ray microanalysis (EDX) spectra reveal very little nitrogen relative to cobalt, further undermining a dominant role of the Co-N moiety in the oxygen reduction catalysis (Figure 2b). This is further supported by the lack of correlation in the distribution of nitrogen and cobalt in the CoTPP catalyst (cf. EDX mapping data in Figure 3). An excellent correlation between the distribution of cobalt and oxygen in Figure 3 seems to indicate that good activity of the CoTPP catalyst may be linked to the presence of cobalt oxides.

A very interesting change to the activity of the CoTPP catalyst is brought about by dilute-acid treatment of catalyst powders. Quite surprisingly, rather than lowering catalyst activity due to leaching, the dilute-acid treatment leads to noticeable improvement in the catalyst ORR performance (Figure 4). Of the pH treatments used, the highest increase in catalytic activity, by up to 100 mV at 50°C -70°C, has been observed at pH 1.0 (an intermediate pH value). This enhancement in the catalytic activity is likely caused by the removal of inactive species present at the catalyst surface, leading to an improved oxygen access to the catalyst sites. Remnant silica after the SiO₂ etch is the most probable reason for the catalyst contamination (cf. EDX proof of Si presence, Figures 2b and 3).

Metal chalcogenides have been identified as another group of materials with good potential for replacing platinum in the PEFC cathode. In the past year, we have established collaboration with the

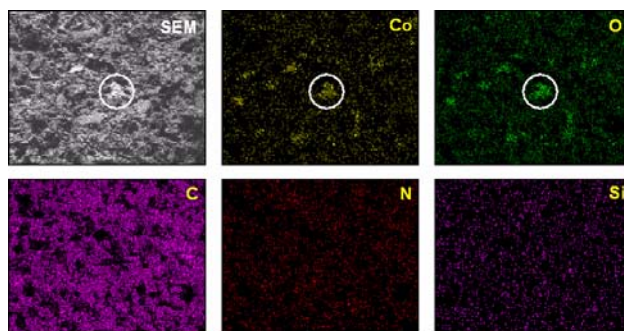


Figure 3. EDX Mapping of the CoTPP Catalyst

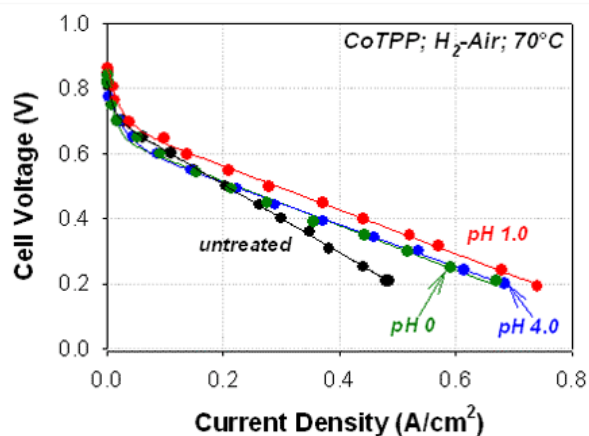
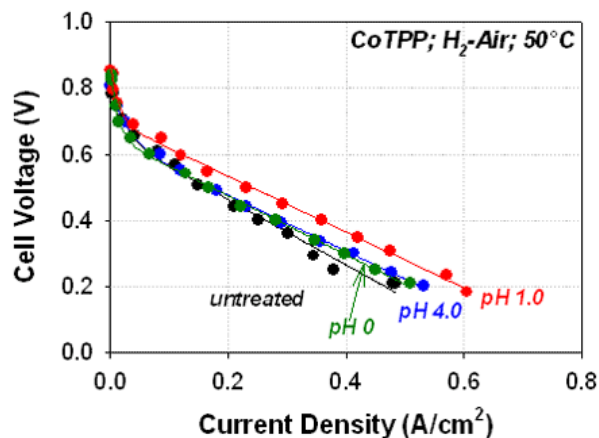


Figure 4. Effect of Dilute-Acid Treatment on Hydrogen-Air Fuel Cell Performance of CoTPP at 50°C and 70°C

University of Illinois Urbana-Champaign (Professor Andrzej Wieckowski) and the University of Poitiers in France (Professor Nicolas Alonso-Vante) to develop well-performing and stable chalcogenide catalyst for oxygen reduction under fuel cell operating conditions. Very promising performance of one such material is shown in Figure 5. Unlike most metalloporphyrins, the chalcogenide catalyst has incurred no performance loss in the life test conducted for over several hundred hours. (The initial 110 hours of that life test is shown in Figure 5b.)

Both metalloporphyrins and chalcogenides are known for their tolerance to methanol, which makes them particularly attractive candidates for use in direct methanol fuel cell (DMFC) cathodes, especially in mixed-reactant DMFCs. Performance of the CoTPP catalyst in DMFCs operating with up to 4.7 M methanol in the anode feed is demonstrated

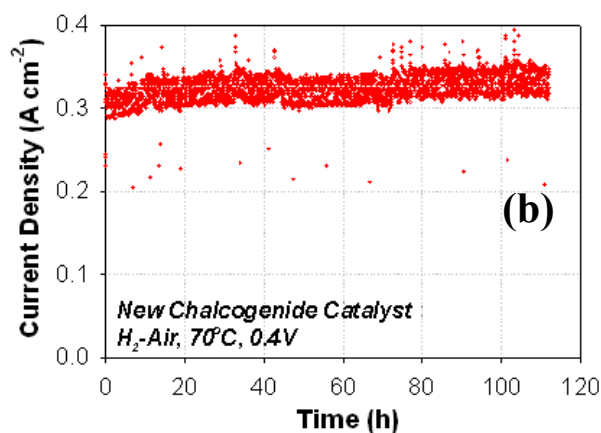
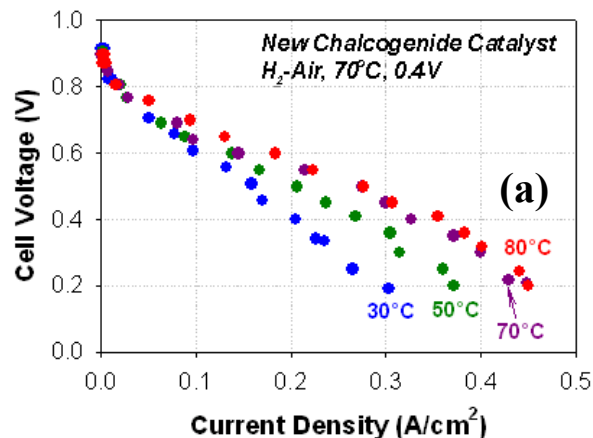


Figure 5 Test Data for the Chalcogenide Catalyst: (a) Polarization Plots at 30°C, 50°C, 70°C, and 80°C; (b) Initial 110 Hours of the Life Test

in Figure 6a. Thanks to high tolerance of the cathode catalyst to crossover methanol, cell performance is virtually independent of methanol concentration. At sufficiently high concentrations, the cell with a methanol-tolerant cathode can outperform a “standard” DMFC, with Pt black used at the cathode catalyst (Figure 6b). Similar, if not better, methanol tolerance has been observed at LANL with chalcogenide catalysts.

Conclusions

The key conclusions from non-precious metal catalysis research at LANL in the past year can be summarized as follows:

- Several metalloporphyrin catalysts show good initial activity and promising stability when used in the PEFC cathode.

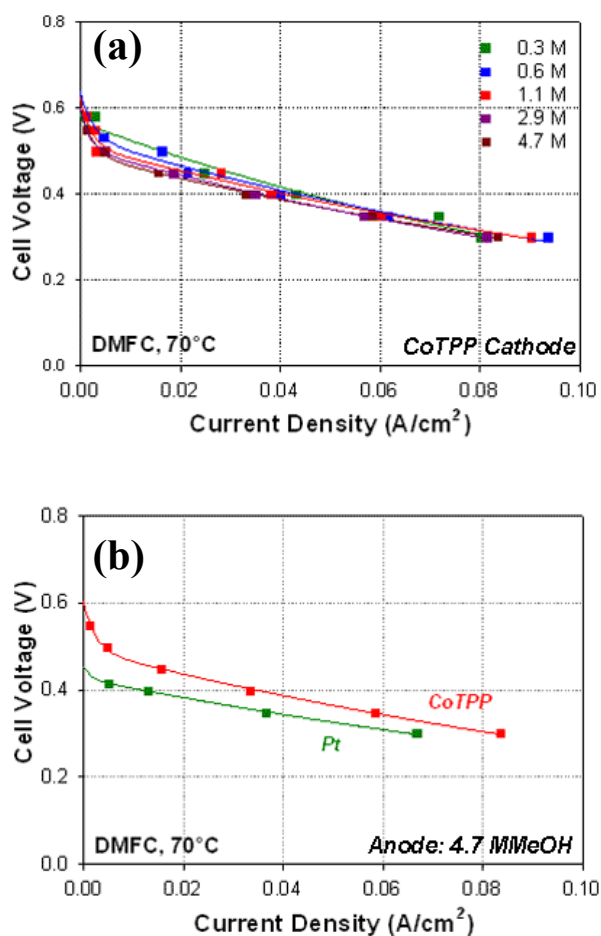


Figure 6. Methanol Tolerance of the CoTPP Catalyst: (a) DMFC Polarization Plots at Various Concentrations of Methanol in the Anode Feed; (b) Comparison of DMFC Polarization Plots Recorded with CoTPP Cathode and Pt-Black Cathode with a Presence of 4.7 M Methanol in the Anode Feed Stream (Pt-Ru black catalyst used at the anode.)

- Dilute-acid treatment improves ORR activity of metalloporphyrins synthesized on the silica support, most likely by removing traces of un-etched silica.
- The results obtained to date do not confirm that N₄ sites play a major role in oxygen reduction on metalloporphyrin catalysts; observed good correlation in the distribution of cobalt and oxygen in CoTPP points to cobalt oxides as important for catalyst activity.
- Chalcogenides may offer comparable, if not higher, ORR activity than metalloporphyrins and better stability under PEFC operating conditions.
- Prohibitively high ORR overpotential on alternative cathode catalysts, *ca.* 200 mV higher than on Pt cathode, has to be overcome to assure sufficient fuel conversion efficiency in the hydrogen-air fuel cell.
- Very good methanol tolerance of metalloporphyrins and chalcogenides makes them attractive candidate catalysts for DMFC applications, in the mixed-reactant systems in particular.

Special Recognitions & Awards

1. Individual Los Alamos National Laboratory Patent & Licensing Awards for E. Brosha, J. Davey, F. Garzon, F. Uribe and P. Zelenay, February 2005.

FY 2005 Presentations

1. 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004. Title: "Non-Platinum Electrocatalysts for Polymer Electrolyte Fuel Cells: Methanol-Tolerant Cathode Catalyst," S. Levendosky, P. Atanassov, B. Piela and P. Zelenay.