Low Pt Loading Fuel Cell Electrocatalysts

Radoslav Adzic (P.I.), Junliang Zhang, Kotaro Sasaki, Tao Huang, Jia Wang, Miomir Vukmirovic

Materials Science Department
Brookhaven National Laboratory, Upton, NY 11973-5000

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Overview

Timeline
- Project start date: 06.2002.
- Project end date: Multi-year
- Percent complete: --

Barriers addressed
1. Precious metal loading, electrocatalysts’ activity
   - Target 2005: 2.7 g/kW
   - Accomplished: 0.14 g/kW cathode
   - 0.33 g/kW cell

2. Electro catalysts’ Durability
   - Target 2005: 2000 hr
   - Accomplished: 3000 hr (cathode)
   - Test in progress: 530 hr (low Pt cell)

Budget
- Total project funding:
  - DOE share: $954K
  - Funding received in FY04: $250K
  - Funding for FY05: $330

Collaborations
- Los Alamos National Laboratory (Fuel cell tests - F. Uribe)
- Battelle Memorial Institute (J. Sayre and A. Kawczak)
- 3M (PdCo catalyst, exploratory activities – R. Atanasoski)
- Plug Power – Test of the PtRu20 anode catalyst in progress: 800hr with a negligible loss in activity (B. Do).

Interactions
- General Motors Co. (F. Wagner)
Objectives

To assist the DOE in developing fuel cell technologies by providing low-platinum-loading electrocatalysts.

For the current year:

• To demonstrate the stability of the Pt monolayer electrocatalysts for $\text{O}_2$ reduction in fuel cell tests (milestone experiment).

• To further the understanding of the properties of Pt monolayer electrocatalysts.

• To improve the activity of Pt monolayer ($\text{Pt/Pd/C}$) electrocatalysts.

• To improve the syntheses of electrocatalysts with ultra low, or no Pt content: $\text{Pt/Au/Ni}$ and $\text{Pd}_2\text{Co}$, and to test them in fuel cells (milestones 2004).

• To explore a novel class of electrocatalysts for $\text{O}_2$ reduction consisting of mixed monolayers of Pt and late transition metals.
Developing of low-Pt-loading electrocatalysts by placing a monolayer of Pt, or mixed Pt - late transition metals monolayers, on nanoparticles of suitable metals or alloys.

This approach uniquely facilitates obtaining electrocatalysts with:

- **Complete Pt utilization (of all atoms that are not blocked by Nafion®)**
- **Ultimately reduced Pt loading**
- **Low coordination of Pt atoms that should enhance their activity**
- **Strained monolayers (tensile or compressive) with shift of the d-band center (Nørskov et al. model) causing increased or decreased activity**
- **Electronic (ligand) effects**

A method for Pt monolayer deposition on metal nanoparticles, involving displacement of a UPD adlayer, was further improved and applied for depositing mixed-metal monolayers.
RDRE measurements show the effect of the substrate

1. Pt/Pd(111) - slight compression, electronic effect and reduced OH coverage – high activity
2. Pt/ Au(111) – Pt is highly expanded - d-band center increases - the bond between Pt and the ORR intermediates is too strong.
Ea for O₂ dissociation is the smallest on Pt_{ML}/Au(111) and largest on Pt_{ML}/Ir(111). The trend is the opposite for the hydrogenation of O. For a good electrocatalyst, the kinetics of both the O-O bond breaking and the hydrogenation of reactive intermediates have to be facile.

Volcano plot → balance between two competing influences (breaking O-O and forming O-H).
Further Improvement of Pt<sub>ML</sub>/Pd/C Electrocatalysts

O<sub>2</sub> reduction on a Pt ML on 5nm Pd nanoparticles; 2.3 – 5.7 µg<sub>Pt</sub>/cm<sup>2</sup>.

1. A higher activity is observed for a 5 nm Pd support than for 9nm particles due to the larger surface area. (Impurity effects were observed with the 5nm Pd/C).

2. The total noble metal mass-specific activity of Pt/Pd/C is 4 times that of Pt/C!
Pt Monolayer on Pd/C Cathode Catalysts
Durability Test at LANL (F. Uribe)

Voltage losses after 2900 hr of testing at constant current (0.6 A/cm²):

<table>
<thead>
<tr>
<th>initial V</th>
<th>final V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>0.51</td>
</tr>
</tbody>
</table>

- Result demonstrates considerable catalyst activity after 2900 hr
- Long-term durability of the Pt-Pd cathode catalyst is thus demonstrated

The catalyst’s performance ranges from 0.17gPt/kW to 0.25gPt/kW, which is below the DOE 2005 target of 1.35gPt/kW (1/2x2.7).
Low Pt Content Fuel Cell

Low-Pt Content Catalysts on both Electrodes (F. Uribe)
--- 0.149 mg total Pt /cm² ---

Test in-progress

H₂/Air Fuel Cell
Anode: 0.050 mg Pt/cm² - PtRu₂₀
Cathode: 0.099 mg Pt/cm² - 6.6% Pt-18 % Pd/C

Catalyst performance: 0.60 g Pt /kW
J: 417 mA/cm²,
Voltage: 0.602 V,
Power: 0.251 W/cm²,

In another test, the cell completed 450hr; performance
0.46 g Pt /kW (terminated by vis major).

Based on the RDE data, the cell voltage should be considerably higher. The reason for this inconsistency (particle size, impurities) will be investigated.
A new class of the ORR electrocatalysts was synthesized – a Pt monolayer that is mixed with a metal with a high coverage of OH or O.

Due to the OH-OH (O) repulsion, PtOH formation decreases, causing an increase in the ORR activity (by a factor of 4 at 0.8V for Pt<sub>80</sub>Ir<sub>20</sub>).

Pt stabilized against oxidation.

DFT calculations show repulsion between PtOH and MOH or MO for some metals, and attraction for others.
Mixed-metal Pt Monolayer Electrocatalysts

Evidence for the decreased PtOH coverage

Single crystals, 0.25ML Ir on Pt(111)

PtOH formation on Pt(111) is suppressed by IrOH on its surface; no effect on H adsorption is observed.

A small oxidation of Pt in PtIr/Pd/C is observed only at 1.17V, while Pt/C is already oxidized at 0.76V (XANES data).
Mixed-metal Pt Monolayer Electrocatalysts

The Pt mass-specific activity of a Pt\textsubscript{0.8}Re\textsubscript{0.2}/Pd/C is about 20 times that of Pt/C.

The total noble metal mass-specific activity is about 4 times that of Pt/C.
PtOH coverage, O₂ reduction rates and the Tafel Slopes

1. Consensus exists that the OH\textsubscript{ads} inhibits the ORR.

2. The intrinsic Tafel slope for Pt (no adsorbates other than the ORR intermediates) is -120mV/dec. The OH adsorption causes low slopes. (Quantitative analysis in J. Phys. Chem., B 108 (2004) 4127).

3. Evidence from XANES data: Decreasing the OH coverage results in higher slopes and higher activity.

\[ \Delta I/I_0 \sim \Theta_{OH} \]

Relative change in peak intensity

\[ \log(j_k/\text{mAm}^{-2}) \]

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

\[ \text{Tafel slope / mV/dec.} \]

\[ 0.1 \text{M HClO}_4 \]

\[ 1.17 \text{ V RHE} \]

\[ -86 \]

\[ -95.6 \]

\[ -112 \]
Milestone for FY 2004—further improvements in 1. Synthesis and 2. Activity

**Synthesis**

Au + Ni co-deposit  At 600°C Au segregates  Pt deposited by replacing Cu

Ni + Au → Au<sub>ML</sub>/Ni → Pt<sub>ML</sub>/Au<sub>ML</sub>/Ni

Asymmetric Au peaks in the XPD spectrum of the AuNi/C catalyst: segregation of alloy nanoparticles

1.03 µg/cm<sup>2</sup> of Pt + 4 µg/cm<sup>2</sup> of Au vs. 12µg/cm<sup>2</sup> of Pt

Pt and (Pt + Au) mass-specific activities are \(~20\) and \(~4\) times that of the commercial Pt/C, respectively
Ultra low Pt-content cathode catalysts fuel cell test (F. Uribe)
Cathode Catalyst: Pt: 1.44 w%; Au: 2.92 w%; Ni: 8.69 w% (13.0 % total metal/C)

Cell: 5 cm²
A: 0.077 mg Pt/cm² (20% Pt/C, ETEK)
C: 0.169 mg Total metal/cm²
(19 µg Pt; 37µg Au; 0.113 mg Ni/cm²)

Target for 2005: 2.7g/kW
Achieved (cell): 0.33g/kW
Achieved (cathode): 0.14g/kW

The long-term stability of the Pt/Au/Ni electrocatalyst has yet to be determined.
Obstruction of the anode gas flow channel ended the test.

<table>
<thead>
<tr>
<th>Composition</th>
<th>g Pt/kW cathode</th>
<th>g Pt+Au/kW cathode</th>
<th>g Pt/kW cell</th>
<th>g Pt+Au/kW cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Performance</td>
<td>0.05</td>
<td>0.14</td>
<td>0.24</td>
<td>0.33</td>
</tr>
</tbody>
</table>
A NON-PLATINUM Pd<sub>2</sub>Co ELECTROCATALYST

Milestone for FY 2004— 1. Activity (improved, RDE)  
2. Fuel Cell test – low activity  
3. Excellent methanol tolerance

11µg/cm<sup>2</sup> of Pd vs. 12µg/cm<sup>2</sup> of Pt; 0.1MHClO<sub>4</sub>; 25°C; 20mV/s

--- 20% Pd<sub>2</sub>Co/C (treated at 900°C) ---

1. The synthesis at 900°C yields large particles of a uniform alloy.
2. The activity of Pd<sub>2</sub>Co in RDE experiments is similar to that of Pt (current density and mass-specific activity).
A NON-PLATINUM Pd$_2$Co ELECTROCATALYST

1. XANES data indicate a pronounced electronic effect in both Pd and Co and an increased stability of Pd.
2. The catalyst has a negligible activity for methanol oxidation and an excellent tolerance to it.
3. Re-protonation of MEA in hot 0.5 M sulfuric acid may cause degradation of this catalyst.

**Methanol tolerance**

- 900RPM
- 0.1 M HClO$_4$
- 11µgPd/cm$^2$
- 10mV/s

Fuel cell test (F. Uribe)
20% Pd$_2$Co/C (treated at 900°C)

**A:** 0.20 mg Pt/cm$^2$ (20% Pt/C ETek)
**C:** 0.18 mg Pd$_2$Co/cm$^2$

**0.1M CH$_3$OH in 0.1M HClO$_4$**
Responses to Reviewers’ Comments from Last Year

1. Expand work on AuNi alloys (2 reviewers) --- The work has been expanded.

2. Continue collaboration with LANL ---- The collaboration has been intensified.

3. Faster tech transfer --- Battelle collaboration; Plug Power tests of the catalyst.

4. Studies of PtOH critical ---- These studies have been continued.

5. More work on PdCo ----- These studies have been continued.
Future Work

Remainder of FY2005

• **Pt$_{\text{ML}}$/Pd/C electrocatalyst**
  - Pd particle size effects; surface segregation; post MEA Z-contrast TEM; fuel cell tests.
• **Pd$_2$Co electrocatalyst**
  - Further synthetic studies; stability of Co.
• **Mixed-metal Pt monolayer electrocatalysts**
  - Basic studies of Pt-M/Pd/C; MOH (MO)-PtOH interactions

FY 2006

• **New strategies to increase the stability of Pt at OCP and under potential cycling conditions**

• **Pt/AuNi/C electrocatalyst**
  - Segregation of Pt, Au; Stability tests; Fuel cell tests.
• **Pd$_2$Co electrocatalyst**
  - Fuel cell tests.
• **Pt monolayers on Pd and other metal alloy nanoparticles**
  - Basic in situ surface science and electrochemical studies.
• **Mixed-metal Pt monolayer electrocatalysts**
  - Electrocatalytic activity, stability and segregation studies; fuel cell tests.
Publications


Presentations

Seven papers at national and three at international meetings,
The major HYDROGEN hazard was associated with the saturation of electrolyte with hydrogen gas in a 100ml electrochemical cell. The gas was vented into the hood, which made its concentration negligible, without possibility of accumulation. In addition, the laboratory air is changed every 7 minutes, which would preclude accumulation of H$_2$ if hood is not operating properly. Presently, the studies involving H$_2$ oxidation are rarely conducted.