New Electrocatalysts For Fuel Cells

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Project ID
#FC10
Overview

Budget

- Total project funding
  - DOE share 100%
- Funding for FY05: $500 K
- Funding for FY06: $253 K

Barriers

- DOE Technical Barriers for Fuel Cell Components
  - Q. Electrode Performance

Partners

- Interactions/ collaborations
  - General Motors Alternative Power Center (GAPC)
  - 3M
Objectives

• Reduce cost by reduction of precious metal loading (long term)
• Improve catalyst durability (long term)
• Bring all ongoing work to a conclusion in FY06
• Publish all work in some form, i.e. either archival literature or government reports
LBNL Materials-by-Design Approach

Model Catalysts
Pure Metals
Alloys
Single Crystals

Surface Structures
vs.
Kinetics
Reaction Mechanisms

Real Catalysts
Carbon supported
pure metals or bimetallic

Taylor made surfaces

“Theory”

Synthesis of
Bimetallic Nanoparticles

Prototype
New Catalyst

Testing in
Fuel Cells

Structure, composition and
particle size
vs.
Kinetics

Commercial Catalyst
Anticipated Gains with Pt Bimetallic Nanoparticles

- Substitution of Pt atoms “buried” in interior of particle with atoms of non-Pt group element atoms

- Possibly higher activity for Pt surface atoms by electronic modification from intermetallic bonding (alloying effect)
  
  Norskov and Hammer theory correlates the position of d-band center to \( H_{ad} \) and \( O_{ad} \) adsorption energies

- Pt loading reduced (without any loss of performance) by a factor of 4–5 seems possible
Outline of Presentation

Putting the finishing touches on the following topics:

• Skin vs. skeleton near-surface structures and the relation to kinetics for the oxygen reduction reaction (ORR)

• Understanding the effect of subsurface transition metal atoms on the activity of Pt$_3$TM surfaces for the ORR – Norskov and Hammer theory of d-band center as measure of electronic effect of subsurface transition metal atoms on heat of adsorption of intermediates

New Results with Pt$_3$Ni(hkl) single crystals point to new opportunities to improve intrinsic activity via control of nanoparticle shape
**Summary: Near-surface characterization of Pt₃TM**

**AES:** absence of carbon and oxygen, Pt enrichment after annealing

**LEISS:** surface composition
- sputtered: Pt –75%, Co – 25%
- annealed: Pt –100% Pt ‘skin’

**UPS:** d – band center position
- sputtered: 2.74 eV
- annealed: 2.86 eV
Summary: Stability of Pt$_3$TM

UHV: Before Transfer

LEISS

Co
1 keV
Ne$^+$

Pt

Intensity [a.u.]

E/E$_0$

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9

UHV: After Rinsing with H$_2$O

LEISS

Co
1 keV
Ne$^+$

Pt

Intensity [a.u.]

Y Axis Title

0 5 10 15 20 25

X Axis Title

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8

H$_2$O rinsing
Summary: Stability of Pt₃TM

**UHV: Before Transfer**

**AES**

3 keV

Pt  
Co₆₅₇  
Co₇₂₀  
Co₇₈₀

1° UHV

**LEIS**

1 keV Ne⁺

Co  
Pt

**UHV: After rinsing with 0.1M HClO₄ and/or After Electrochem. Exp.**

0.1M HClO₄ rinsing

**AES**

3 keV

O₅₂₀  
C₀₆₅₇  
Co₇₂₀  
Co₇₈₀

2° UHV

Co leaching out from the surface layers and formation of a Pt “skeleton” structure
Summary: ORR activity vs. d-band center Pt$_3$TM

$(1-\Theta_{ad})$ term

$(1-\Theta_{ad})$ term and $\Delta G_{ad}$ term

Kinetic Current Density [mA/cm$^2$] vs. d-band center [eV]

@ 0.85 V$_{RHE}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Sputtered</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_3$Ti</td>
<td>3.03 eV</td>
<td>3.37 eV</td>
</tr>
<tr>
<td>Pt$_3$V</td>
<td>2.94 eV</td>
<td>3.20 eV</td>
</tr>
<tr>
<td>Pt$_3$Fe</td>
<td>2.89 eV</td>
<td>3.05 eV</td>
</tr>
<tr>
<td>Pt$_3$Co</td>
<td>2.74 eV</td>
<td>2.86 eV</td>
</tr>
<tr>
<td>Pt$_3$Ni</td>
<td>2.69 eV</td>
<td>2.72 eV</td>
</tr>
<tr>
<td>Pt-poly</td>
<td>2.53 eV</td>
<td>2.54 eV</td>
</tr>
</tbody>
</table>
ORR activity vs. d-band center: Pt$_3$TM annealed(skin) vs sputtered(skeleton) surfaces

- Pt$_3$Co
- Pt$_3$Fe
- Pt$_3$V
- Pt$_3$Ni
- Pt$_3$Ti
- Pt-poly

Current Density [mA/cm$^2$]

d-band center [eV]
**Summary: Skin vs. Skeleton near-surface structure**

1. Complete segregation of Pt over Pt₃M surfaces after annealing in UHV
   - Only Pt atoms over Pt₃(Co, Ni, Fe)
   - Possible to create two different surfaces in UHV: Pt-skin and Pt₃M

2. Alloying components are dissolved **instantaneously** from the surface in contact with acid electrolyte. Pt-skeleton surface is formed

3. Pt-skin, Pt-skeleton and Pt-poly have the same surface composition but different electronic properties || Pt-skin has protective role

4. Different position of d-band center provides different adsorption properties

5. The same/similar Tafel slope, activation energy, peroxide production → ORR pathway

6. Blocking species are less adsorbed on Pt-skin, kinetics determined by \((1-\Theta)\) term

7. With decrease of atomic number, d-band center shift increases, kinetics determined by both \((1-\Theta)\) term and \(\Delta G_{ad}\) term
Pt₃Ni(hkl): Surface Characterization | LEED

- Pt₃Ni(100) (5x1) superstructure
- Pt₃Ni(110) c(4x2) superstructure
- Pt₃Ni(111) - Does not have a superstructure - p(1x1)
- Pt₃Ni(110) c(4x2) superstructure with different arrangement of surface atoms
- Different possible compositions

- c(4x2) superstructure missing row

Pt - Green
Ni - Red
Pt₃Ni(hkl): Surface Characterization

- Complete Pt enrichment on the annealed Pt₃Ni(hkl) surfaces

LEISS:

- Complete Pt enrichment on the annealed Pt₃Ni(hkl) surfaces

LEISS:

- Complete Pt enrichment on the annealed Pt₃Ni(hkl) surfaces

Pt₃Ni(100)

Pt₃Ni(110)

Pt₃Ni(111)
Pt$_3$Ni(100): EC Characterization

Activity Improvement Factor: 2.3

\[ i_k [\text{mAcm}^{-2}] \]

\[ E \text{ [V] vs RHE} \]

- Pt(100): $270 \pm 0.3$
- Pt$_3$Ni(100): $190 \pm 0.2$

- $i_k @ 0.850 \text{V}$: $3 \pm 0.3$
- $i_k @ 0.875 \text{V}$: $1.7$
- $i_k @ 0.900 \text{V}$: $0.9$
- $i_k @ 0.925 \text{V}$: $0.5$
- $i_k @ 0.950 \text{V}$: $0.2$

0.1M HClO$_4$
60°C
Pt$_3$Ni(110): EC Characterization

Activity Improvement Factor: 2.1

<table>
<thead>
<tr>
<th>$i_k$ @ 0.850V</th>
<th>11.5 ± 1</th>
<th>23 ± 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_k$ @ 0.875V</td>
<td>≈ 5.0</td>
<td>≈ 10.7</td>
</tr>
<tr>
<td>$i_k$ @ 0.900V</td>
<td>≈ 2.2</td>
<td>≈ 5.1</td>
</tr>
<tr>
<td>$i_k$ @ 0.925V</td>
<td>≈ 0.7</td>
<td>≈ 1.9</td>
</tr>
<tr>
<td>$i_k$ @ 0.950V</td>
<td>≈ 0.2</td>
<td>≈ 0.7</td>
</tr>
</tbody>
</table>
Pt$_3$Ni(111): EC Characterization

**Activity Improvement Factor: > 10**

$I_k$ @ 0.850V: $9 \pm 1$

$I_k$ @ 0.875V: $\approx 4.4$

$I_k$ @ 0.900V: $\approx 1.9$

$I_k$ @ 0.925V: $\approx 0.8$

$I_k$ @ 0.950V: $\approx 0.3$

<table>
<thead>
<tr>
<th>E [V] vs. RHE</th>
<th>Pt(111)</th>
<th>Pt$_3$Ni(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.850V</td>
<td>$\approx 46$</td>
<td></td>
</tr>
<tr>
<td>0.900V</td>
<td>$\approx 18$</td>
<td></td>
</tr>
<tr>
<td>0.925V</td>
<td>$\approx 5.7$</td>
<td></td>
</tr>
<tr>
<td>0.950V</td>
<td>$\approx 1.7$</td>
<td></td>
</tr>
</tbody>
</table>

0.1M HClO$_4$

20°C

Activity Improvement Factor: > 10
**Pt₃Ni(hkl): UPS Characterization**

<table>
<thead>
<tr>
<th>Surface</th>
<th>Pt (100)</th>
<th>Pt₃Ni(100)</th>
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</thead>
<tbody>
<tr>
<td>d-band center</td>
<td>2.90 eV</td>
<td>3.14 eV</td>
</tr>
<tr>
<td>Δ d-band</td>
<td>0.24 eV</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface</th>
<th>Pt (110)</th>
<th>Pt₃Ni(110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-band center</td>
<td>2.70 eV</td>
<td>2.53 eV</td>
</tr>
<tr>
<td>Δ d-band</td>
<td>-0.17 eV</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface</th>
<th>Pt (111)</th>
<th>Pt₃Ni(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-band center</td>
<td>2.76 eV</td>
<td>3.09 eV</td>
</tr>
<tr>
<td>Δ d-band</td>
<td>0.33 eV</td>
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</tbody>
</table>
Pt$_3$Ni(111): ORR Activity

[Graph showing ORR activity with Pt$_3$Ni(111) and Pt(111) electrodes under different conditions.]
Publications and Presentations

Journal Publications


Future Plans

FY2007
P.I. Retires from Berkeley Lab and program in its present form concludes

Good night and good luck!