Non-Platinum Bimetallic Cathode Electrocatalysts

Debbie Myers
Argonne National Laboratory

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Project ID: FCP28

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Overview

Timeline
- Project start data: January, 2007
- Project end data: December, 2010
- Percentage complete: 10%

Budget
- Total project funding:
  - DOE: $5,434 K
  - Contractor share: $172 K
- Funding received for FY'07:
  - DOE: $945 K
  - Contractor share: $29 K

Barriers
- Barriers addressed
  A. Durability
  B. Cost
  C. Electrode performance

Partners
- William A. Goddard, III, California Institute of Technology (Caltech)
- John Regalbuto, University of Illinois at Chicago (UIC)
- Clemens Heske, University of Nevada at Las Vegas (UNLV)
- Karren More, Oak Ridge National Laboratory (ORNL)
- Piotr Zelenay, Los Alamos National Laboratory (LANL)
Objectives

- Develop a non-platinum cathode electrocatalyst for polymer electrolyte fuel cells to meet DOE targets that:
  - Promotes the direct four-electron oxygen reduction reaction (ORR) with high electrocatalytic activity
    \[ \text{0.44 A/mg}_{PGM}; \text{720 } \mu \text{A/cm}^2 \text{ at 0.9 V}_{iR-\text{free}} \]
  - \( O_2 \) reduction reaction (ORR) in acidic media
    - Two-electron transfer
      \[ O_2 + 2H^+ + 2e^- = H_2O_2 \]
    - Four-electron transfer
      \[ O_2 + 4H^+ + 4e^- = 2H_2O \]
  - Is chemically compatible with the acidic electrolyte and resistant to dissolution
    \( <40\% \text{ electrochemical area loss over 5000 h@} \leq 80^\circ\text{C and 2000 h@} >80^\circ\text{C} \)
  - Is low cost
    \( \$5/KW, 0.3 \text{ mg PGM/cm}^2 \)

FY’07 Objective

- Synthesize and evaluate the oxygen reduction activity and stability of nanoparticles of three palladium alloy systems
Approach

- Bimetallic systems (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 bimetallic systems is based on surface segregation energies and d-band center shift
  - Examples: Bimetallics of palladium, iridium, and rhodium

- How this project addresses the technical barriers
  - A. Durability: altering oxophilicity of catalyst to prevent oxidation-related degradation
  - B. Cost: lowering PGM loading by replacing PGM in electrocatalyst particle core with base metal
  - C. Electrode performance: modifying surface electronic properties to enhance ORR activity
Noble metals were chosen based on stability and tendency to form surface “skins”

- Noble metals are the most stable in acidic environment
  - Pd $E^{o'}$ for dissolution = 0.987 V
  - Rh $E^{o'}$ for dissolution = 0.76 V
  - Ir $E^{o'}$ for dissolution = 1.156 V
  - Pt $E^{o'}$ for dissolution = 1.188 V

- Base metals were chosen due to their ability to modify the electronic properties of the noble metal and for the tendency of the noble metal to form a protective skin on the noble metal-base metal alloy

- Tendencies of noble metals to segregate to the surface of base metal hosts have been calculated by J. Nørskov and co-workers [A.V. Ruban, H.L. Skriver, J.K. Nørskov, Phys. Rev. B, 59 (1999)15990.]
The d-band centers of candidate noble metals can be shifted towards desired values 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 desirable d-band center and thus a high ORR activity (LBNL)
**Project tasks**

- Perform computational studies to guide choice of systems and compositions (Caltech)
- Fabricate and characterize model systems-bulk electrodes to guide choice of systems and compositions (UNLV, Argonne)
- Synthesize nano-particles on high-surface-area carbon support (Argonne, UIC)
- Characterize nano-particle ORR activity, composition, electronic structure, and morphology (Argonne, ORNL, UNLV, UIC)
- Determine stability via dissolution measurements, mechanisms of degradation, and predict lifetime via modeling (Argonne)
- Fabricate, test, and characterize membrane-electrode assemblies with newly-developed electrocatalyst (LANL, ORNL)
  - determine performance and durability using accelerated test protocol
Oxygen reduction activity is highly dependent on Pd:Cu ratio and post-deposition heat treatment (0.8 V, room temp.)

- Catalysts prepared by co-impregnation of Vulcan carbon with metal precursors and post-deposition heat treatment in a reducing atmosphere
Oxygen reduction activity is highly dependent on Pd:Cu ratio and post-deposition heat-treatment (0.9 V, room temp.)
Post-heat treatment acid treatment improved oxygen reduction activity of Pd:Cu catalysts (0.8 V, room temp.)
Post-heating acid treatment improved oxygen reduction activity of Pd:Cu catalysts (0.9 V, room temp.)
Highest ORR activity was seen for catalysts showing formation of ordered PdCu phase
Co-impregnation synthesis technique leads to large poly-disperse alloy particles

<table>
<thead>
<tr>
<th>Pd: Cu Molar Ratio</th>
<th>Particle size (nm)</th>
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<tbody>
<tr>
<td></td>
<td>300°C</td>
</tr>
<tr>
<td>1:9</td>
<td>10.8 ± 2.1</td>
</tr>
<tr>
<td>1:3</td>
<td>8.1 ± 2.8</td>
</tr>
<tr>
<td>1:1</td>
<td>6.1 ± 1.6</td>
</tr>
<tr>
<td>3:1</td>
<td>9.1 ± 3.3</td>
</tr>
<tr>
<td>9:1</td>
<td>6.5 ± 1.8</td>
</tr>
</tbody>
</table>
Synthesis of nano-particle bimetallic carbon-supported electrocatalysts

- Goals
  - Achieve noble metal-base metal bimetallic core with noble metal skin
  - Minimize particle size, maximize surface area/gram PGM
  - Achieve uniform and controllable particle size and composition

- Techniques
  - Colloidal synthesis
  - Strong electrostatic adsorption

20 nm
Single-phase colloidal technique is being developed to form mono-disperse bimetallic nano-particles (Argonne)

- Chemical reduction of metal precursors in the presence of organic capping molecules (e.g., oleylamine and oleic acid)
  - capping molecules stabilize small particles, limit particle growth

- Pre-formed particles loaded on carbon support
  - capping molecules maintain particle dispersion

- Removal of capping molecules through thermal or electrochemical decomposition
  - capping molecules can be removed at moderate temperatures
**Strong electrostatic adsorption technique for synthesis of core-shell bimetallic nano-particles (UIC)**

- SEA technique has been demonstrated by UIC for Pt-Co bimetallics

- Impregnate at pH between pHs of zero charge (PZCs) for selective adsorption and formation of bimetals.

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**SEA for Mixed Oxides, Bimetals**

- Diagram showing pH vs. particle size (diameter or length) for different oxides and bimetals.
Computational analyses are being used to guide the choice of bimetallic systems and compositions (Caltech)

- Quantum mechanical calculations
  - Detailed reaction mechanisms and rate-limiting processes
  - Binding energies and structures for possible intermediates (i.e., O, H, O₂, H₂, OH, OOH, H₂O)
  - How alloying and nano-structure affect the ORR rates

- Large-scale molecular dynamics simulations using ReaxFF
  - Trends in chemisorption energies of oxygen-containing species
  - Effect of nano-particle size, alloying elements, surface defects and segregations, step edges, and kinks on the barriers and rates of the ORR
Comparison of the energetics of $O_2$ reduction via OH formation on candidate metals (Caltech)

ΔH-Pt = -0.29 eV
ΔH-Pd = -0.45 eV
ΔH-Cu = -0.59 eV
ΔH-Rh = +0.08 eV
ΔH-Ir = +0.04 eV

Pd, Cu have more favorable energetics for OH formation than Pt
Rh and Ir, less favorable than Pt
Comparison of the energetics of $O_2$ reduction via OOH formation on candidate metals (Caltech)

$\Delta H - Pt = -1.62 \text{ eV}$
$\Delta H - Pd = -1.78 \text{ eV}$
$\Delta H - Cu = -2.36 \text{ eV}$
$\Delta H - Rh = -2.64 \text{ eV}$
$\Delta H - Ir = -2.46 \text{ eV}$

Pd, Cu, Rh, Ir have more favorable energetics for OOH formation than Pt.
Calculated barrier for OH formation is lowest on Pd (Caltech)

- Calculations on Pt indicate that the rate determining step is:
  \[ H_{\text{ads}} + O_{\text{ads}} \rightarrow OH_{\text{ads}} \]
- Pd has the lowest barrier for this step compared to the pure metals Pt, Ir, and Cu and to Pt₃Ni alloy (along \( \mu_{2/3} \)).
Model systems (bulk electrodes) will be used to guide the choice of bimetallic systems (UNLV)

- Used to establish relationship between physicochemical properties and ORR activity

- Model systems
  - Fabrication by e-beam evaporation
  - Surface composition verification by XPS

- Electronic characterization (UPS, IPES, STS, KPFM)
  - Energy of d-band
  - Density of occupied and unoccupied electronic states

- Oxygen reduction activity, reaction mechanism, and stability
  - Electrochemical measurements via hanging meniscus technique
  - Post-test spectroscopic and microscopic characterization to determine changes in composition, morphology, and electronic properties
Catalyst activity and structural characterization of carbon-supported nano-particle catalysts

- Determine oxygen reduction activity and reaction mechanism (4 e- or 2 e-)
  - Thin-film rotating ring-disk technique

- Verify that desired structures, compositions, and particles sizes are obtained
  - TEM, EDAX, XRD, XAS, XPS, XES, IR of adsorbed CO

- Characterize nano-particle electronic structure
  - Soft X-ray and UV spectroscopies
Accelerated durability testing of carbon-supported nanoparticle catalyst

- Potentiostatic and potential cycling dissolution rates
- Equilibrium concentration of dissolved metallic components of electrocatalysts
- Mechanism of dissolution reaction via rotating ring-disk experiments
- Modeling of performance degradation (beginning with Pt/C commercial electrocatalyst)
Electrocatalysts that pass activity and durability screening tests will be tested in MEAs

- Membrane-electrode assembly fabrication, testing, and characterization
  - MEA fabrication
  - MEA performance and durability testing
    - Pre- and post-test analyses using TEM, XRD, and SAXS

LANL H₂-Air MEA Fabrication Procedure

- Make Carbon Supported Catalyst Ink
- Paint and Oven Dry Decals: Repeat Until Desired Catalyst Loading Achieved
- Clean and Cation Exchange PEM to Na⁺ Form. Dry on Heated Vacuum Table For decal Hot Pressing
- Hot Press Decals Onto the PEM
- Cation Exchange PEM w/Electrodes to H⁺ Form and Dry on a Heated Vacuum Table
- Assemble the PEM w/Electrodes, Gas Diffusion Layers (GDLs), and Gaskets into Fuel Cell Hardware for Testing

ORNL TEM analyses of LANL MEA
Summary of Progress

- Milestone (12/07): Synthesize and evaluate the oxygen reduction reaction (ORR) activity and stability of nano-particles of three palladium alloy systems with goals of:
  - specific activity: 720 $\mu$A/cm²; mass activity: 0.44 A/mg (@900 mV$_{iR\text{-free}}$); volumetric activity: >130 A/cm³ (@800 mV$_{iR\text{-free}}$)

- Progress:
  - Synthesized a series of carbon-supported Pd-Cu catalysts via co-impregnation; determined the effect of Pd:Cu ratio, post-deposition heat treatment temperature, and acid treatment on the phases formed, particle size, particle size distribution, and ORR activity
    - Highest room temperature ORR mass activity observed: 0.82 A/mg Pd (800 mV); 0.016 A/mg Pd (900 mV)
  - Formed palladium-copper alloy on carbon support with smaller particle size and narrower size distribution using colloidal technique
  - Synthesized 1-3 nm Pd particles on various high surface area carbon supports using the strong-electrostatic adsorption technique
  - Calculated the energetics of the oxygen reduction reaction on candidate noble metals and copper
**Future work**

- Remainder of the first year
  - Synthesize and fully characterize two additional palladium-base metal systems
  - Utilize electrochemical methods for removing the capping agents from the carbon-supported colloidal bimetallics to retain small particle size during capping agent removal
  - Form carbon-supported palladium-base metal nano-particles using the strong electrostatic adsorption technique
  - Complete calculation of the reaction step barriers in the oxygen reduction reaction
  - Calculate the thermodynamically favorable alloy atomic structure
  - Determine the effect of temperature treatment on the surface segregation of alloy components from bulk electrodes
  - Fully characterize the electronic structure of Pd-Cu bulk electrodes

- Next year
  - Explore three iridium-base metal systems and fabricate and test MEAs using promising palladium-base metal catalysts
Team members

- Argonne National Laboratory: Xiaoping Wang, Nancy Kariuki, Suhas Niyogi, Bilge Yildiz, and Jennifer Mawdsley

- California Institute of Technology: William A. Goddard, III, Boris Merinov, Yao Sha, and Ted Yu

- University of Illinois at Chicago: John R. Regalbuto and Lawrence DSouza

- University of Nevada, Las Vegas: Clemens Heske, Timo Hofmann, and Lothar Weinhardt

- Los Alamos National Laboratory: Piotr Zelenay

- Oak Ridge National Laboratory: Karren More