Low Pt Loading Fuel Cell Electrocatalysts

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(This presentation does not contain any proprietary or confidential information). Project ID # FC17

DOE Hydrogen Program Review, May 23-26, 2005

Overview

Timeline

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

Budget

Total project funding:

- DOE share: $954K
- Funding received in FY04: $250K
- Funding for FY05: $330

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. Electrocatalysts' Durability

Target 2005: **2000 hr**
Accomplished: **3000 hr (cathode)**
Test in progress: **530 hr (low Pt cell)**

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 $PtRu_{20}$ 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 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 (**Pt/Pd/C)** electrocatalysts.
- To improve the syntheses of electrocatalysts with ultra low, or no Pt content: **Pt/Au/Ni** and **Pd_2Co**, and to test them in fuel cells (milestones 2004).
- To explore a novel class of electrocatalysts for O_2 reduction consisting of **mixed monolayers of Pt and late transition metals**.

Approach

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:

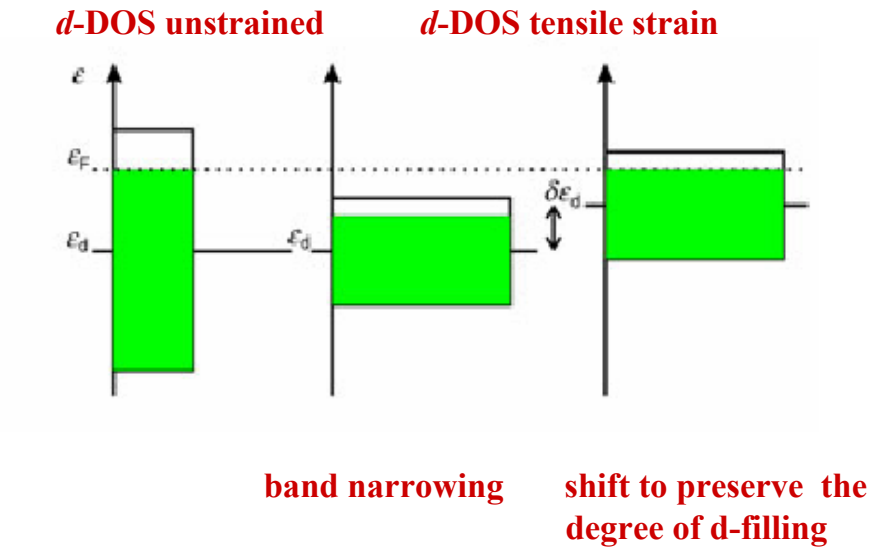
Complete Pt utilization (of all atoms that are not blocked by Nafion®)

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

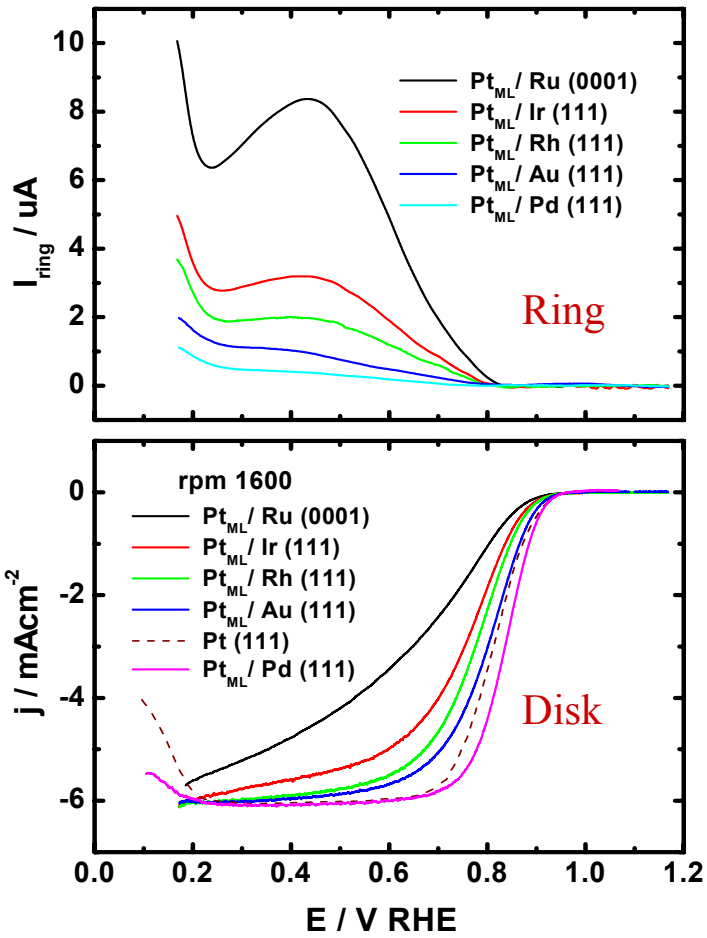
Electronic (ligand) effects



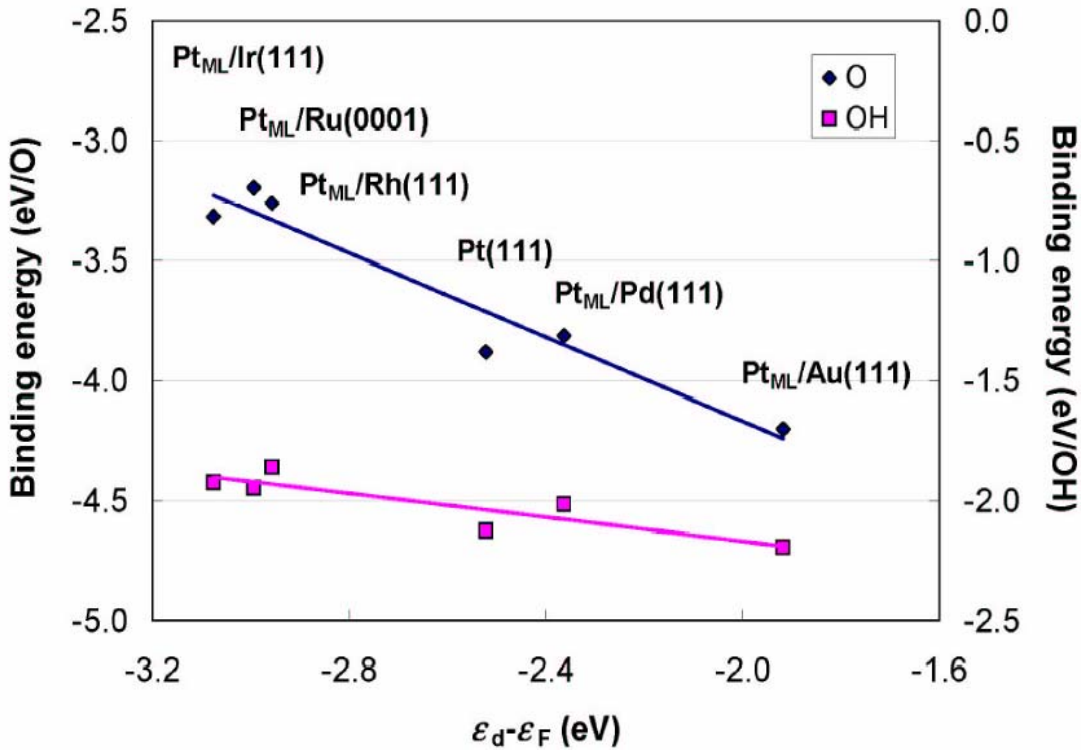
A method for Pt monolayer deposition on metal nanoparticles, involving displacement of a UPD adlayer, was further improved and applied for depositing mixed-metal monolayers.

SUBSTRATE EFFECTS ON Pt MONOLAYER ACTIVITY
- ACTIVITY - CENTER OF THE *d*-BAND VOLCANO PLOT

RDRE measurements show the effect of the substrate



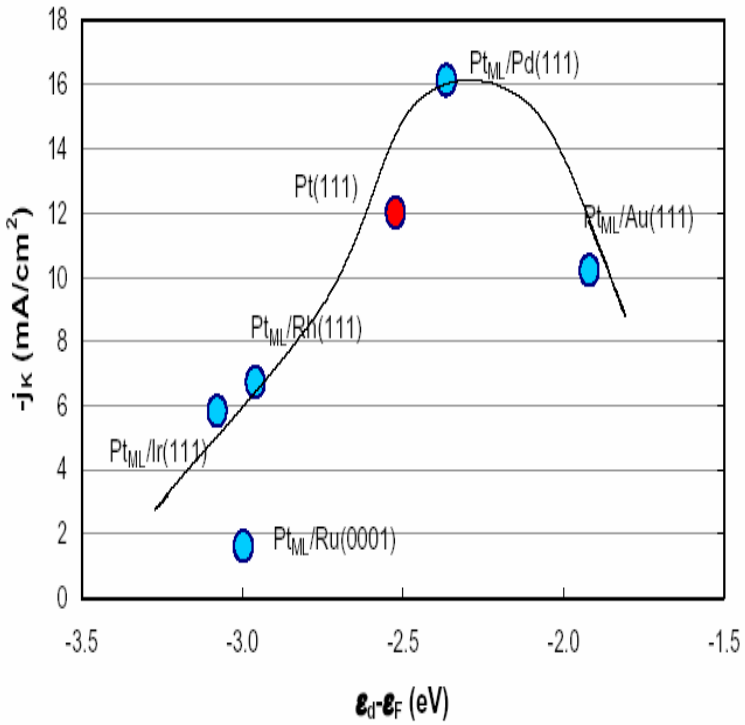
d-band centers - DFT Calculations
by M. Mavrikakis, U. Wisconsin



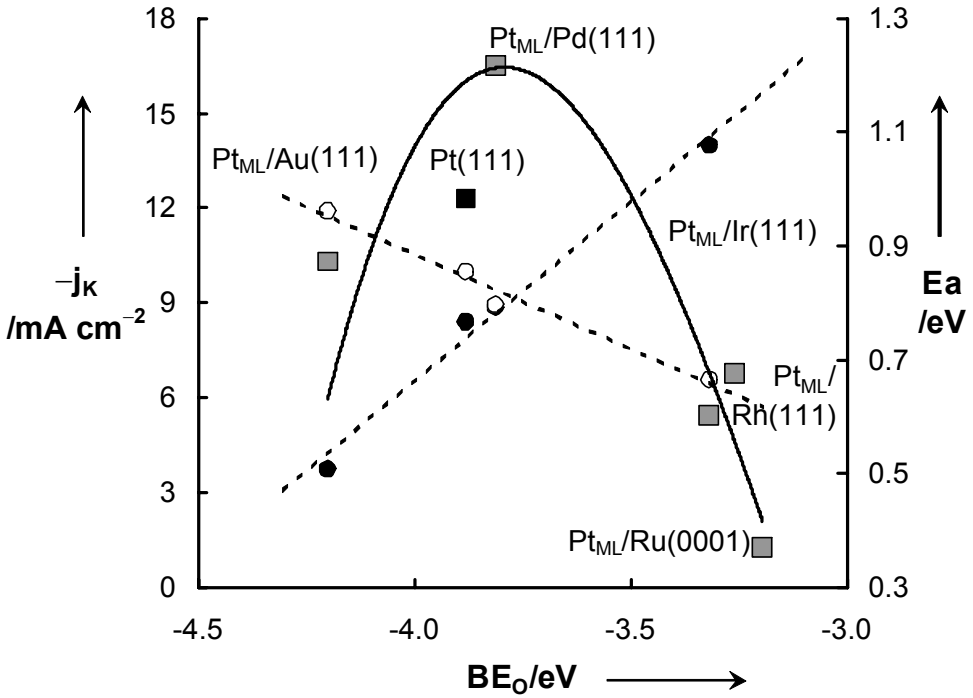
1. Pt/Pd(111)- slight compression, electronic effect and reduced OH coverage – high activity
2. Pt/ Au(111) – Pt is highly expanded - *d*-band center increases - the bond between Pt and the ORR intermediates is too strong.

SUBSTRATE EFFECTS ON Pt MONOLAYER ACTIVITY
- ACTIVITY - CENTER OF THE *d*-BAND VOLCANO PLOT-

Volcano plot: activity vs. calculated *d*-band centers of Pt MLs



Activation energies for O_2 dissociation (●) and OH formation (○)



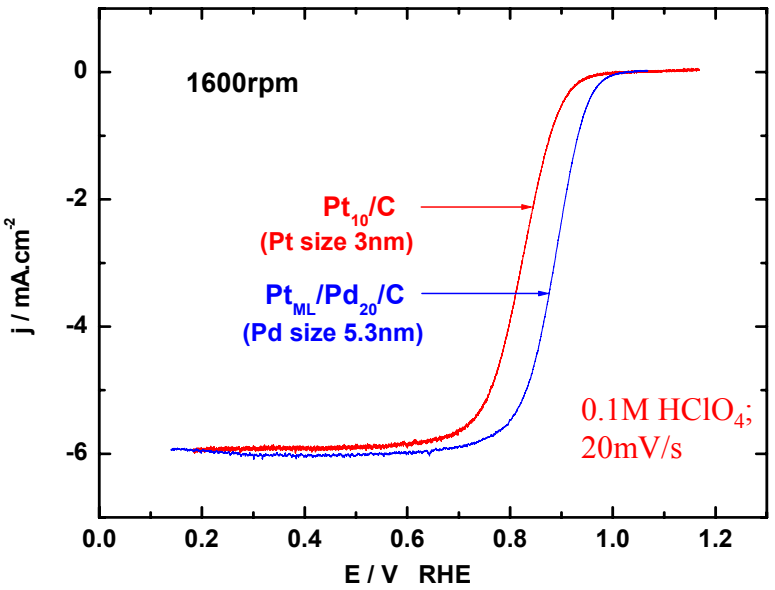
Angew. Chem. Int. Ed.. 2005, 44, 2132.

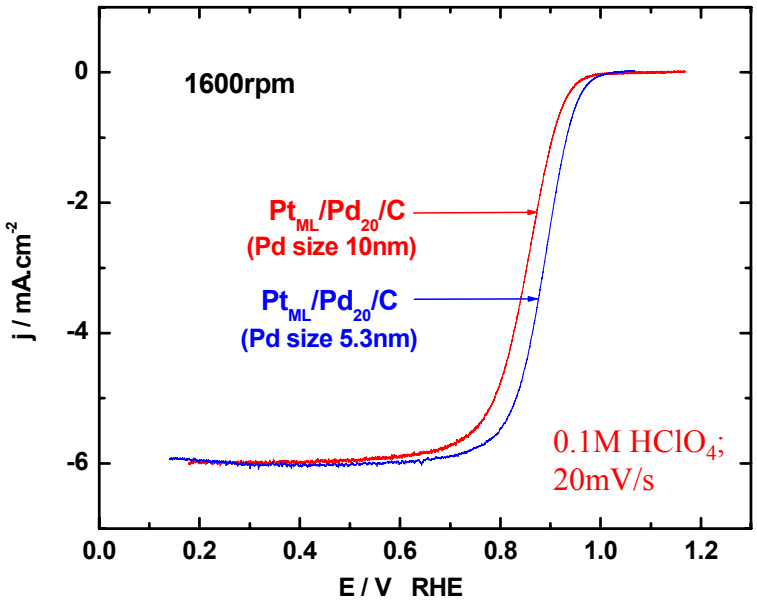
Ea for O_2 dissociation is the smallest on Pt_{ML}/Au(111) and largest on Pt_{ML}/Ir(111). The trend is the opposite for the hydrogenation of O. For a good electrocatalyst, the kinetics of both the O-O bond breaking and the hydrogenation of reactive intermediates have to be facile.

Volcano plot → balance between two competing influences (breaking O-O and forming O-H).

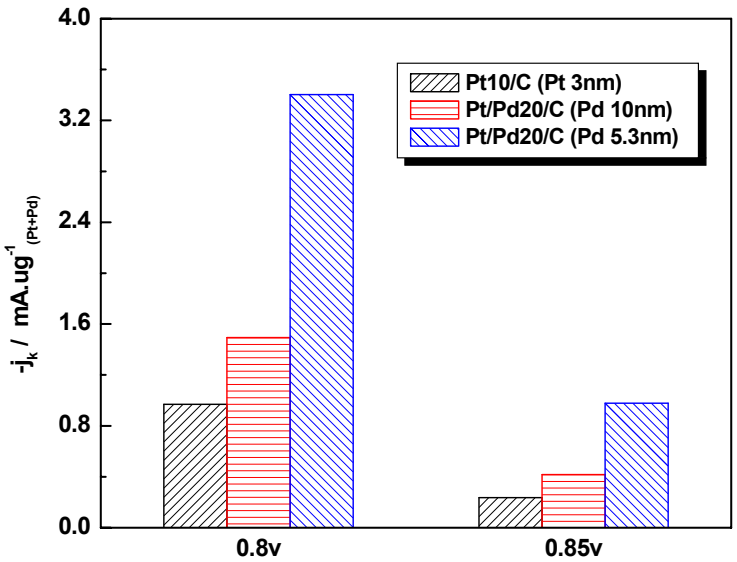
Further Improvement of Pt_{ML}/Pd/C Electrocatalysts

O_2 reduction on a Pt ML on **5nm** Pd nanoparticles; 2.3 – 5.7 $\mu g_{Pt}/cm^2$.





Total noble metal mass-specific activity

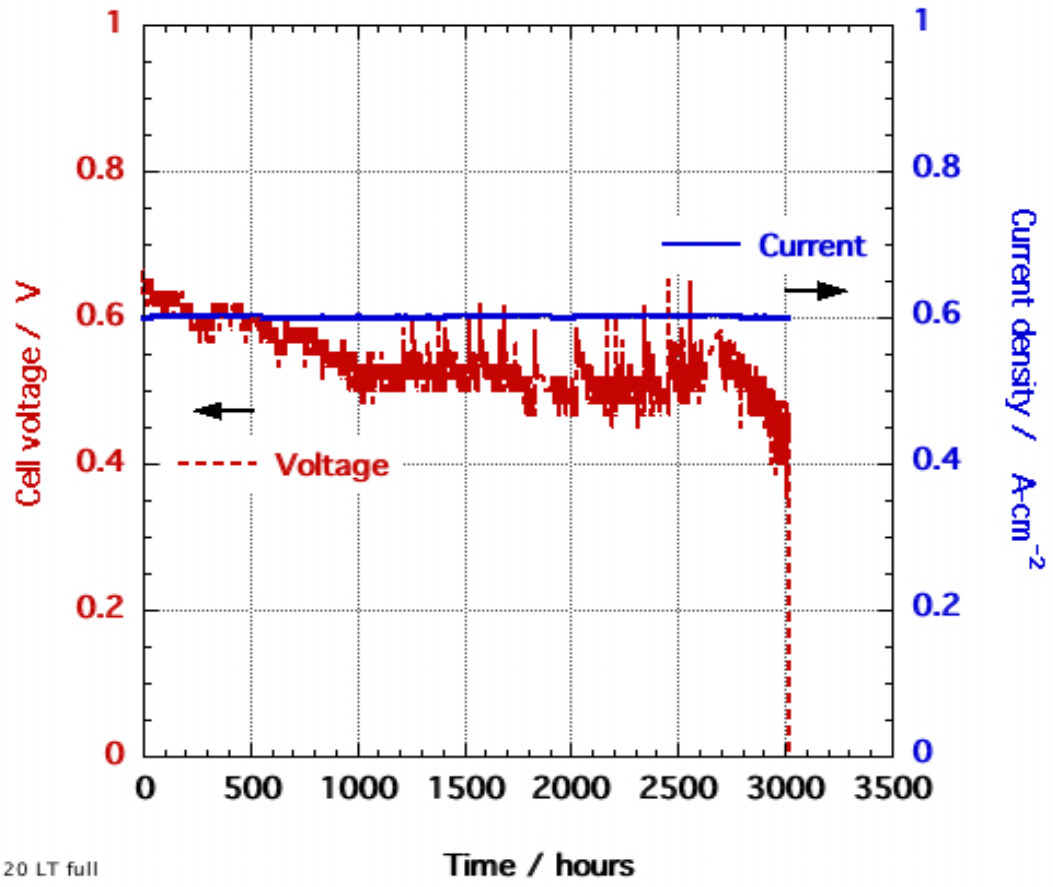


1. A higher activity is observed for a 5 nm Pd support than for 9nm particles due to the larger surface area. (Impurity effects were observed with the 5nm Pd/C).

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)

77 µg Pt/cm^2 (4% Pt - 20% Pd)



Voltage losses after 2900 hr of testing at constant current (0.6 A/cm^2):

initial V	final V
0.65	0.51

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

H_2/Air Fuel Cell 50 cm^2; 80ºC.

Test terminated after 3011hr for reasons other than catalyst's failure

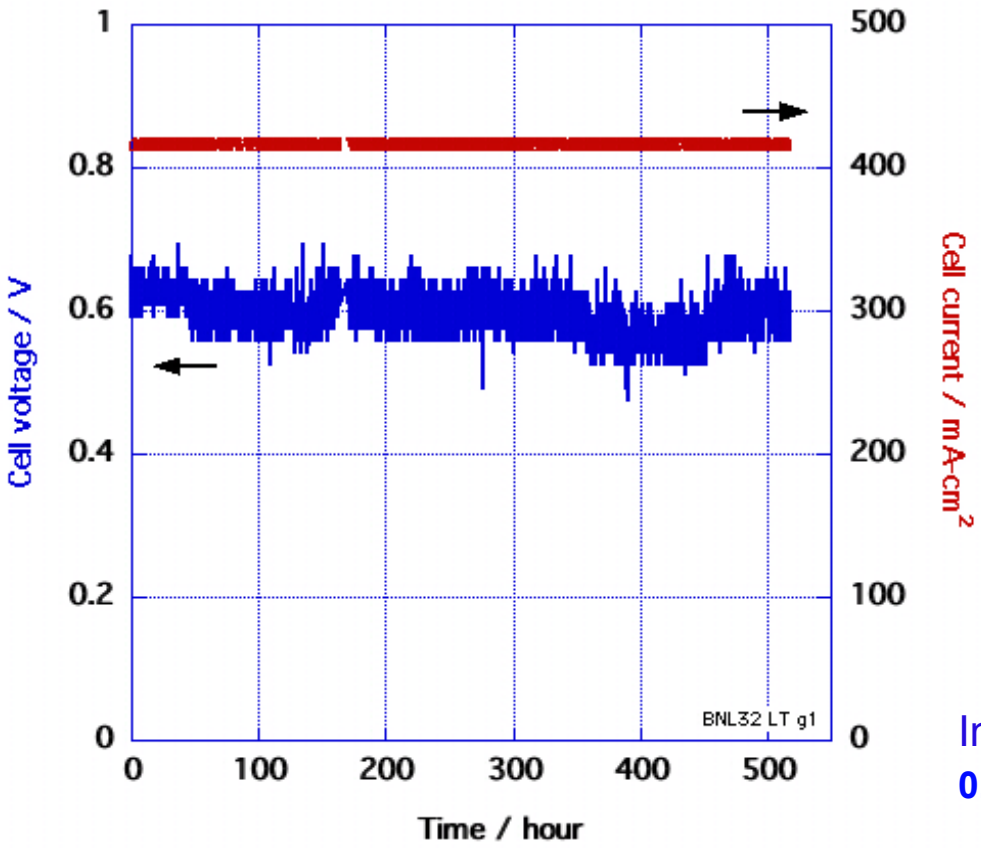
The catalyst's performance ranges from **0.17gPt/kW to 0.25gPt/kW,** which is below the **DOE 2005 target of 1.35gPt/kW** (1/2x2.7).

Low Pt Content Fuel Cell

Low-Pt Content Catalysts on both Electrodes (F. Uribe)
--- 0.149 mg total Pt /cm^2 ---

Test in-progress

Constant current test (0.4 A/cm^2)



H_2/Air Fuel Cell

Anode: 0.050 mg Pt/cm^2 - $PtRu_{20}$

Cathode: 0.099 mg Pt/cm^2 - 6.6%Pt-18 % Pd/C

Catalyst performance: 0.60 g Pt /kW

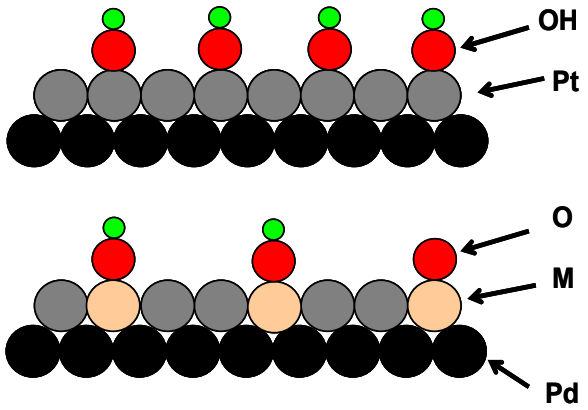
J: 417 mA/cm^2,
Voltage: 0.602 V,
Power: 0.251 W/cm^2,

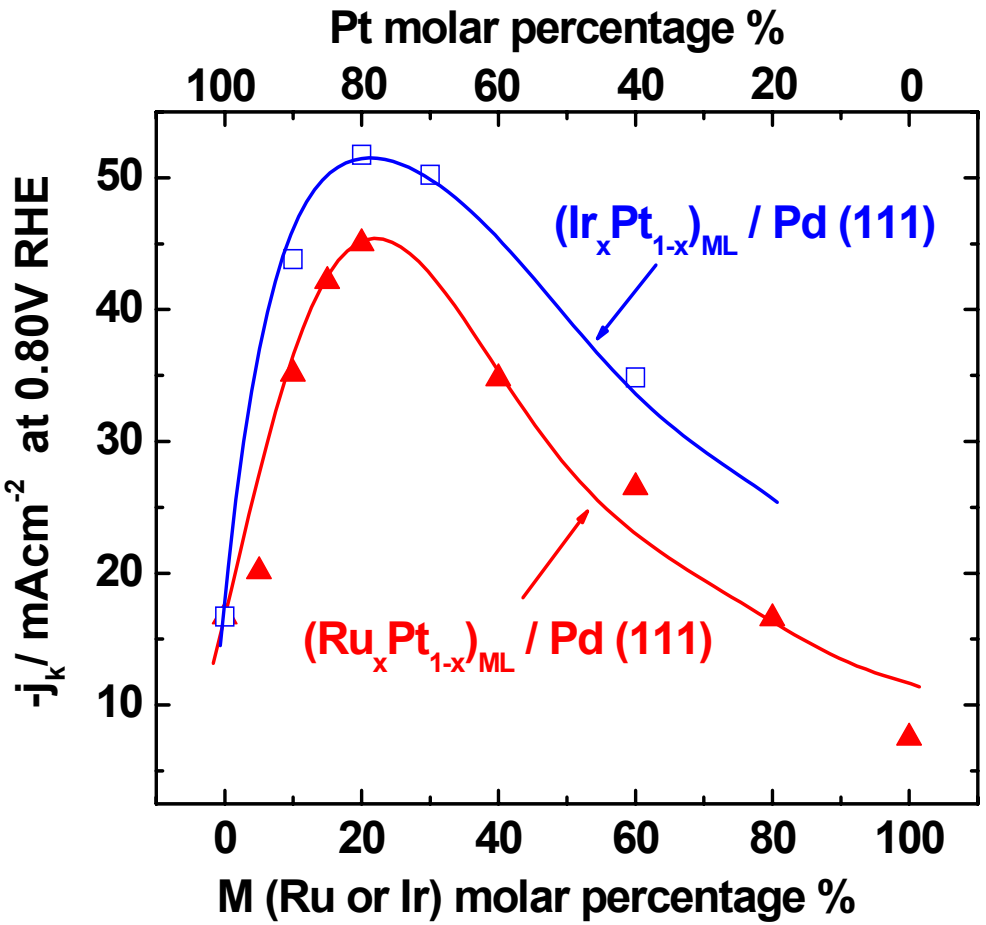
In another test, the cell completed 450hr; performance **0.46 g Pt /kW** (terminated by *vis major*).

Based on the RDE data, the cell voltage should be considerably higher. The reason for this inconsistency (particle size, impurities) will be investigated.

Mixed-metal Pt Monolayer Electrocatalysts

Sketch of the OH-OH or OH –O repulsion





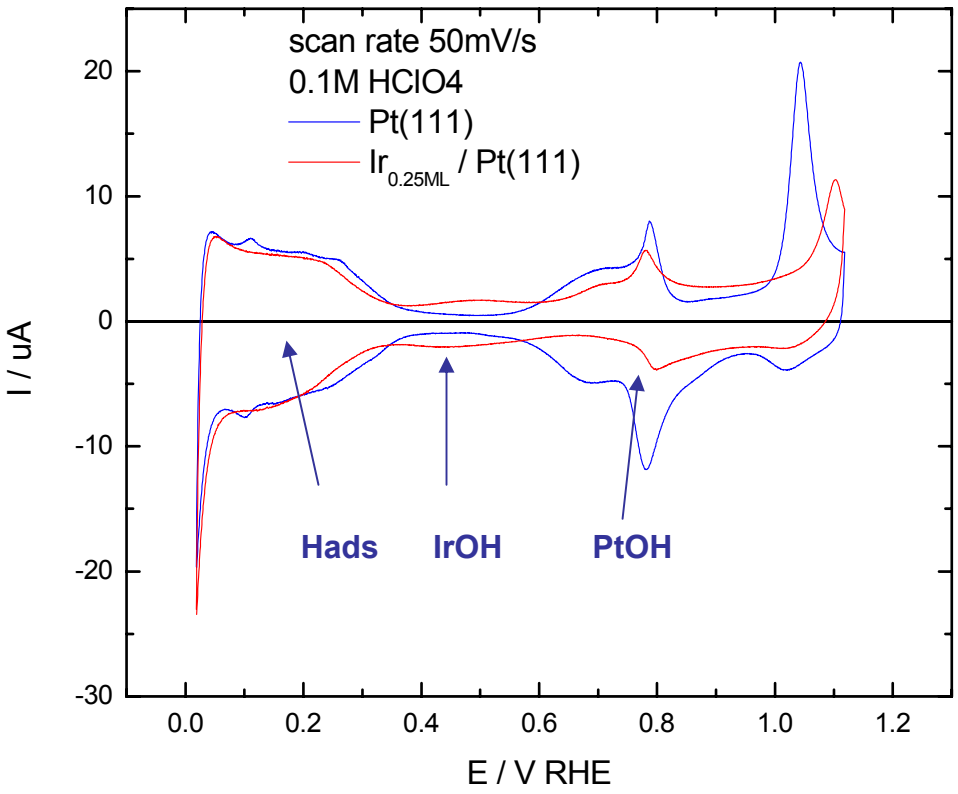
Maximum activity for $Pt_{80}M_{20}$.

- 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 $Pt_{80}Ir_{20}$).
- Pt stabilized against oxidation.
- DFT calculations show repulsion between PtOH and MOH or MO for some metals, and attraction for others.

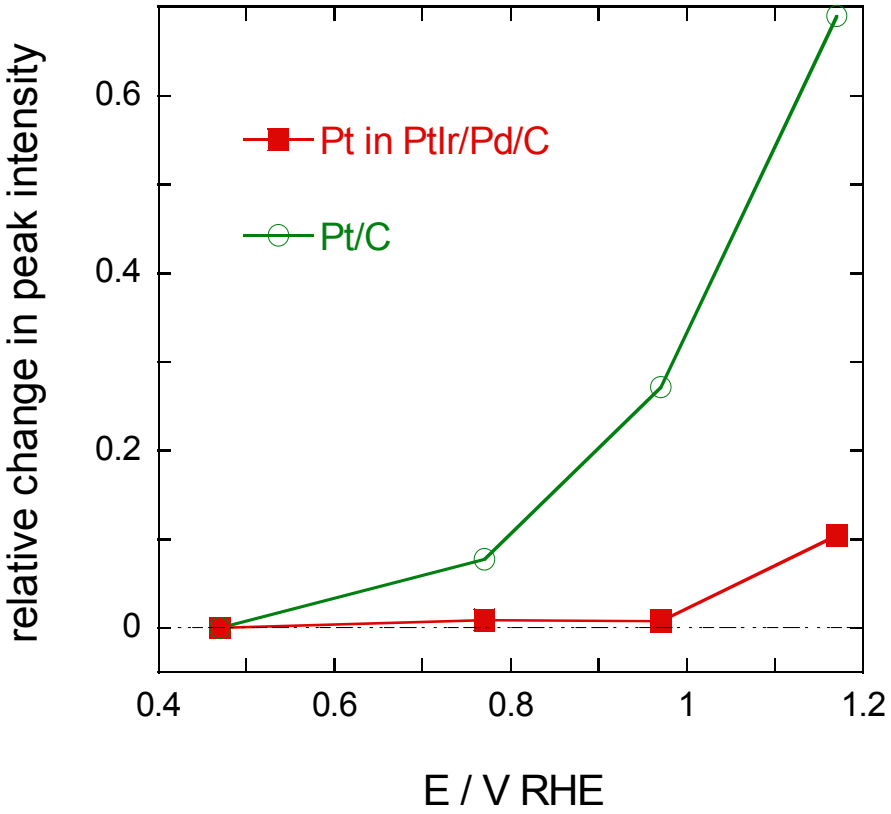
Mixed-metal Pt Monolayer Electrocatalysts

Evidence for the decreased PtOH coverage

single crystals, 0.25ML Ir on Pt(111)



$Pt_{80}Ir_{20}$/Pd/C nanoparticles

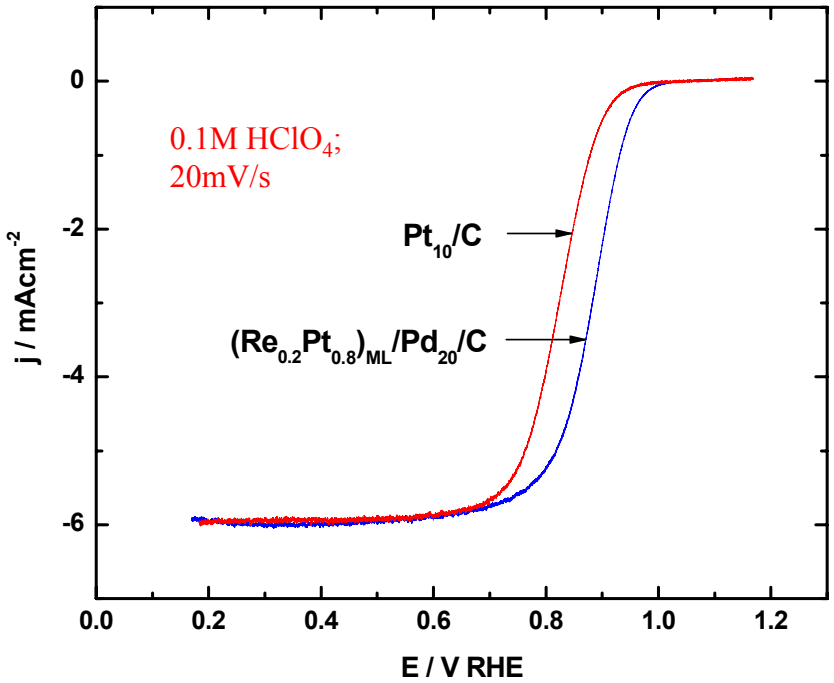


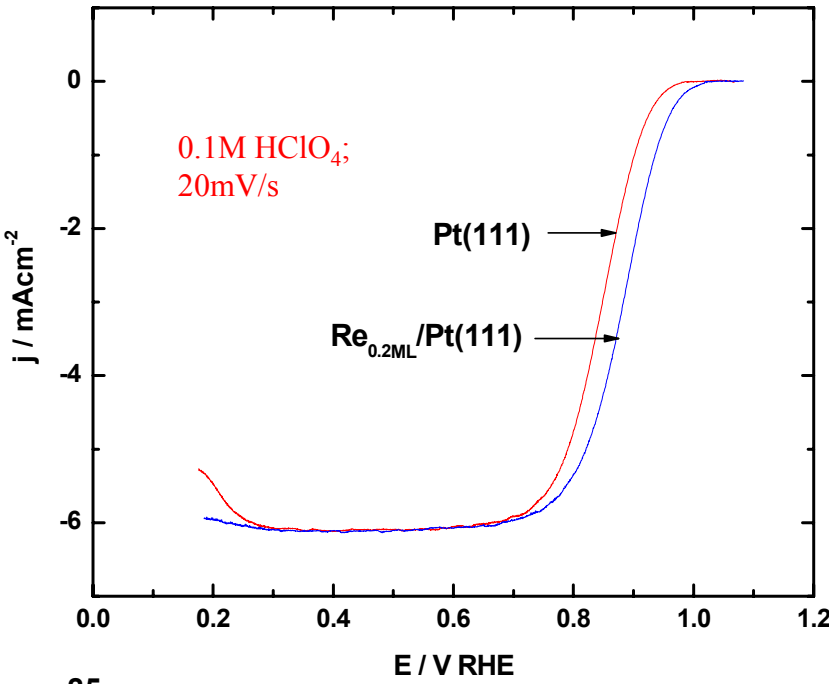
PtOH formation on Pt(111) is suppressed by IrOH on its surface; no effect on H adsorption is observed.

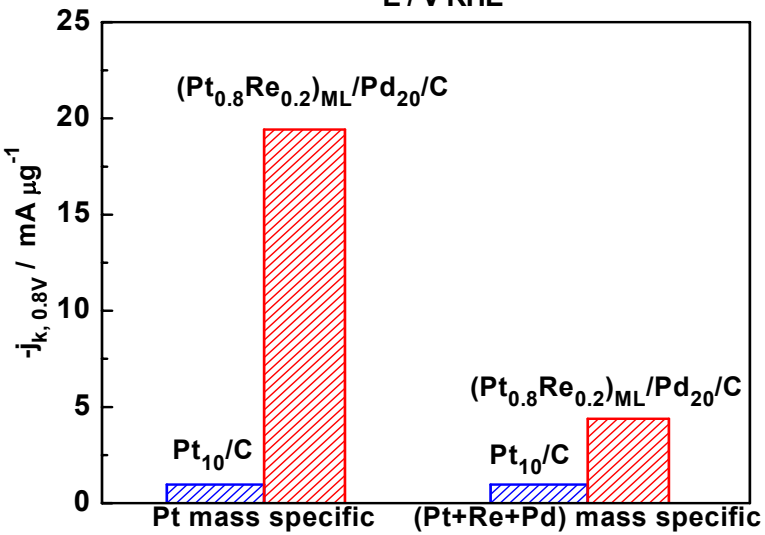
A small oxidation of Pt in PtIr/Pd/C is observed only at 1.17V, while Pt/C is already oxidized at 0.76V (XANES data).

Mixed-metal Pt Monolayer Electrocatalysts

$Pt_{0.8}Re_{0.2}$/Pd/C and $Re_{0.2ML}$/ Pt(111)





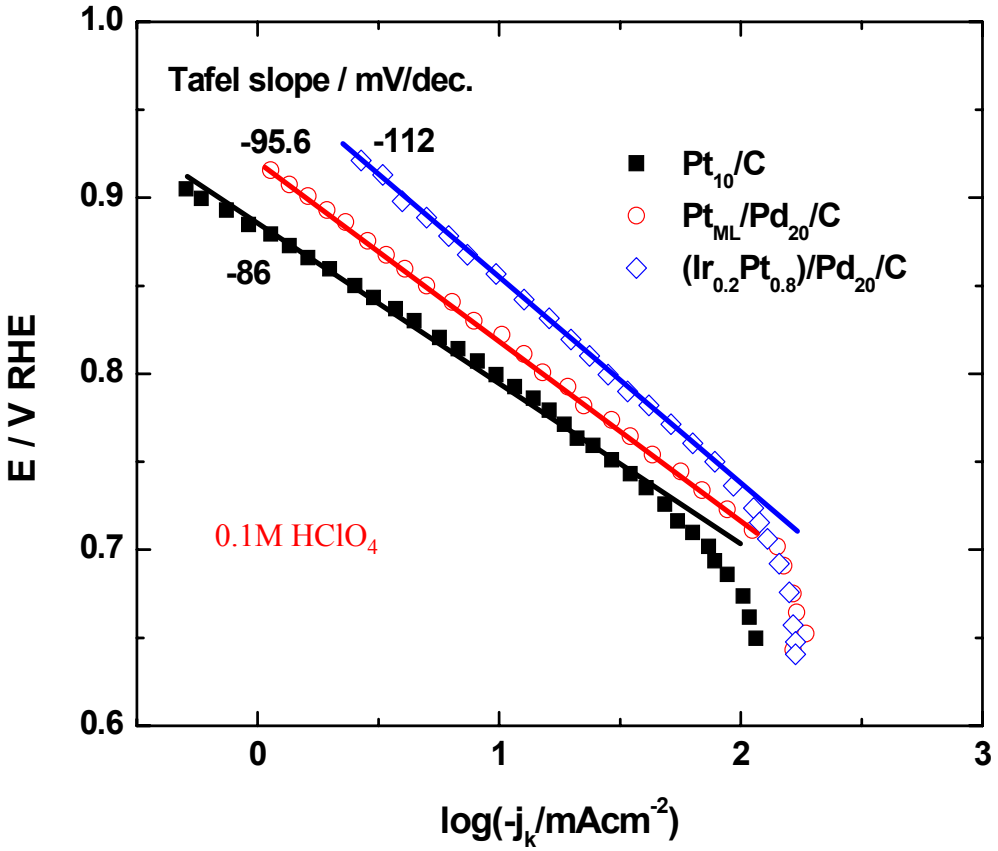


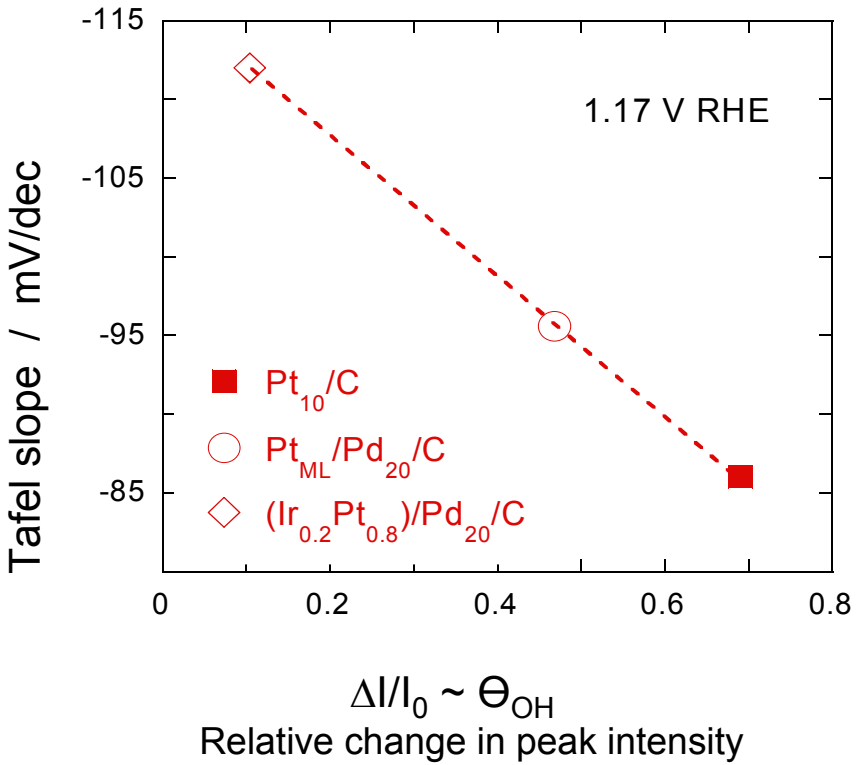
The **Pt mass-specific activity** of a $Pt_{0.8}Re_{0.2}$/Pd/C is about **20 times** that of **Pt/C**.

The **total noble metal** mass-specific activity is about **4 times** that of Pt/C.

PtOH coverage, O_2 reduction rates and the Tafel Slopes

1. Consensus exists that the OH_{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: **Deceasing the OH coverage results in higher slopes and higher activity.**



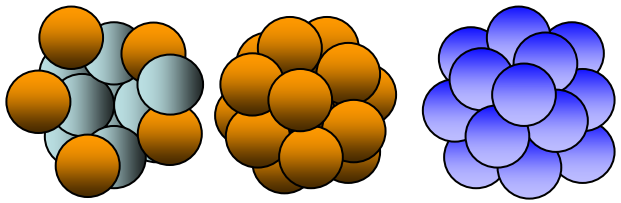


Pt MONOLAYERS ON METAL ALLOY SUBSTRATES: **Pt/Au/Ni/C**

Milestone for FY 2004—further improvements in 1. Synthesis and 2. Activity

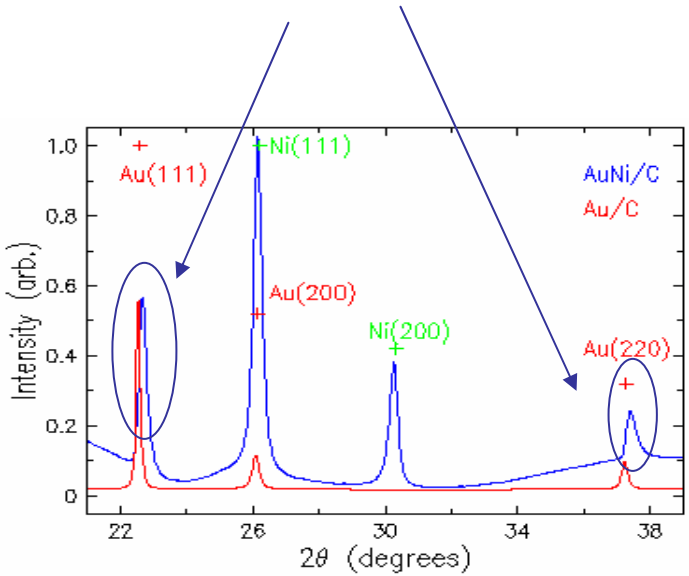
Synthesis

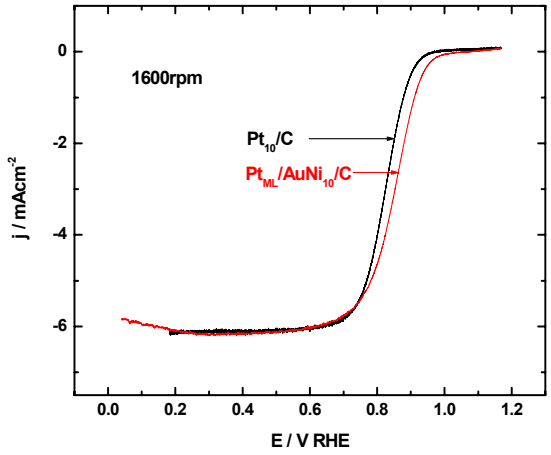
Au + Ni co-deposit — At 600°C Au segregates — Pt deposited by replacing Cu

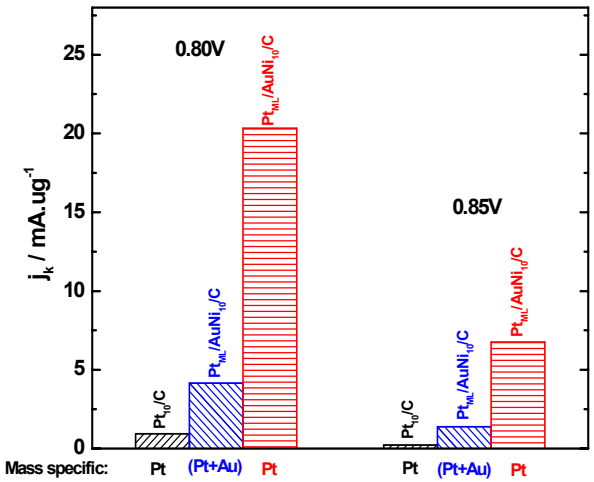


Ni + Au → Au_{ML}/Ni → $Pt_{ML}/Au_{ML}/Ni$

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





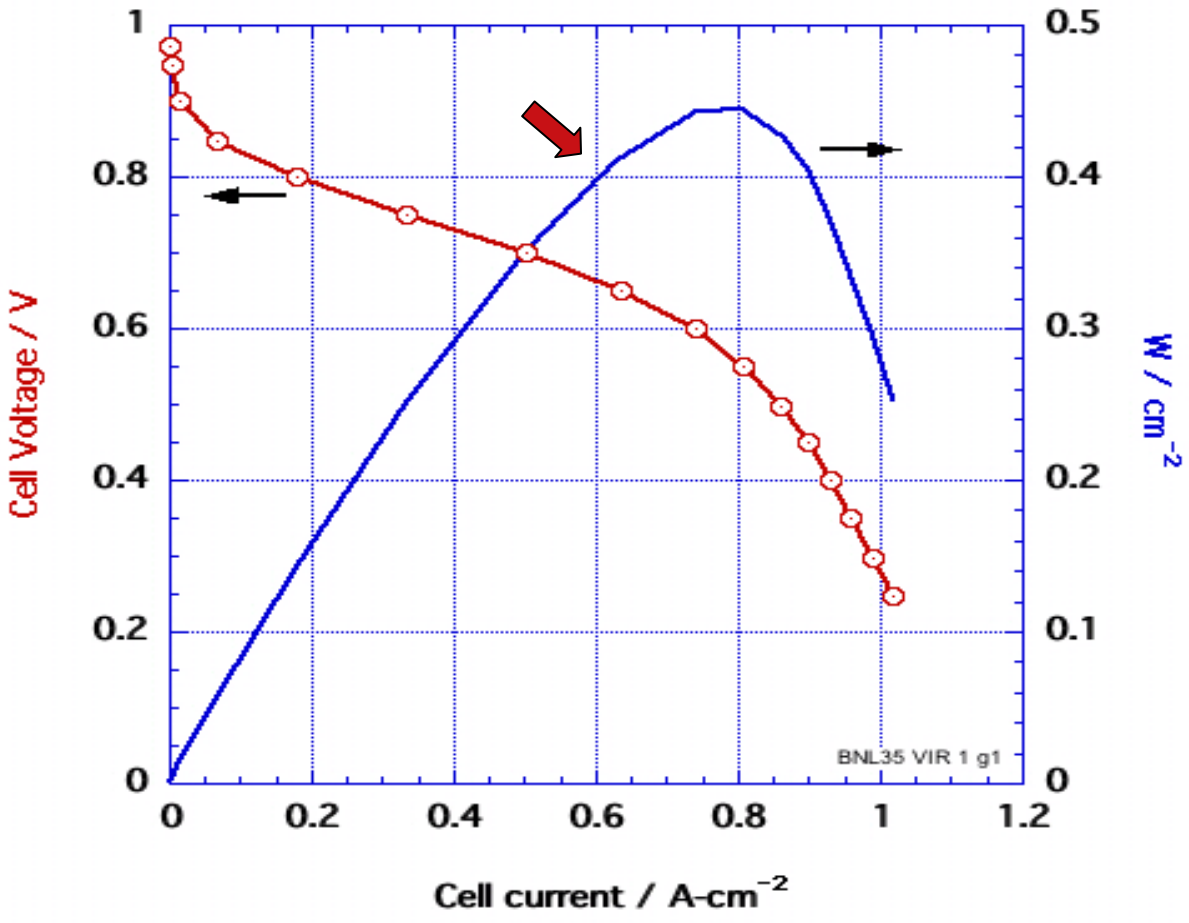


1.03 μg/cm^2 of Pt + 4 μg/cm^2 of Au *vs.* 12μg/cm^2 of Pt

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 cm^2
A: 0.077 mg Pt/cm^2 (20% Pt/C, ETEK)
C: 0.169 mg Total metal/cm^2
(19 µg Pt; 37µg Au; 0.113 mg Ni/cm^2)

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.

Catalyst performance at 0.6 A/cm^2

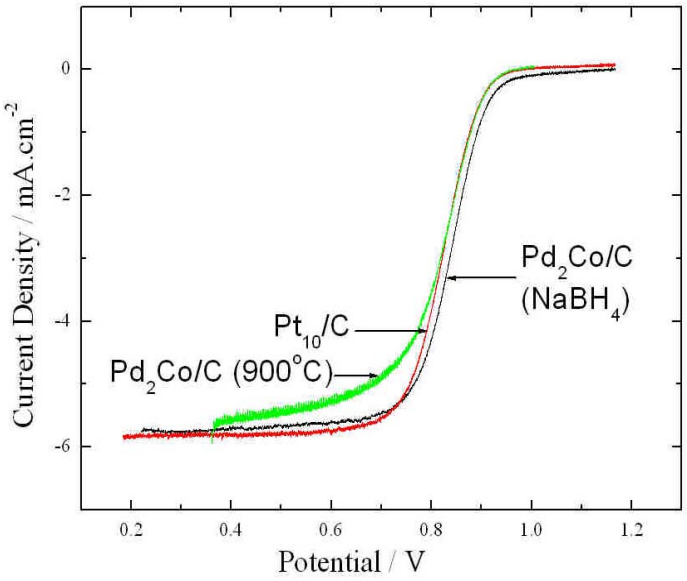
Composition	g Pt/kW cathode	g Pt+Au/kW cathode	g Pt/kW cell	g Pt+Au/kW cell
Performance	0.05	0.14	0.24	0.33

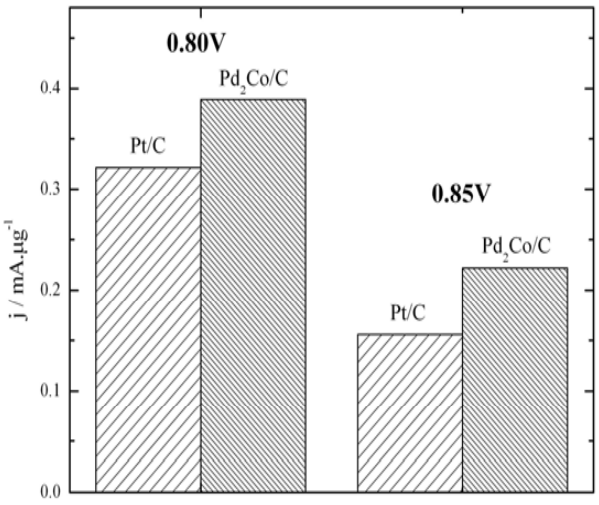
A NON-PLATINUM Pd_2Co ELECTROCATALYST

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

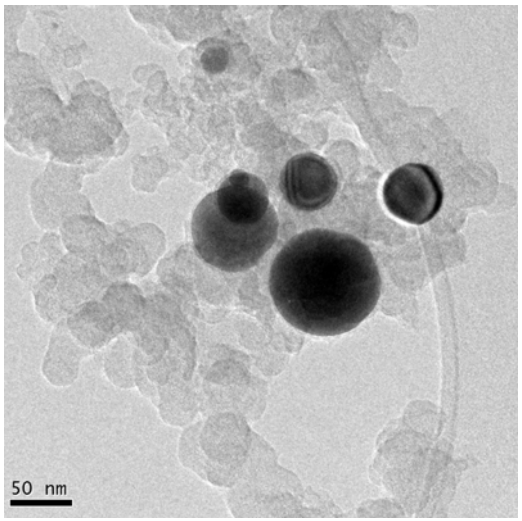
11μg/cm^2 of Pd *vs.* 12μg/cm^2 of Pt; 0.1M$HClO_4$; 25°C; 20mV/s

--- 20% Pd_2Co/C (treated at 900°C) ---





Pd or Pt mass-specific activity



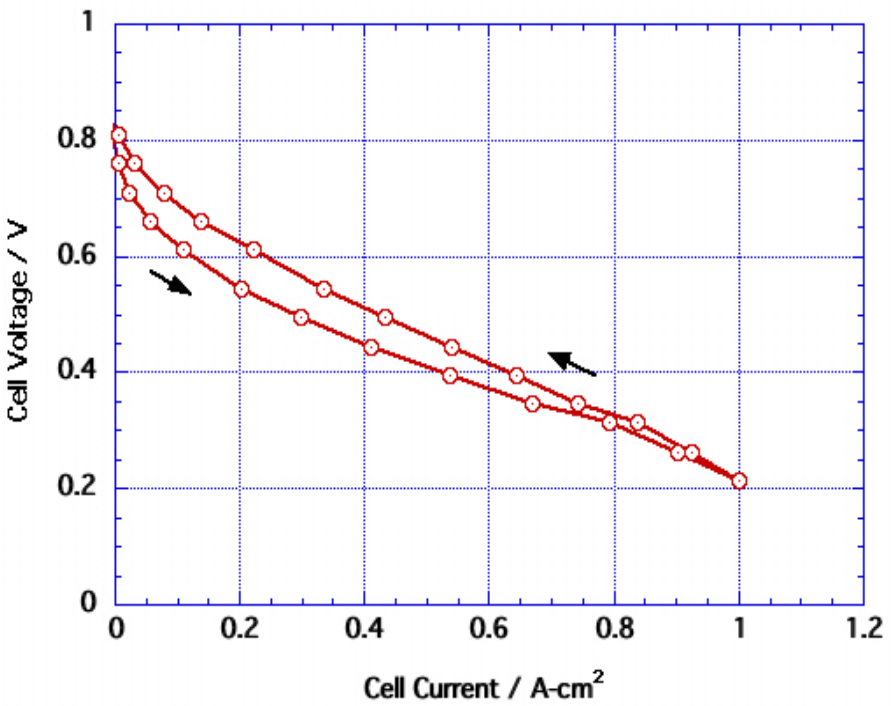
1. The synthesis at 900°C yields large particles of a uniform alloy.
2. The activity of Pd_2Co in RDE experiments is similar to that of Pt (current density and mass-specific activity).

A NON-PLATINUM Pd_2Co ELECTROCATALYST

BROOKHAVEN NATIONAL LABORATORY

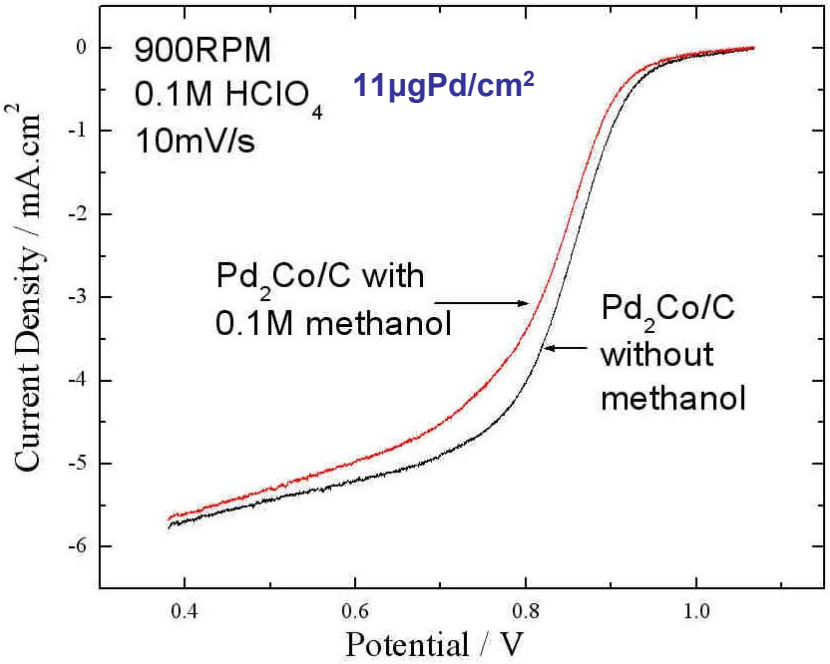
Fuel cell test (F. Uribe)

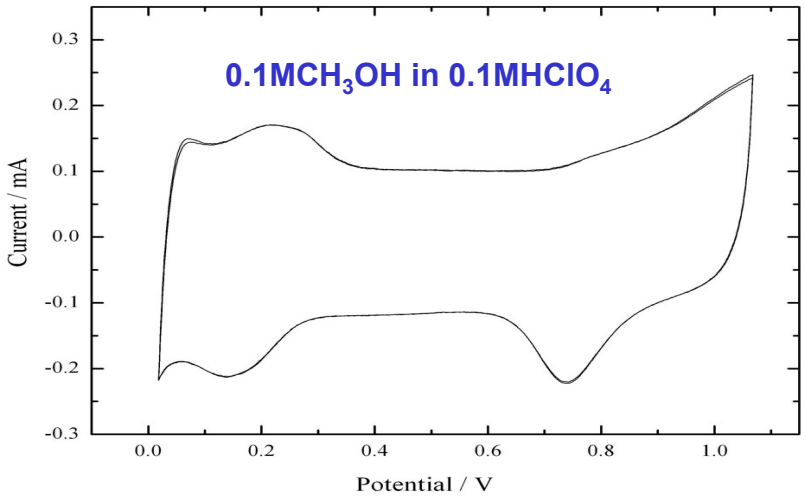
20% Pd_2Co/C (treated at 900°C)



A: 0.20 mg Pt/cm^2 (20% Pt/C ETEK)
C: 0.18 mg Pd_2Co /cm^2

Methanol tolerance





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.

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_{ML}/Pd/C electrocatalyst**
  - Pd particle size effects; surface segregation; post MEA Z-contrast TEM; fuel cell tests.
- **Pd_2Co 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_2Co 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

1. J.X. Wang, N.M. Markovic, R.R. Adzic "Kinetic Simulation of O_2 reduction on Pt(111) in Acid Solutions: Intrinsic Kinetic Parameters and anion adsorption effects", *J. Phys. Chem. B* 108 (2004) 4127.

2. K. Sasaki, J.X. Wang, M. Balasubramanian, J. McBreen, F. Uribe, R.R. Adzic, Ultra-low Platinum Content Fuel Cell Anode Electrocatalyst with a Long-term Performance Stability, Electrochimica. Acta, (special issue) 49 (2004) 3873.

3. J. Zhang, Y. Mo, M.B. Vukmirovic, R. Klie, R. R. Adzic, Platinum Monolayer Electrocatalysts for O_2 Reduction: Pt Monolayer on Pd(111) and on Carbon-supported Pd Nanoparticles, J. Phys. Chem. B, J. Phys. Chem. B, 108 (2004) 10955.
4. J. Zhang, M. B. Vukmirovic, Y. Xu, M. Mavrikakis, R. R. Adzic, Controlling the Catalytic Activity of Platinum Monolayer Electrocatalysts for Oxygen Reduction with Different Substrates, Angew. Chem.. Int. Ed.. 2005, 44, 2132.

5. J. Zhang, M.B Vukmirovic, K. Sasaki, F. Uribe, R.R. Adzic, Platinum monolayer electrocatalysts for oxygen reduction: substrates effects and a long-term stability, J.Serb. Chem. Soc. In press.

6. K. Sasaki, J. Zhang, J. Wang, F. Uribe, R.R. Adzic, Platinum submonolayer-monolayer electrocatalysts – an electrochemical and x-ray absorption spectroscopy study, Research on Chemical Intermediates, in press.

Presentations

Seven papers at national and three at international meetings,

Hydrogen Safety

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.