Novel Non-Precious Metals for PEMFC: Catalyst Selection Through Molecular Modeling and Durability Studies

2005 DOE Hydrogen, Fuel Cells Infrastructure Technologies Program Review

Branko N. Popov
Department of Chemical Engineering
University of South Carolina,
Columbia, South Carolina 29208
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Project ID# FC15

University of South Carolina — Center for Electrochemical Engineering
# Overview

## Timeline
- **Project Start Date**: 31/9/2003
- **Project End Date**: 30/9/2007
- **Percent Complete**: 35%

## Technical Barriers and Targets
- **Electrode performance**
  - Perform at least as good as the conventional Pt catalysts currently in use in MEAs
- **Durability**
  - 2000 hours operation with less than 10% power degradation
- **Material Cost**
  - Cost at least 50% less as compared to a target of 0.2 g (Pt loading)/peak kW

## Budget
- **Total Project Funding**
  - DOE Share - $1376.292 K
  - Contractor Share - $351.207K
- **FY 03**: $200K
- **FY 04**: $125K
- **FY 05**: $425K
- **FY 06**: $395K
- **FY 07**: $231.292K

## Partners / Collaborations
- **Case Western University**
  - Molecular Modeling
- **Northeastern University**
  - Structural Studies / Chalcogenides
Objectives

- Develop transition metal supported catalysts for oxygen reduction using:
  - Low cost transition metal and nitrogen precursors
  - Modified carbon support
- Optimize number of the catalytic sites as a function of
  - Carbon pretreatment.
  - Chemical composition of catalyst.
  - Post treatment of catalyst.
- Improve understanding of reaction mechanism of oxygen reduction on non-precious catalysts through
  - Theoretical molecular modeling. (Case Western Reserve University)
  - Electrochemical characterization.
  - Structural studies (XPS, EXAFS, XANES). (North Eastern University)
  - Correlation between the catalyst composition, heat treatment and catalytic sites for oxygen reduction.
- Accomplish low cost catalyst through
  - Mass production methods.
  - Non precious metals.
  - Low cost precursors.
- Accomplish stable non precious catalysts with
  - High durability (corrosion resistant alloy catalysts).
  - Low peroxide generation.
  - High activity towards oxygen reduction.
Our Approach

- **Molecular Modeling**
  - **New Nitrogen Precursors**
    - Development of Co based alloys from nitrogen containing precursors.
  - **Carbon Surface Modification**
    - Introduce carbon surface functional groups to increase the adsorption and dispersion of Co metal chelate.
  - **Surface Modifiers**
    - Increase porosity, dispersion and surface area of the Co catalyst with the use of surface modifiers.
  - **Bimetallic Alloys**
    - Development of bimetallic alloys such as Co-Fe and Ru-Fe.

- **Structural Studies**

- **RRDE/ MEA Test**

- **Durability Studies**
Accomplishments

• Metal free catalyst was developed with carbon surface modification.
  – Onset potential for oxygen reduction = 0.7 V vs. RHE.
  – FOUR electron pathway for ORR.

• Active Co-chelate /C catalysts 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.
  – FOUR electron pathway for ORR.

• Active Co-chelate/ C catalyst was developed with the use of surface modifiers.
  – Two surface modifiers were identified (SM1 and SM2- USC product) to increase the activity of the non precious metal catalyst (Co, Fe and Co-Fe).
  – FOUR electron pathway for ORR.

• Ru based catalyst synthesized by our methodology has a performance equivalent to that of ETEK 20% Pt/C catalyst under RRDE test conditions.

• Bimetallic Ru-Co and Ru-Fe prepared by the methodology developed at USC shows performance comparable to that of ETEK 20% Pt/C catalyst under RRDE test conditions.
Development of Metal Free Catalyst

Modeling: Structure Model for Nitrogenated Carbon

- Introducing various oxygen and nitrogen groups on the surface of the carbon increases the activity towards oxygen reduction.
- However, oxygen reduction is predominantly through two electron pathway.
- This agrees with the structure model for nitrogenated carbon.

K1 – Un-Oxidized, K2 – Oxidized

Introducing various oxygen and nitrogen groups on the surface of the carbon increases the activity towards oxygen reduction.

H bonds by 1.02 eV on N and \( U^0 = -1.0 \text{ V} \) for the reaction:

\[
\text{H}^+ + \text{e}^- + \text{surface} \rightarrow \text{H-surface}
\]

H bonds by 2.31 eV on C, and \( U^0 = 0.2 \text{ V} \). This means H will be oxidatively removed from the surface to create a catalytically active radical site.

Introducing various oxygen and nitrogen groups on the surface of the carbon increases the activity towards oxygen reduction.

\[
\text{O}_2 + \text{H}^+ + \text{e}^- + \text{surface} \rightarrow \text{H-surface}
\]

\( U^0 = 0.88 \text{ V} \)

Introducing various oxygen and nitrogen groups on the surface of the carbon increases the activity towards oxygen reduction.

\[
\text{H}^+ + \text{e}^- \rightarrow \text{surface} + \text{H}_2\text{O}_2
\]

\( U^0 = 0.51 \text{ V} \)
Oxidation of carbon by HNO₃ introduces quinone groups on the carbon which favors nitrogen adsorption.

 Adsorption of monomeric nitrogen precursors on oxidized carbon
  - Onset potential for ORR – 0.7 V vs. RHE
  - TWO electron pathway for ORR

 Adsorption of polymeric nitrogen precursors in oxidized carbon
  - Onset potential for ORR - 0.7 V vs. RHE
  - FOUR electron pathway for ORR
**Effect of Carbon Activation on Co-chelate/C Performance to Oxygen Reduction Reaction**

- Presence of quinone groups on carbon surface favors nitrogen adsorption.
- Introduction of Co in the catalyst structure increases the activity and shifts ORR mechanism from two electron to four electron.
- Developed chelate catalysts show less than 100 mV overpotential in comparison to ETEK 20% Pt/C
Investigating Relative Amounts of Oxygen Using XPS

The decrease in the intensity of Co peak can be attributed to the formation of a graphitic envelop around the transition metal with high temperature treatment.

Oxidation increases only the amount of quinone groups on carbon and not the total oxygen content.

After heat treatment more amount of oxygen is retained in the catalysts dispersed on oxidized carbon. Thus quinone groups help in activity in addition to increasing dispersion.

K – Ketjen Black EC 300 J, V – Vulcan XC-72, B – Black Pearl 2000
1 – Un-Oxidized, 2 – Oxidized, ND – Chelating agent, HT – After heat treatment
Activity to Oxygen Reduction Reaction of Co-chelate Loaded on Different Carbons

✔ Ketjen Black EC-300 J (K) with the highest mesoporous area shows the highest activity (highest disk and lowest ring currents)

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Area (m²/g)</th>
<th>Micropores (m²/g)</th>
<th>Mesopores (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcan XC 72</td>
<td>254</td>
<td>118</td>
<td>100</td>
</tr>
<tr>
<td>Ketjen Black EC 300J</td>
<td>886</td>
<td>55</td>
<td>680</td>
</tr>
<tr>
<td>Black Pearl 2000</td>
<td>1500</td>
<td>720</td>
<td>540</td>
</tr>
</tbody>
</table>

1 – Un-Oxidized, 2 – Oxidized, ND – Chelating agent
TEM image of Co-chelate Loaded on Different Carbons

K – Ketjen Black EC 300 J, V – Vulcan XC-72, B – Black Pearl 2000
1 – Un-Oxidized, 2 – Oxidized, ND – Chelating agent
The Effect of Nitrogen Donors and Surface Modifier

The scan rate is 5mV/s. Rotation rate 900 rpm in 0.5M H₂SO₄.

✓ The activity of the catalyst is dependent on the nitrogen donor used.
✓ Surface modifier increases the activity of the catalyst
  ✓ Increases the dispersion.
  ✓ Forms part of the catalytic site.
Effect of Surface Modifiers

SM1 = [0]  
17 nm

SM1 = [0.62]  
6 nm

SM1 = [3.2]  
12 nm

SM1 = [46]  
16 nm
Stability Test for Co Catalyst in RRDE Test Conditions

The scan rate is 5mV/s. Rotation rate 900 rpm in 0.5M H₂SO₄.
Performance Studies of Co-based Catalysts in Fuel Cell Station after 24 hrs

Anode: 0.4mg/cm$^2$ of 20wt% Pt/C

Operating Conditions: H$_2$/O$_2$, 75°C, 1atm, Nafion 112
Ru catalysts prepared by USC chelate method show improved activity than MoRuSe catalysts.

%H$_2$O$_2$ produced is less than 2% for the synthesized catalysts.

ND: Nitrogen containing compound

SM: Surface modifier
TEM Image of Ru Chelate and Chalcogenide Catalyst

RuN_x  MoRuSe
Bimetallic Catalysts for Oxygen Reduction Reaction

RuFeNx Catalysts for ORR

The scan rate is 5mV/s. Rotation rate 900 rpm in 0.5M H₂SO₄.

✓ Alloying 13wt% Ru with 7 wt% Fe show comparable performance to ETEK 20% Pt/C and 20%Ru/C.
✓ Synergistic effect between Ru and Fe is observed.
Bimetallic Catalysts for Oxygen Reduction Reaction

ORR - Various Bimetallic Catalysts

Stability of RuCo Catalysts

 ✓ Activity of Ru catalyst with alloying follow
    ✓ Ru > RuFe > RuCo > Ru-Cr > Ru-Ti > Ru-Pb

 ✓ Ru and Ru-Fe catalysts show activity similar to ETEK 20% Pt/C.

The scan rate is 5mV/s. Rotation rate 900 rpm
Electrolyte 0.5M H₂SO₄.

Tₐ – 77 °C, Tₐ – 75 °C, Tcell – 75 °C, 5 cm², Nafion112
Loading – 1.2 mgRu/cm², Ambient Pressure.
Comparison of Performance of USC Co and Ru Based Catalyst vs. Pt

Ru catalysts prepared by USC chelate method with surface modifiers show performance close to that of 20% ETEK Pt/C catalysts
Initial *In-situ/Ex-situ* XAFS Results (NEU)

- In-situ XAFS studies to analyze the stability on Ru based catalysts
- Analyze the evolution of catalyst structure of Co and Fe catalyst with heat treatment.
- Develop cluster model to predict the structure of the active site.
Response to Reviewer’s Comments

• Lack of Industrial Collaboration
  – USC has collaboration with Fuji Film Inc, Faraday Technologies which are complimentary to this research.
  – Northeastern University’s collaboration with ETEK is complimentary to this research.
• Approach is a “Wish List”. Tasks listed are very large and difficult
  – Initial studies were primarily aimed at screening the catalysts.
  – Current research focuses on Co, Fe and Co-Fe bimetallic catalysts.
• NEU and CWRU don’t seem actively engaged in the effort.
  – The project was at initial stages during the 2004 review program.
  – CWRU has been contributing to understand the role of nitrogenated species on the activity.
  – In situ and ex-situ XAFS studies are being conducted by NEU to analyze the catalyst structure and stability.
**Future Work**

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### Activity

- Enhancement of the intrinsic activity of Co based catalysts.
- Development of Fe chelate based catalysts.
- Development of Fe-Co chelate based catalysts.
- Effect of chain length and different surface functionalities on the ORR kinetics.
- Extensive material characterization/structural analysis of the developed Co chelate catalyst – Attain insight on the nature of the active site.
- Search for new surface modifiers and carbon surface treatments to increase the number of active sites.

### Stability

- Modify carbon surface functional groups to anchor chelate metal catalysts strongly.
- To increase the reversibility of the redox system for oxygen reduction.
- Use of Pressure / Temperature variants to increase the stability.
- Encapsulation of the catalyst in more stable materials such as carbide, nitride and zeolite.
- Extensive fuel cell testing to evaluate the stability of the catalyst
Publications and Presentations

Publications


Presentations


Hydrogen Safety

- All reactors are operated in a vented area.
- Hydrogen detector is placed near the hydrogen source.
- Reactors using high concentrations of hydrogen have additionally installed a burning flame to eliminate exhausting gas.
- All the reactors have being design using leak-proof joints.
- Ambient atmosphere pressures are used at all times in the reaction vessels and fuel cell stations.
- Only personnel trained in how to operate the reactors and emergency procedures is allowed to use the reactor set-up.
  - At least one person trained must present during runs in case of an emergency shutdown.
Furnace for Hydrogen Treatment at High Temperature and Safety Equipment

PEM Fuel Cell Dual Station with a Hydrogen Sensor
1. What is the most significant hydrogen hazard associated with this project? Please be specific in your answer.

The most significant hydrogen hazard is the fuel cell test station that we use to test the catalysts. However, the hydrogen flow rate used does not exceed 600 cm³/min.

2. What are you doing to deal with this hazard? Please list pertinent safety measures you are implementing and/or plan to implement.

In order to prevent any accident safety features such as fail close H₂ valve, fail open N₂ valve, low voltage trip, low gas flow trip, high temperature alarm, and H₂ sensor with audible alarm are activated when the system is in operation. In addition, the system is positioned close to the hood in order to vent the used gas. Operation and emergency procedures are accessible in the case of an accident.