

Low Pt Loading Fuel Cell Electrocatalysts

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

Chemistry Department
Brookhaven National Laboratory, Upton, NY 11973-5000

(This presentation does not contain any proprietary or confidential information.) Project ID # FC09

Overview

Timeline

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

Budget

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

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 PtRu₂₀ anode catalyst: **2390 hr** showed a small loss in activity (B. Do).
- General Motors Co. planning stage (F. Wagner)

Barriers addressed

1. **Precious metal loading**
2. **Electrocatalysts' Activity**
3. **Electrocatalysts' Durability**

Target 2010: 0.3 g/kW

Target 2010: 5000hr

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 ($\text{Pt}_{80}\text{Ir}_{20}/\text{Pd}/\text{C}$) 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.

APPROACH

Pt monolayer electrocatalysts

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)

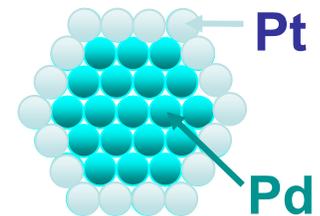
For 3-5nm nanoparticles **~25% of atoms** are on the surface,
~75% are not available for catalysis.

Three types of Pt electrocatalysts:

1. Pt on Pd nanoparticles

Improved activity

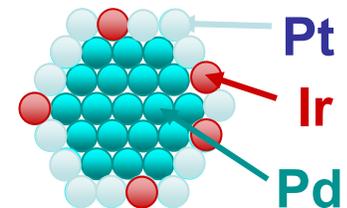
Improved durability



2. Mixed-metal Pt on Pd nanoparticles

Even higher activity

Durability tests at LANL
and Battelle

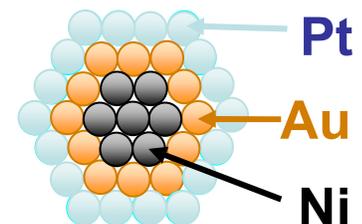


3. Pt on noble/non-noble core-shell nanoparticles

Yet higher activity

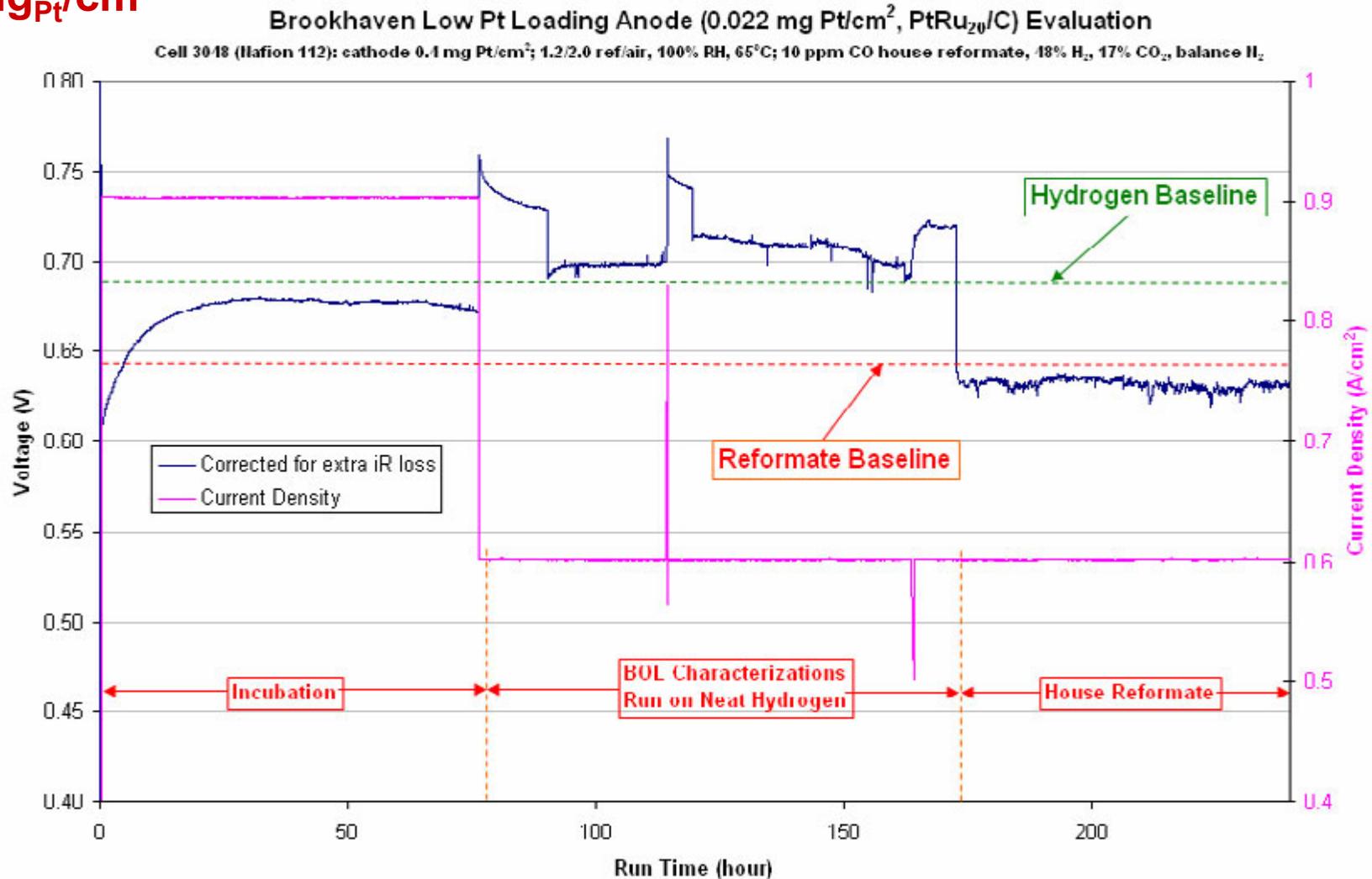
per mass of noble metal

Durability to be tested



Long-term test (one segment) of the anode PtRu₂₀ electrocatalyst at PLUG POWER

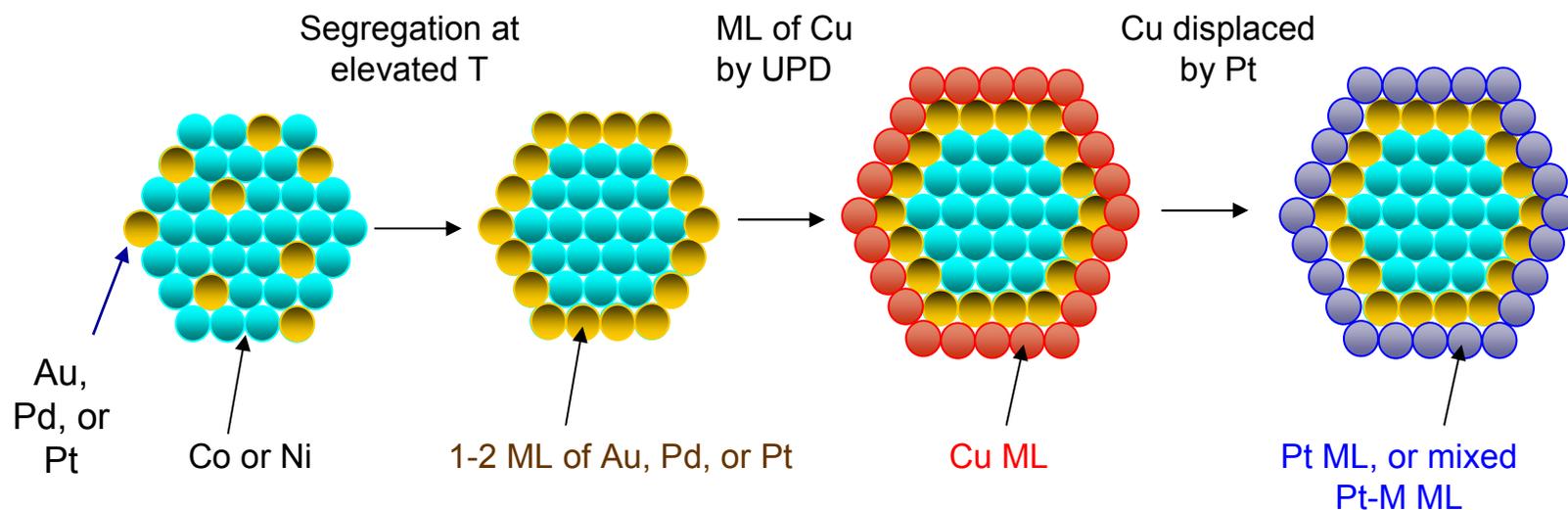
0.022 mg_{Pt}/cm²



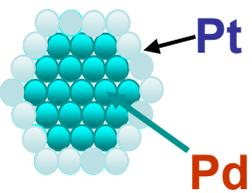
Compared to commercial MEA baselines (0.6 mg Pt/Ru/cm²):
Higher than neat H₂ baseline; lower than reformat baseline.
Total run time: 2394 hours

New class of catalysts: Pt monolayer on *noble metal - non-noble metal core-shell* nanoparticles

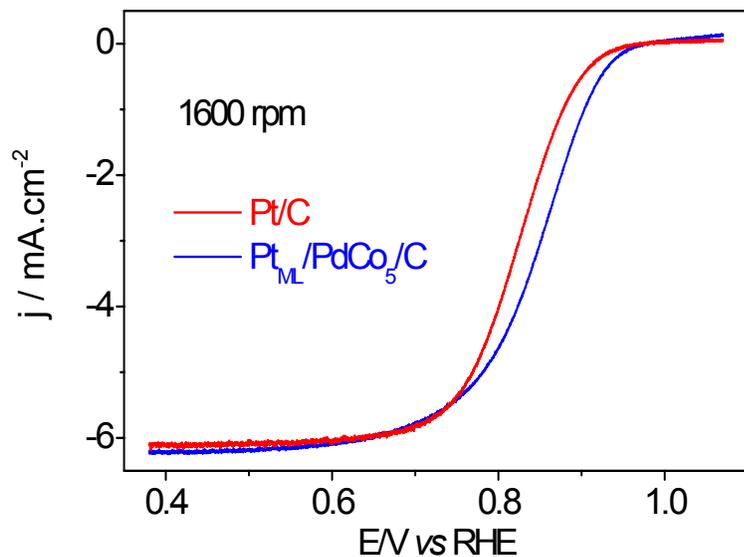
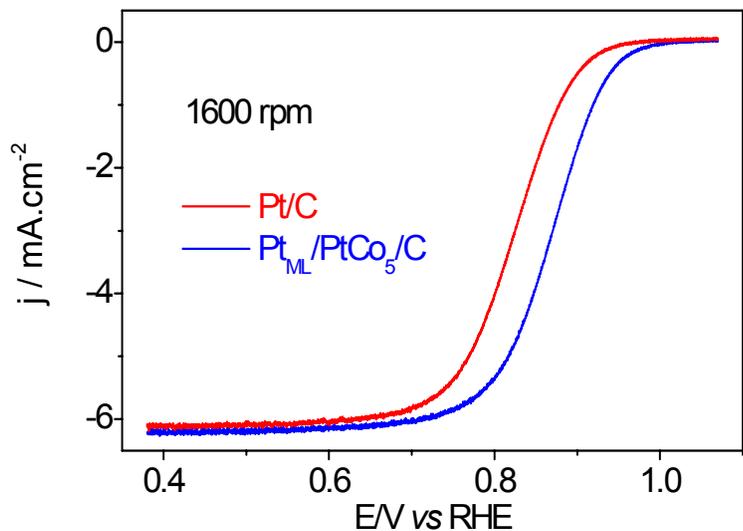
Synthetic route



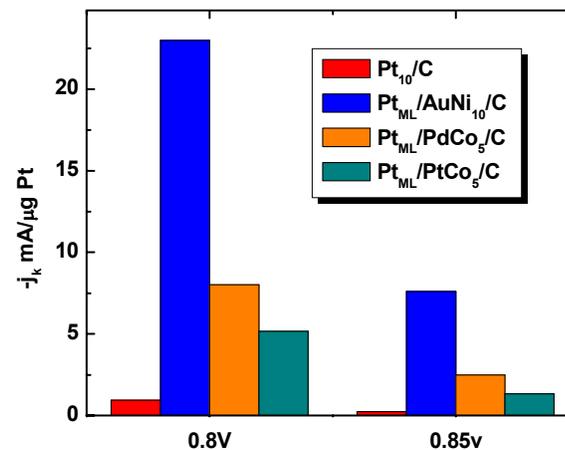
New class of electrocatalysts that facilitate a **further decrease of noble metal content** while possessing a very high activity.



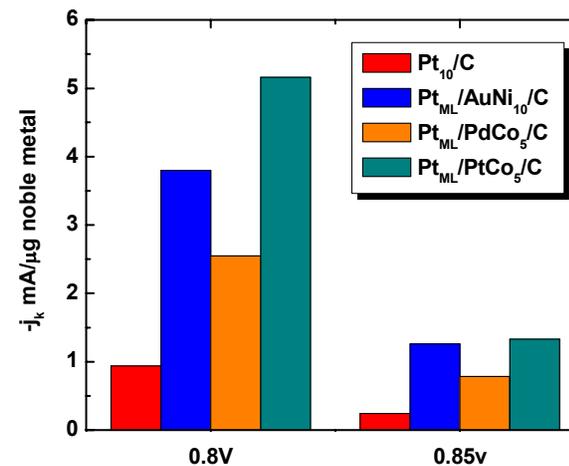
O₂ Reduction Kinetics and Mass Activities of Pt_{ML}/PtCo₅/C and Pt_{ML}/PdCo₅/C



Pt mass activity



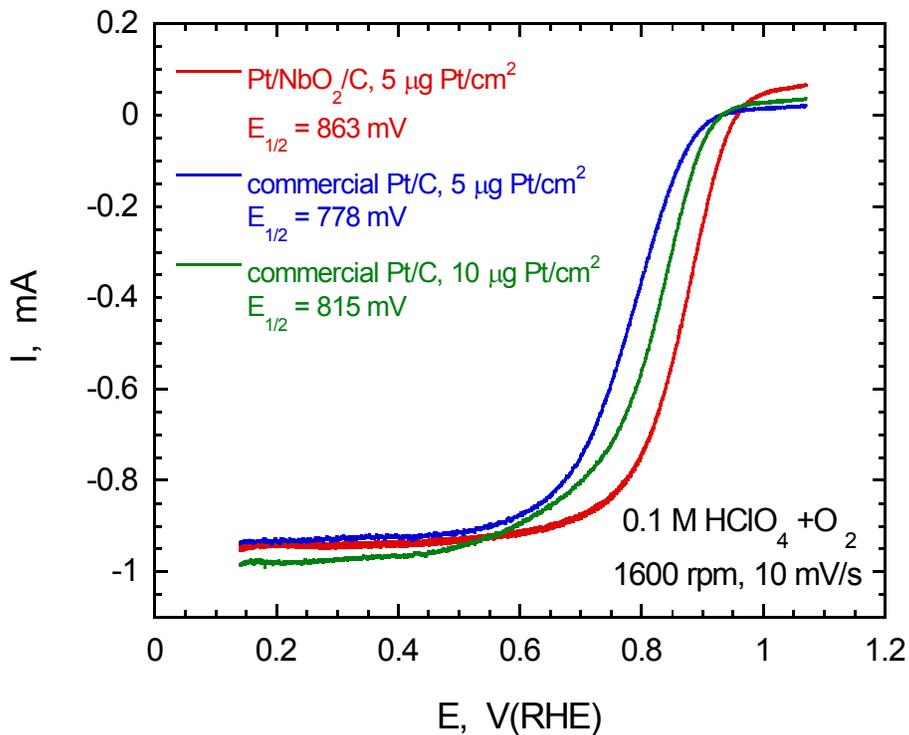
Total noble metal mass activity



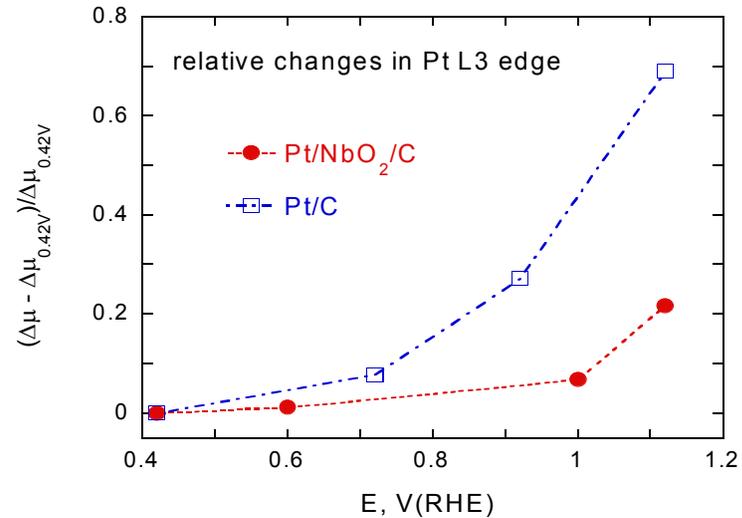
2- to 5-fold increase in noble metal mass activity with Pt on core-shell nanoparticles

O₂ Reduction Kinetics and Mass Activities of Pt_{ML}/NbO₂/C and Pt/C/C

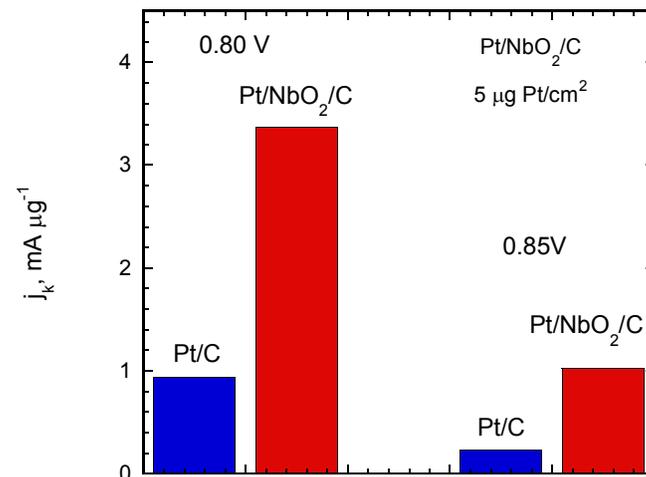
Pt is not observed by XRD in Pt/NbO₂/C



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

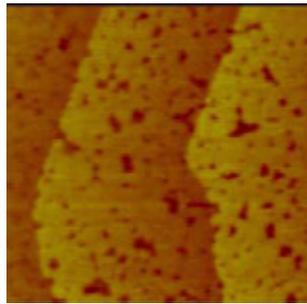


XANES shows a small oxidation of Pt/NbO₂/C compared to Pt/C.

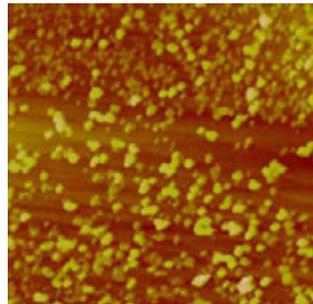


Formation of Au clusters on Pt electrodes

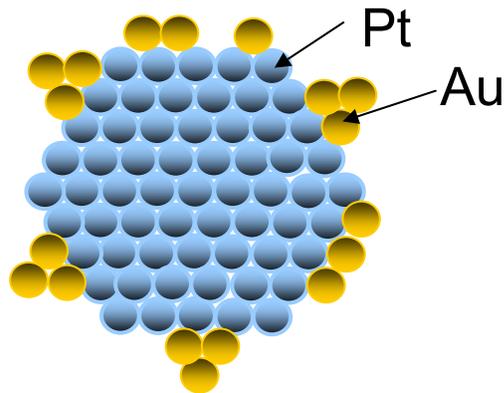
2D Au deposited on Pt(111); 3D formed after several cycles to 1.2V in O₂ saturated solution



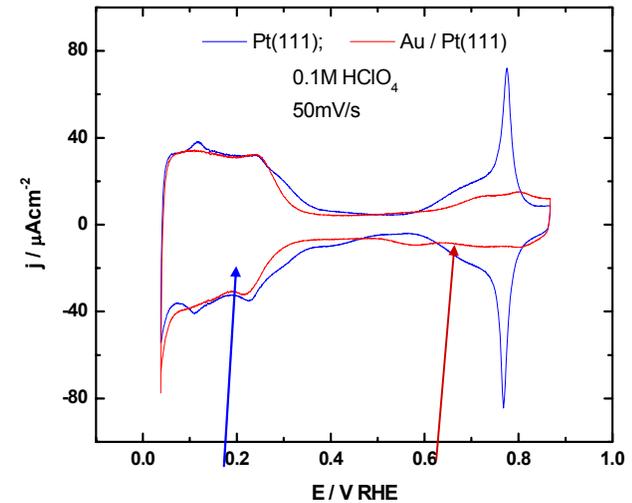
115 nm x 115 nm



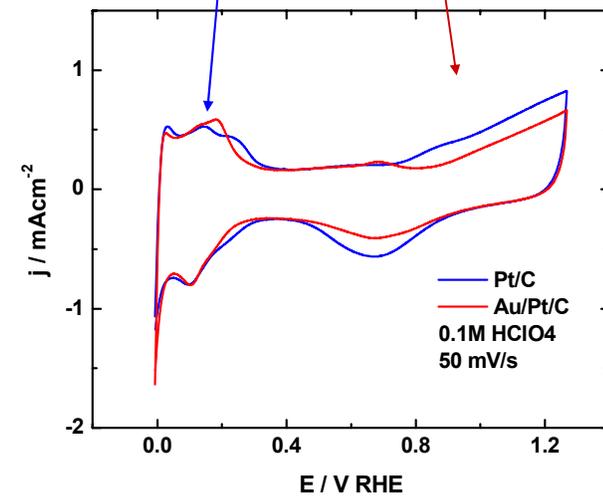
120 nm x 120 nm



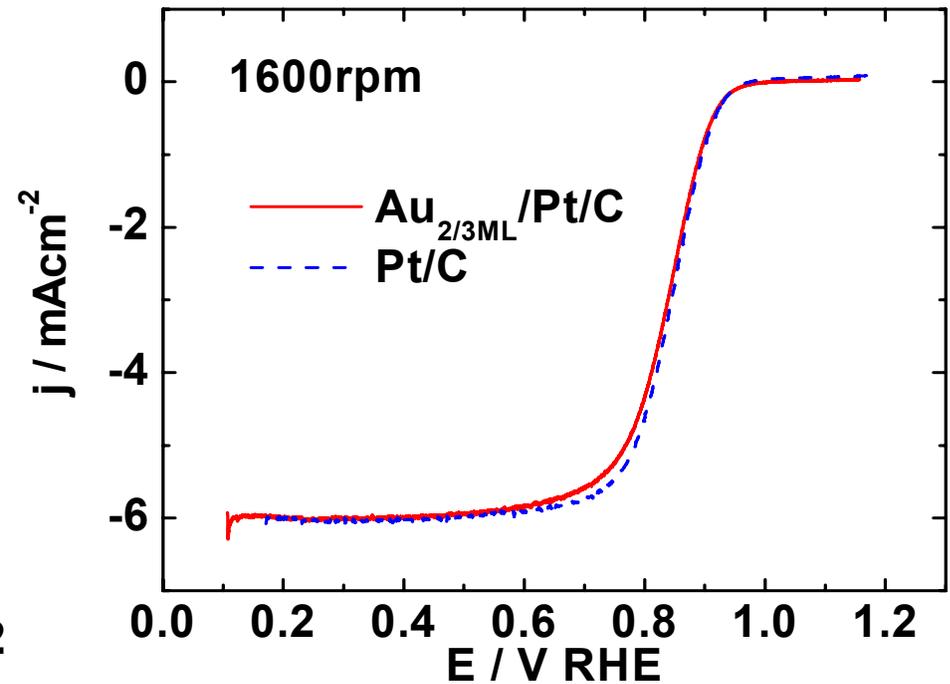
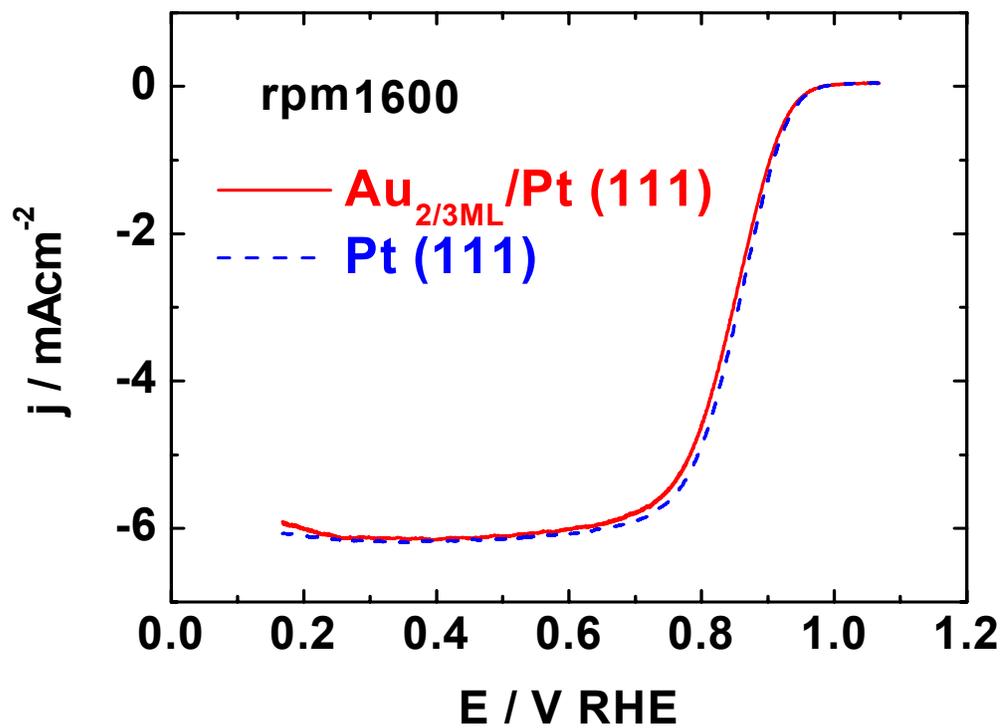
Model of Au clusters on Pt nanoparticle



No effect on H ads. Inhibition of OH ads.



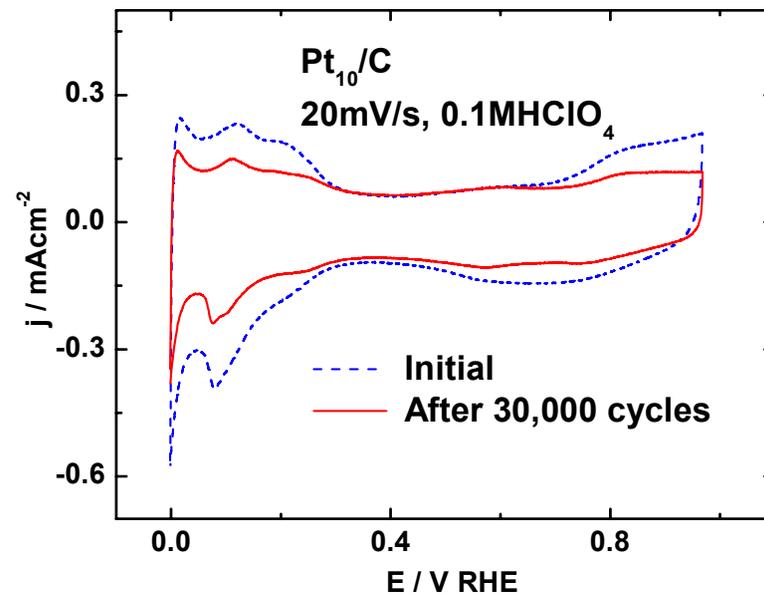
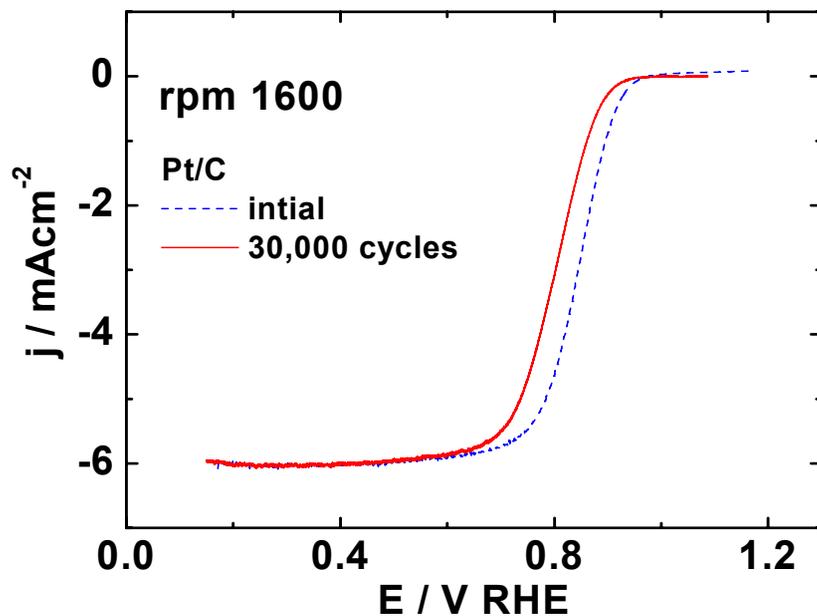
Effect of submonolayer of Au clusters on O₂ reduction on Pt(111) and Pt/C



Small inhibition of O₂ reduction by Au, not in proportion to Au coverage

Effect of potential cycling on the activity of Pt/C in the ORR

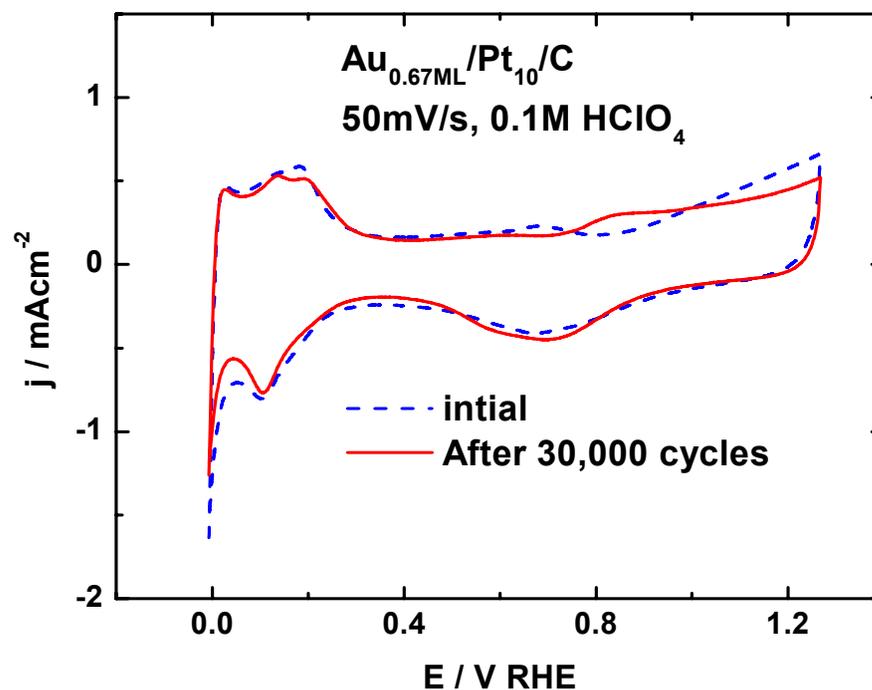
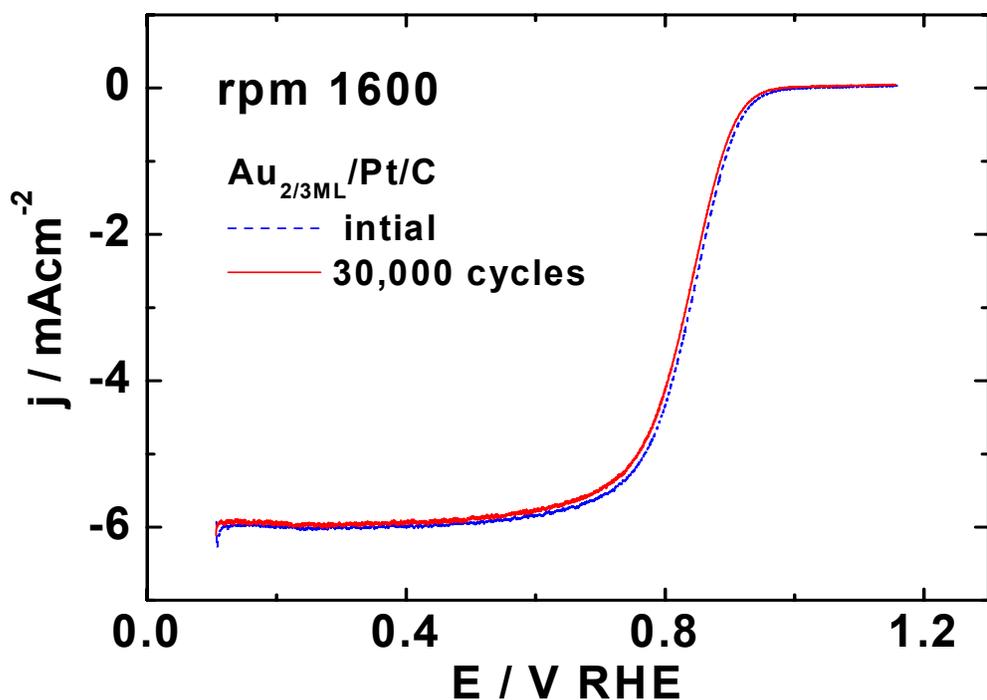
30,000 cycles from 0.6 to 1.1V at 25°C in O₂-saturated solution



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

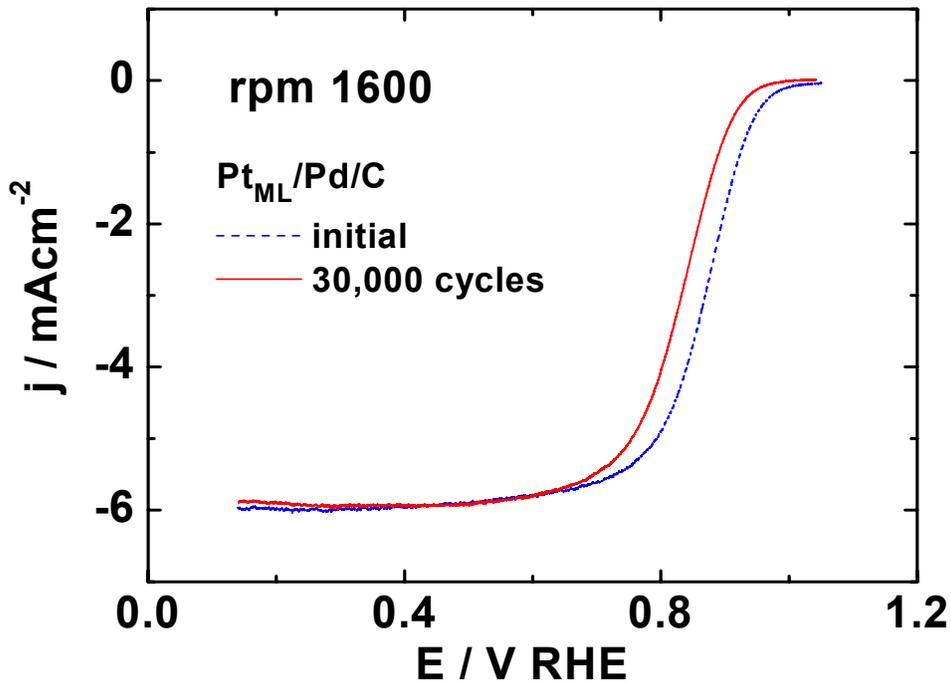
30,000 cycles from 0.6 to 1.1V at 25°C in O₂-saturated solution



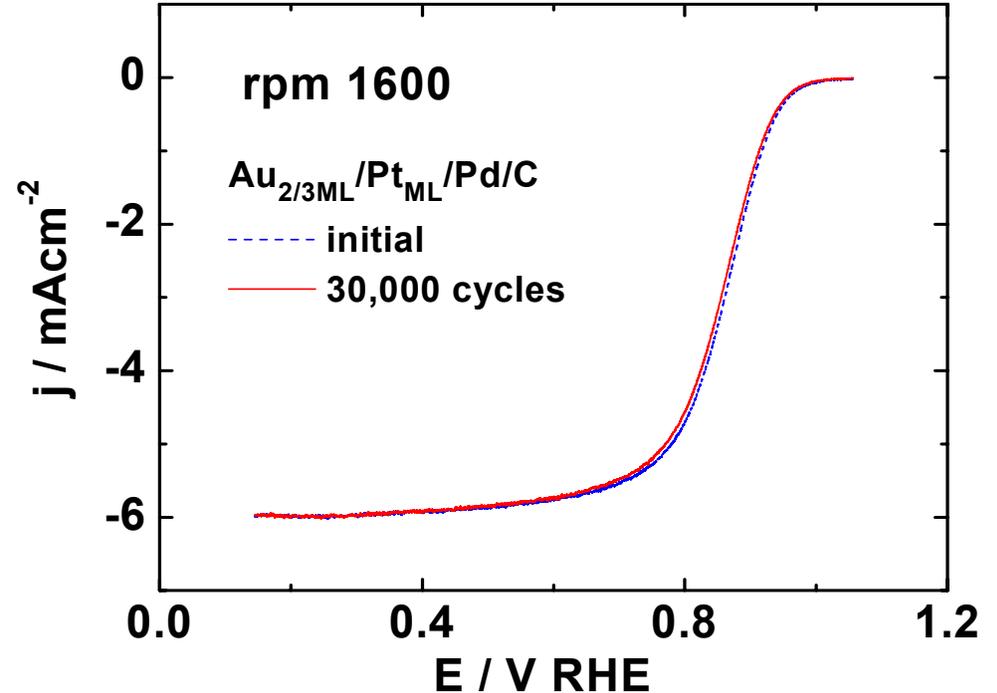
A negligible shift in $E_{1/2}$ and a loss of surface area

Stabilization of Pt_{ML}/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 O₂-saturated solution



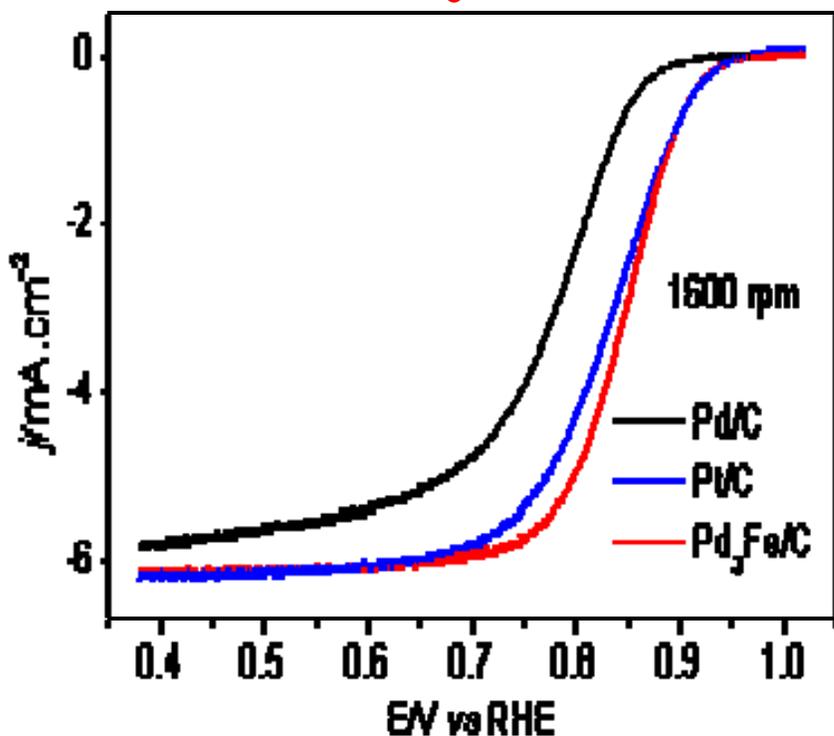
A negative shift of 26mV in $E_{1/2}$



A negligible shift in $E_{1/2}$

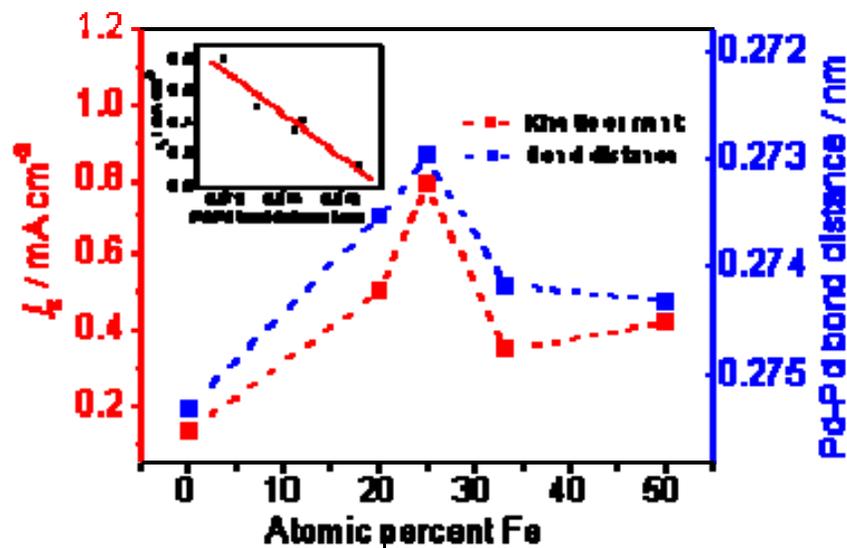
Pd₃Fe alloy O₂ reduction electrocatalyst

Pd₃Fe

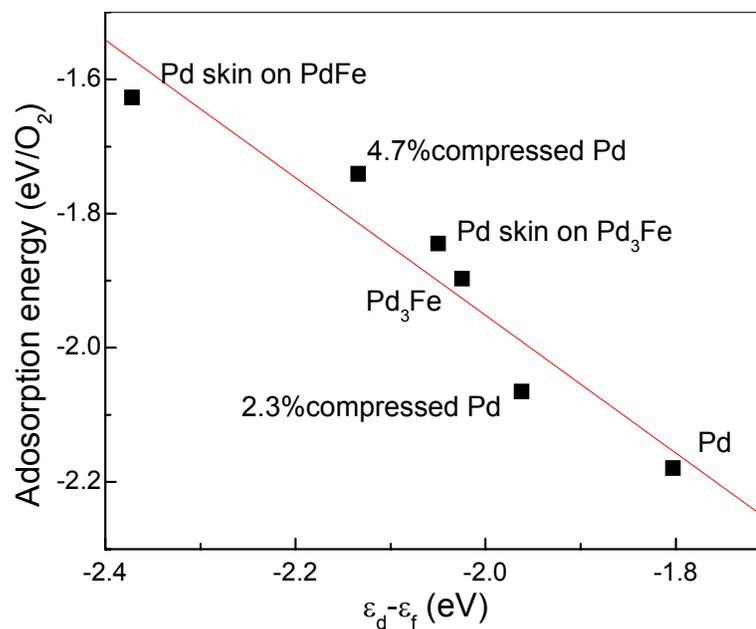


The activity of Pd₃Fe/C is as high as that of commercial Pt/C.

Compressive strain-induced downshift of the *d* - band center decreases the activity of Pd and the blocking effect of OH, O₂, O₂⁻, H₂O₂.



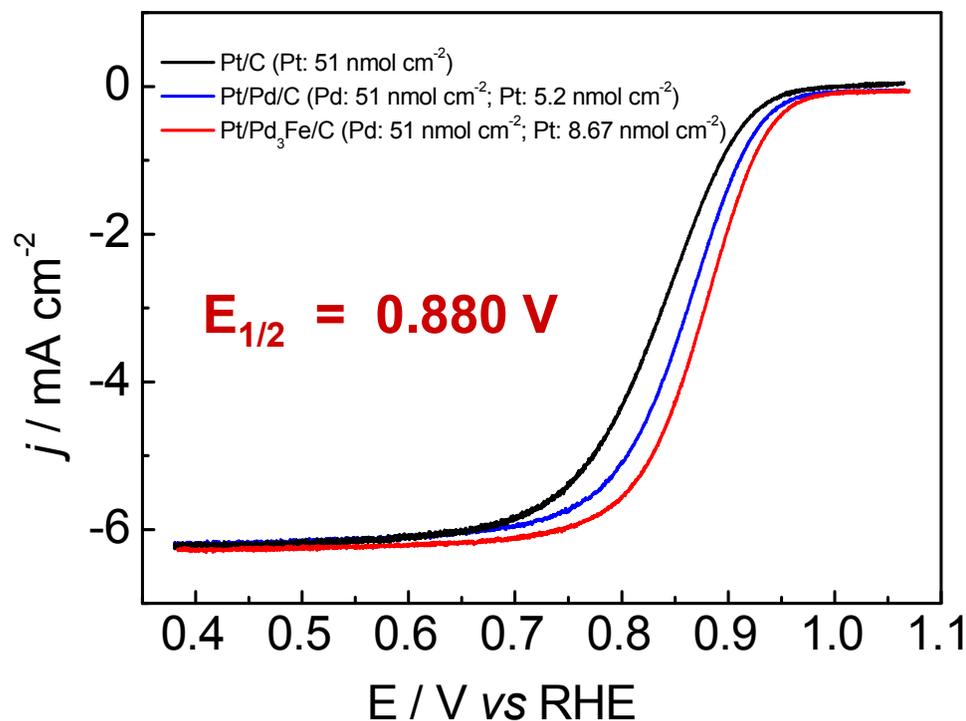
The optimal Pd-Pd distance is 0.273 nm.



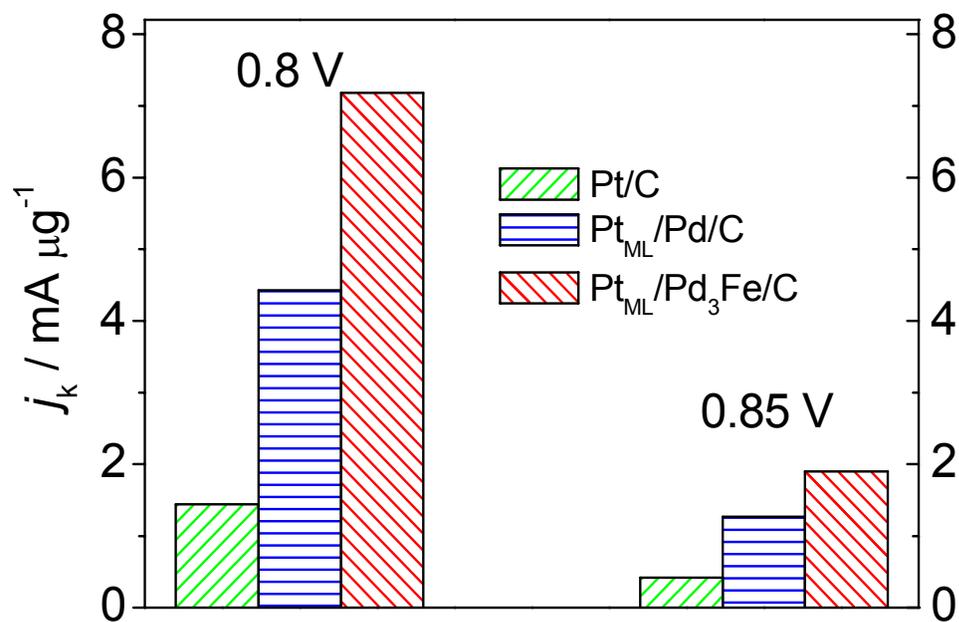
Fine tuning of the Pt-substrate interaction: Very high activity of Pt_{ML}/Pd₃Fe/C

Comparison between Pt_{ML}/Pd₃Fe/C, Pt_{ML}/Pd/C and Pt/C

Pd/C particle size of 9 nm.



Total noble mass activity



Pt_{ML}/Pd₃Fe/C has **0.14g/kW**, which meets **0.15g/kW**,
i.e., 1/2 of 0.3g/kW, the DOE's target for 2010

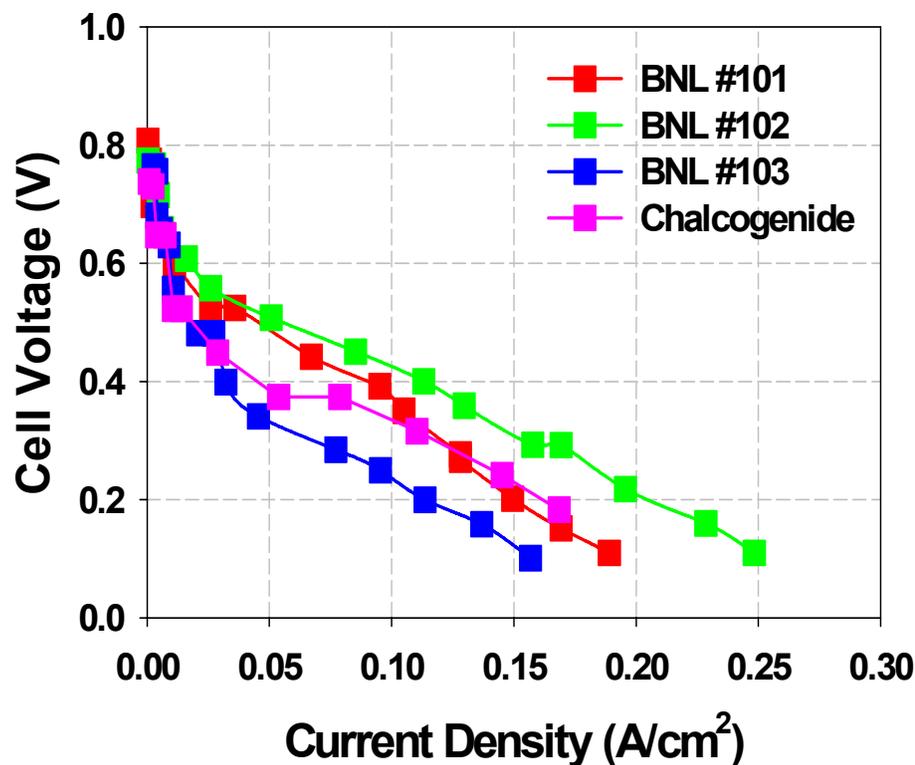
Total noble metal mass activity is about
5 times that of the commercial Pt catalyst.

Methanol tolerance of the Pd₂Co electrocatalyst

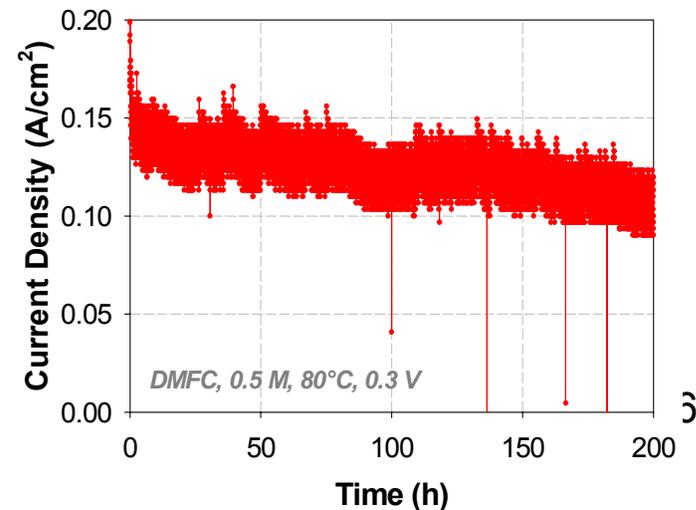
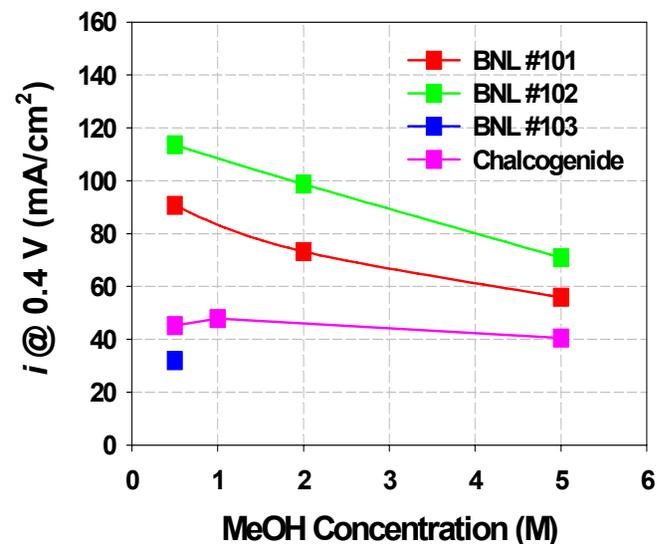
Pd₂Co

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.

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



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



Dual-Pathway Kinetic Equation for the Hydrogen Oxidation Reaction on Pt Electrodes

The Butler-Volmer equation,

$j_k = j_0 (e^{2.3\eta/b} - e^{-2.3\eta/b})$, appears to be inappropriate for describing the kinetics of the H₂ oxidation reaction (HOR) on a Pt electrode (1,2).

1. Gasteiger, et al., Power Sources, 127 (2004), 162.
2. Chen, Kucernak, J. Phys. Chem. B 108 (2004) 13984.
3. J. X. Wang, T. E. Springer, R. R. Adzic, J. Electrochem. Soc. Submitted.

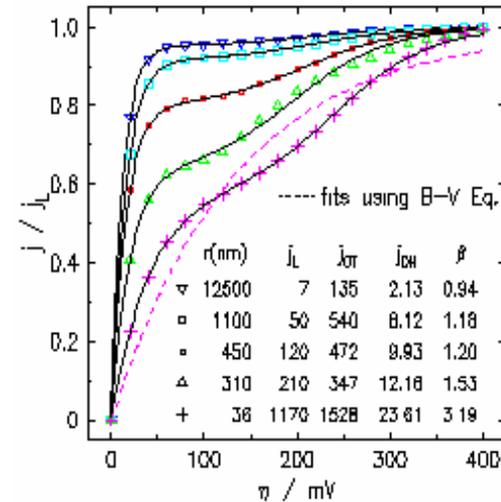
Based on the Tafel-Heyrovsky-Volmer mechanism, we derived a new equation, ref. 3, to describe the HOR on Pt over the entire potential region:

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

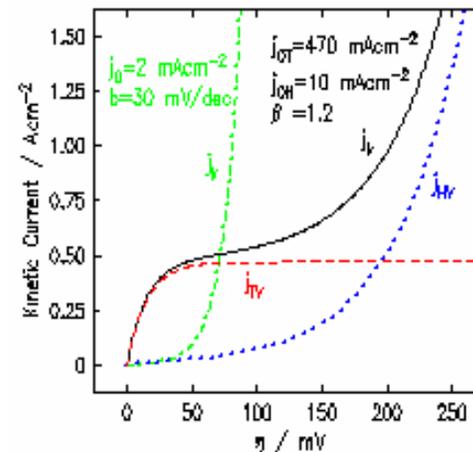
A fast, inverse exponential rising of kinetic current at small overpotentials through the Tafel-Volmer pathway, j_{TV} , and a gradual rise at $\eta > 50$ mV through the Heyrovsky-Volmer pathway, j_{HV} .

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

- **Pt_{ML}/Pd/C electrocatalyst**
 - Post fuel cell tests Z-contrast TEM, XANES.
- **Pd₂Co 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/PdCo₅/C.
- **Pt/AuNi/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.

Summary: Pt monolayer electrocatalysts

BNL ANODE PtRu₂₀/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 Pd₂Co and Pd₃Fe have activities similar to that of Pt; Methanol tolerance of Pd₂Co confirmed in a fuel cell test at LANL.
6. NbO₂ 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 50cm² 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

1. J. Zhang, F.H.B. Lima, M. H. Shao, K. Sasaki, J.X. Wang, J. Hanson, R. R. Adzic, Platinum monolayer on non-noble metal - noble metal core-shell nanoparticles electrocatalysts for O₂ reduction, *J. Phys. Chem. B*, 109 (2005) 22701-22704.
2. M.H. Shao, P. Liu, R.R. Adzic, Superoxide is the intermediate in the oxygen reduction reaction on platinum electrode. *J. Am. Chem. Soc.* (submitted).
3. J. Zhang, M. B Vukmirovic, K. Sasaki, F. Uribe, R. R. Adzic, Platinum monolayer electrocatalysts for oxygen reduction: effect of substrates, and long-term stability, *J. Serb. Chem. Soc.*, 70 (2005) 513-525 (75th Anniversary issue).
4. J. X. Wang, F. A. Uribe, and R. R. Adzic, Parameterizing H₂/air-PEMFC polarization curves, and quantifying cell performance and major voltage losses”, *Electrochem. Solid-State Lett.* (submitted).
5. M.H. Shao, K. Sasaki, R.R. Adzic, Pd-Fe nanoparticles as electrocatalysts for oxygen reduction. *J. Am. Chem. Soc.* 128 (2006) 3536.

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