Low Pt Loading Fuel Cell Electrocatalysts

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Overview

### Timeline
- Project start date: 06.02.
- Project end date: Multi-year
- Percent complete

### Barriers addressed
1. Precious metal loading
2. Electrocatalysts’ Activity
3. Electrocatalysts’ Durability

### Budget
- Total project funding: $1314K
- DOE share: $1314K
- Funding received in FY05: $330K
- Funding for FY06: $360K

### Budget

### Collaborations
- Los Alamos National Laboratory (Fuel cell tests - F. Uribe, P. Zelenay)
- Battelle Memorial Institute (CRADA Scale-up of synthesis - J. Sayre and A. Kawczak)
- 3M (PdCo catalyst, exploratory activities – R. Atanasoski)
- Plug Power – Test of the PtRu$_{20}$ anode catalyst: 2390 hr showed a small loss in activity (B. Do).
- General Motors Co. planning stage (F. Wagner)
Objectives

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

--- During the current year
• To demonstrate the stability of Pt mixed metal monolayer (Pt$_{80}$Ir$_{20}$/Pd/C) and Pt/Au/Ni/C electrocatalysts in fuel cell tests.

• To explore a novel class of electrocatalysts for O$_2$ reduction consisting of Pt monolayer on noble metal -non-noble metal core-shell nanoparticles.

• Further studies of the electrocatalysts with low, or no Pt.

• Scale – up of synthesis based on displacement of a Cu monolayer.

• Addressing the problem of Pt dissolution under potential cycling regimes.

• Testing the effects of Au clusters on Pt stability.
Why Pt monolayer catalysts?

- Complete Pt utilization (of all atoms that are not blocked by Nafion®)
- Ultimate reduction of Pt loading
- Increased activity

(Six patents pending)

For 3-5nm nanoparticles ~25% of atoms are on the surface, ~75% are not available for catalysis.

Three types of Pt electrocatalysts:

1. **Pt on Pd nanoparticles**
   - Improved activity
   - Improved durability

2. **Mixed-metal Pt on Pd nanoparticles**
   - Even higher activity
   - Durability tests at LANL and Battelle

3. **Pt on noble/non-noble core-shell nanoparticles**
   - Yet higher activity per mass of noble metal
   - Durability to be tested
Compared to commercial MEA baselines (0.6 mg Pt/Ru/cm²):
Higher than neat H₂ baseline; lower than reformate baseline.
Total run time: 2394 hours
New class of catalysts: Pt monolayer on *noble metal* - *non-noble metal core-shell* nanoparticles

**Synthetic route**

- Segregation at elevated T
- ML of Cu by UPD
- Cu displaced by Pt

New class of electrocatalysts that facilitate a **further decrease of noble metal content** while possessing a very high activity.
O₂ Reduction Kinetics and Mass Activities of Ptₘₐₙ/PtCo₅/C and Ptₘₐₙ/PdCo₅/C

Pt mass activity

Total noble metal mass activity

2- to 5-fold increase in noble metal mass activity with Pt on core-shell nanoparticles
O₂ Reduction Kinetics and Mass Activities of Pt_{ML}/NbO₂/C and Pt/C/C

Pt is not observed by XRD in Pt/NbO₂/C

Pt_{ML}/NbO₂/C has 3 times higher mass activity than the commercial Pt/C

XANES shows a small oxidation of Pt/NbO₂/C compared to Pt/C.
Formation of Au clusters on Pt electrodes

2D Au deposited on Pt(111); 3D formed after several cycles to 1.2V in O₂ saturated solution

115 nm x 115 nm  120 nm x 120 nm

No effect on H ads.  Inhibition of OH ads.

Model of Au clusters on Pt nanoparticle
Effect of submonolayer of Au clusters on O$_2$ reduction on Pt(111) and Pt/C

Small inhibition of O$_2$ reduction by Au, not in proportion to Au coverage
Effect of potential cycling on the activity of Pt/C in the ORR

30,000 cycles from 0.6 to 1.1V at 25°C in O₂-saturated solution

A negative shift of 40mV in E_{1/2} and a loss of surface area of 45%
Stabilization of Pt/C by a submonolayer of Au clusters under a potential cycling regime

30,000 cycles from 0.6 to 1.1V at 25°C in O₂-saturated solution

A negligible shift in E₁/₂ and a loss of surface area
Stabilization of $\text{Pt}^{\text{ML}}/\text{Pd/C}$ by a submonolayer of Au nanoparticles under a potential cycling regime

30,000 cycles from 0.6 to 1.1V at 25°C in $\text{O}_2$-saturated solution

A negative shift of 26mV in $E_{1/2}$

A negligible shift in $E_{1/2}$
Compressive strain-induced downshift of the $d$-band center decreases the activity of Pd and the blocking effect of OH, $O_2$, $O_2^-$, $H_2O_2$.

The activity of Pd$_3$Fe/C is as high as that of commercial Pt/C.

The optimal Pd-Pd distance is 0.273 nm.
Fine tuning of the Pt-substrate interaction: Very high activity of Pt\(_{\text{ML}}/\text{Pd}_3\text{Fe}/\text{C}\)

Comparison between Pt\(_{\text{ML}}/\text{Pd}_3\text{Fe}/\text{C}\), Pt\(_{\text{ML}}/\text{Pd}/\text{C}\) and Pt/\text{C}

Pd/\text{C} particle size of 9 nm.

\[
\begin{align*}
E_{1/2} &= 0.880 \text{ V} \\
\end{align*}
\]

Pt\(_{\text{ML}}/\text{Pd}_3\text{Fe}/\text{C}\) has 0.14g/kW, which meets 0.15g/kW, i.e., 1/2 of 0.3g/kW, the DOE's target for 2010.

Total noble metal mass activity is about 5 times that of the commercial Pt catalyst.
Methanol tolerance of the Pd$_2$Co electrocatalyst

Pd$_2$Co

XANES data indicates pronounced electronic effects in Pd-Co and an increased stability of Pd, its activity being close to that of Pt(10%)/C.

BNL#101-103 are from one sample obtained by different acid wash procedure.

Fuel cell methanol tolerance test by P. Zelenay et al., LANL

[Graphs showing cell voltage and current density versus MeOH concentration]
The Butler-Volmer equation, 
\[ j_k = j_0 \left( e^{2.3\eta/b} - e^{-2.3\eta/b} \right), \]
appears to be inappropriate for describing the kinetics of the H$_2$ oxidation reaction (HOR) on a Pt electrode (1,2).


Based on the Tafel-Heyrovsky-Volmer mechanism, we derived a new equation, ref. 3, to describe the HOR on Pt over the entire potential region:

\[ j_k = j_{0T} \left( 1 - e^{-F\eta/(2RT)} \right) + j_{0H} \left( e^{F\eta/2RT} - e^{-F\eta/(2+\beta)RT} \right) \]

A fast, inverse exponential rising of kinetic current at small overpotentials through the Tafel-Volmer pathway, \( j_{TV} \), and a gradual rise at \( \eta > 50 \) mV through the Heyrovsky-Volmer pathway, \( j_{HV} \).

The anode behavior in a PEM fuel cell can now be well understood.

New basis for fuel cell modeling, optimization, and diagnosis.

Measured (symbols, from ref [2]) and fitted (solid lines using the Eq.) polarization curves for the HOR on Pt microelectrodes

Calculated kinetic current (solid line), components, \( j_{TV} \) (dashed line) and \( j_{HV} \) (dotted line), the kinetic current from the Butler-Volmer equation (dotted-dashed line).
Future Work

Remainder of FY2006

• \( \text{Pt}_{\text{ML}}/\text{Pd}/\text{C} \) electrocatalyst
  - Post fuel cell tests Z-contrast TEM, XANES.

• \( \text{Pd}_2\text{Co} \) electrocatalyst
  - Stability studies; and fuel cell tests.

• Mixed-metal Pt monolayer electrocatalysts
  - Stability studies. Effects of Au clusters in MEA’s under potential cycling regimes.

FY 2007

• Stabilization effects of Au clusters:
  - RDE and MEA studies under potential cycling conditions with Pt/Pd/C; Pt/PdCo\(_5\)/C.

• \( \text{Pt}/\text{AuNi}/\text{C} \) electrocatalyst
  - Segregation of Pt, Au; Stability tests; Fuel cell tests.

• Further reduction of Pd content: Pt monolayers on core-shell nanoparticles
  - Basic in situ surface science and electrochemical studies; stability and fuel cell tests.
BNL ANODE PtRu$_{20}$/C electrocatalyst:
Durability and CO tolerance confirmed in a 2400h test at Plug Power. The performance of 0.063 g$_{Pt}$/kW meets the 2010 target of 0.15g/kW, i.e., 1/2 of 0.5g/kW (Ru not counted).

BNL CATHODE electrocatalysts:
1. Novel class of electrocatalysts developed: Pt monolayer on noble metal - non-noble metal core-shell nanoparticles. The performance of 0.14g/kW meets the target for 2010 of 0.15g/kW.
2. MEA test of Pt/Au/Ni/C failed, attributable to inadequate synthesis.
3. Scale up of catalysts synthesis to 1g/batch accomplished.
4. Au cluster submonolayer has a pronounced stabilization effect on Pt under potential cycling regime. It is a highly promising solution to that problem.
5. The Pd$_2$Co and Pd$_3$Fe have activities similar to that of Pt; Methanol tolerance of Pd$_2$Co confirmed in a fuel cell test at LANL.
6. NbO$_2$ is a promising support for Pt monolayer catalysts.
Responses to Previous Year Reviewers’ Comments

1. Include repeated potential cycling tests as part of durability screening of promising candidates… --- The tests have been started.

2. Do small-scale development of the processes needed to make 50cm$^2$ MEA and, eventually, short-stack quantities of catalysts through the UPD-replacement process. --- The synthesis has been scaled up to make 1 g of the catalyst per day.

3. Should try to reduce the amount of Pd sooner in timeline (2 reviewers) -- Pt monolayer on noble metal -non-noble metal core-shell nanoparticles provide such a possibility.

4. A more appropriate industry collaboration would be with companies that make catalysts,--- BNL is open for collaboration.
Publications


Presentations

Five papers at national and three at international meetings,
Critical Assumptions and Issues

• Stability of Au clusters on Pt surfaces

• Stability of surface segregation induced by annealing

• The extent of mixing in bimetallic systems at 80-100°C

• Electronic effects vs. strain effects