

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

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)

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)

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 O₂ 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 **Pd₂Co**, and to test them in fuel cells (milestones 2004).
- To explore a novel class of electrocatalysts for O₂ 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:

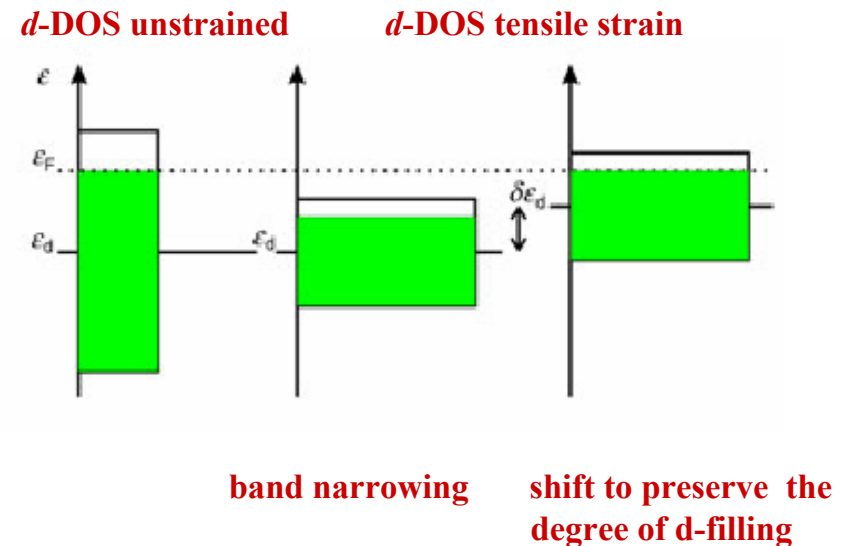
Complete Pt utilization (of all atoms that are not blocked by Nafion®)

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

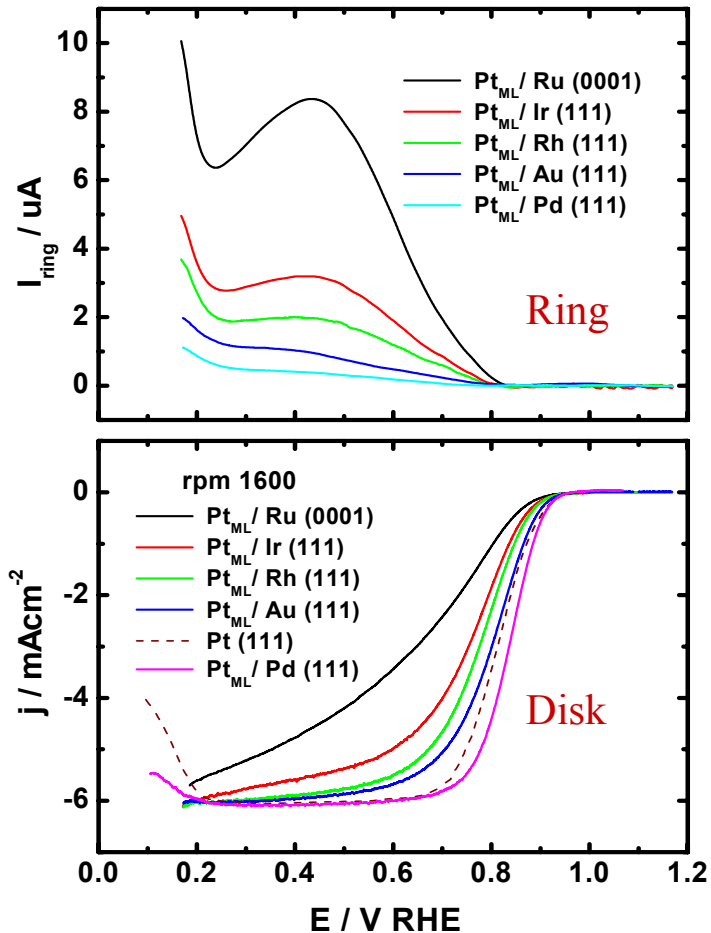


A method for Pt monolayer deposition on metal nanoparticles, involving displacement of a UPD adlayer, was further improved and applied for depositing mixed-metal monolayers.

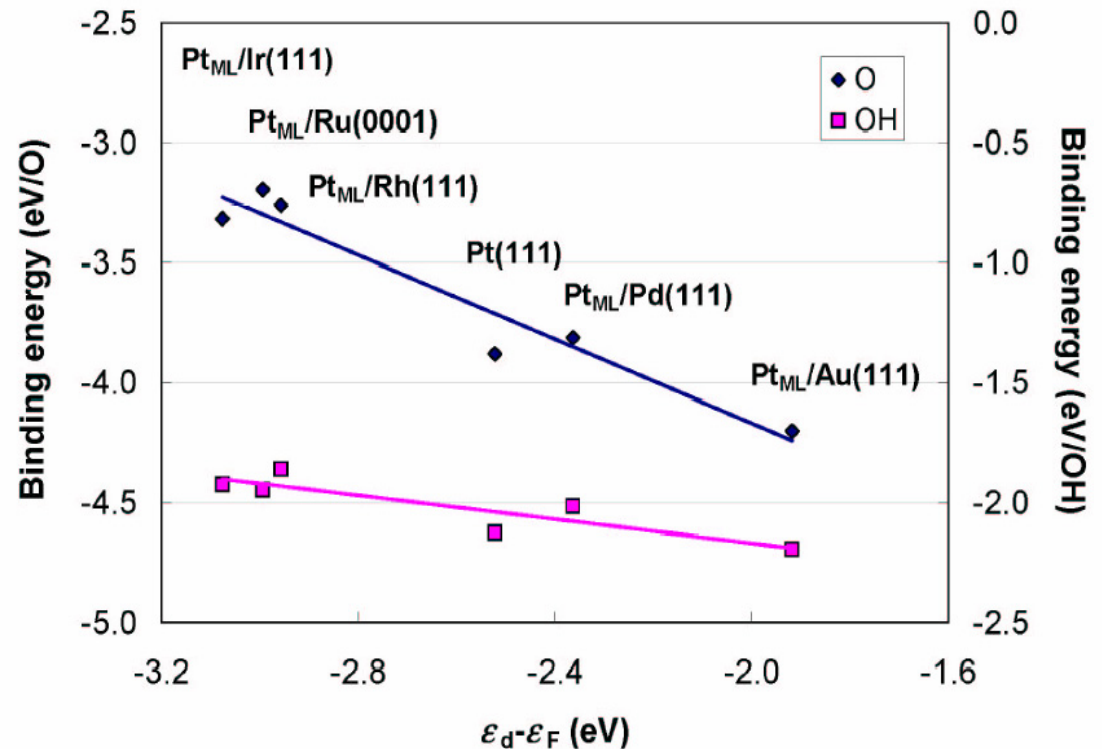
SUBSTRATE EFFECTS ON Pt MONOLAYER ACTIVITY

- 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

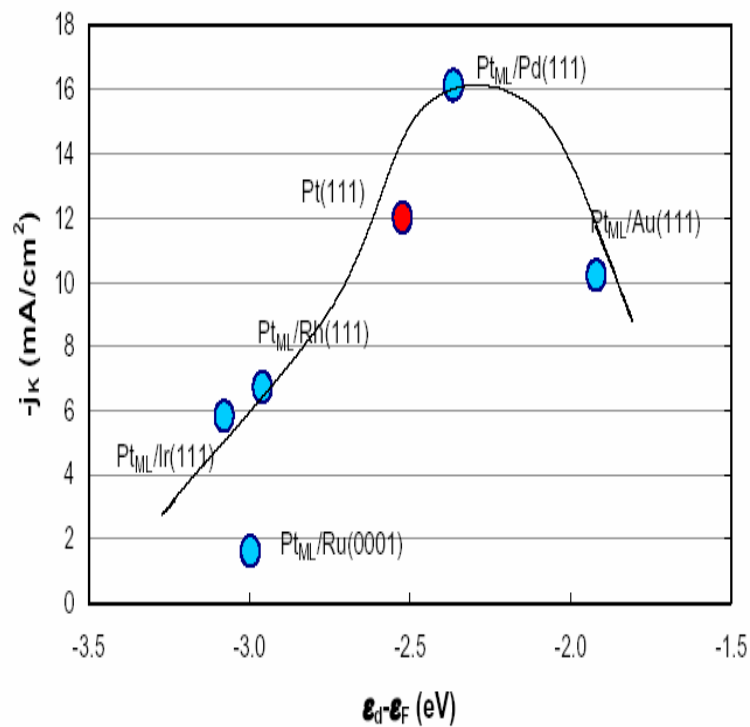


1. Pt/Pd(111)- slight compression, electronic effect and reduced OH coverage – high activity
2. Pt/ Au(111) – Pt is highly expanded - *d*-band center increases - the bond between Pt and the ORR intermediates is too strong.

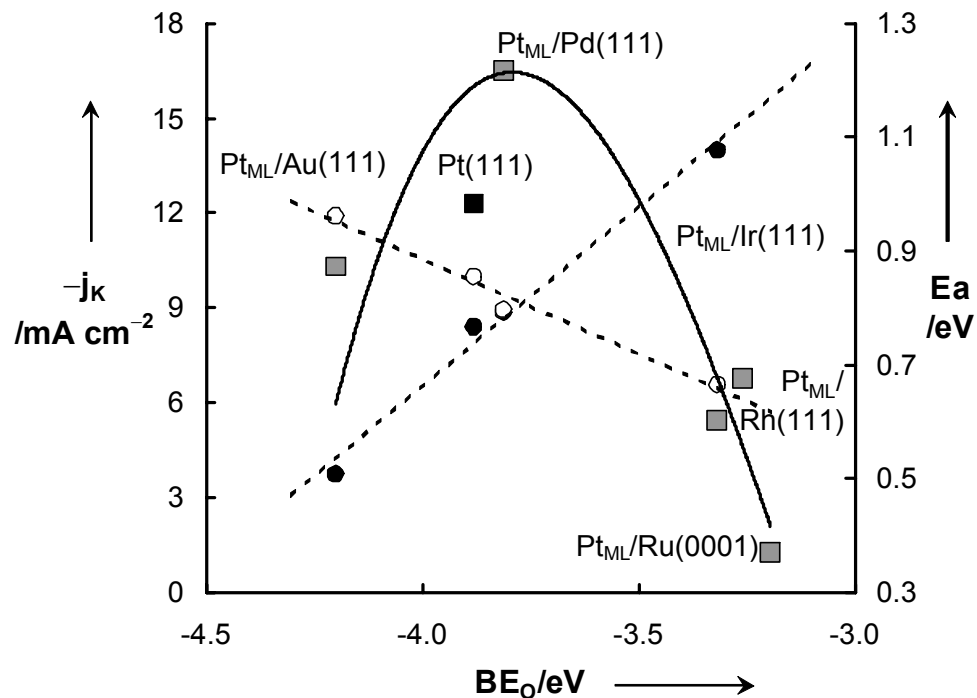
SUBSTRATE EFFECTS ON Pt MONOLAYER ACTIVITY

- ACTIVITY - CENTER OF THE *d*-BAND VOLCANO PLOT-

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



Activation energies for O₂ dissociation (●) and OH formation (○)



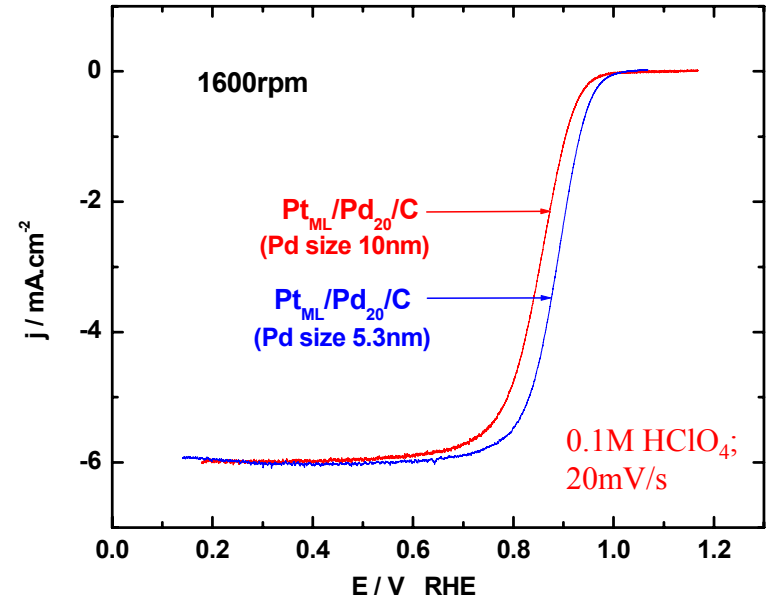
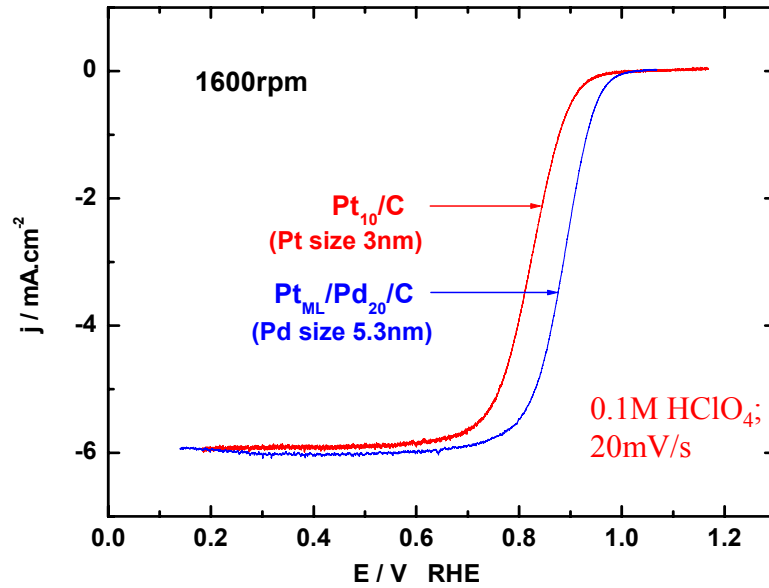
Angew. Chem. Int. Ed.. 2005, 44, 2132.

E_a 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.

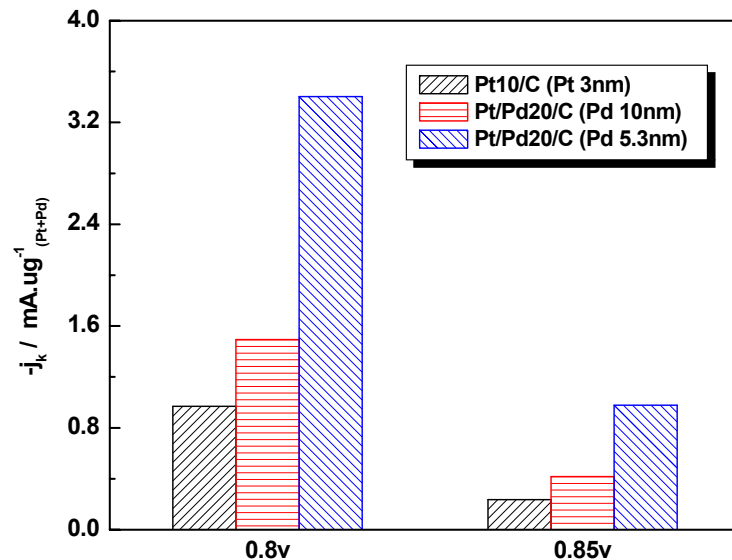
Volcano plot → balance between two competing influences (breaking O-O and forming O-H).

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

O₂ reduction on a Pt ML on 5nm Pd nanoparticles; 2.3 – 5.7 μg_{Pt}/cm².



Total noble metal mass-specific activity



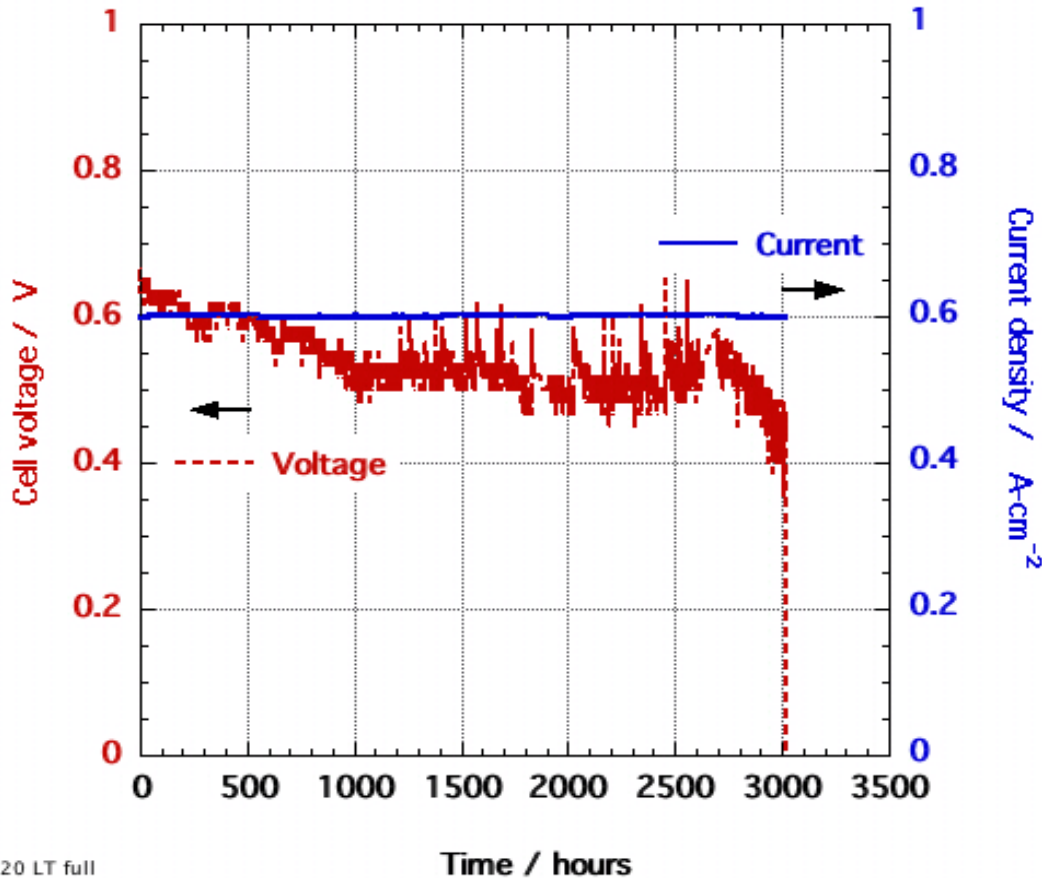
1. A higher activity is observed for a 5 nm Pd support than for 9nm particles due to the larger surface area. (Impurity effects were observed with the 5nm Pd/C).

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 $\mu\text{g Pt}/\text{cm}^2$ (4% Pt - 20% Pd)



Voltage losses after 2900 hr of testing at constant current ($0.6 \text{ A}/\text{cm}^2$):

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 ; 80°C .

BNL 20 LT full

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

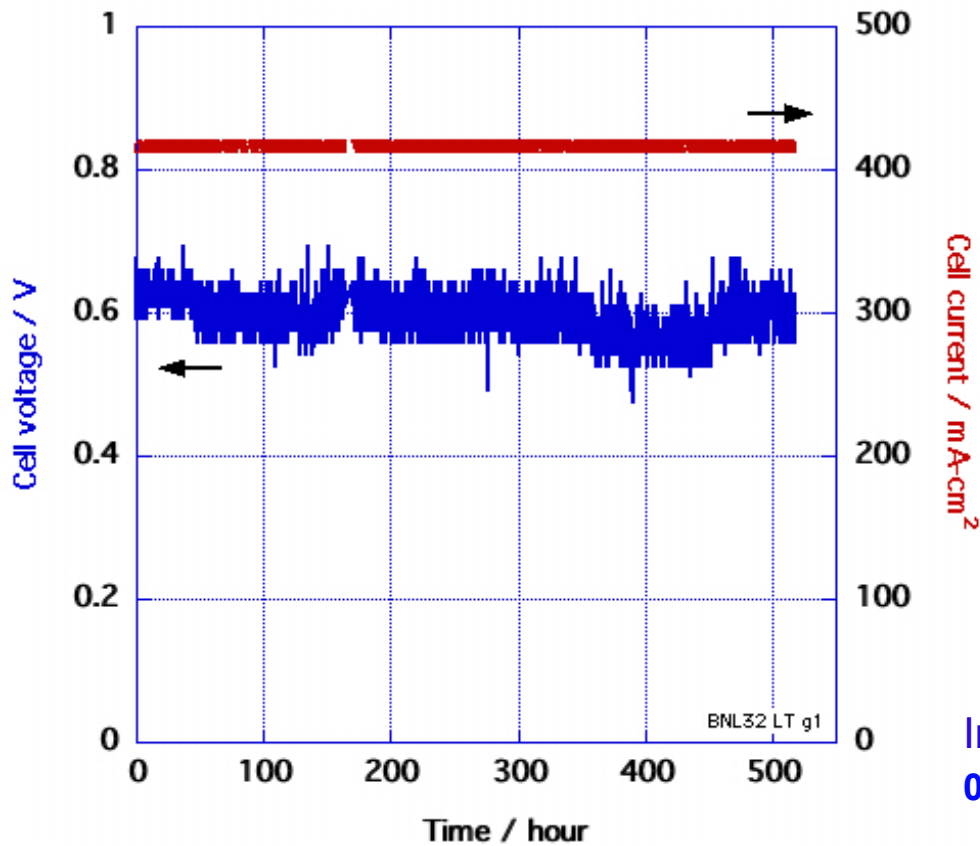
The catalyst's performance ranges from $0.17\text{gPt}/\text{kW}$ to $0.25\text{gPt}/\text{kW}$, which is below the DOE 2005 target of $1.35\text{gPt}/\text{kW}$ ($1/2 \times 2.7$).

Low Pt Content Fuel Cell

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

Test in-progress

Constant current test (0.4 A/cm²)



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,

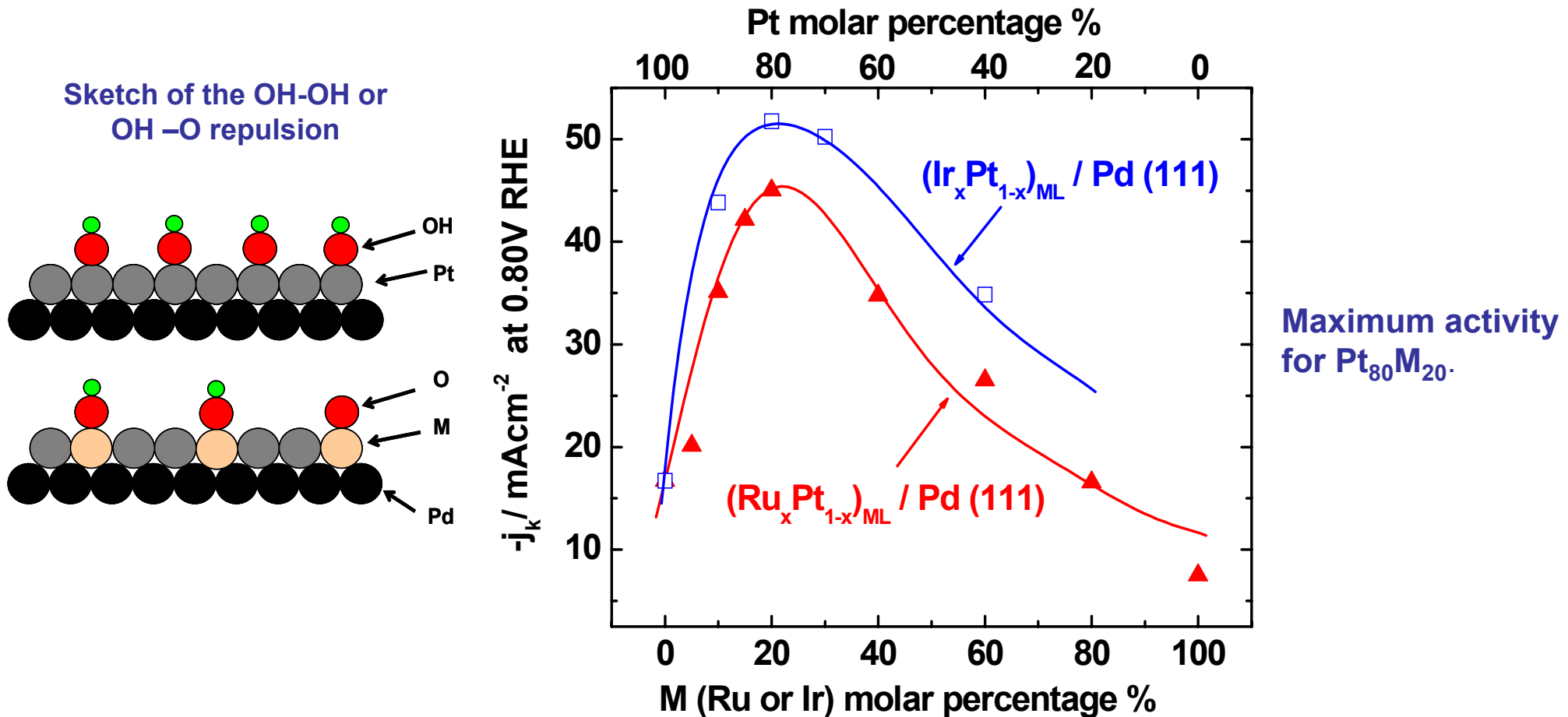
Voltage: 0.602 V,

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.

Mixed-metal Pt Monolayer Electrocatalysts

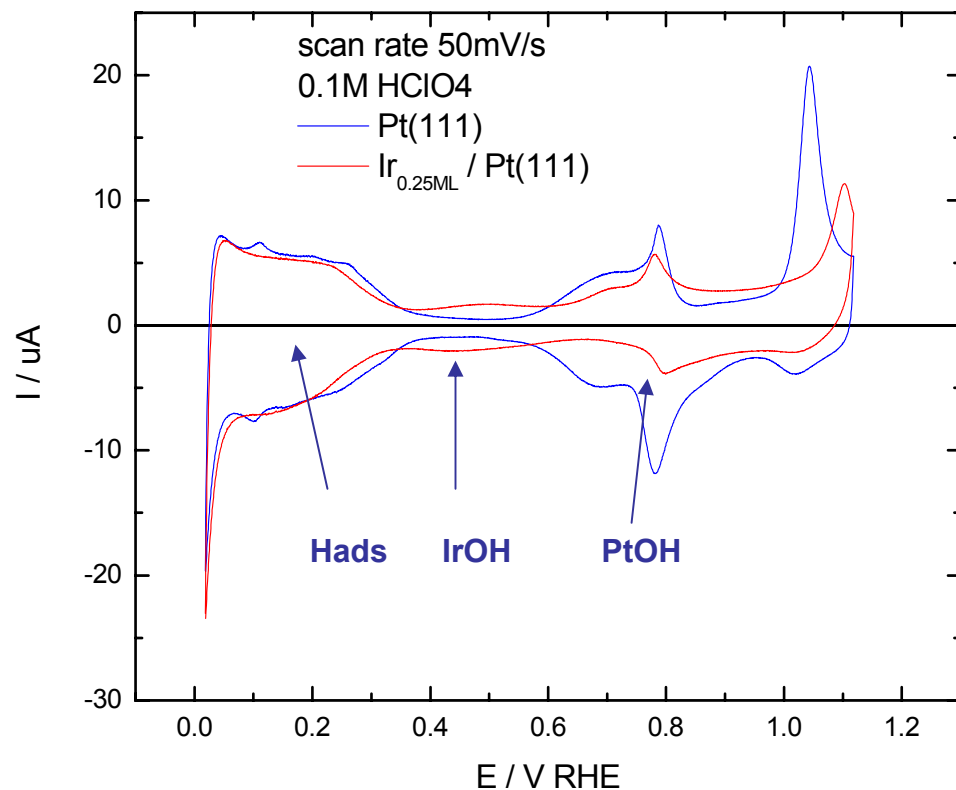


- A new class of the ORR electrocatalysts was synthesized – a Pt monolayer that is mixed with a metal with a high coverage of OH or O.
- Due to the OH-OH (O) repulsion, PtOH formation decreases, causing an increase in the ORR activity (by a factor of 4 at 0.8V for $\text{Pt}_{80}\text{Ir}_{20}$).
- Pt 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

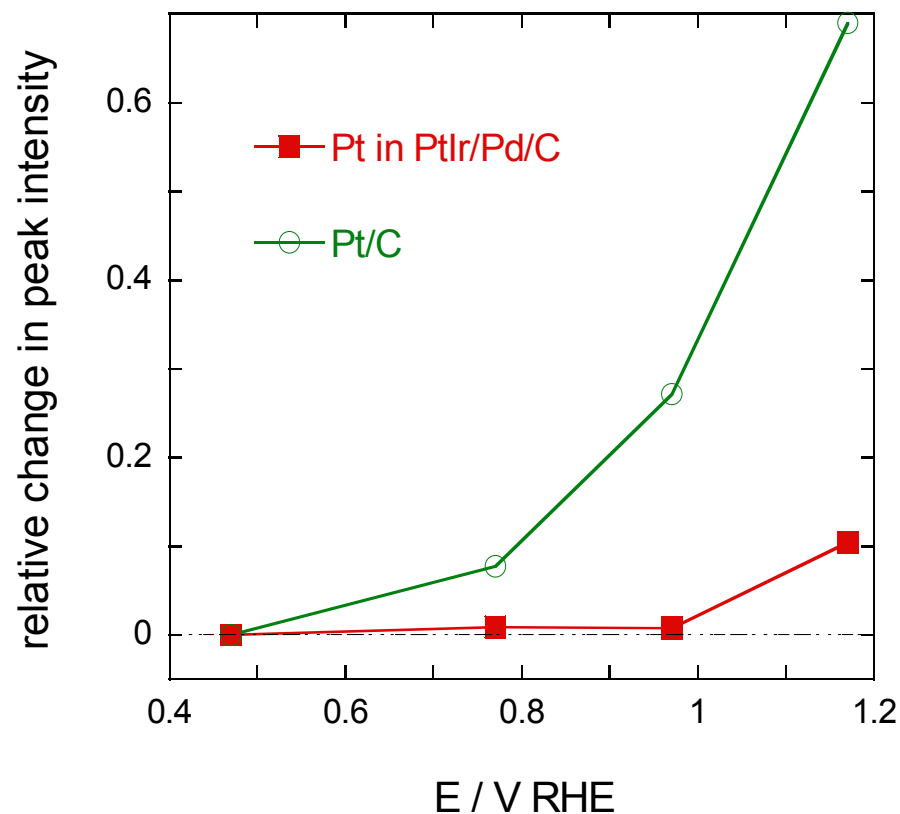
Evidence for the decreased PtOH coverage

single crystals, 0.25ML Ir on Pt(111)



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

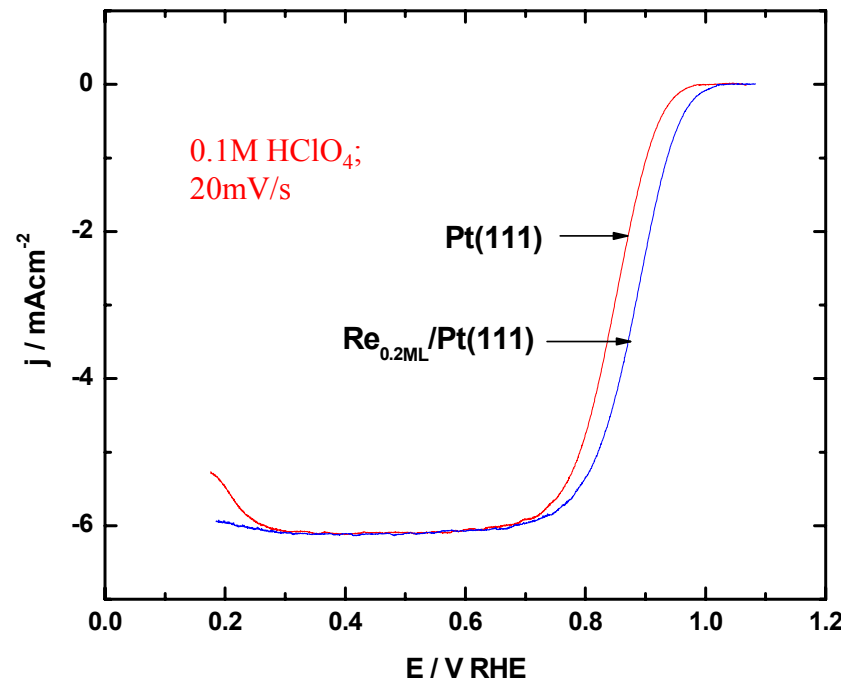
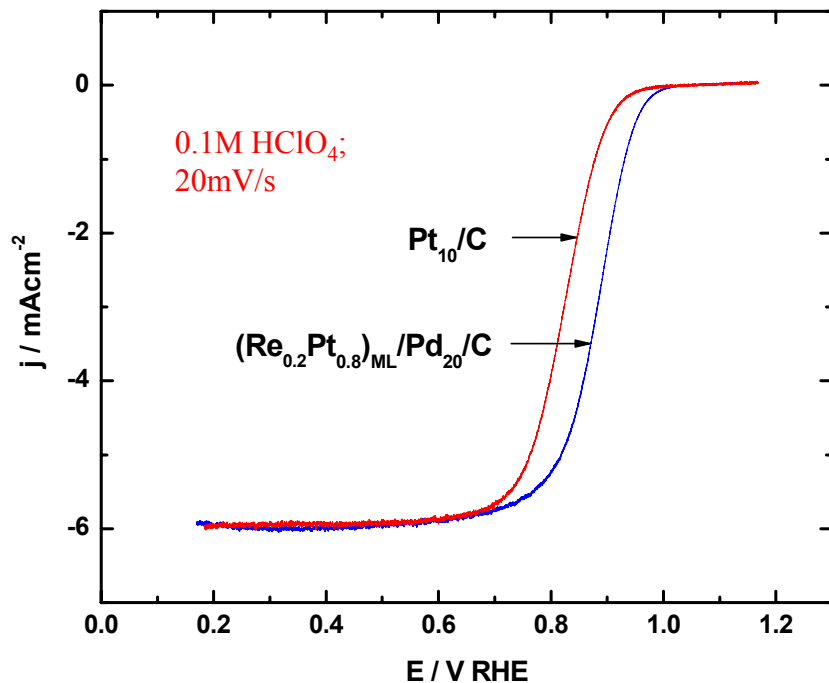
Pt₈₀Ir₂₀/Pd/C nanoparticles



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).

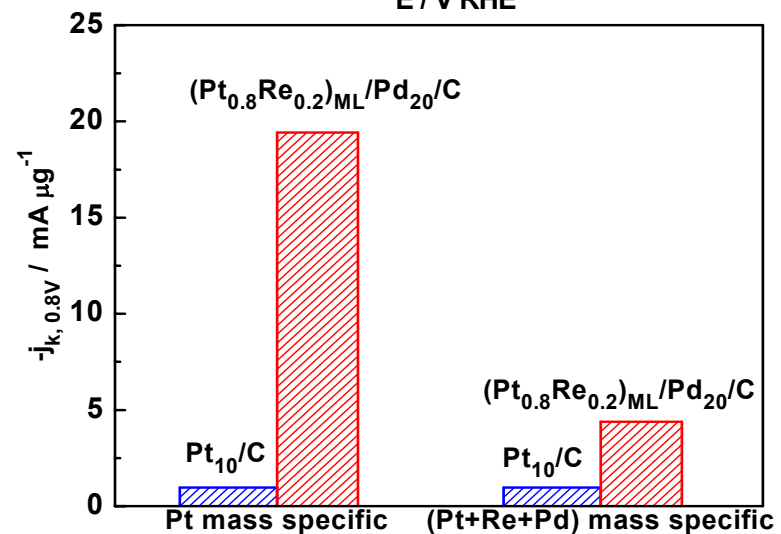
Mixed-metal Pt Monolayer Electrocatalysts

$\text{Pt}_{0.8}\text{Re}_{0.2}/\text{Pd}/\text{C}$ and $\text{Re}_{0.2\text{ML}}/\text{Pt}(111)$



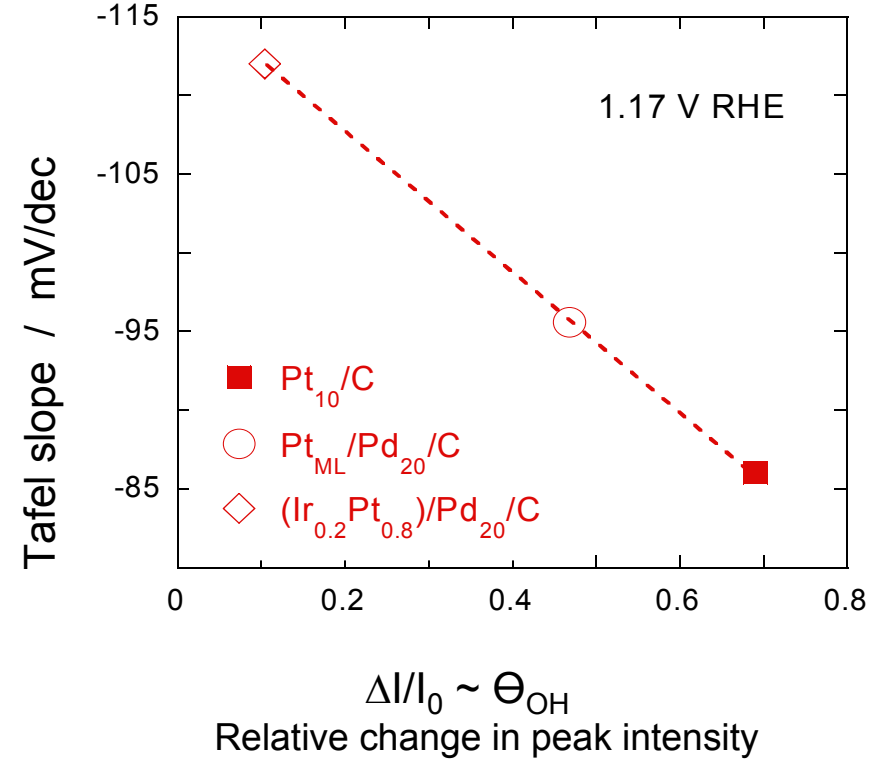
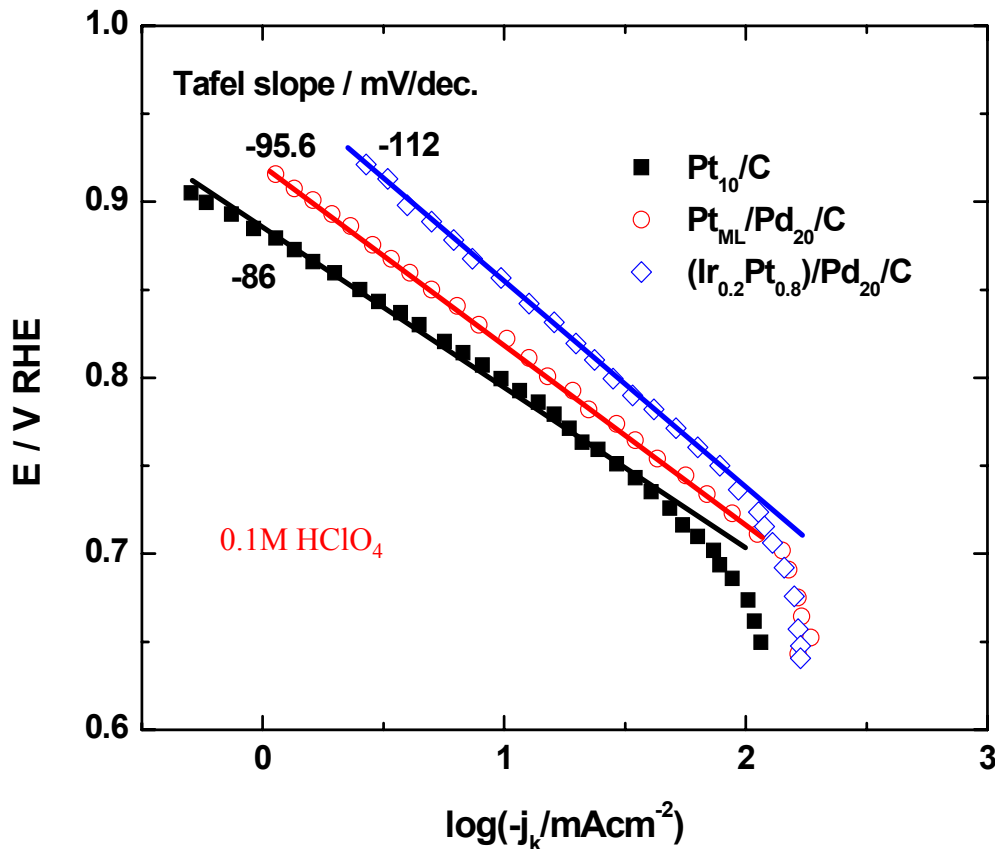
The **Pt mass-specific activity** of a $\text{Pt}_{0.8}\text{Re}_{0.2}/\text{Pd}/\text{C}$ is about **20 times** that of **Pt/C**.

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



PtOH coverage, O₂ reduction rates and the Tafel Slopes

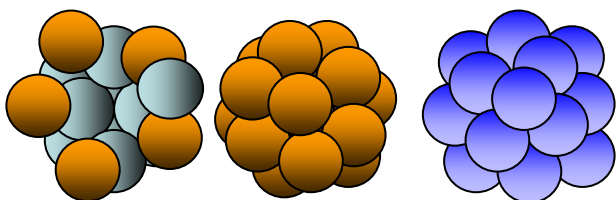
1. Consensus exists that the OH_{ads} inhibits the ORR.
2. The intrinsic Tafel slope for Pt (no adsorbates other than the ORR intermediates) is -120mV/dec. The OH adsorption causes low slopes. (Quantitative analysis in J. Phys. Chem., B 108 (2004) 4127).
3. Evidence from XANES data: **Decreasing the OH coverage results in higher slopes and higher activity.**



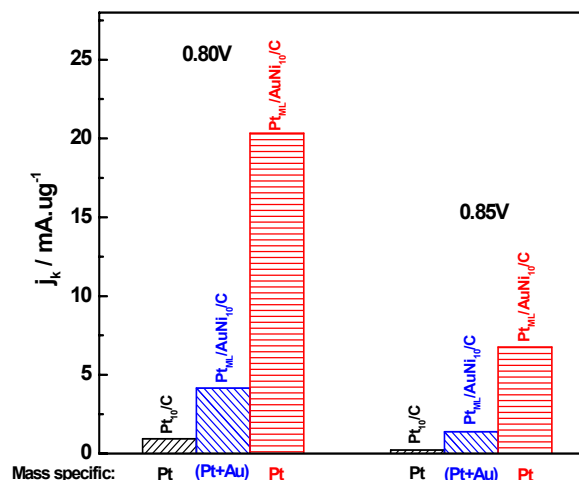
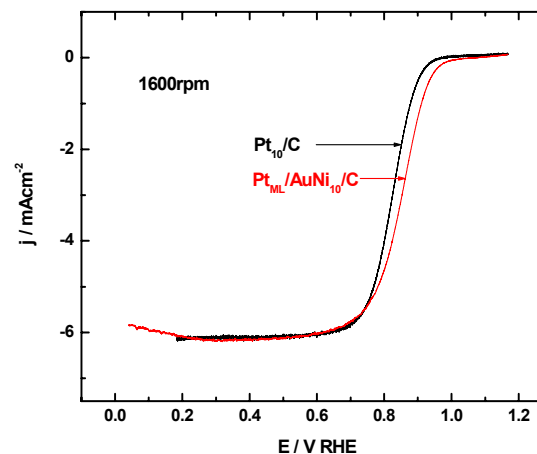
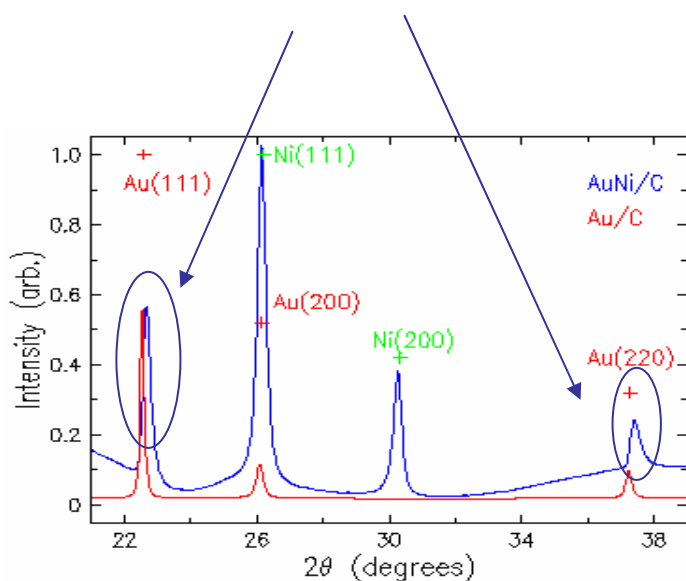
Milestone for FY 2004—further improvements in 1. Synthesis and 2. Activity

Synthesis

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



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

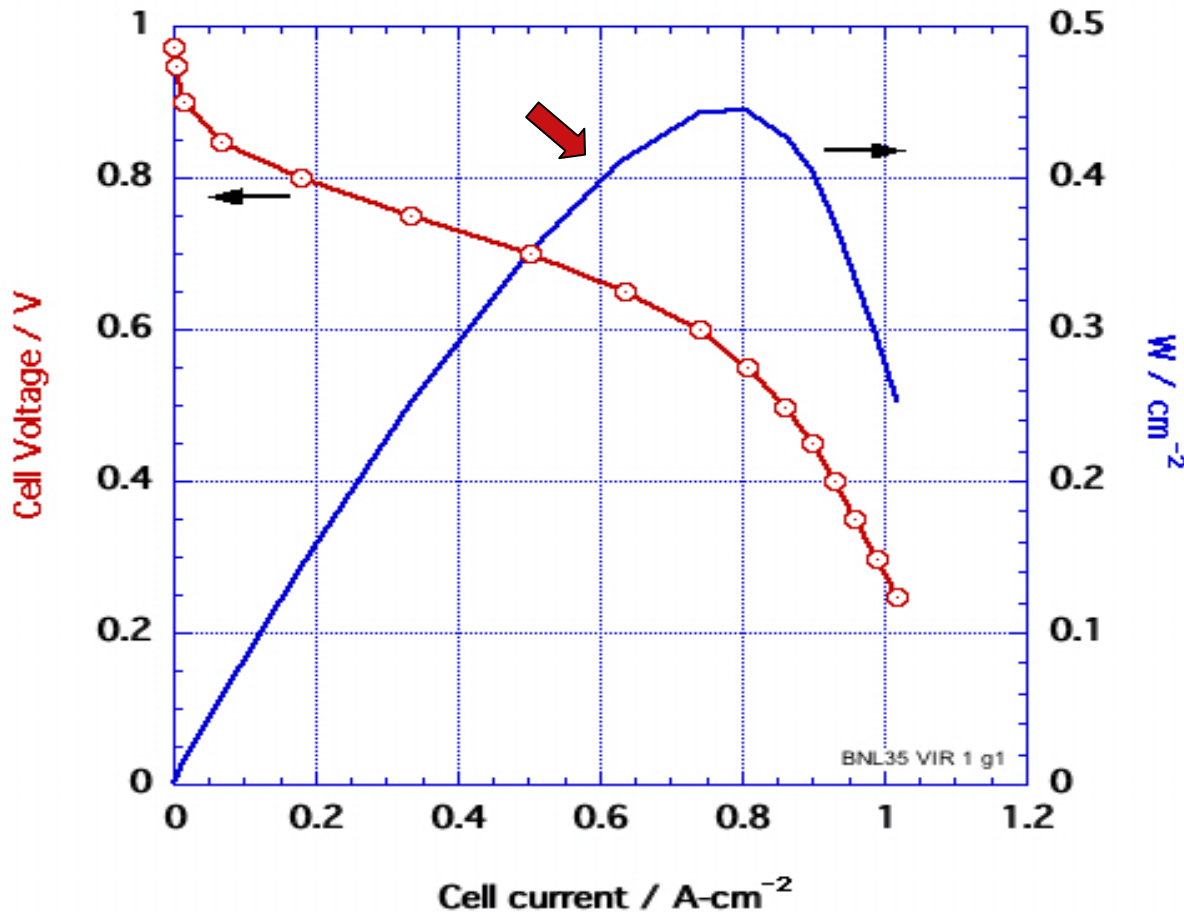


1.03 $\mu\text{g}/\text{cm}^2$ of Pt + 4 $\mu\text{g}/\text{cm}^2$ of Au vs. 12 $\mu\text{g}/\text{cm}^2$ of Pt

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 cm²

A: 0.077 mg Pt/cm² (20% Pt/C, ETEK)

C: 0.169 mg Total metal/cm²

(19 μg Pt; 37 μg 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.

→ Catalyst performance at 0.6 A/cm²

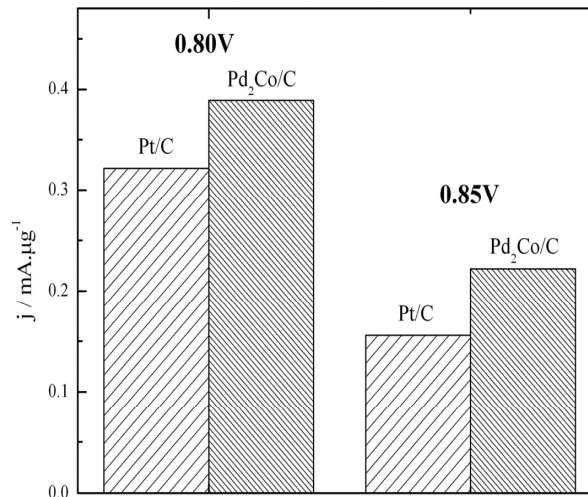
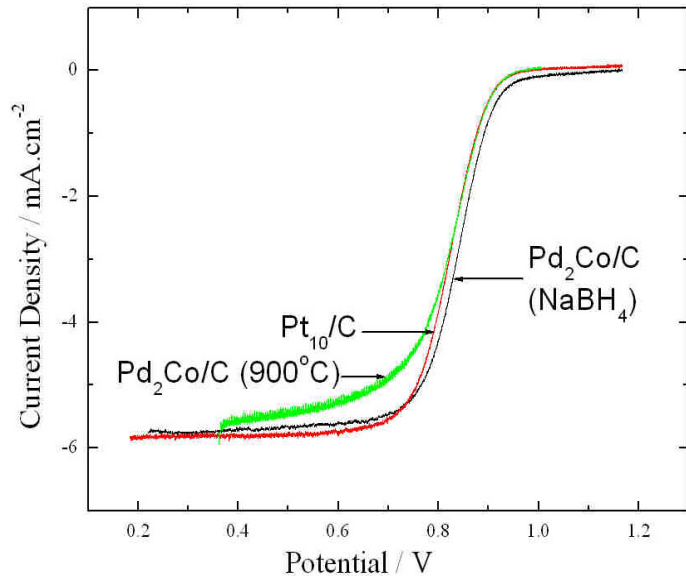
Composition	g Pt/kW cathode	g Pt+Au/kW cathode	g Pt/kW cell	g Pt+Au/kW cell
Performance	0.05	0.14	0.24	0.33

A NON-PLATINUM Pd₂Co ELECTROCATALYST

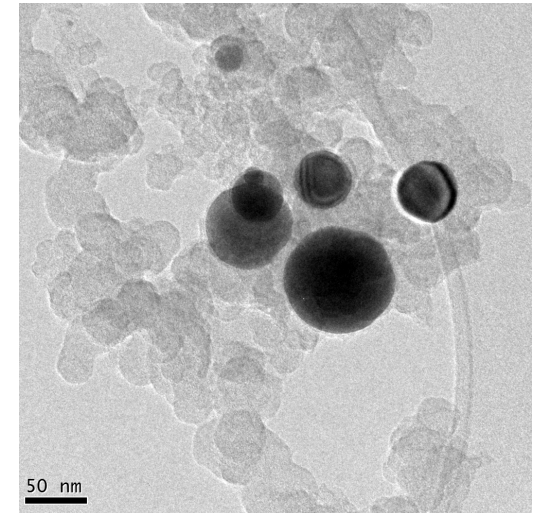
Milestone for FY 2004— 1. Activity (improved, RDE) 2. Fuel Cell test – low activity
3. Excellent methanol tolerance

11μg/cm² of Pd vs. 12μg/cm² of Pt; 0.1MHClO₄; 25°C; 20mV/s

--- 20% Pd₂Co/C (treated at 900°C) ---

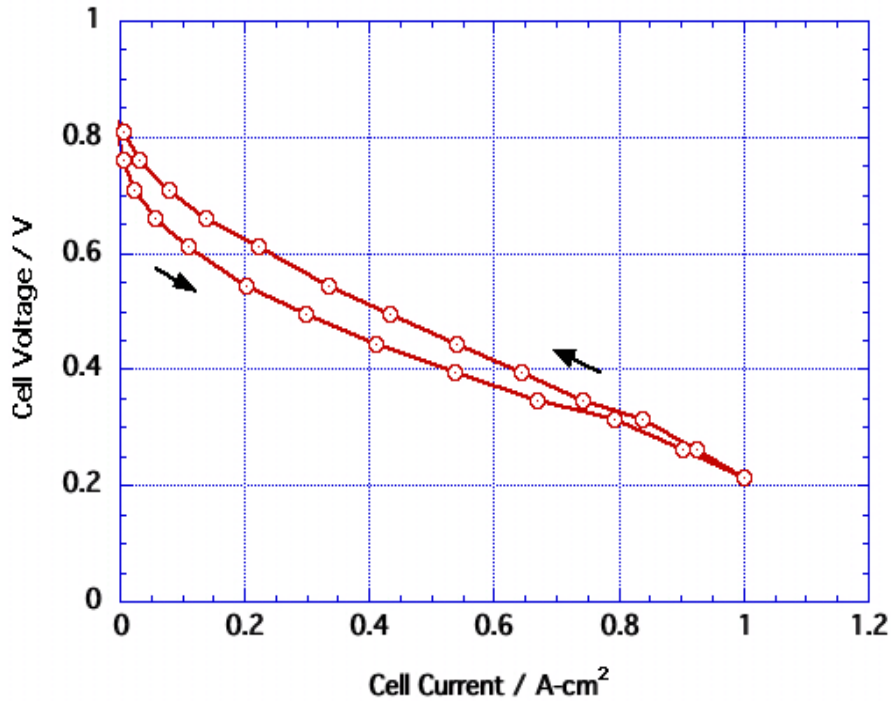


Pd or Pt mass-specific activity



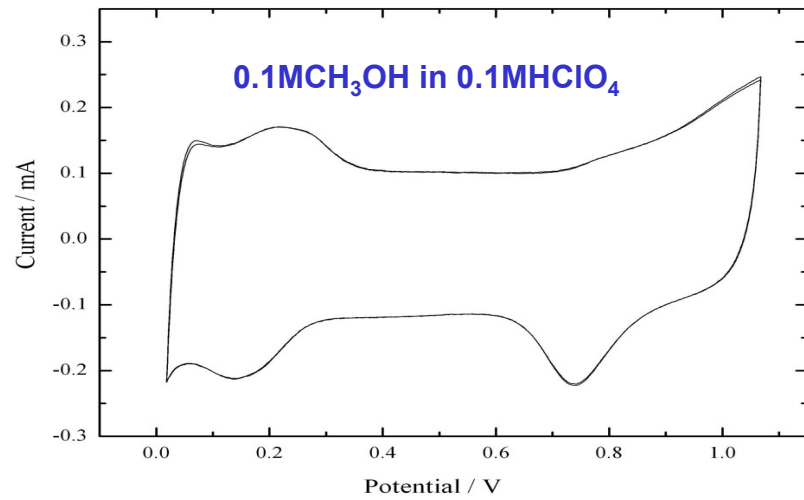
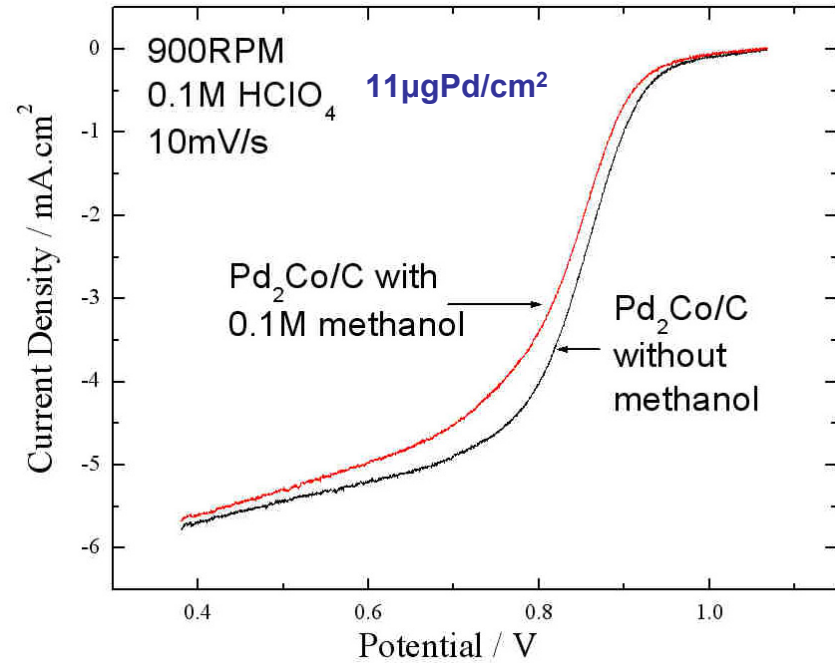
1. The synthesis at 900°C yields large particles of a uniform alloy.
2. The activity of Pd₂Co in RDE experiments is similar to that of Pt (current density and mass-specific activity).

Fuel cell test (F. Uribe) 20% Pd₂Co/C (treated at 900°C)



A: 0.20 mg Pt/cm² (20% Pt/C ETEK)
C: 0.18 mg Pd₂Co /cm²

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.
- **Pd₂Co 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.
- **Pd₂Co 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 O₂ 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 O₂ 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 H₂ if hood is not operating properly. Presently, the studies involving H₂ oxidation are rarely conducted.