Non-Pt Catalysts for PEFCs

Xiaoping Wang, Deborah Myers, and Nancy Kariuki
Argonne National Laboratory

May 16-19, 2006

This presentation does not contain any proprietary or confidential information
Project ID # FCP 29
**Overview**

**Timeline**
- Project start date: October FY’03
- Project end date: Open
- Percentage complete: n/a

**Budget**
- Total funding: $750 K
- Funding for FY’05: $150 K
- Funding for FY’06: $300 K

**Barriers**
- Barriers addressed
  - B. Cost
  - C. Electrode performance

**Partners**
- Los Alamos National Laboratory
- Prof. John Regalbuto, University of Illinois at Chicago
- Collaborations with BES-funded groups on characterization
- Regularly providing updates and soliciting feedback from FreedomCAR Fuel Cell Technical Team
Objective

- Develop a non-platinum cathode electrocatalyst for polymer electrolyte fuel cells to meet DOE targets
  - Promotes the direct four-electron transfer with high electrocatalytic activity (comparable to that of Pt) \((0.44 \text{ A/mgPt or 720 } \mu\text{A/cm}^2 @0.9V)\)
    - \(O_2\) reduction reaction (ORR) in acidic media (e.g., in PEFC)
      - Two-electron transfer
        \[ O_2 + 2H^+ + 2e^- = H_2O_2 \]
      - Four-electron transfer
        \[ O_2 + 4H^+ + 4e^- = 2 \text{H}_2\text{O} \]
      - Four-electron process is desirable due to its higher efficiency and non-corrosive product
  - Chemically compatible with the acidic polymer electrolyte (\(5000h @80^\circ\text{C}, < 40\%\) electrochemical area loss)
  - Low cost (\($8/KW, 0.3 \text{ mg PGM/cm}^2$\))
Approach

- **Bi-metallic systems (e.g., base metal, noble metal)**
  - Surface segregation of minor noble metal component to form protective layer
  - Base metal component chosen to modify d-band center of noble metal making it more “Pt-like”
  - Choice of bi-metallic systems is based on the surface segregation energies and d-band center shift
  - Examples: Bi-metallics of iridium, rhodium, and palladium
  - Alternative supports to modify electronic properties of small metal particles (e.g., titania)

- **Metal centers attached to electron-conducting polymer backbones**
  - Allows easy control of spacing between metal centers
  - Electron conductor in close proximity to reaction site can promote high catalyst utilization
The d-band centers of candidate noble metals can be shifted to desired value by alloying with base metals

- There is a relationship between the d-band center of the metal and its ORR activity - Nørskov-Hammer theory and results of LBNL group
- Pt₃Co has high ORR activity and, thus, a desirable d-band center (LBNL)
Progress vs. FY '06 Milestones

- Synthesize and determine the ORR activity of two metal center-polymeric, two bimetallic, and one ACNT systems (06/06)
  - Two metal center-polymeric systems
    - Synthesized and tested two metal center moieties
    - Identification of electron conducting polymers as backbone is underway
  - Two bimetallic systems
    - Competed one Ir-based bimetallic system for material synthesis (nine compositions) and testing, including materials characterization
    - Synthesized one Pd-based bimetallic system (five compositions); testing and characterization is underway
    - Finished three more Au-based bimetallic systems
  - One Aligned Carbon Nanotube system
    - Tested ORR activity

- Determine the long-term stability of the electrocatalyst with the highest ORR activity (09/06)
Solid solutions of Ir-BM nanoparticles have been formed on Vulcan carbon

XRD shows that a solid solution is formed at 400°C
TEM shows catalysts to have 2- to 10-nm diameter particles
The Ir to base metal ratio affects the ORR activity

Current at 0.75 V vs. SHE, 400ºC heat-treated

Neg. scan
Pos. scan

Ir to BM molar ratio

(1:0) (9:1) (3:1) (1:1) (46:54) (38:62) (3:7) (1:3) (1:4) (1:9) (0:1)
Acid treated Ir:BM catalyst showed improved ORR activity

- TEM image indicates that acid treatment did not change particle size
- EDX results shows molar ratio of Ir to BM stayed the same after acid treatment
ORR current decreased as the heat treatment temperature increased (Ir:BM)
Coarsening of Ir:BM particles occurred at higher heat treatment temperatures.
Nanoparticles of Pd-base metal alloy have been formed on Vulcan carbon

- TPR to determine the condition that yields reduced form of the metal

- XRD indicates alloy formation

- Bimodal size distribution:
  - 2-5 nm and 10-20 nm
  - 10-20 nm particles more evenly distributed
Base metal increased ORR activity of palladium
Base metals enhance the ORR activity of Ir and Pd, but further improvement is needed

<table>
<thead>
<tr>
<th>Supported metallic system</th>
<th>Ir-based</th>
<th>Pd-based</th>
<th>DOE 2010 target 0.9 V</th>
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</thead>
<tbody>
<tr>
<td>ORR mass activity at 0.8 V per mg metal</td>
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<td></td>
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</tr>
<tr>
<td>Ir</td>
<td>Ir-BM</td>
<td>BM</td>
<td>Pd</td>
</tr>
<tr>
<td>20 μA</td>
<td>65 μA</td>
<td>3 μA</td>
<td>8.4 mA</td>
</tr>
</tbody>
</table>
Nanocrystalline cores encapsulated in a monolayer of organic molecular or surfactant shell have several advantages

- Size and surface properties of nanoparticles are controllable
- Organic shell protects nanoparticles from agglomeration
  - *Stable and highly monodisperse nanoparticles*
- Interparticle interactions of the shell molecules confers spatial controllability in the assembly of the particles on support materials
- Deliberate tailoring of the surface of the metallic core with suitable shell structures enables the morphology of the bimetallic composition to be very well controlled
- Large volumes of pre-engineered nanoparticles can be efficiently produced

*New synthetic approach for desired structure/morphology of bimetals --- Metal core-organic shell approach*
A procedure has been devised for bimetallic system

Step 1: Seed preparation

Metal Precursor (e.g. Base metal(acac)$_3$) Stirring/N$_2$ Organic capping agent Reduction Capped base metal seed nanoparticles
Octyl ether Δ Δ Δ

Step 2: Seed growth

Second metal precursor (e.g. Ir(acac)$_3$) Stirring/N$_2$ Organic capping agent Reduction Ir on base metal Core-shell nanoparticles
Octyl ether Δ Δ Δ

Step 3: Assemble on support and remove the shell for activation

Ir on base metal Core-shell nanoparticles support O$_2$/N$_2$ H$_2$/N$_2$ Ir on base metal Core-shell Nanoparticles on support Δ Δ
TEM shows nanoparticle size and monodispersity control---better shaped and more uniform particles than traditional method

- TEM of Ir on BM reveals size growth associated with overdeposition of Ir on BM nanoparticles used as seeds
- EDX analysis confirmed bimetallic composition consistent with synthetic feed amounts of metal precursors
ORR activity of cobalt metal centers attached to polymer backbones begins at 0.6 V
Summary

- Both supported Ir- and Pd-based bimetallic systems showed an ORR activity better than supported Ir and Pd alone
  - ORR started at potential of 0.85 V and 0.93 V, respectively for Ir- and Pd-based system

- XRD and TEM analysis indicates alloy formation and nanosize particles for both systems

- ORR activity was strongly influenced by type and composition of bimetallic system and catalyst preparation and processing conditions (e.g., acid treatment and heat treatment temperature)

- New synthetic approach is being explored to obtain desired structure/morphology
Future work

- Perform elevated temperature RRDE experiment to determine $O_2$ reduction mechanism (2e$^-$ or 4e$^-$ transfer) for Ir-based system

- For Pd-based system
  - ORR activity testing and TEM work for other compositions prepared

- Prepare and test the ORR activity of additional bimetallic systems identified

- Surface and bulk characterization to verify the desired catalyst composition/structure, particle size, and electronic properties by using various techniques such as XRD, TEM, SEM, FTIR of adsorbed CO, and TPD of CO

- Explore different synthesis methods and temperature treatments

- Perform electrochemical and chemical stability studies

- Fabricate and test a membrane-electrode assembly using newly-developed electrocatalysts
Acknowledgments

- J. Vaughey and T. Cruse for XRD
- J. Mawdsley for TEM
- M. Ferrandon for TPR and TPD
- J. Yang and D.J. Liu for preparing ACNT system
Publications

- “Polymer Electrolyte Fuel Cell Cathode Electrocatalysts”, Xiaoping Wang, Romesh Kumar, and Deborah J. Myers, Poster and Abstract, 2005 Fuel Cell Seminar, Palm Springs, CA, November 14-18, 2005
Response to FY ’05 Reviewers’ Comments

- “The work on bimetallic (Au-based), transition metal carbides and nitrides, and metal centers attached to electron-conducting polymer backbone is too broad area for such relatively small project”
  - *We have focused our effort on bimetallic systems*

- “Need to pull in other characterization techniques to better understand behavior of bimetallic system (microscopy, etc.).”
  - *We are characterizing catalysts by TEM, XRD, EDX, CO Temperature Programmed Desorption*

- “See no evidence that the claimed LANL collaboration is underway”
  - *Once material shows adequate activity in screening tests, LANL will fabricate MEAs*

- “The reason for the choice of the new catalysts was not evident”

- “Screening large number of non-Pt catalysts based on Au is no guarantee that one of the proposed catalyst formulations will work”
  - *We have elaborated on the rationale behind the choice of bimetallic systems in this presentation*