

VII.C.2 Novel Non-Precious Metal Catalysts for PEMFC: Catalyst Selection through Molecular Modeling and Durability Studies

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Objectives

- Synthesize low-cost non-precious metal electrocatalyst for the oxygen reduction reaction by using a mass production method.
- Study the role of surface groups such as O, S, etc.
- Develop methodology for the synthesis of metal-free catalysts.
- Develop methodology for the synthesis of active Co- and Fe-based electrocatalysts.
- Demonstrate the potential of novel non-precious electrocatalysts to substitute Pt catalysts currently used in membrane electrode assemblies (MEAs).

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

Approach

- Increase the number of the catalytic sites by modifying carbon substrates using various activation processes and heat treatments.
- Develop a procedure to synthesize low-cost cobalt or iron complex from various nitrogen donors.

- Optimize the process parameters such as metal-to-nitrogen ratio, wt% of metal on carbon, and the effect of carbon activation.
- Use surface modifiers to increase the porosity, surface area and activity of the catalyst.

Accomplishments

- Metal-free catalyst was developed with carbon surface modification.
 - Onset potential for oxygen reduction = 0.73 V vs. the standard hydrogen electrode (SHE).
 - The four-electron pathway for the oxygen reduction reaction (ORR) was achieved.
- Active Co-chelate/C catalyst was developed with the use of activated carbon.
 - A methodology was developed to increase the active sites of the catalyst. Introduction of quinone-hydroquinone groups on the carbon surface increases the number of active sites by favoring the anchoring of Co-chelate complexes on carbon substrate. The four-electron pathway for the ORR was achieved.
 - Co-based catalyst synthesized from low-cost precursors showed better performance than the complex macrocyclic CoTMPP [5,10,15,20-tetrakis(4-methoxy-phenyl)-21H,23H-porphine cobalt] catalysts. The half-wave potential of Co-chelate-based catalyst was as high as 0.72 V vs. SHE ($E_{1/2}$ of Pt/C = 0.8 V vs. SHE).
 - Active Co-chelate/C catalyst was developed by using surface modifiers.
 - Two surface modifiers were identified (SM1 and SM2 – University of South Carolina products) to increase the activity of the non-precious metal catalysts (Co, Fe and Co-Fe). The four-electron pathway for the ORR was achieved.
- Ru-based catalyst synthesized by a procedure developed at the University of South Carolina showed performance equivalent to that of ETEK 20% Pt/C catalyst under rotating ring disc electrode (RRDE) test conditions.
- Bimetallic Co-Ru and Fe-Ru showed performance comparable to that of ETEK 20% Pt/C catalyst under RRDE test conditions.

Future Directions

- Develop Co and Fe catalysts and Fe-Co bimetallic catalyst. Extensive material characterization/structural analysis and durability studies will be performed in order to optimize the performance of the catalyst. The objective is to increase the activity and decrease the catalyst loading as suggested by a USCAR committee during the last Review Meeting.
- Search for new surface modifiers and carbon surface treatments to increase the number of active sites.
- Encapsulate the catalyst in more stable materials such as carbide, nitride and zeolite.
- Develop metal-free catalyst for oxygen reduction.
- Study the structure-property relation of developed metal-free catalysts.
- Calculate water oxidation potential and O₂ adsorption properties on carbon nitrides.
- Investigate alternative active Co sulfide structures.

Introduction

Currently Pt and Pt alloys are widely used as anode and cathode materials in polymer electrolyte membrane fuel cells (PEMFCs). Despite a cathodic overpotential loss of 20%, Pt and its alloys are still

preferred because of their resistance towards corrosion in acidic media. In the last few years, several transition metal compounds such as macrocycle-based metal containing porphyrin system [1,2], chevreel phase type compounds (e.g., Mo₄Ru₂Se₈) and other transition metal

chalcogenides have been proposed as selective catalysts for the oxygen reduction reaction (ORR)[3]. However, further increase in activity and stability of the catalyst is essential for PEMFC applications.

The goal of the present project is to develop a highly active and stable non-precious metal catalyst through a mass production method.

Approach

Non-precious catalysts were prepared from low-cost precursors of transition metals and nitrogen donors. The approach is to increase the number of active sites for the oxygen reduction reaction. Carbon surface modification with various chemical and heat treatments was performed to anchor the chelate-type catalyst leading towards increased dispersion. Surface modifiers that increase the porosity and dispersion of the catalyst will be identified. Bimetallic alloys such as Fe-Co, Co-Ru and Fe-Ru will be synthesized to increase the stability of the catalysts.

Results

Development of Metal-Free Catalysts

The metal-free catalysts were synthesized by chemical modification of carbon substrate followed by heat treatment. Oxygen groups were introduced with different chemical treatments such as oxidation with HNO_3 (K2) and treatment with NaOH (K3). Prior to oxidation, the carbons were pre-washed in HCl (K1). Nitrogen groups were introduced by two methods: (i) heat treatment at elevated temperatures in the presence of ammonia and (ii) adsorption of nitrogen from various nitrogen donors followed by heat treatment at elevated temperatures.

Figure 1a shows the disk currents of several modified carbons. Carbon oxidized with HNO_3 , K2, showed higher ORR currents compared to K1. The increased activity can be attributed to the quinone hydroquinone oxygen surface groups generated on the surface of the carbon with HNO_3 treatment. The presence of quinone groups on HNO_3 -oxidized carbons (K2) was identified electrochemically by the quinone/hydroquinone redox couple which occurs at approximately 0.55 V vs. SHE. Further increase in

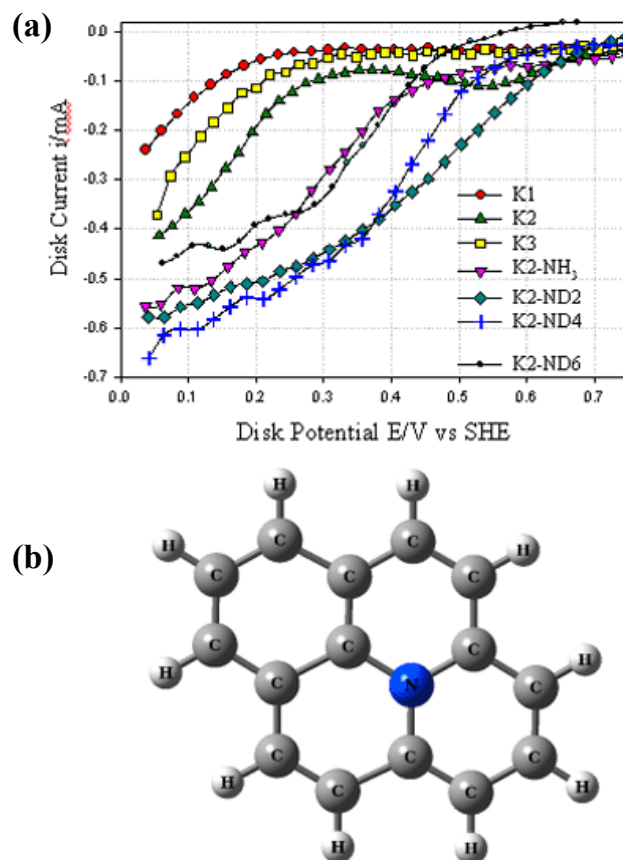


Figure 1. (a) Disk Currents Obtained on RRDE for Metal-Free Catalysts in 0.5 M H_2SO_4 Solution Saturated with O_2 (b) Model of a Nitrogenated Carbon Used for ab-initio MP2 Calculations

activity towards ORR has been obtained with the introduction of nitrogen groups. It's observed that the activity is a strong function of the nature of the nitrogen donor (ND) used for synthesis of carbon. Nitrogenated carbon obtained by the adsorption of nitrogen donors has better performance than K2-NH_3 . The presence of quinone hydroquinone groups is known to favor the adsorption of nitrogen donors, leading to nitrogen-rich, metal-free catalysts. Several nitrogen precursors were tested for ORR. High onset potential of 0.7 V vs. SHE for ORR was obtained for K2-ND2 catalysts. However, higher ring currents were obtained for the nitrogenated carbons, showing that the ORR follows a two-electron reduction. This system has been modeled by ab initio MP2 calculations assuming a nitrogenated carbon structure as shown in Figure 1b. A linear relationship between Gibbs energies and internal energies discovered in this lab was applied to

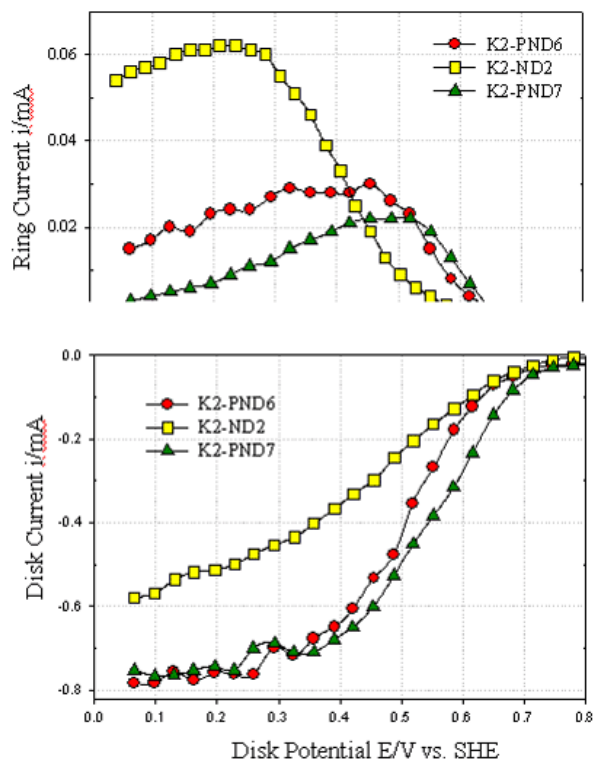


Figure 2. Disk and Ring Current Plots for Metal-Free Catalysts in 0.5 M H_2SO_4 Solution Saturated with Oxygen

predicting potentials for forming reaction intermediates on electrode surfaces to study H_2O_2 generation [4]. The mechanistic study shows that for nitrogenated carbon, the predominant reaction is towards peroxide generation.

It is crucial to eliminate peroxide generation in the metal-free catalysts for ORR. To eliminate the peroxide generation, the metal-free catalysts were modified with several chemical and heat treatments. Figure 2 shows the disk and ring currents of nitrogen donors ND6 and ND7 deposited on oxidized carbon. Also shown for comparison is the monomeric ND2 adsorbed on K2. The disk currents shown in Figure 2 indicate an activation potential of 0.7 V and 0.73 V for deposited K2-PND6 and K2-PND7, respectively. Also, K2-PND7 exhibits higher disk currents when compared with the carbon-based catalyst loaded with nitrogen donors. The ring currents on K2-PND7 are reduced to approximately half of what is observed in K2-ND2, indicating an increased selectivity of this catalyst for four-electron reduction of oxygen.

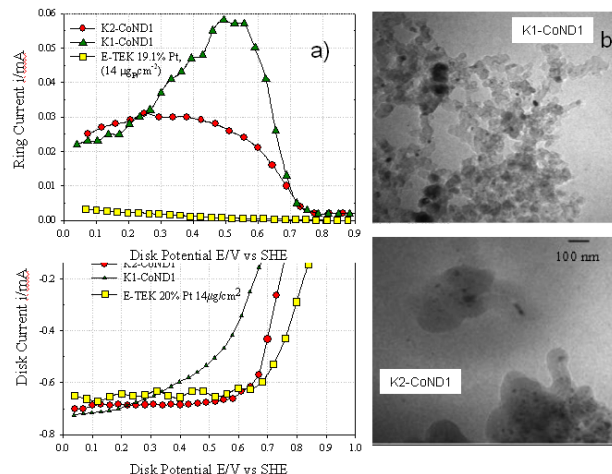


Figure 3. (a) Disk Currents for Co-Chelate Catalysts Adsorbed on K1 and K2, in 0.5 M H_2SO_4 Saturated with O_2 (b) TEM Images of K1-CoND1 and K2-CoND1

Such high kinetic rates and selectivity towards four-electron reduction on metal-free catalysts have not been reported previously.

Development of Co-Chelate Catalysts

Effect of Carbon Pretreatment: The effect of oxidation on the dispersion and the activity of cobalt-chelate complexes was studied by testing samples of heat-treated CoND1 on oxidized carbon K2 and on un-oxidized carbon K1. The results are shown in Figure 3a. The electrocatalyst K2-CoND1(HT) showed better activity than K1-CoND1(HT). The catalyst supported on un-oxidized carbon exhibits activation overpotential of 470 mV towards oxygen reduction. The diffusion-limited plateau of the polarization curve for K1-CoND1(HT) shown in Figure 3a is not well defined as usually observed with the Pt catalysts. The model proposed by Jiang *et al.* [5] shows that the plateau is more inclined when the distribution of active sites is less uniform and the reaction is slower. However, with the use of HNO_3 -treated oxidized carbon, activity towards oxygen reduction increases. A single steep reduction wave with a well-developed limiting plateau similar to that of Pt catalysts is observed. The activation overpotential for oxygen reduction on K2-CoND1(HT) decreases by 60 mV compared to K1-CoND1(HT). Figure 3a gives the ring currents as a function of the disk potential of the two catalysts.

The ring currents on K2-CoND1(HT) are less compared to those on K1-CoND1(HT). This suggests that on oxidized carbon, the selectivity of the catalyst for the four-electron reduction of oxygen to water is increased. Nitrogen fixation on carbon from nitrogen-containing precursors increases with the amount of oxygen surface groups, with one atom of nitrogen being added for every oxygen atom in the quinone structure. The presence of such quinone groups on the carbon surface forms acidic sites on the carbon surface which favor the absorption of basic CoND1 complex. This phenomenon results in an increase in dispersion of the catalyst. Figure 3b shows the transmission electron microscopy (TEM) images of heat-treated CoND1 samples supported on oxidized carbon and un-oxidized carbon. The average particle size of the catalyst supported on K1 support is 23.7 nm, while the particle size for the catalyst loaded on K2 support is 9.5 nm. Thus, the surface quinone groups cause a better dispersion of the CoND1 complex. By increasing the number of oxygen groups on the carbon support, the dispersion of the catalysts as well as their ultimate performance is increased.

Effect of Surface Modifier: Surface modifiers were used to increase the dispersion and activity of the catalysts. The effects of the surface modifiers on the cobalt-chelate catalyst were studied in detail. Figure 4a shows the linear sweep voltammograms measured at 900 rpm in 0.5 M H₂SO₄ for Co-chelate catalyst prepared with two different surface modifiers, namely SM1 and SM2. Also shown for comparison is the performance of 20% ETEK Pt/C catalyst. Single-step reduction currents with well-developed limiting currents plateaus are observed at 900 rpm for Co-chelate catalysts prepared with surface modifiers. The shape of the voltammogram shows a very well-defined mass transfer and kinetic regions similar to those obtained for the oxygen reduction on a platinum electrode. With the use of surface modifiers, a drastic increase in the activity of the Co-chelate catalysts can be observed. The onset potential for ORR increases by 40-70 mV with the use of surface modifiers. The use of surface modifiers is expected to increase the porosity and dispersion of the catalyst. Figure 4b shows the TEM images of Co-chelate catalysts in the absence and presence of surface modifiers. The particle size of the Co-chelate catalysts decreases from 17 nm to 6

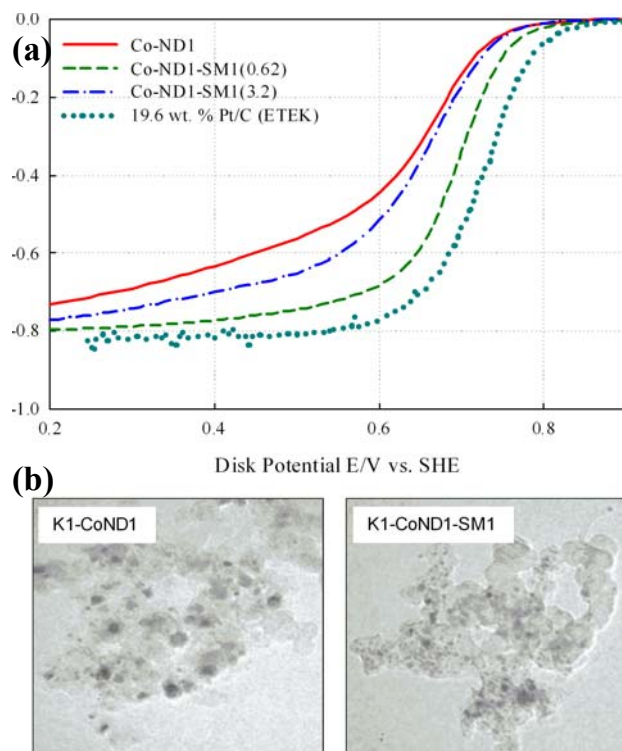


Figure 4. (a) Disk Currents for Co-Chelate Catalysts with Surface Modifiers, in 0.5 M H₂SO₄ Saturated with O₂ (b) TEM Images of K1-CoND1 and K1-CoND1-SM1

nm with the use of surface modifier (SM1). Apart from increasing dispersion of the catalyst, the surface modifiers are expected to form a part of the active sites of the catalyst.

Development of Ru-Chelate Catalysts for ORR

Ru-based chalcogenide compounds such as MoRuSe have intrinsic disadvantages, including low reaction rate of synthesis and high-cost carbonyl precursors. In order to synthesize transition metal-supported catalysts for oxygen reduction which are less expensive and more stable, a chelating method has been developed using low-cost transition metal salts and nitrogen precursors. Figure 5a shows the linear sweep voltammograms at 900 rpm in 0.5 M H₂SO₄ saturated with oxygen for various Ru catalysts. The activity of Ru-chelate catalyst, namely Ru-ND2, is improved in comparison with expensive MoRuSe catalysts. Further increase in activity for Ru-ND2 catalyst is obtained with the use of surface modifier (SM1). The onset potential for ORR is as high as 0.9 V vs. SHE. Ru catalysts prepared from

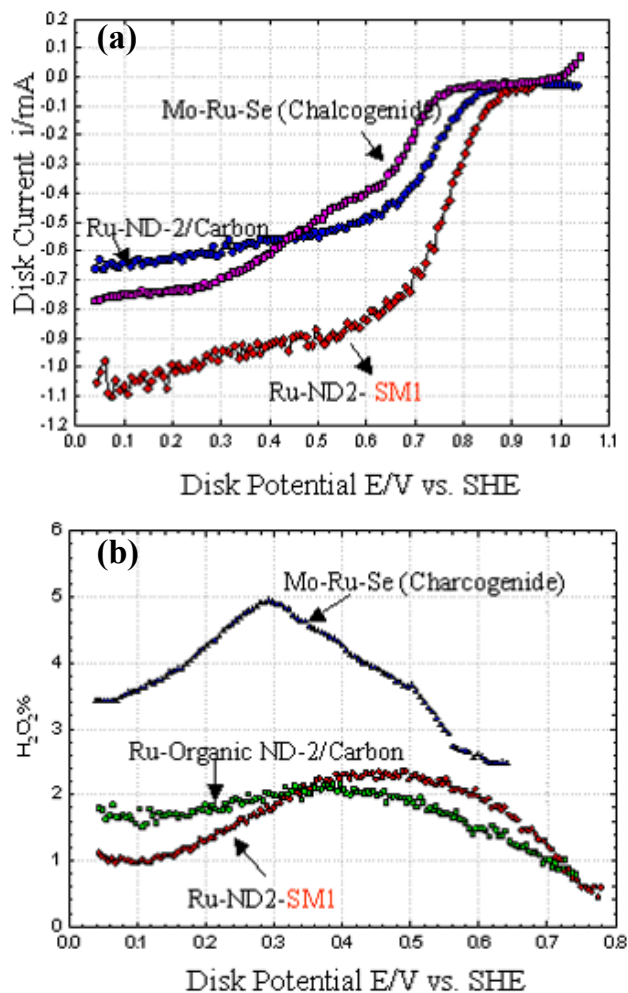


Figure 5. (a) Disk for Ru-Based Catalysts in 0.5 M H_2SO_4 Saturated with O_2 (b) % H_2O_2 Produced for Ru-Based Catalysts

chelates with the use of surface modifier show activity comparable to that of Pt/C. Such high activity for ORR on Ru has not been reported before. Also, from Figure 5b it can be seen that the amount of peroxide produced in Ru-chelate catalysts is less than 2%, close to that of platinum.

Stability of Developed Catalysts

The stability of the catalyst is the key criterion for the development of non-precious metal catalysts. Preliminary studies on the stability of bimetallic Ru-Co catalyst were conducted in rotating disk electrode (RDE) and fuel cell test stations. In the RDE test, the catalyst was tested in a corrosive environment of 0.5 M H_2SO_4 saturated with oxygen and polarized at 0.5

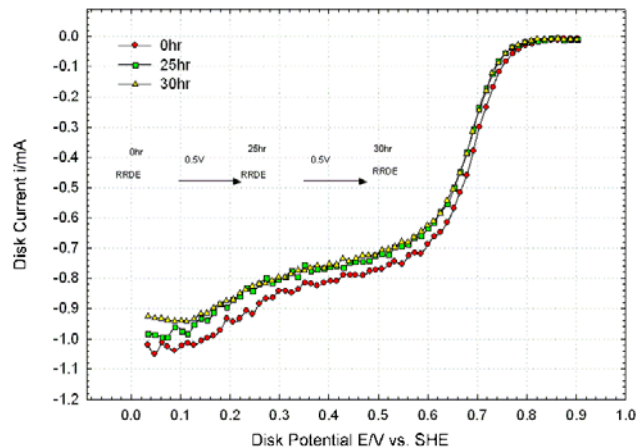


Figure 6. Stability of Ru-Co Chelate Catalyst in 0.5 M H_2SO_4 Saturated with O_2

V vs. SHE. The linear sweep voltammograms were obtained at regular intervals. The current-potential plots for the catalyst are shown in Figure 6. Over a period of 30 h, the loss in performance is very low. This emphasizes the good stability of the catalyst. Long-term stability studies of metal-free catalyst and Co- and Fe-based catalysts are currently in progress.

Conclusions

It has been shown that metal-free catalysts with activity as high as 0.7 V onset potential for ORR can be attained. Functional groups on the surface of the carbon play an important role in the activity and stability of the catalysts developed. The use of surface modifier increases the dispersion and decreases the particle size of the catalysts. Surface modifiers are also expected to form a part of the active sites in the catalysts. Ru-chelate catalysts with the use of surface modifiers show performance comparable to that of ETEK 20% Pt/C.

Special Recognitions & Awards/Patents Issued

1. Crystal Flame Innovation Award in Research from FuelCell South was presented to Prof. Branko Popov's research group for their work in the field of non-precious catalyst development and preparation of thin film assemblies with nanostructured catalysts by pulse deposition technique.

FY 2005 Publications/Presentations

1. N. P. Subramanian, S. P. Kumaraguru, H. Colon, H. Kim and B. N. Popov, "Studies on Co Based Catalysts Supported on Modified Carbon for PEMFC Cathodes," *J. Power Sources*, in press.
2. N. P. Subramanian, S. P. Kumaraguru, H. Kim, B. N. Popov, "Development of Metal Free Catalysts for PEMFC Cathodes," submitted to *J. Power Sources*, July 2005.
3. R. A. Sidik and A. B. Anderson, "Molecular Modeling of Water Oxidation and O₂ Reduction on Non-Noble Metal Oxygen Reduction Catalysts: Cobalt Sulfide."
4. S. P. Kumaraguru and B. N. Popov, "New Catalyst Materials for Fuel Cells Applications," SERMACS, November 2004, Durham, NC, Invited.
5. B. N. Popov, "Overview of Fuel Cell Research at CEE", FuelCell South Annual Conference, May 2005, Columbia, SC, Invited.
6. S. P. Kumaraguru, N. P. Subramanian, H. Colon, H. Kim and B. N. Popov, "Novel Non Precious Metal Catalysts for PEMFC Applications," *206th Meeting of the Electrochem Soc.*, October, 2004, Honolulu, HI, Contributed.
7. N. P. Subramanian and B. N. Popov, "Analysis of Carbon Substrates Used in Non-Precious Metal Catalysts for Fuel Cell Applications," *206th Meeting of the Electrochem Soc.*, October, 2004, Honolulu, HI, Contributed.

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