# Project: LOW PLATINUM LOADING CATALYSTS

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**(This presentation does not contain any proprietary or confidential information.)**

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# OBJECTIVES

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

- To demonstrate the possibility of synthesizing novel electrocatalysts for $O_2$ reduction with a monolayer level Pt loadings.
- To further characterize of the $PtRu_{20}$ electrocatalyst for $H_2$/CO oxidation and long term tests.
- To gain understanding of the activity of Pt monolayer and the $PtRu_{20}$ electrocatalysts.

# PROJECT SAFETY

- All the work on this project is performed within the controls identified in the Experimental Safety Review (ESR) Form for this Project.

- Personnel have all the training identified by ESR.

- CO sensor installed at the CO tolerance experiment. Hazard evaluation of this experiment was performed.

- For the work at synchrotron, the safety procedures and the training requirements of NSLS are followed.

BUDGET

TOTAL FUNDING FOR THE PROJECT (FY 02-04):  $624.000

FUNDING IN FY 04: $250.000

# TECHNICAL BARRIERS AND TARGETS

The DOE's Technical Targets for Fuel Cell Stack Systems Operating on Hydrogen (Gasoline Reformate)

| | year | 2003 | 2005 | 2010 |
|---|---|---|---|---|
| precious metal loading | g/kW | <2.0 | 0.6 | 0.2 |
| durability | hours | >2000 | >2000 | >5000 |
| CO tolerance (2% air bleed) | ppm | 50 | 500 | 1000 |

# APPROACH

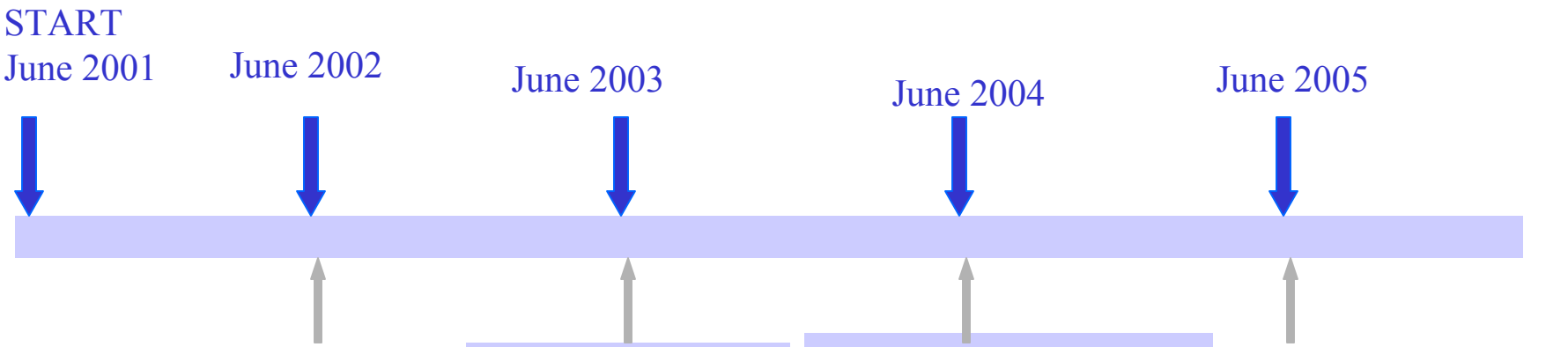
**Development of low-Pt-loading electrocatalysts by placing a submonolayer-to-monolayer of Pt on nanoparticles of suitable metals or alloys to obtain electrocatalysts with the following characteristics:**

- ultimately reduced Pt loading
- enhanced activity of Pt
- complete utilization of Pt

**Two methods for Pt monolayer deposition were developed:**

1. Electroless (spontaneous ) Pt deposition on Ru.
2. Pt deposition by replacing a UPD metal adlayer.

# PROJECT TIMELINE




Proof of principle, characterization of a Pt submonolayer anode electrocatalyst.

Optimization, MEA tests, $O_2$ reduction electrocatalysts.

Pt loading reduced to 1/10 of the standard value.

1000 h MEA tests completed with $PtRu_{20}$.

$O_2$ reduction Pt monolayer electrocatalysts demonstrated.

Electrocatalyst obtained that does not show any loss in activity in a 870 h test.

Optimization of $O_2$ reduction monolayer electrocatalysts, MEA tests.

Anticipated Pt loading 1/5 of the current standard.

# TECHNICAL ACCOMPLISHMENTS

BROOKHAVEN NATIONAL LABORATORY

ANODE

- Stability tests at LANL (F. Uribe) show **no loss of voltage after 870 h** for the $PtRu_{20}$ electrocatalyst with 18 μg Pt/cm$^2$ (20% Ru; 2% Pt, 3% air bleed), and small losses after 1000 h with 18 μg Pt/cm$^2$ (10% Ru; 1% Pt, 4% air-bleed) and very small losses in a 600 h test with 19 μg Pt/cm$^2$ (2% air-bleed) of combined $CO/H_2$ and $H_2$ operation.

- The DOE durability target of 2000h for 2005 can be reached with this electrocatalyst.

- The DOE target for 2005 for noble metals of 0.6 g/kW (0.3 g/kW for anode) is met for Pt: **only 0.063 g Pt/kW is necessary**. If Ru is counted, 0.630 g total metal is needed.

CATHODE

- A Pt monolayer on C-supported metal or metal alloy nanoparticles can be an active catalyst for $O_2$ reduction.

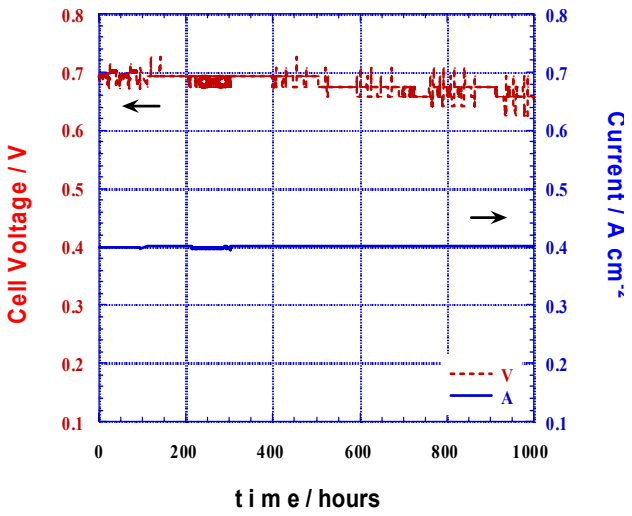
- The Pt mass-specific activity of Pt/Pd/C is 5-8 times higher than that of Pt(10%)/C. The (Pt + Pd) mass activity is 2.5 times higher. Fuel cell tests (F. Uribe) are quite promising.

- A PdCo/C electrocatalyst was synthesized. Its activity is comparable to that of Pt.

- A Pt/AuNi/C electrocatalyst was synthesized whose activity is similar to that of Pt.

# LONG-TERM FUEL CELL TESTS AT LANL (F. Uribe)

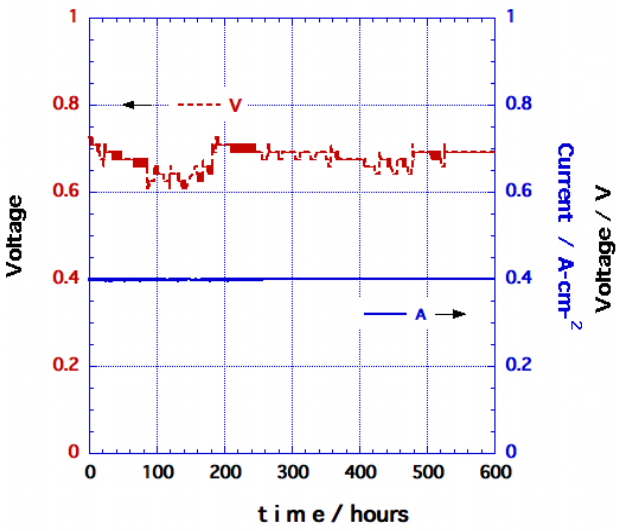
## 17 µg Pt/cm² (10% Ru; 1% Pt)




**Voltage losses after 1000 hr:**
* with neat $H_2$: 40 mV
with $H_2$+CO+4% air: 60 mV

Cell=50 cm2 ; T= 80 C;
A: 0.19 mg /cm2(10%Ru, 1%Pt) C: 0.23 mg Pt /cm2(20% Pt/C, ETEK)
Total run time = 1000 hours at constant current. 710 hours of operation with clean H2 and 290 hours with H2 + 50 ppm CO + 4 % air bleed.

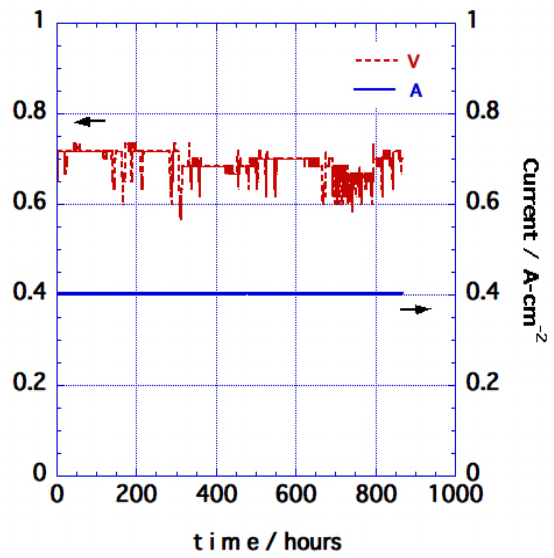
## 19 µg Pt/cm² (10% Ru; 1% Pt)




**Voltage losses after 600 hr:**
* with neat $H_2$: 20 mV (0.71-0.69 V)
* with $H_2$+CO+2% air: 20 mV (0.66-0.64 V)

Cell 50 cm² cell / T= 80 C
A: 0.19 mg BNL/cm² (10% Ru; 1% Pt)
C: 0.22 mg Pt/cm² (ETEK)
$H_2$ 471 hr; $H_2$ + CO 50 ppm +2% air bleed, *129 hr*

## 18 µg Pt/cm² (20% Ru; 2% Pt)



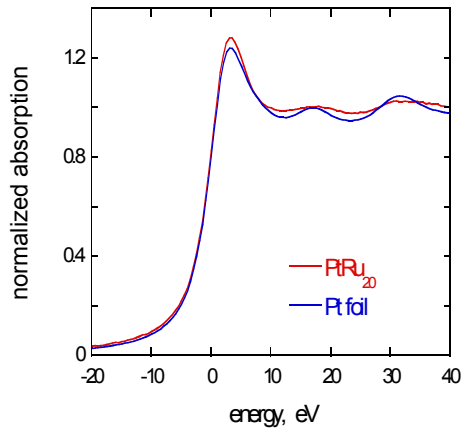

**No voltage losses after 868 hr:**

| | initial V | final V |
|---|---|---|
| * with $H_2$: | 0.717 | 0.717 |
| * with $H_2$+CO+3% air: | 0.697 | 0.701 |

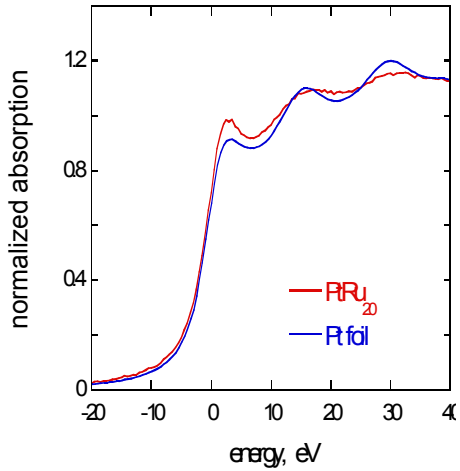
Cell 50 cm² cell / T= 80 C
A: 0.20 mg BNL/cm² (20% Ru; 2% Pt)
C: 0.24 mg Pt/cm² (ETEK)
Running Mode: 20 A current
a) $H_2$ at @ 1.3 stoich
b) $H_2$ at @ 1.3 stoich + CO 50 ppm +3% air bleed
Air flow: constant @ 2100 sccm

In addition to CO tolerance, **the very strong surface segregation** of Pt is a key factor in its stability.

# ELECTRONIC EFFECTS *vs*. BIFUNCTIONAL MECHANISM IN CO TOLERANCE OF THE $PtRu_{20}$ ELECTROCATALYST




**relative to $L_3$ Pt edge**

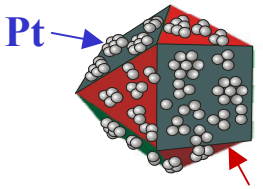


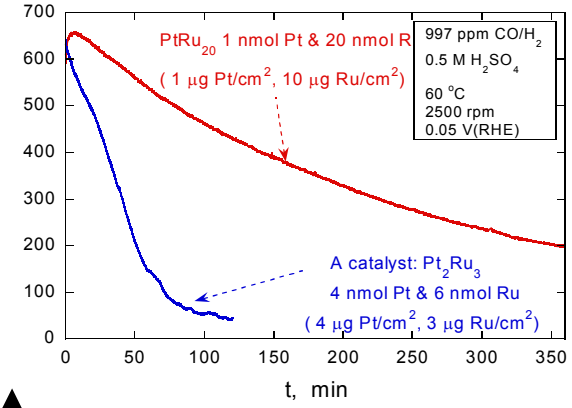

**relative to $L_2$ Pt edge**

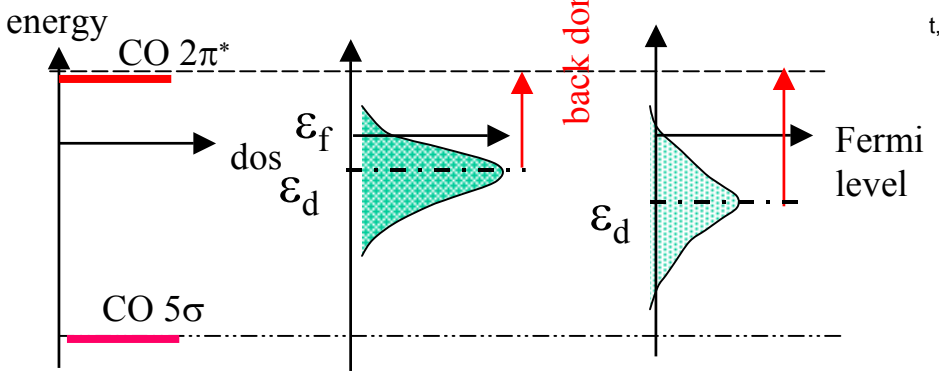
d band vacancy

**$PtRu_{20}$ 0.345 (0.41V)**

**Pt foil 0.30**




## CO

- σ electron from CO to Pt
- Back donation of Pt d electron to CO 2π*

## Pt

Strong CO adsorption

## $PtRu_{20}$

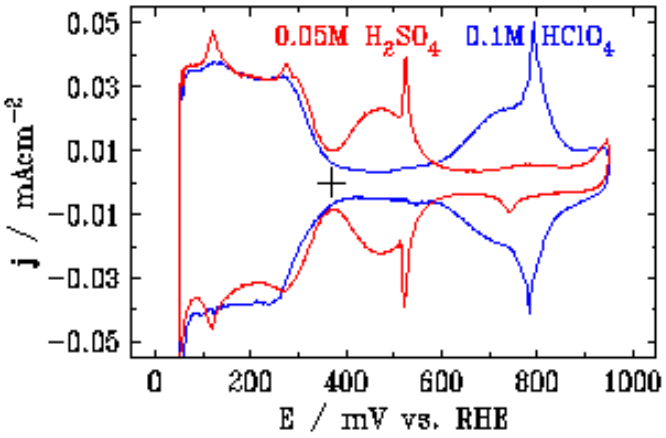
- Lower d-electron density
- Lower d-band center $\varepsilon_d$ (Nørskov's model)

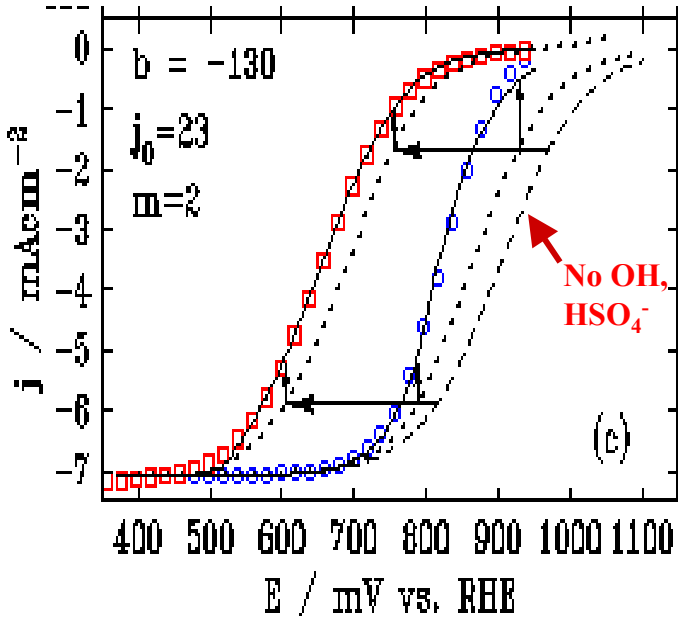
Back donation decreases

Weaker CO adsorption

Conclusion: Both the electronic effects and the "bifunctional " mechanism are operative for this electrocatalyst.

# INHIBITION OF $O_2$ REDUCTION ON Pt BY ANION ADSORPTION




The kinetic currents are calculated as a function of E and the anion adsorption isotherm, $\theta_A(E)$ using

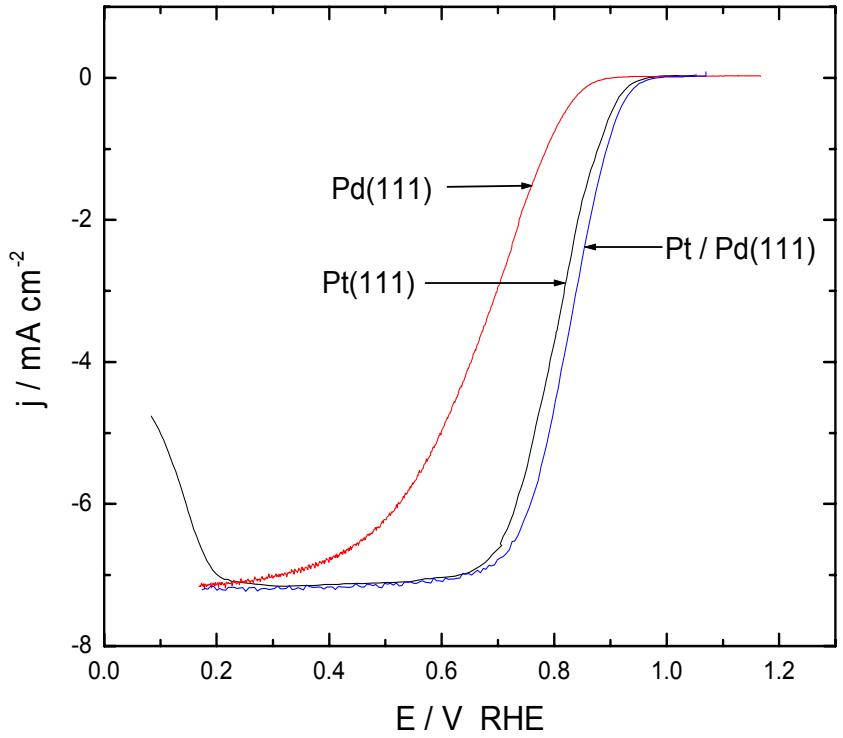
$$j_k(E) = -j_0 (1 - \gamma_A \theta_A(E))^m \exp(-2.3(E - E^0 - \varepsilon_A \theta_A(E))/b),$$

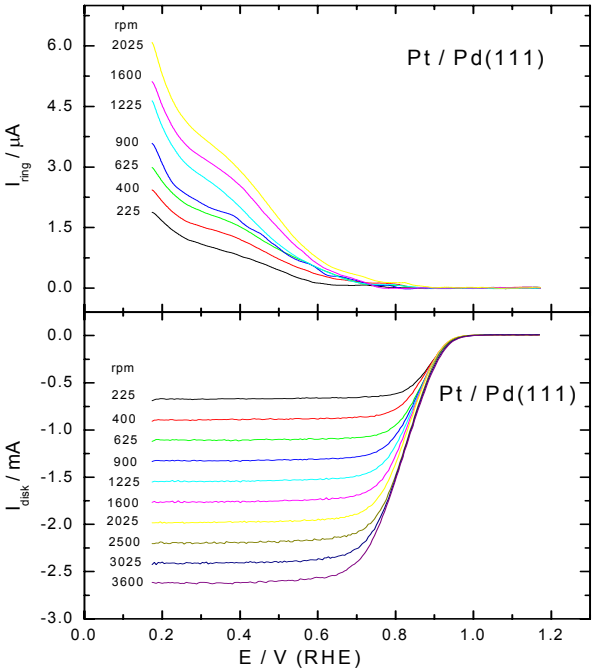
where $j_0$ and **b** are the **intrinsic kinetic parameters,** $\gamma_A$ is the **geometric blocking factor,** and $\varepsilon_A$ is the **electronic effect** of adsorbed anions.

- The best fits yielded the intrinsic Tafel slope in the range –118 to –130 mV/dec.
- In addition to site blocking, both OH and bisulfate have a negative electronic effect on ORR kinetics, with the effect of the latter being much stronger.
- The deviation of the apparent Tafel slope in $HClO_4$ from its intrinsic value can be fully accounted for by the site blocking and electronic effects of adsorbed OH ions, which vary with coverage over the mixed kinetic-diffusion controlled region.

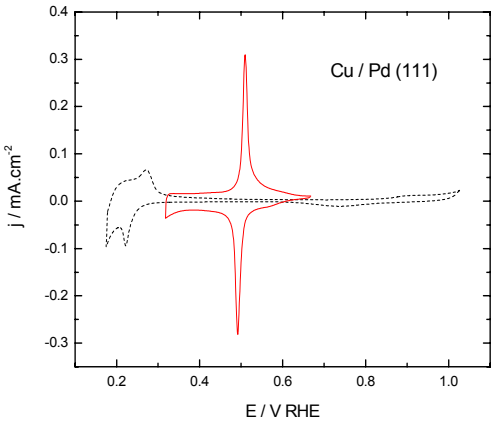
Wang et al. J. Phys. Chem., in press.

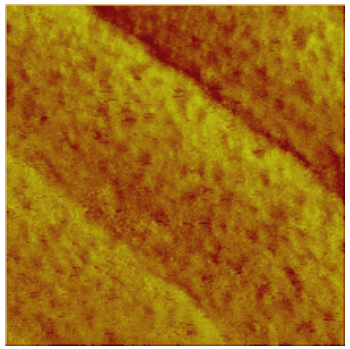
# $O_2$ REDUCTION ON $Pt_{1ML}/Pd(111)$



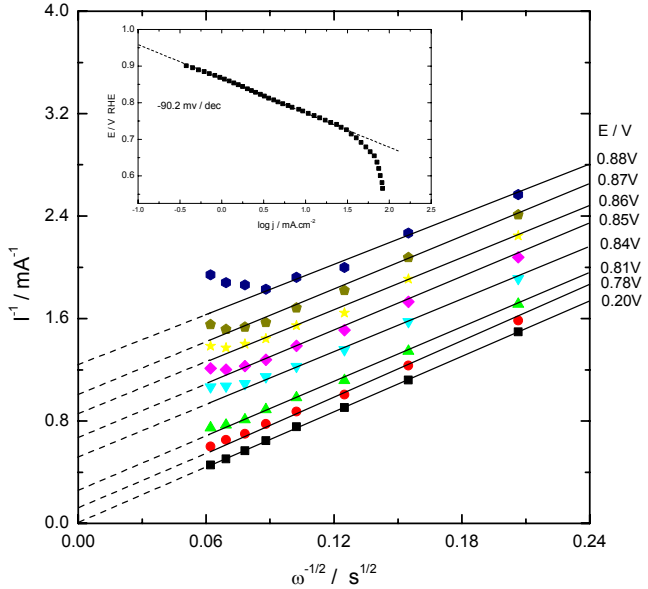

The reduced coverage of PtOH appears to be the cause of enhanced activity.



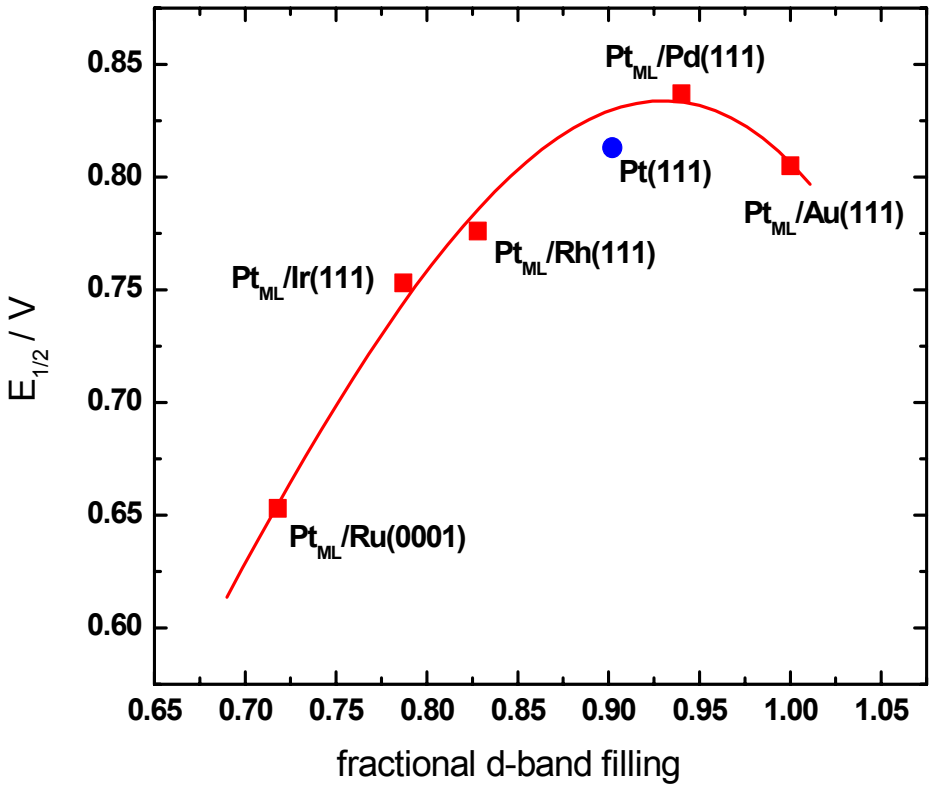



250 nm
x
250 nm

$Pt_{ML}/Pd(111)$

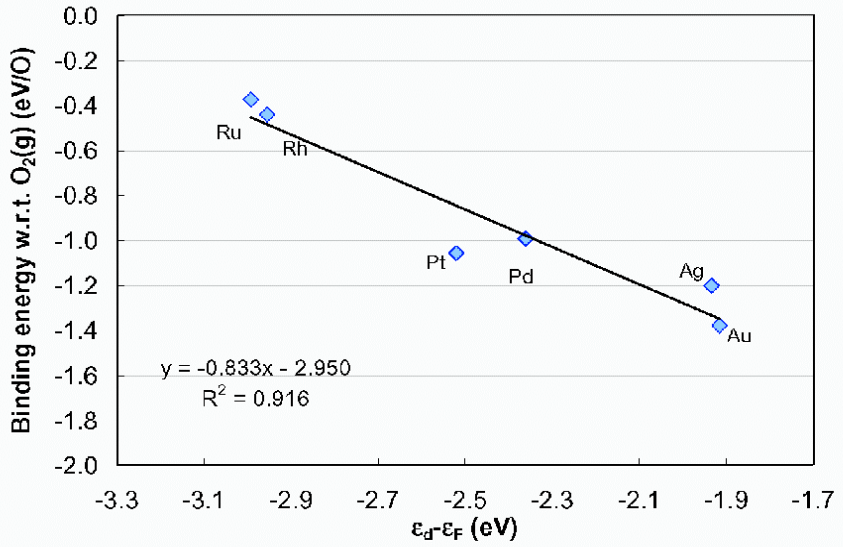


# ACTIVITY OF Pt MONOLAYERS AS A FUNCTION OF THE FRACTIONAL FILLING OF THE d-BAND OF SUBSTRATES




## Adsorption energies of atomic oxygen on Pt monolayers vs. d-band centers

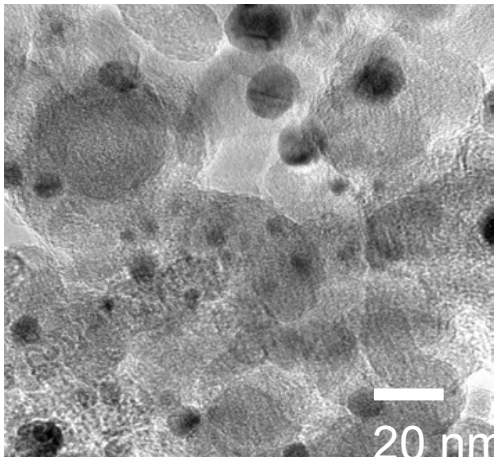
fcc(111); (2x2x4) unit cell; top two layers relaxed; PW91 functional

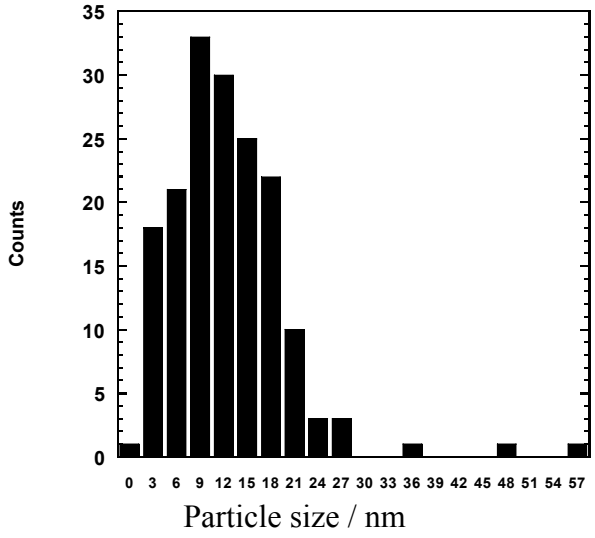


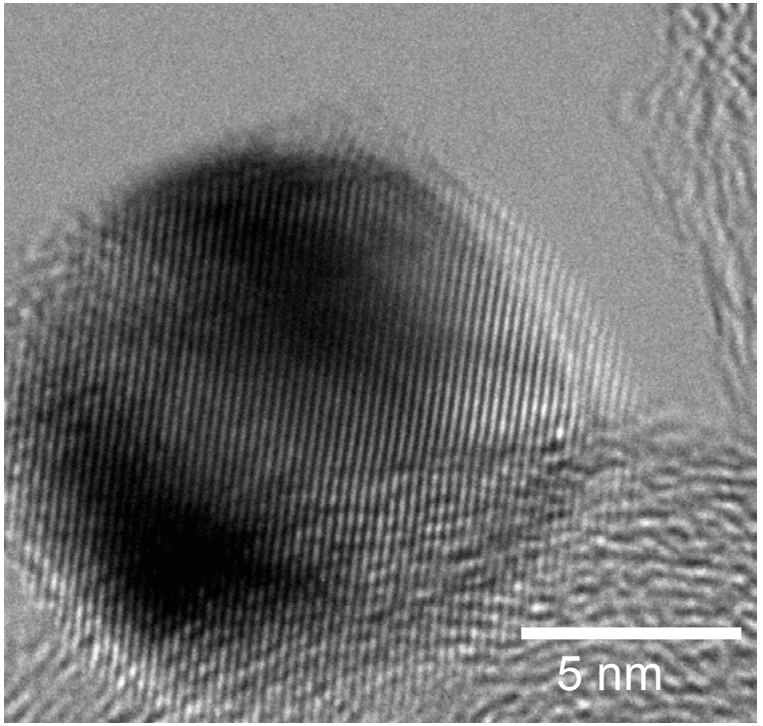

DFT calculations by M. Mavrikakis, U. Wisconsin.

# HRTEM OF Pd NANOPARTICLES ON C

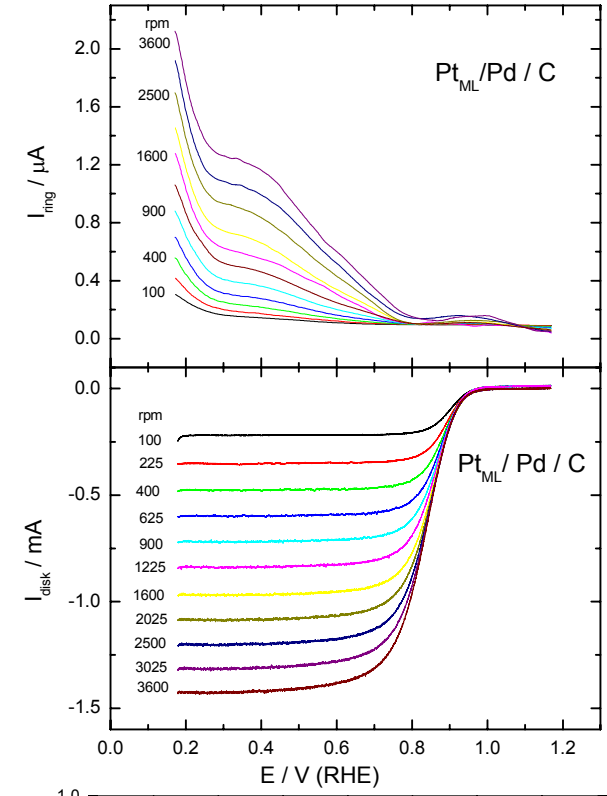
## Pd(10%) / Vulcan XC-72 commercial

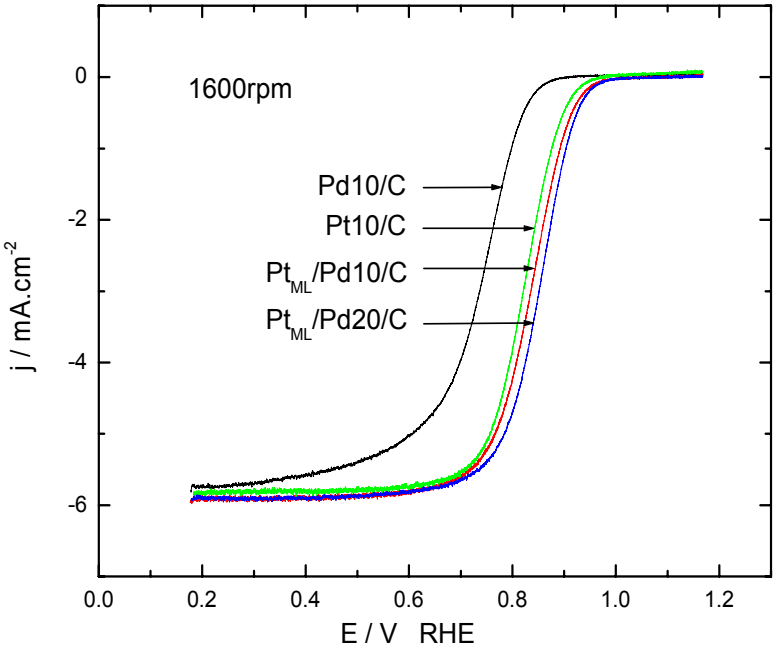


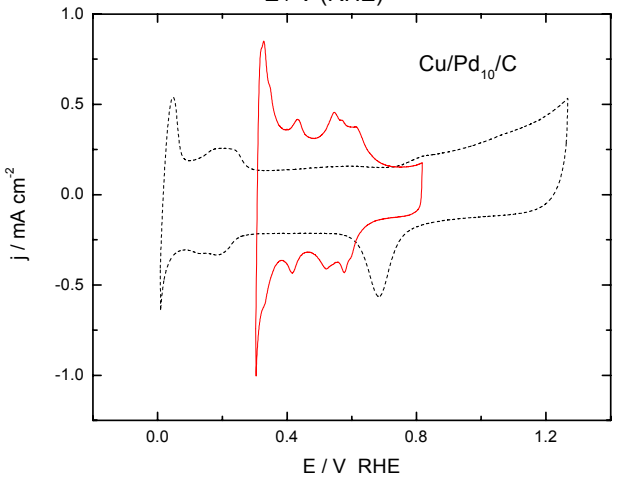



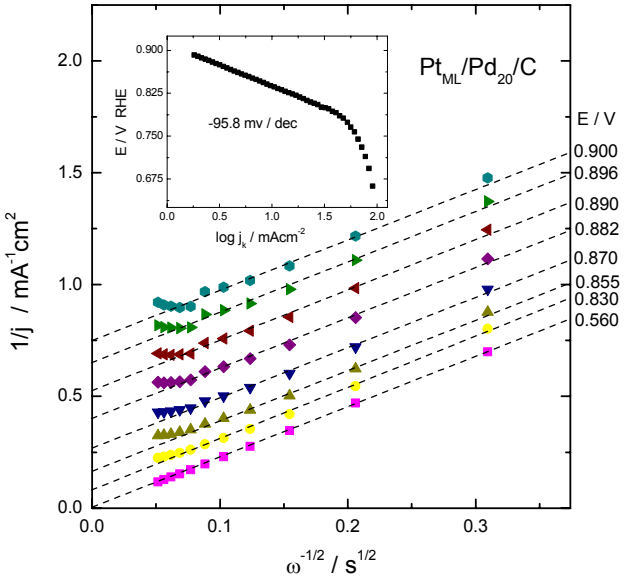



# $O_2$ REDUCTION ON Pt/Pd/C

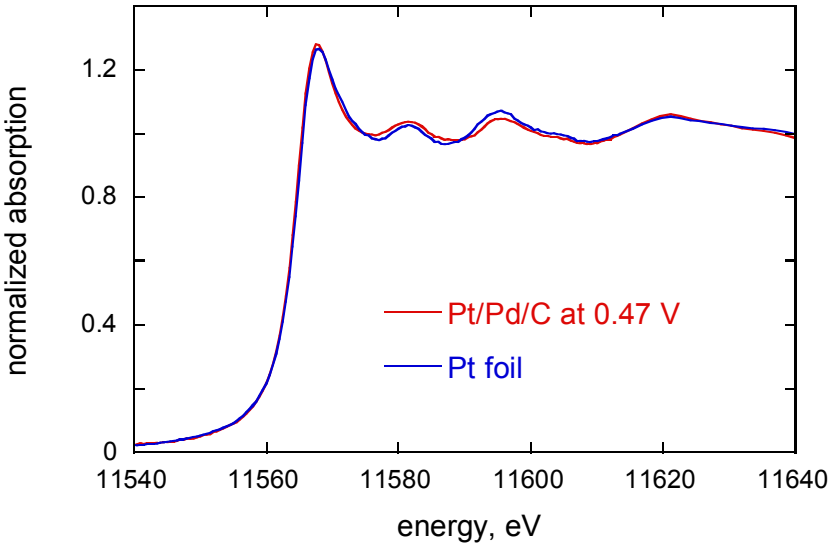


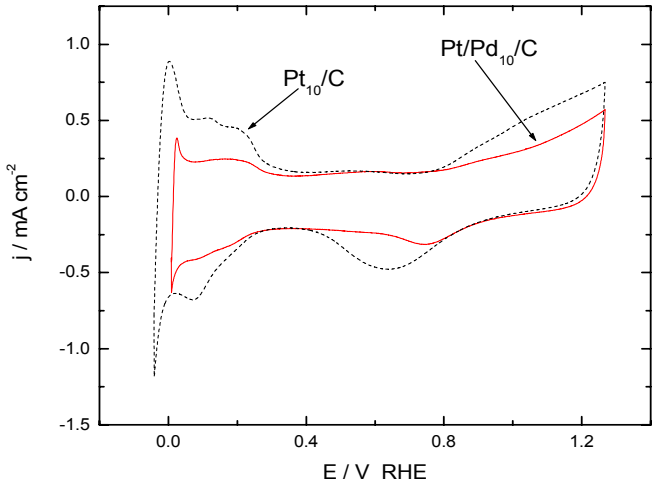



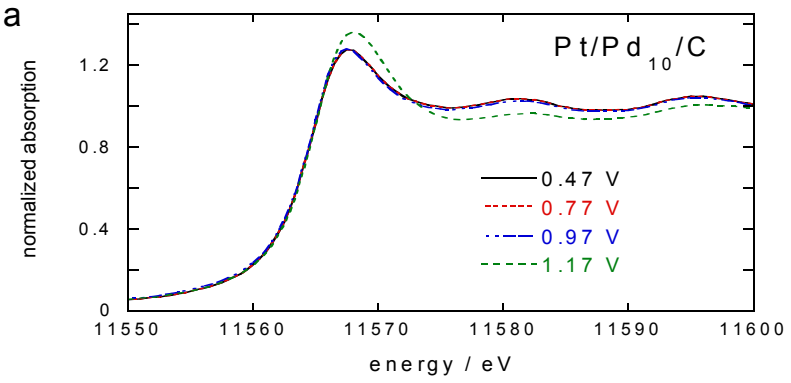
# *IN SITU* XANES MEASUREMENTS WITH Pt/Pd/C

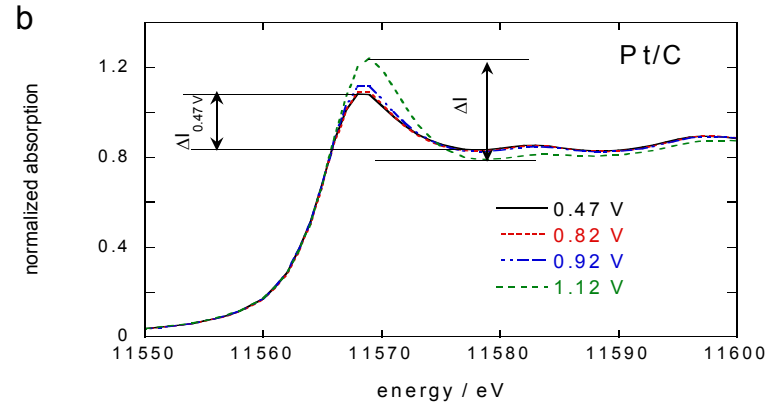


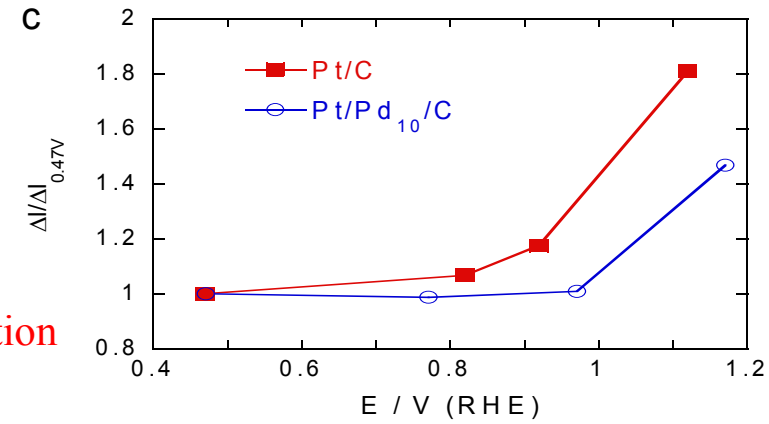

XANES reveals a small change in the Pt d band.



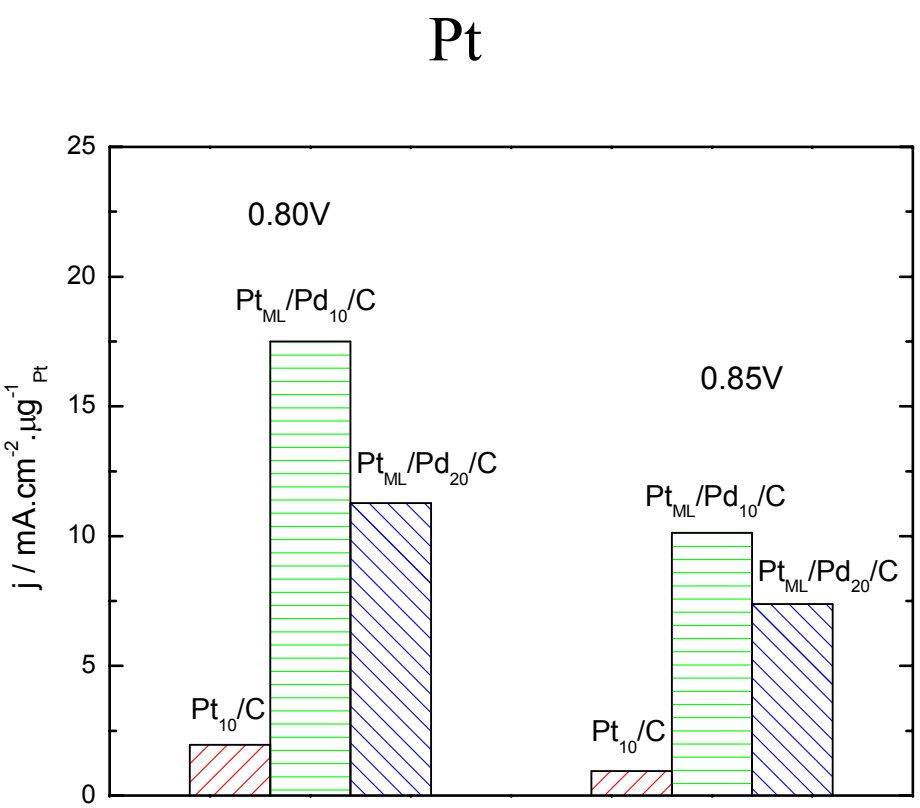

Voltammetry and XANES show delayed Pt oxidation at high potentials in comparison with Pt/C.

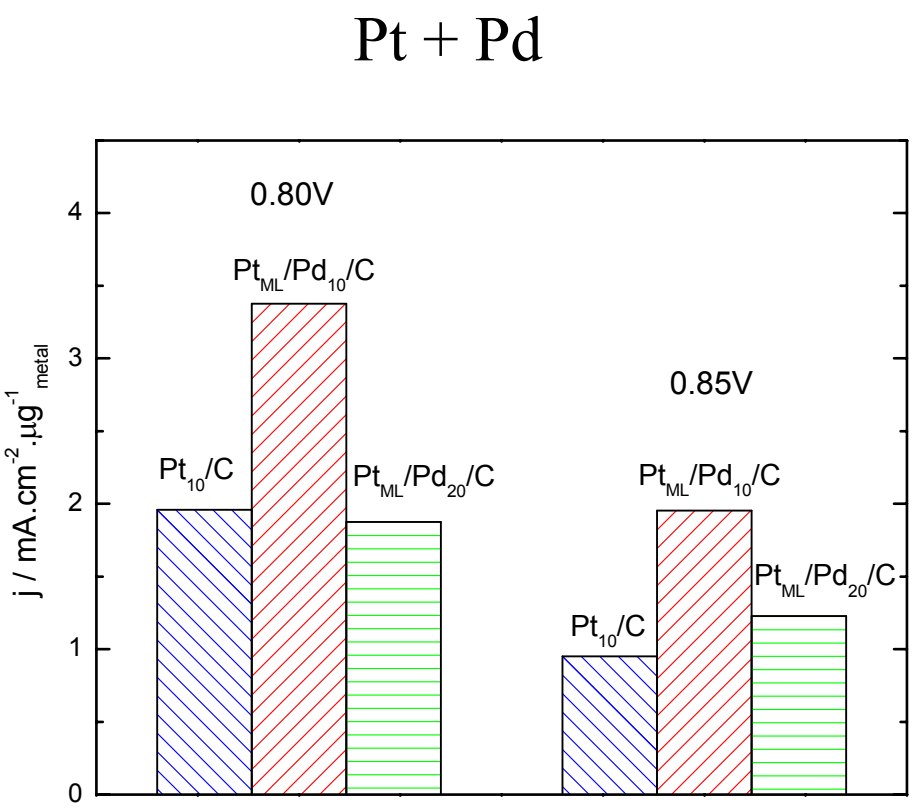


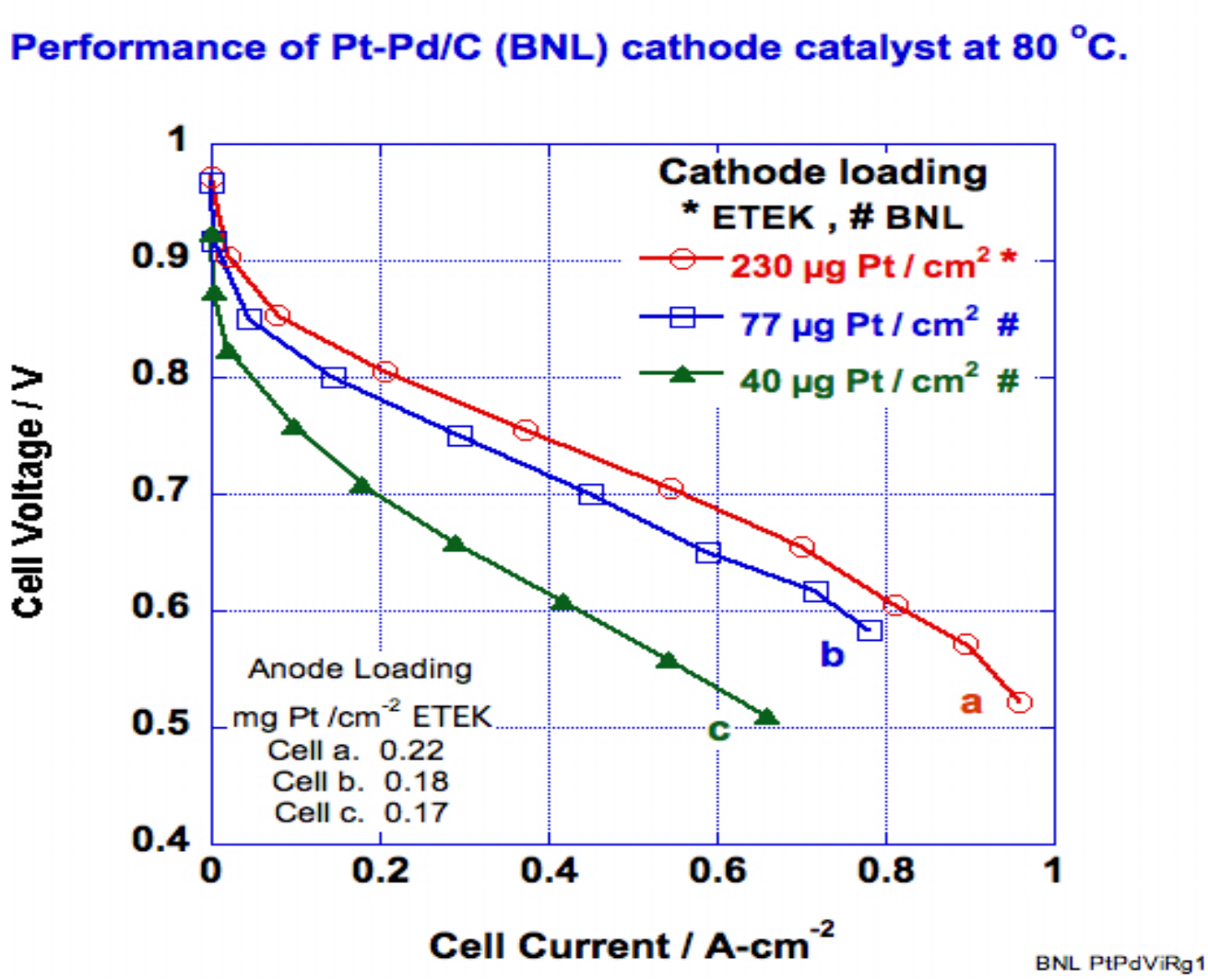



# Pt and (Pt + Pd) MASS-SPECIFIC ACTIVITY OF $Pt_{ML}/Pd/C$ FOR $O_2$ REDUCTION



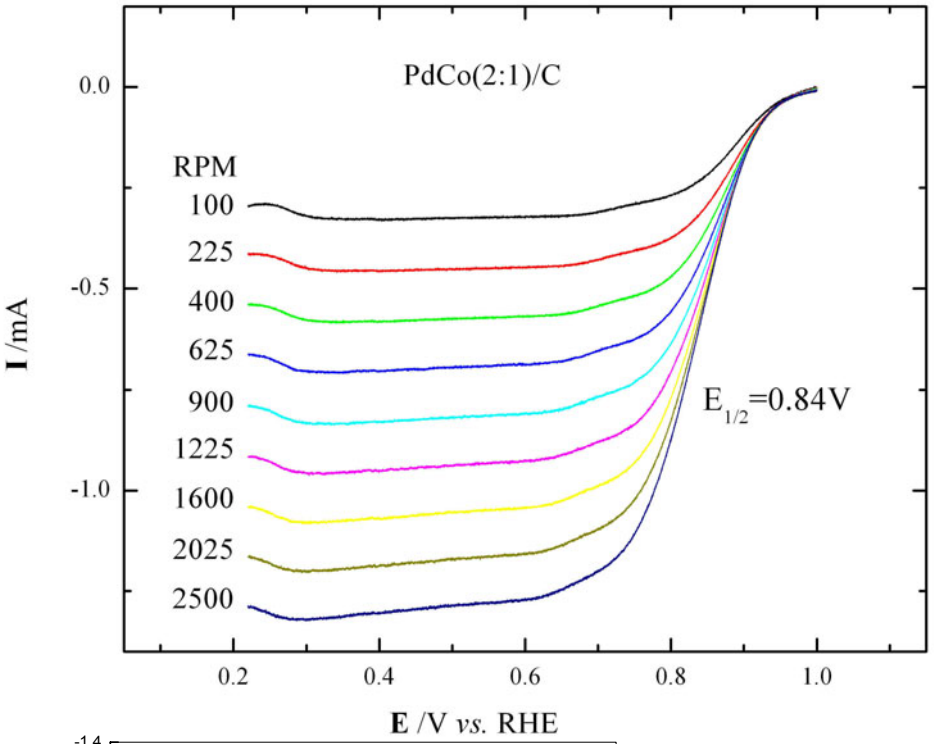
# FUEL CELL TESTS OF Pt/Pd/C AT LANL (F. Uribe)

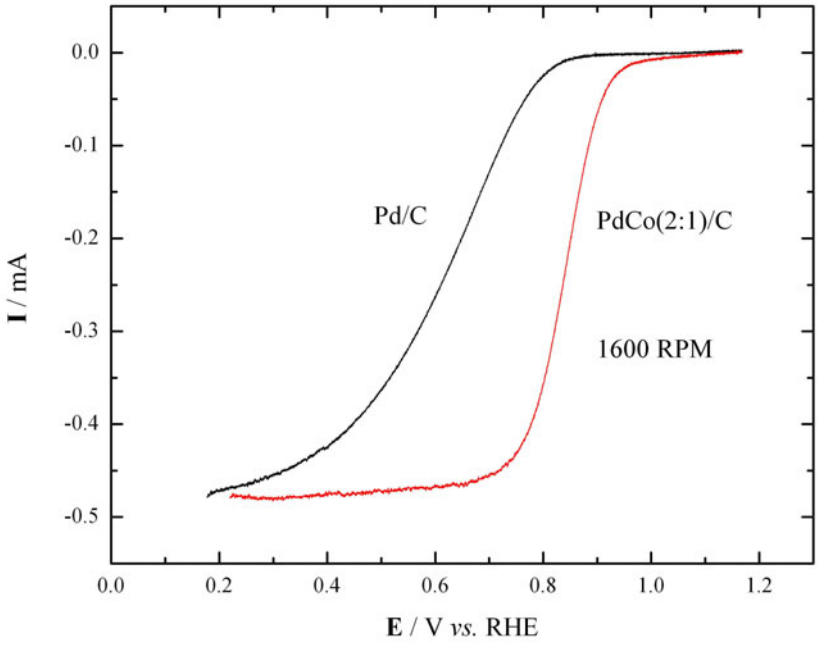


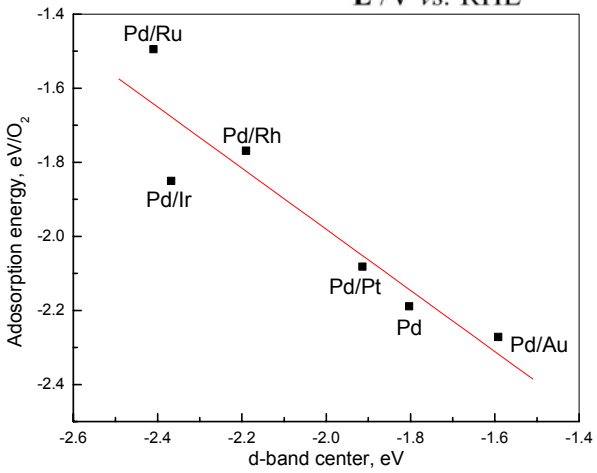

Performance of Pt-Pd/C (4% Pt-20% Pd) cathode catalyst at 80 °C. Membrane: Nafion® N1135.

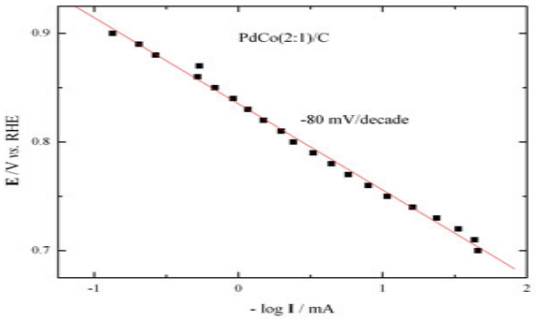
Anode loadings in mg Pt/cm2: Cell **a:** 0.22 ; Cell **b:** 0.18 ; Cell **c**: 0.17.

# $O_2$ REDUCTION ON PdCo/C

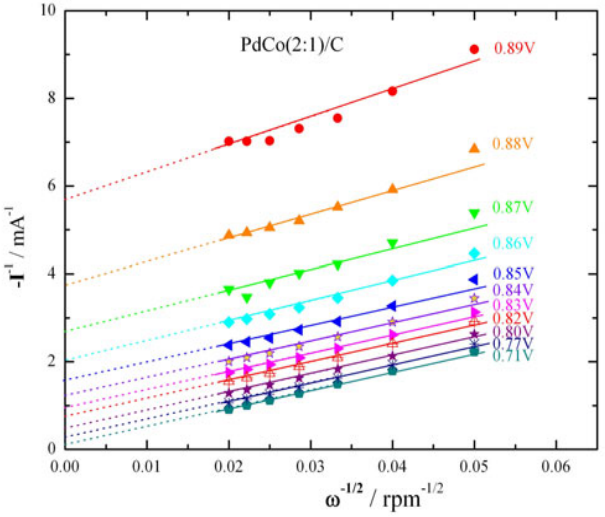


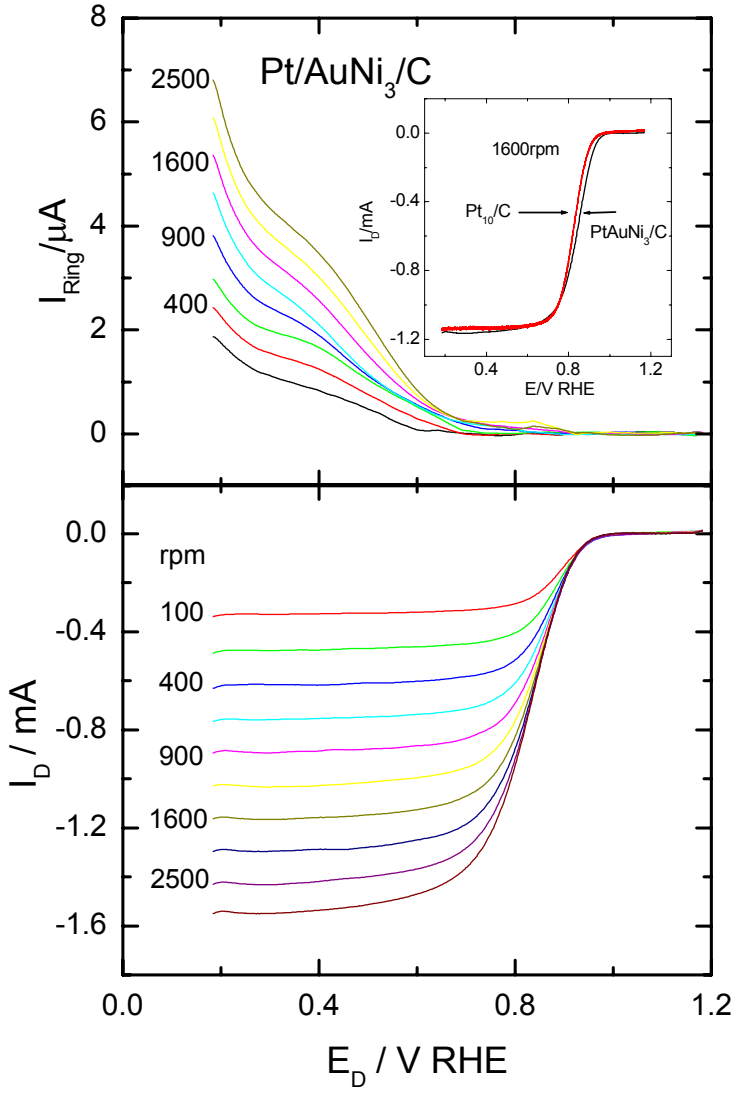



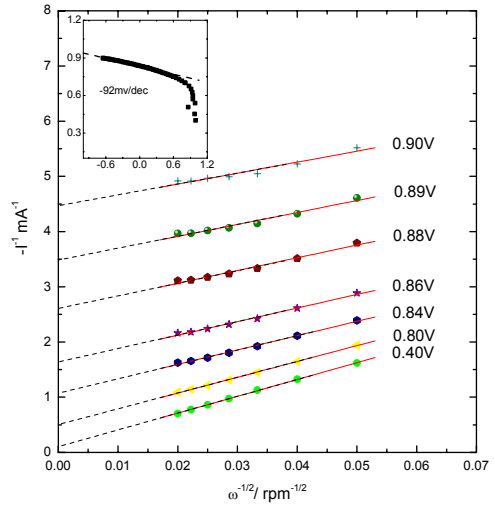



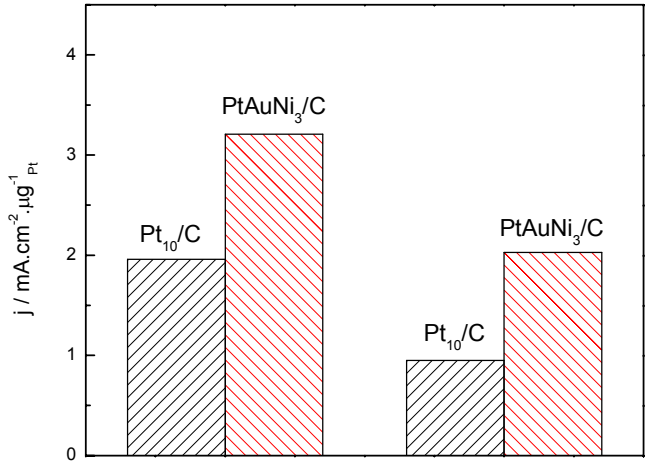

DFT calculation by P. Liu, BNL



# $O_2$ REDUCTION ON Pt/AuNi/C




Further reduction of Au and the use of an immiscible $Au_{ML}Ni$ alloy seem possible.

# INTERACTIONS AND COLLABORATIONS

1. Los Alamos National Laboratory Dr. Francisco Uribe – long-term fuel cell tests of electrocatalysts.
2. Plug Power, visit, discussions.
3. Interest expressed in the $PtRu_{20}$ electrocatalyst and collaboration.

Publications from collaborations:

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, Electrochim. Acta, in press.

K. Sasaki, Y. Mo, J.X. Wang, M. Balasubramanian, F. Uribe,J. McBreen, R.R. Adzic,
Pt submonolayers on metal nanoparticles – novel electrocatalysts for $H_2$ oxidation and $O_2$ Reduction, Electrochim. Acta, 48 (2003) 3841.

J.X. Wang, N.M. Markovic, R.R. Adzic, Kinetic Analysis of $O_2$ reduction on Pt(111) in Acid Solutions: Intrinsic Kinetic Parameters and Anion Adsorption Effects, J. Phys. Chem. in press.

# Responses to Previous Year Reviewers' Comments

Q. Distinction from Wieckowski's catalyst not clear.

A. His: Ru on Pt for methanol oxidation; ours: Pt on Ru for $H_2$/CO oxidation.

Q. Not clear how structure/phase behavior (of CO) is exploited to design practical catalysts.

A. Knowing adsorbate's mobility, lateral interactions and adsorption sites can help in designing electrocatalysts.

Q. Cathode materials of higher importance and needs to be expanded.

A. The work on cathode materials has been expanded.

# FUTURE WORK

## $H_2$ oxidation

1. Pt submonolayers on non-noble metal alloy nanoparticles.

## $O_2$ reduction

1. Further development of a Pt/Pd/C electrocatalyst. Tests at LANL.
2. Further development of immiscible Au-non-noble metal alloy nanoparticles as support for Pt.
3. Multi-metal monolayers to reduce PtOH coverage and to modify the electronic properties of Pt.
4. Non-noble metal alloys as support for Pt.