IV.C.6 Novel Non-Precious Metals for PEMFC: Catalyst Selection through Molecular Modeling and Durability Studies

Branko N. Popov
University of South Carolina
301, Main Street, Rm.2C02
Columbia, SC 29208
Phone: (803) 777-7314; Fax: (803) 777- 8265; E-mail: popov@engr.sc.edu

DOE Technology Development Manager: Donna Lee Ho
Phone: (202) 586-8000; Fax: (202) 586-9811; E-mail: Donna.Ho@ee.doe.gov

Subcontractors:
Dr. Alfred Anderson, Case Western Reserve University, Cleveland, OH
Dr. Sanjeev Mukerjee, North Eastern University, Boston, MA

Objectives

- Synthesize novel non-precious-metal electrocatalysts, with activity and stability similar to Pt, for the oxygen reduction reaction.
  - High activity toward oxygen reduction reaction
  - Mass production method
  - Corrosion resistance
  - Low cost
- Improve understanding of the reaction mechanism of oxygen reduction on non-precious catalysts through:
  - Theoretical molecular modeling
  - Electrochemical characterization
  - Structural studies (x-ray photoelectron spectroscopy – XPS, extended x-ray absorption fine structure, x-ray absorption near edge structure)
  - Correlation between the catalyst composition, heat treatment and catalytic sites for oxygen reduction
- Demonstrate the potential of the novel non-precious electrocatalysts to replace Pt catalysts currently used in 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:

- Q. Electrode Performance
- P. Durability
- O. Stack Material and Manufacturing Cost

Approach

- Develop supported and unsupported catalysts for oxygen reduction
  - Nitrogen contained precursors
  - Transition metal precursors
  - Chalcogenide compounds

- Optimize number of the catalytic sites as a function of:
  - Carbon pretreatment
  - Chemical composition of catalyst
  - Post treatment of catalyst
- Create a low-cost catalyst through use of
  - Mass production methods
  - Non-precious metals
  - Low-cost precursors
  - Development of a metal-free catalyst

Accomplishments

- A novel method to synthesize oxygen reduction catalysts from simple metal nitrate precursors has been developed.
- Hydrogen peroxide generation in cobalt-based catalysts has been eliminated by alloying the transition metal catalyst.
- Cr-X and Co-X alloys have shown improved catalytic activity towards oxygen reduction and decreased activity for H_2O_2 generation.
- Cr-X (from nitrate precursor), Co-X (from nitrate precursor) and Fe-X (from nitrogen precursor) alloys have performance comparable to Pt under rotating ring-disk electrode (RRDE) test conditions.
- Fe-X (from nitrogen precursor), Co-X and treated MoRuSe show the best performance for oxygen reduction.
- Post treatment is critical in order to obtain a high catalyst performance.
- Thermal and chemical treatments have been devised to improve the catalytic activity of chalcogenide and macrocycle-based catalysts.
- Modification of carbon by various chemical and thermal treatments increases the population of catalytically active sites.
- A methodology to generate a metal-free catalyst has been developed.

Future Directions

- Continue with the synthesis of low-cost transition metal catalysts from simple metal nitrates and nitrogen containing precursors to study the effects of: (i) metal/nitrogen ratio, (ii) temperature and (iii) pressure on oxygen overvoltage, performance and stability of the catalyst. The goal is to develop a catalyst which will show an oxygen overvoltage close to that of Pt with increased performance and stability.
- Prepare a metal-free catalyst from various nitrogen containing precursors and study the effects of temperature and pressure on the population of the catalytically active sites.
- Study the role of alloying elements in the kinetics of oxygen reduction and catalyst stability.
- Increase the stability of macrocyle-based catalyst by substituting the peripheral groups of the polydentate ligands attached to the central metal atoms of the macrocycles.
- Improve understanding of reaction mechanism of oxygen reduction on non-precious catalysts through molecular modeling.
- Perform structural characterization, fuel cell testing and stability studies of the optimized catalyst.

Introduction

Several transition metal compounds have been proposed as oxygen reduction reaction selective catalysts. Prominent among them are macrocycle-based metal-containing porphyrin systems, chevrel phase type compounds (e.g., $Mo_4Ru_2Se_8$) and other transition metal chalcogenides. An M-N_4 type moiety is known to be the active catalytic site for oxygen reduction. Other than macrocycles, these M-N_4 moieties can be generated from low-cost precursors. The ingredients necessary to generate a catalyst are (i) a transition metal, (ii) a source of nitrogen (e.g NH_3, acetonitrile) and (iii) high-temperature pyrolysis.[1,2]

In the present work, transition metals such as Fe, Co and Cr were studied for oxygen reduction. In addition, studies on different carbon susbstrates with thermal and chemical treatments were performed to generate a metal-free catalytic site. The performances of these catalysts were evaluated based on three main criteria: (i) activity towards oxygen reduction, (ii) oxygen reduction pathway type (two-electron or four-electron), and (iii) amount of hydrogen peroxide generated.

Approach

Our goal is to develop non-precious metal catalysts by mass production methods from low-cost precursors. The approach is based on (i) generating metal-free catalyst sites on carbon supports by using chemical and temperature treatments and by doping the precursor with non-precious metals and (ii) development of non-precious catalyst from low-cost metal salts followed by heat treatments. Our studies also address improvement of chalcogenide-based catalysts and increasing the stability of macrocyclic compounds by chemical and thermal treatments.

Results

1. Pretreatment Optimization Studies of Carbon Supports

An attempt was made to generate a metal-free catalytic site for the oxygen reduction reaction. In addition, to produce transition metal catalysts with higher levels of activity, the surfaces of Ketjenblack,
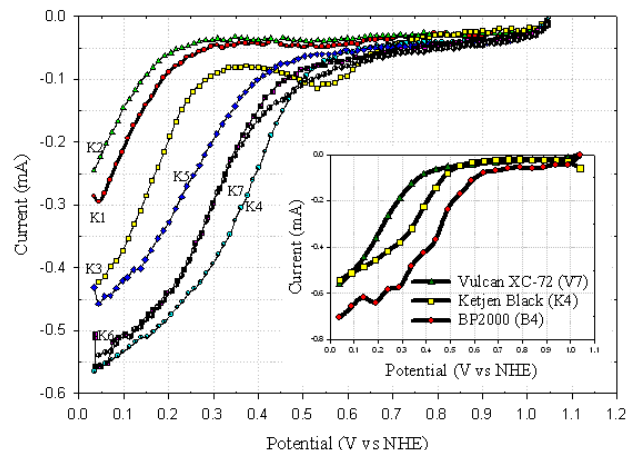

Figure 1. Oxygen Reduction Activity of Ketjen Black with Various Treatments; (inset) Comparison of Performance of Treated Ketjen Black (treatment K4), Black Pearl 2000 (treatment K4) and Vulcan XC 72 (treatment V7)

Black pearl 2000 and Vulcan XC-72 supports were modified using chemical and thermal pretreatments.

Figure 1 shows the performance of untreated and treated Ketjenblack samples. A comparison of the best-performing Ketjenblack, Black pearl 2000 and Vulcan XC-72 is shown in the Figure 1 inset. Combining treatments 1 and 4 resulted in the highest electrocatalytic activity for Ketjenblack and Black pearl 2000. Vulcan shows the best electrocatalytic performance when a combination of chemical and thermal treatments (treatment 7) are used to create the catalytically active sites on carbon. The results indicate that a nitrogen precursor and high temperature are necessary to generate a metal-free catalytic site. The nature of the active groups present on the carbon surface determines the number of active sites.

Our future work will include optimization of carbon modification processes. Modified carbon will be used for impregnation of optimized transition metal alloys. XPS studies will be conducted on carbon surfaces in order to identify the surface groups present on both treated and untreated carbons.

2. Transition Metal Based Catalysts for Oxygen Reduction

The electrochemical results obtained for the Cr, Co and Fe catalysts synthesized by treatments I and

Table 1. Summary of Electrochemical Results Obtained for Cr, Co and Fe Catalysts.

Catalyst	Treatment	Ep (V vs. RHE)	E1/2 (V vs. RHE)	Avg. no. of electrons	% H$_2$O$_2$ at 0.5 V vs. RHE
Co	I	0.499	0.4635	2.9	54.52
Fe	I	0.406	0.399	3.27	36.49
Cr	I	0.5	0.4336	3.59	20.29
Co	II	0.515	0.4725	2.923	53.81
Fe	II	0.4705	0.4275	3.31	34.20
Cr	II	0.5655	0.4807	3.05	47.49

Table 2. Summary of Electrochemical Results of Co and Cr Alloy Catalysts

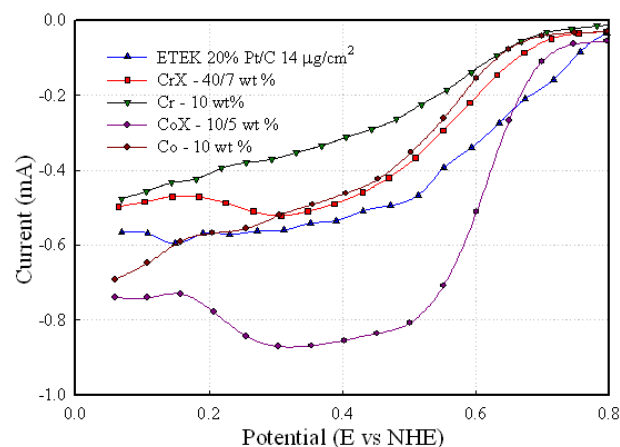| Catalyst	Treatment	E peak (V vs. RHE)	E half (V vs. RHE)	No. of Electrons	% H$_2$O$_2$ at 0.5 V vs. RHE
Cr	III	0.6175	0.532	3.57	20.7
CrX	III	0.605	0.572	3.93	3.5
Co	IV	0.54	0.49	2.85	57.5
Co-X	IV	0.63	0.61	3.95	2.5
8 µg Pt/cm2	-	-	0.576	3.8	13.2

II are presented in Table 1. Co shows the highest half-wave potential (E$_{1/2}$), followed by Cr and Fe (*E ½ --- Co > Cr >Fe*) for treatment I. However, the percent peroxide produced on Co is relatively high compared to that on Cr and on Fe. As shown in Table 1, the Cr catalyst exhibits the smallest peroxide generation, followed by Fe. In addition, the number of electrons exchanged on the Cr catalyst is close to four, suggesting a four-electron pathway for the oxygen reduction reaction. Cr shows the highest half-wave potential (E$_{1/2}$), followed by Co and Fe (*E ½ --- Cr > Co >Fe*) for heat treatment II. However, this treatment yields a high percentage of H$_2$O$_2$ generation. Therefore, treatment I is used in our catalyst optimization studies.

Co and Cr were selected as potential oxygen reduction catalysts for proton exchange membrane fuel cells (PEMFCs). To develop a commercial non-precious-metal catalyst, it is necessary to (i) increase the oxygen reduction activity of both Cr and Co, (ii) decrease the peroxide generation and (iii) increase the stability.

Figure 2 shows a comparison of disc currents for Cr/C, Cr-X/C, Co/C, Co-X/C and commercial ETEK Pt/C. The disc currents were obtained by using 900 rpm and a scan rate of 5 mV/s. The results of this study are summarized in Table 2. The half-wave potential for the 40 wt% Cr-X alloy catalyst is 0.572 V vs. NHE. More importantly, the percentage of peroxide produced decreases significantly, while the number of electrons is almost 4. The catalytic activity obtained for the CrX/C alloy catalyst is comparable to that of 8 µg Pt/cm^2 (ETEK 20%). The

Figure 2. Oxygen Reduction Activity of Co/C, Cr/C, Co-X/C, Cr-X/C and Pt/C at 900 rpm and Scan Rate of 5 mV/sec

peroxide generation is about 1/3 of the amount generated in 8 µg Pt/cm^2 (ETEK 20%).

As shown in Figure 2, the E$_{1/2}$ for Co-X/C increases from 0.49 V vs. RHE observed for the Co/C catalyst to 0.61 V vs. RHE. The E$_{1/2}$ estimated for the commercial E-TEK platinum electrode with a loading of 14 µg Pt/cm^2 is 0.62 V.

The RRDE ring currents are shown in Figure 3. The results clearly indicate that the ring current decreases after Co and Cr are alloyed with X. The production of hydrogen peroxide decreases dramatically after Co is alloyed with X. In the case of Co-X/C, the number of electrons transferred is very close to 4 and hydrogen peroxide production at 0.5 V vs. RHE is less than 3%.
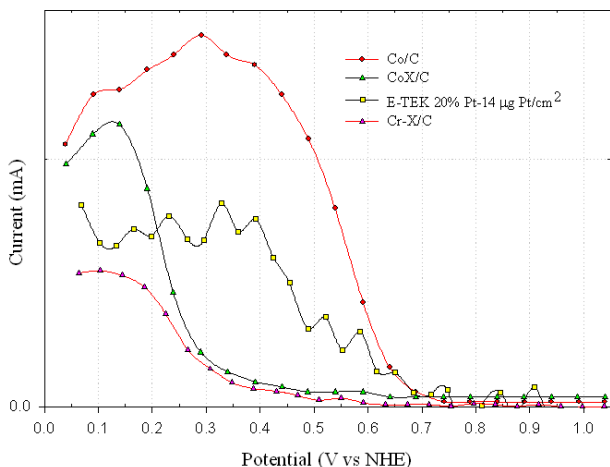
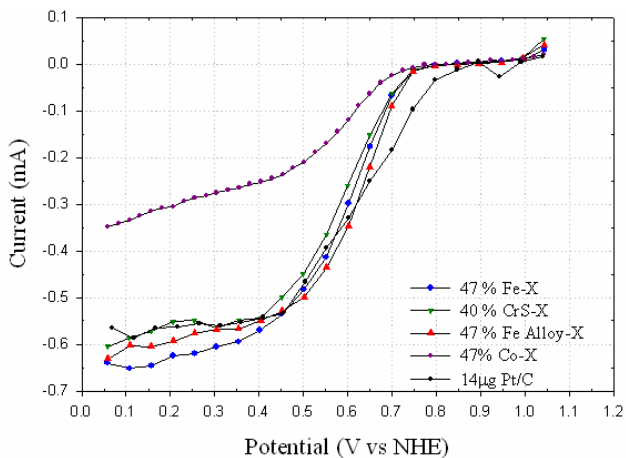**Figure 3.** Ring Currents of Cr/C, Co/C, Cr-X/C, Co-X/C and Pt/C obtained at 900 rpm with a Scan Rate of 5 mV/sec

Figure 4. Oxygen Reduction Activity of Fe and Cr Alloys Prepared From Nitrogen Containing Precursors

3. Synthesis of Fe-, Cr-, Cu- and Co-Based Alloys from Nitrogen Containing Precursors

Catalyst preparation involved loading of transition metals such as iron, cobalt, copper or chromium salt onto a carbon support generated from precursors containing nitrogen. The activation overpotential observed for iron- and chromium-based catalysts is approximately 0.72 V vs. NHE.

Figure 4 shows the effect of alloying element X on the performance of the transition metal catalyst. The oxygen activation overpotential remains almost the same for all catalysts. However, the half potential
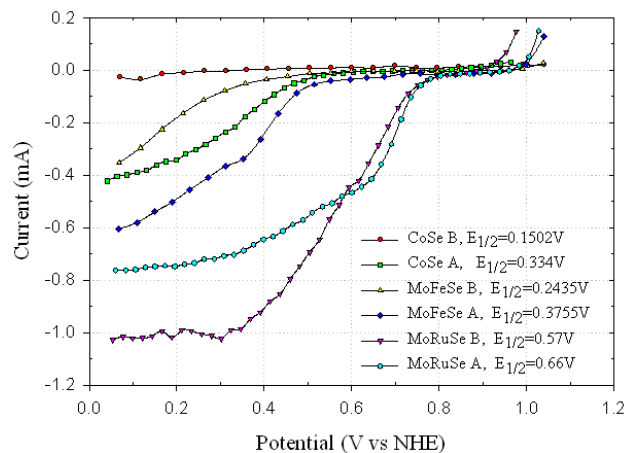

Figure 5. Effect of Treatment on Oxygen Reduction Activity of Unsupported Chalcogenide-Based Catalysts: (A) Before treatment (B) After treatment

increases by approximately 100 mV when the transition metal is alloyed with X. This increase matches and in some cases exceeds the performance of the platinum-based catalyst. The highest performance is obtained for the iron alloy-based catalyst, which has a half potential of 0.623 V vs. NHE.

4. Chalcogenide-Based Catalyst for Oxygen Reduction Reaction

Several types of catalysts based on transition metal chalcogenides were prepared and tested. Mo-Ru-Se shows the best performance, with a value of 0.57 V vs. NHE for $E_{1/2}$ (Mo-Ru-Se > Mo-Co-Se > Mo-Fe-Se > Mo-Ru > Se > Co-Se > Co-Ru-Se). Performance of the catalysts before and after the post treatments is shown in Figure 5. The most promising result is obtained for Mo-Ru-Se**;** the half-wave potential of this catalyst increases by 90 mV and reaches 0.66 V after the post treatment. This value is comparable to that for the Pt catalyst (E-TEK) with the loading of 20 $\mu g/cm^2$. Future work will include (i) development of a Ru-free catalyst, (ii) performance optimization studies and (iii) fuel cell and stability performance studies of the catalyst.

5. Macrocycle-Based Compounds for Oxygen Reduction

Figure 6 shows the polarization curves for heat-treated macrocycle catalysts adsorbed on black pearl
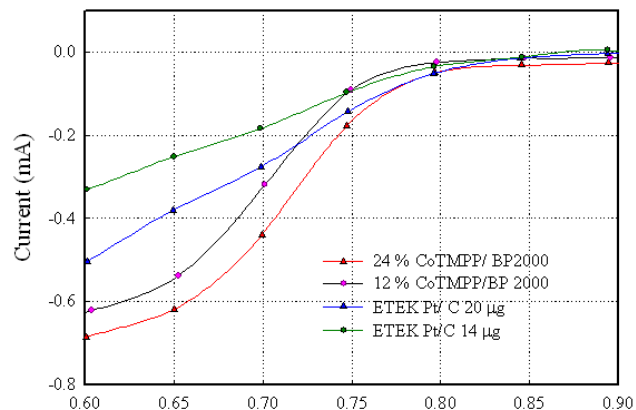
Figure 6. Oxygen Reduction Activity of CoTMPP Catalysts and Commercial ETEK Pt/C

2000. As shown in Figure 6, an increase in weight percentage results in improvement of the catalyst performance. The stability studies indicated that the macrocycle-based catalysts suffer from poor stability. Currently, research is being carried out to optimize the catalytic activity and stability by alloying the macrocycle compounds with Fe and Se.

Conclusions

- A novel method to synthesize oxygen reduction catalysts from simple metal nitrate precursors has been developed.

- Hydrogen peroxide generation in cobalt-based catalysts has been eliminated by alloying the transition metal catalyst.
  - Co/C catalysts show improved activity towards oxygen reduction. Unalloyed Co/C catalysts show higher H_2O_2 generation.
  - Oxygen reduction follows a four-electron path for Cr/C catalyst.
  - Cr-X and Co-X alloys shows improved activity towards oxygen reduction and decreased activity for H_2O_2 generation.
  - Cr-X alloys, Co-X alloys and Fe-X (from nitrogen precursor) alloys have performance comparable to Pt under RRDE test conditions.

- Fe-X (from nitrogen precursor), Co-X and treated MoRuSe show the best performance for oxygen reduction.

References

1. P. Gouerec, A. Biloul, O. Contamin, G. Scarbeck, M. Savy, J. Riga, L. T. Weng and P. Betrand, *J. Electroanal. Chem.*, 422, 61 (1997).

2. F. Jaouen, S. Marcotte, J.-P. Dodelet and G. Lindbergh, *J. Phys. Chem. B*, 107, 1376 (2003).