Project: LOW Pt LOADING ELECTROCATALYSTS

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WHY Pt MONOLAYER ELECTROCATALYSTS ?

- ultimate reduction of Pt loading
- complete Pt utilization – every Pt atom counts
- low coordination of Pt atoms should enhance their activity
- strained overlayer - enhanced activity
- compressed overlayer - decreased activity
- coverage dependent electronic properties

OBJECTIVES

1. Development of novel electrocatalysts with a monolayer level Pt loadings.
2. Elucidation of their catalytic action.

PROJECT TIMELINE

START
June 2001

June 2002

June 2003

June 2004

Proof of principle, characterization of electrocatalysts, tests in MEAs

Optimization, MEA tests, reduction of Ru loading, O_2 reduction electrocatalysts

Replacement of Ru for H_2 oxidation, O_2 reduction electrocatalysts, MEA tests

ACCOMPLISHMENTS

- The (√19 x √19)6CO phase determined by SXS on Pt(111) and a fast (2 x 2) ↔ (√19 x √19) phase transition found. H_2 oxidation less inhibited by this phase than by the (2 x 2) adlayer.

- A considerable improvement of the 1%Pt /10%Ru/C catalyst has been achieved. The "life" for the oxidation of 1000 ppm CO/H_2 at 2500 rpm extended from <3h to >6h. Stability tests at LANL show a good activity after 222h of combined CO/H_2 and H_2 operation.

Loadings in anode: 18μg Pt/cm^2 + 180 μg Ru/cm^2
DOE Target for 2004: 300 μg/cm^2 for anode and cathode

- Pt on C-supported Au nanoparticles can be an efficient catalyst for O_2 reduction. The Pt mass specific activity 2.5 times higher than that of Pt10%/C achieved. Stability needs to be investigated.

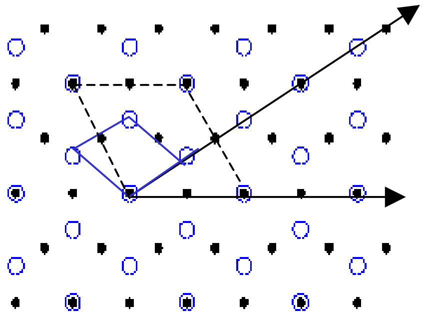
- Pt on C-supported W nanoparticles (synthesized by D. Mahajan, BNL) appear promising as a catalyst for H_2 oxidation.

CO ADSORPTION AND H_2 OXIDATION ACTIVITY ON Pt(111)

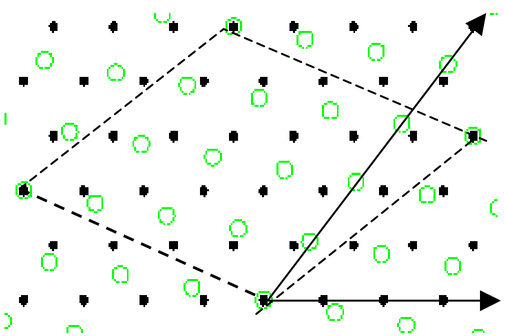
BROOKHAVEN NATIONAL LABORATORY

New insights into the structure and phase behavior from *in situ* SXS

(2x2)-3CO, θ=0.75

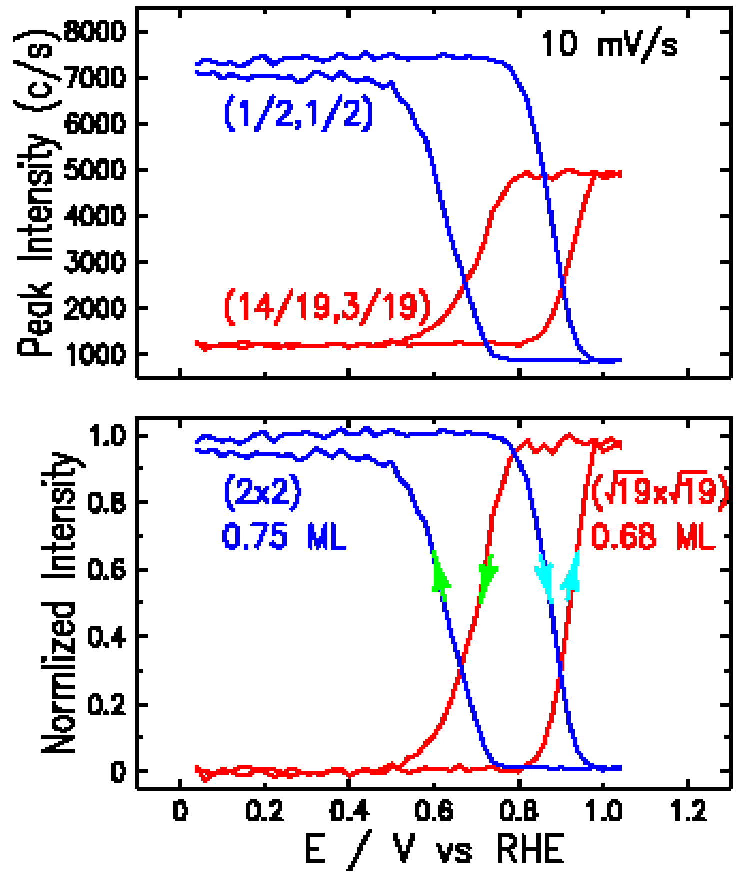


(√19x√19)-13CO θ=0.68



CO 1 atop, 6 near-atop, 6 near-bridge. The near-atops prefer to surround the atop.

(2x2)-3CO ↔ (√19x√19)-13CO phase transition

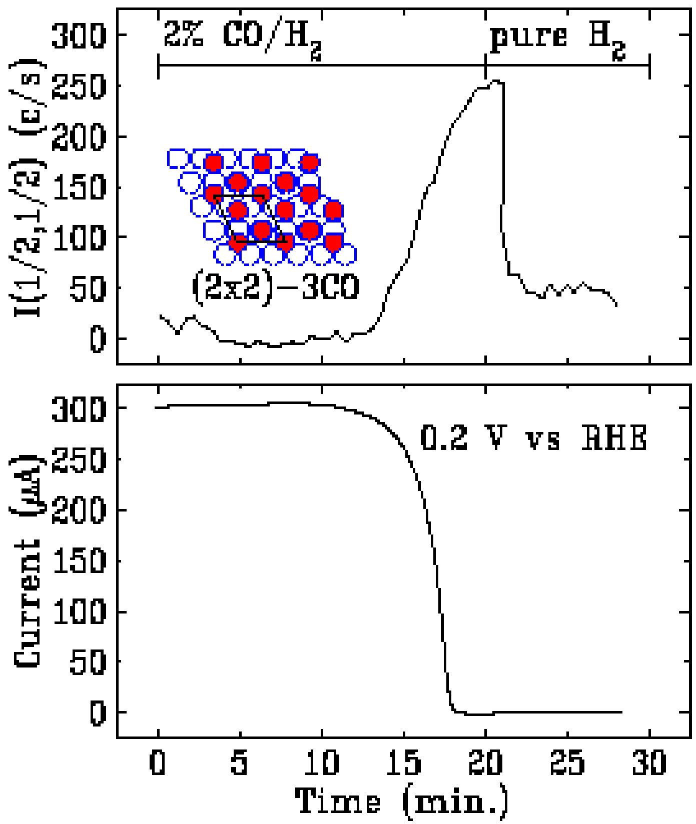


Both phases can exist over wide potential region depending on CO concentration

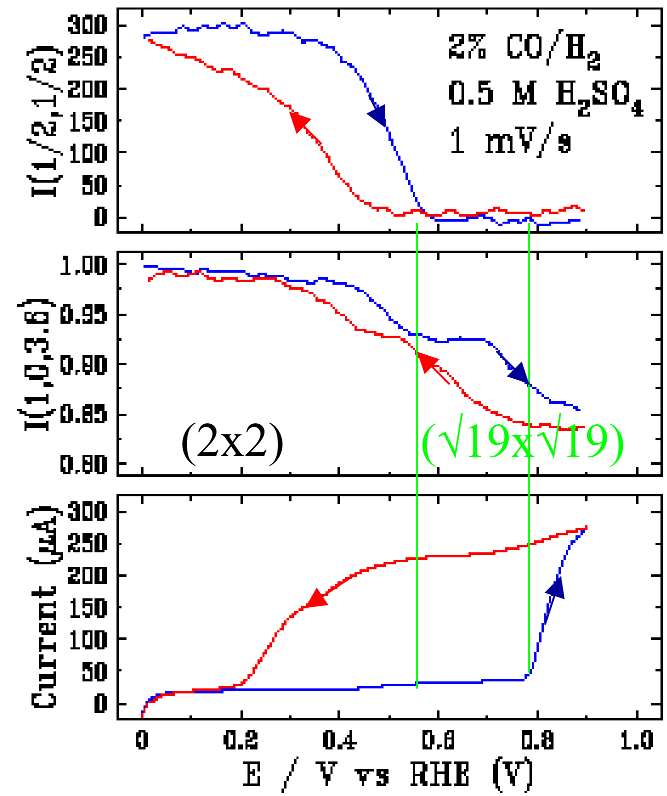
Fast phase transition – small energy barrier between different sites

CO ADSORPTION AND H_2 OXIDATION ACTIVITY ON Pt(111)

Phase behavior in 2% CO/H_2 in sulfuric acid solution



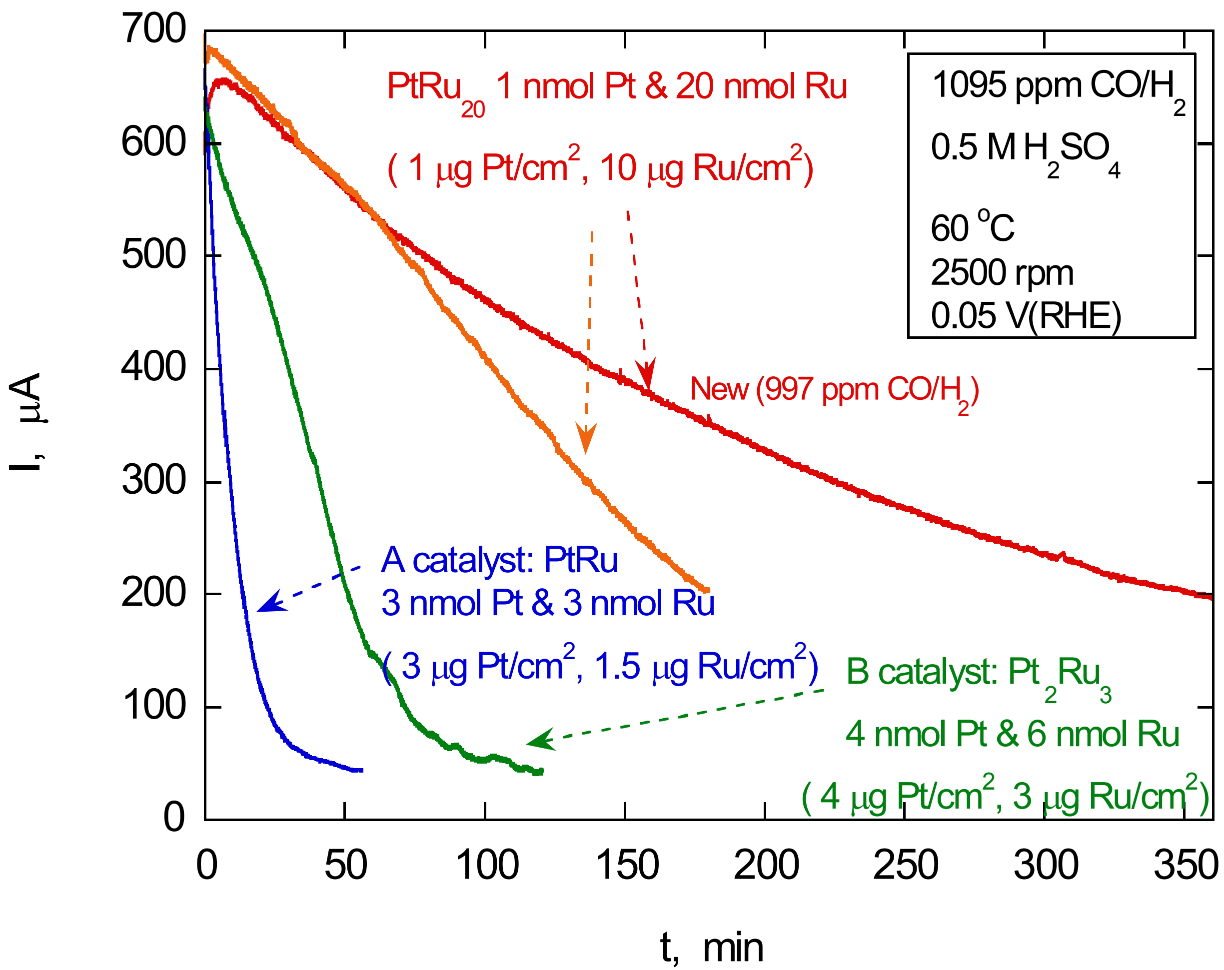
The (2x2) phase forms in small patches, which completely inhibit H_2 oxidation.



Larger hysteresis in activity than in CO phase transitions. Smaller inhibition by the low-coverage (√19x√19) phase.

IMPROVEMENT OF A $PtRu_{20}$ ELECTROCATALYST

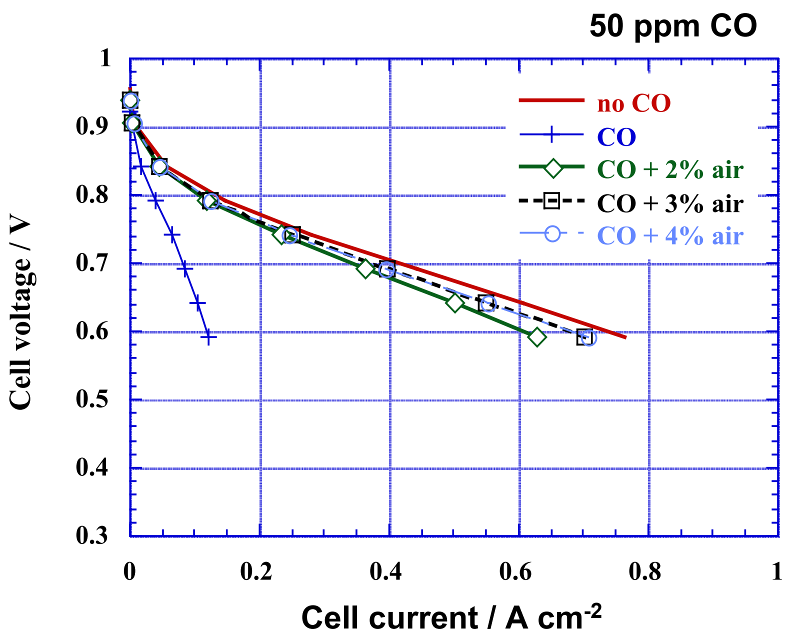
- Mixed Pt-other noble metal (Os, Re, Ir) adlayers on Ru are not better than $PtRu_{20}$
- Optimization of the preparation procedure resulted in an improved CO tolerance of $PtRu_{20}$

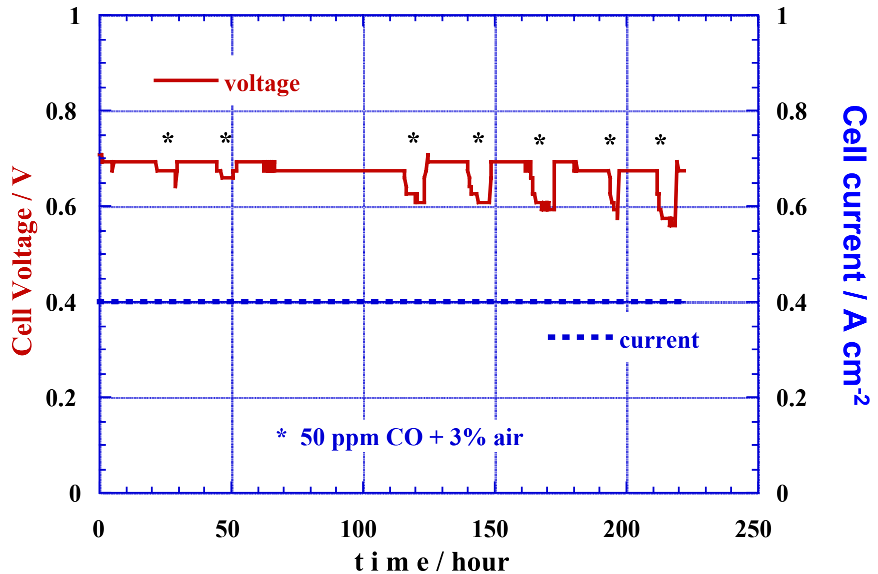


Low Pt Content Catalyst Long Term Test*

Carbon supported 1 w% Pt - 10 w%Ru catalyst (BNL)

Anode Pt Loading: 19 μg/cm^{-2}





50 cm^2 H_2/Air cell at 80 °C
A: 0.21 mg total metal/cm^2
C: 0.20 mg Pt/ cm^2
1.5 H_2 stoich

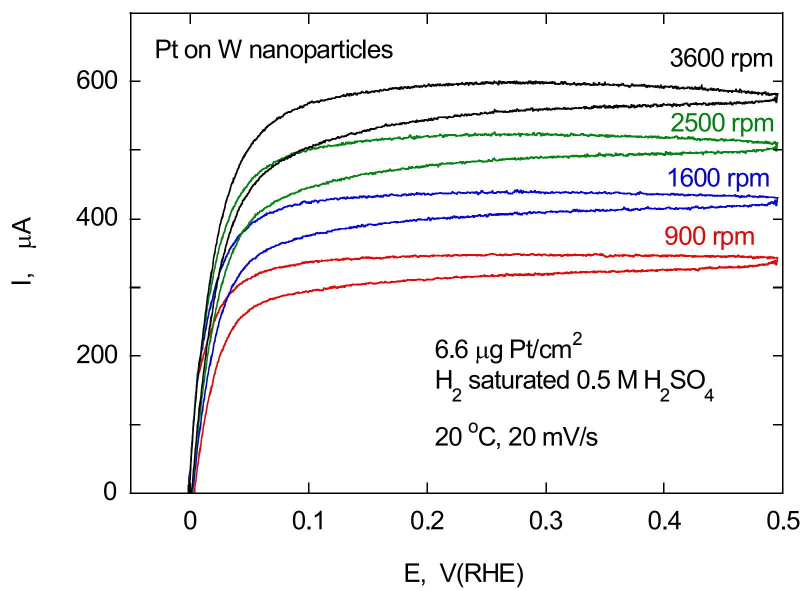
- **48.5 hrs operation with 50 ppm + 3% air CO**
- **Performance losses of 100 mV after 222 hr of operation at 0.4 A/cm^2 or 17 mV for H_2.**

*The results obtained by Francisco Uribe and coworkers, LANL

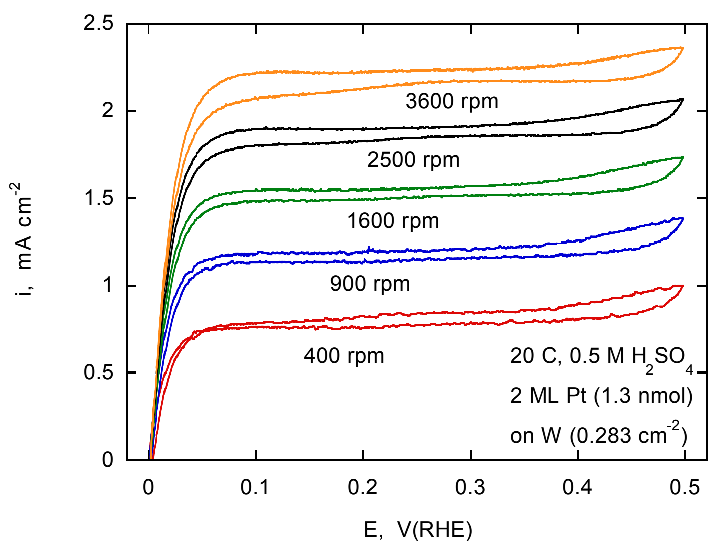
REDUCTION OF Ru CONTENT IN Pt/Ru ELECTROCATALYSTS

- RuNi, RuCo nanoparticles were deposited on XC-72 by wet impregnation and then Pt was deposited spontaneously. Compositions determined by EDX after Pt deposition. Activity of these catalysts is somewhat lower than that of Pt/Ru, CO tolerance similar.
- Pt/Wpoly and Pt/W/C have a good activity for H_2 oxidation but poor CO tolerance.

H_2 oxidation on Pt/W/C



H_2 oxidation on Pt_{2ML}/Wpoly

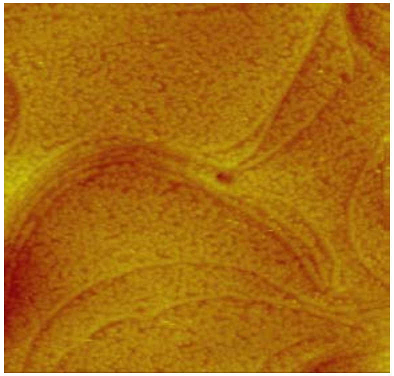


O_2 REDUCTION ON Pt MONOLAYERS on C-SUPPORTED METAL NANOPARTICLES

Pt MONOLAYER ON Au(111) BY REPLACING A Cu UPD ADLAYER

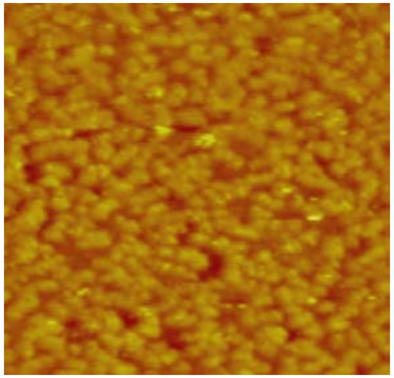
$Cu_{UPD}/Au + Pt^{2+} \rightarrow Pt/Au + Cu^{2+}$

320x320nm

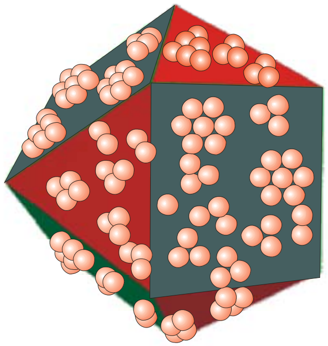


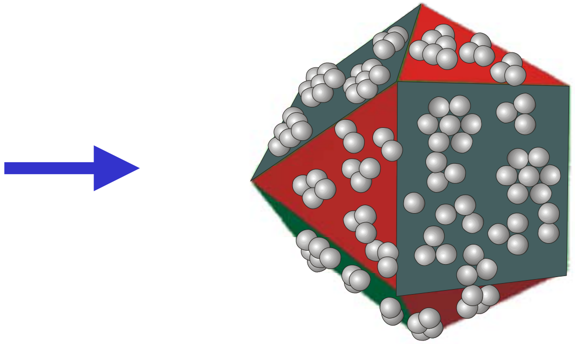
No step edge effects

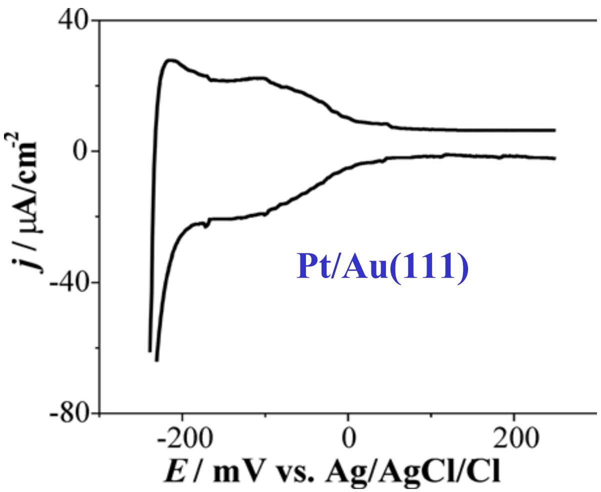
105x105nm

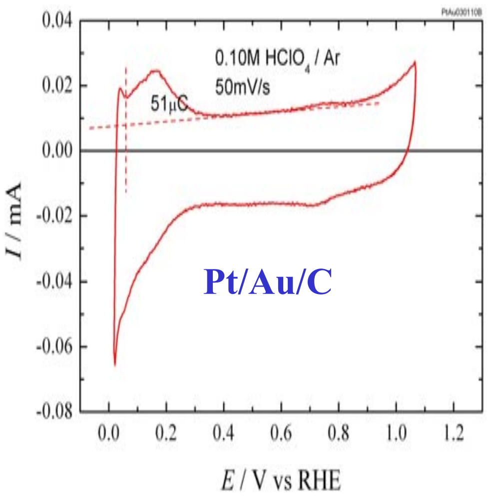


Low coordination of Pt atoms

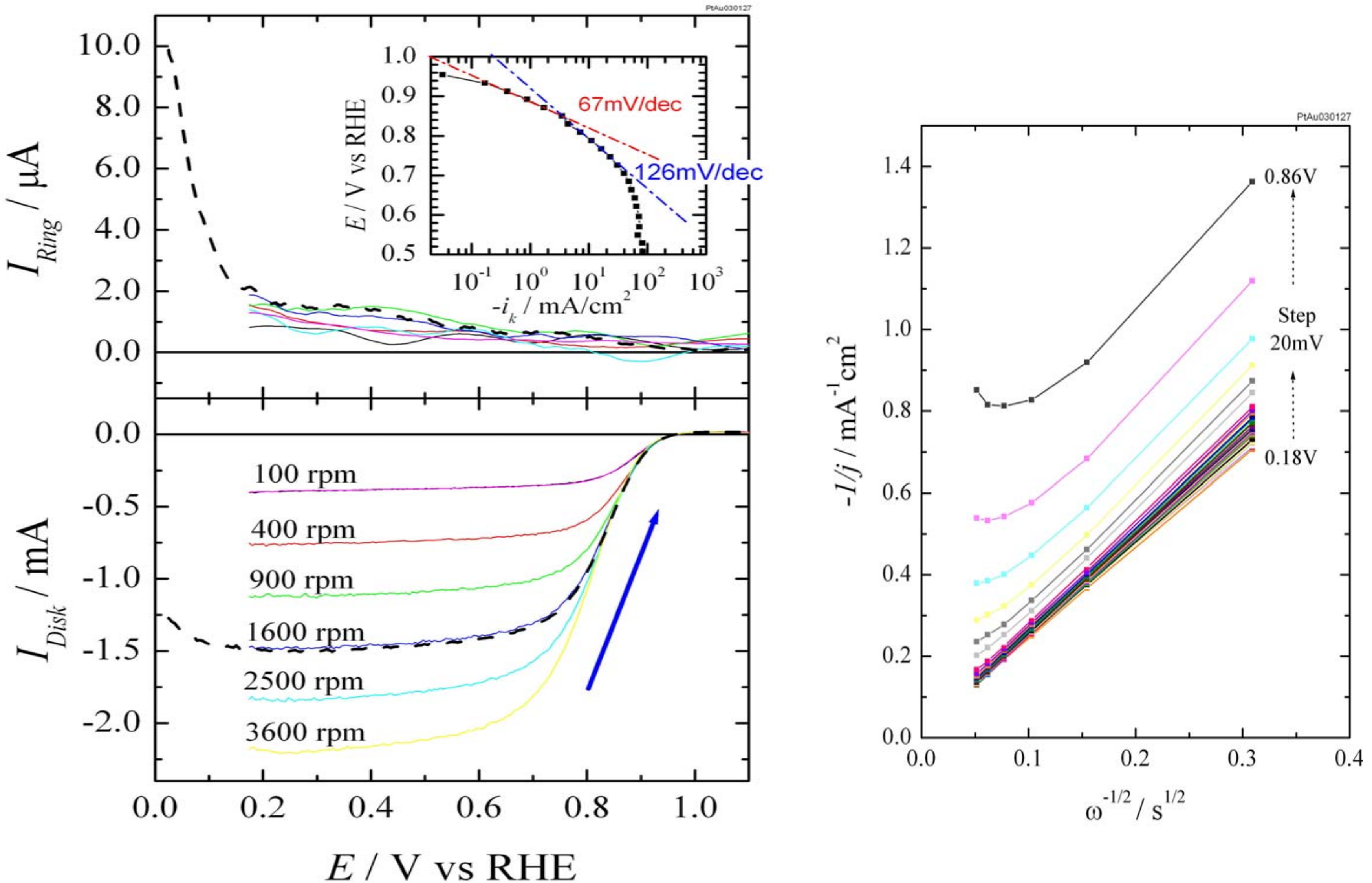






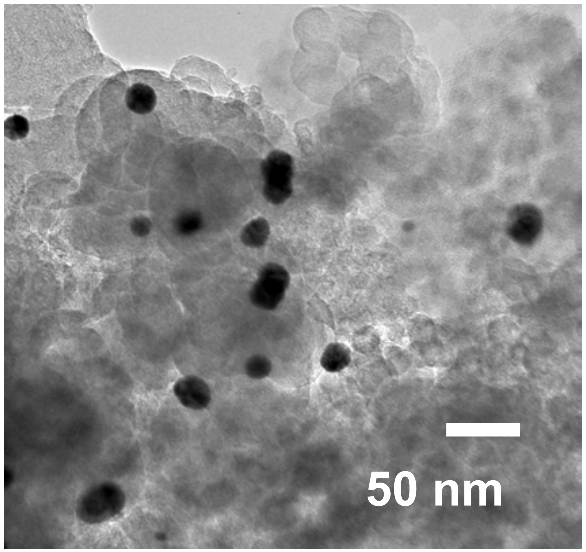


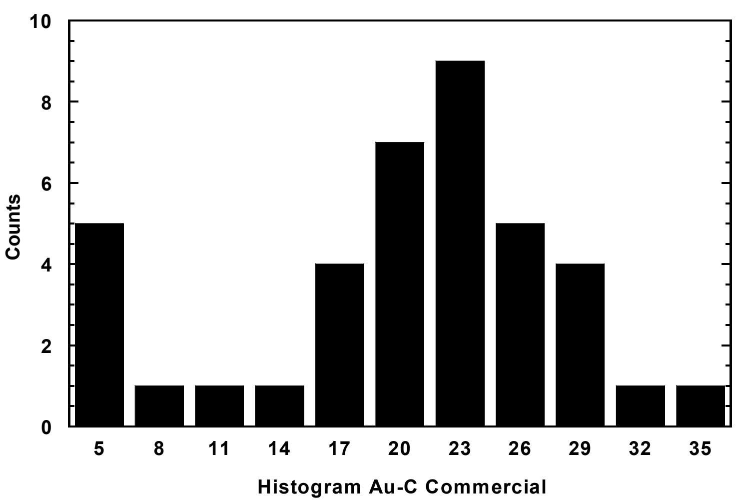
O_2 REDUCTION ON $Pt_{1ML}/Au(111)$

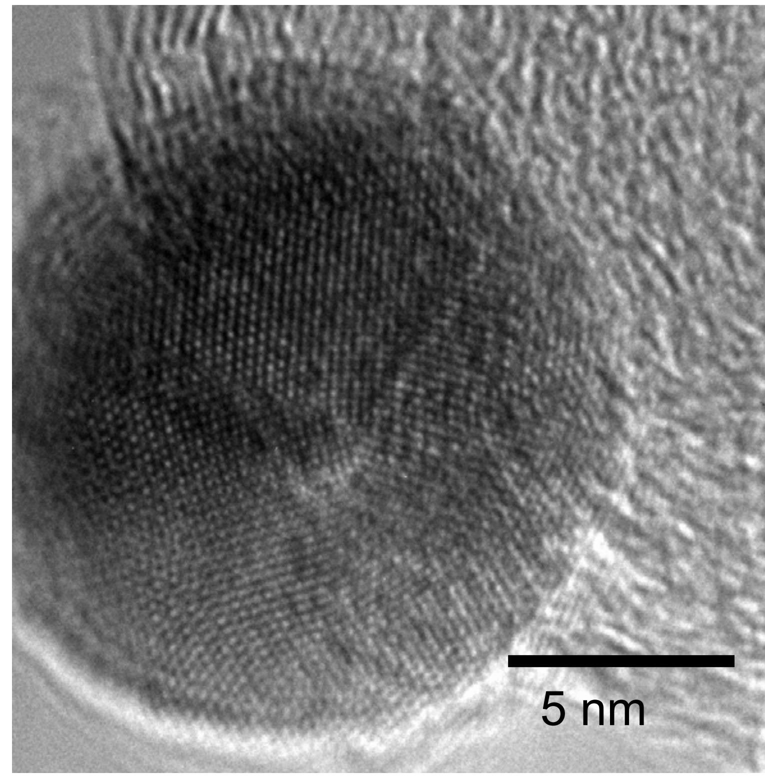


HRTEM OF Au NANOPARTICLES ON C

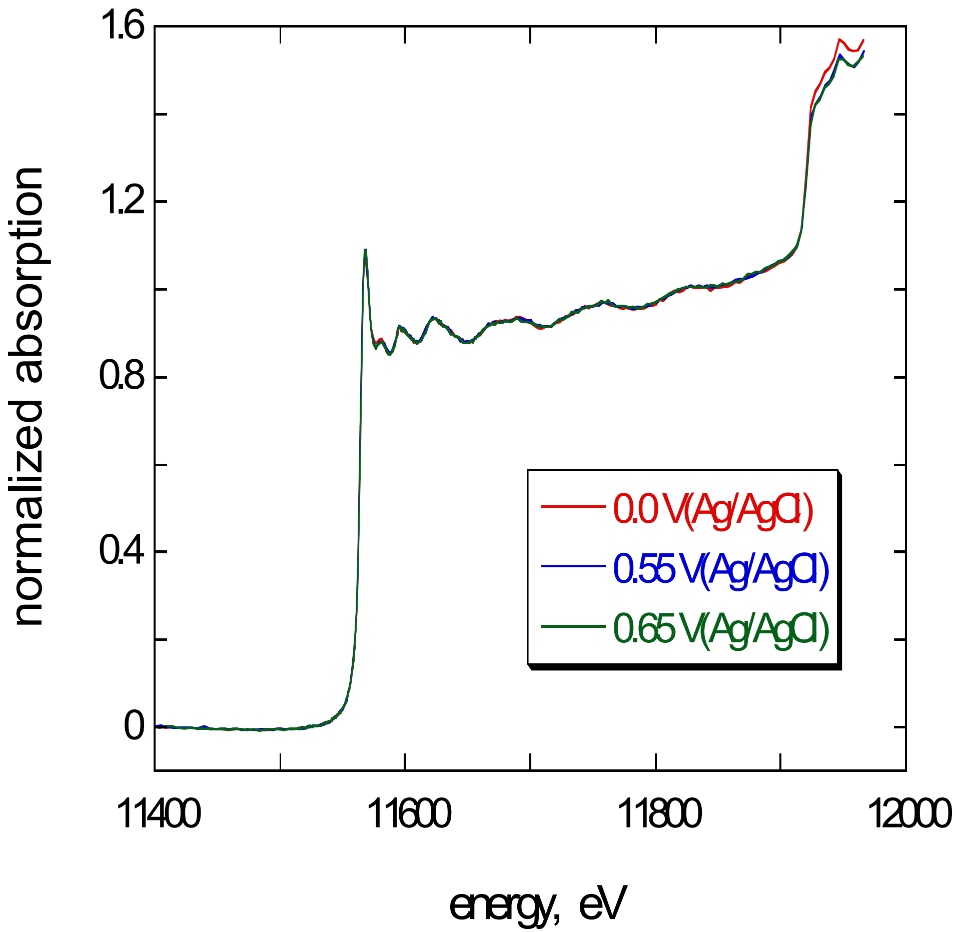
Au(10%) / Vulcan XC-72 commercial

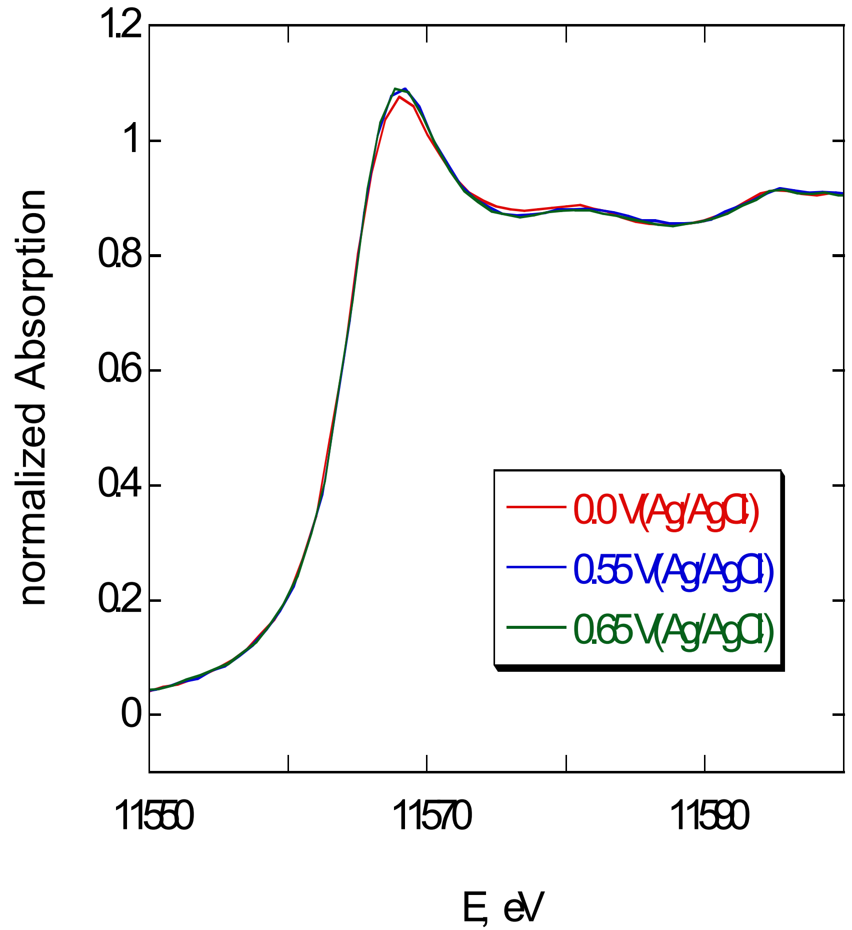






IN SITU XAS OF Pt/Au/C

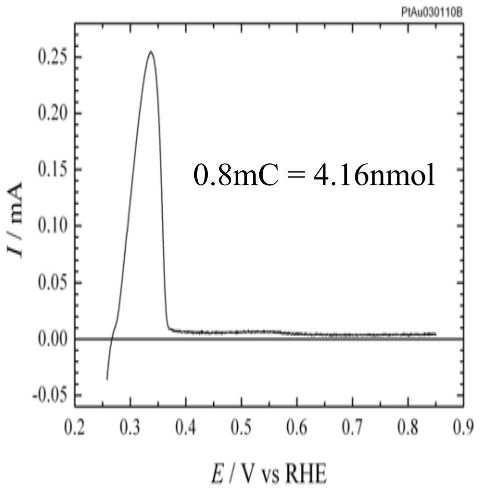


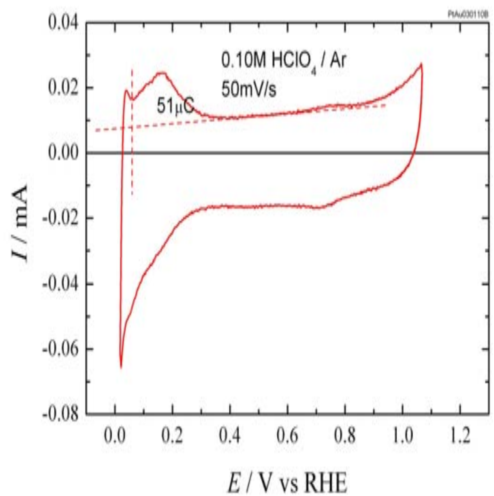


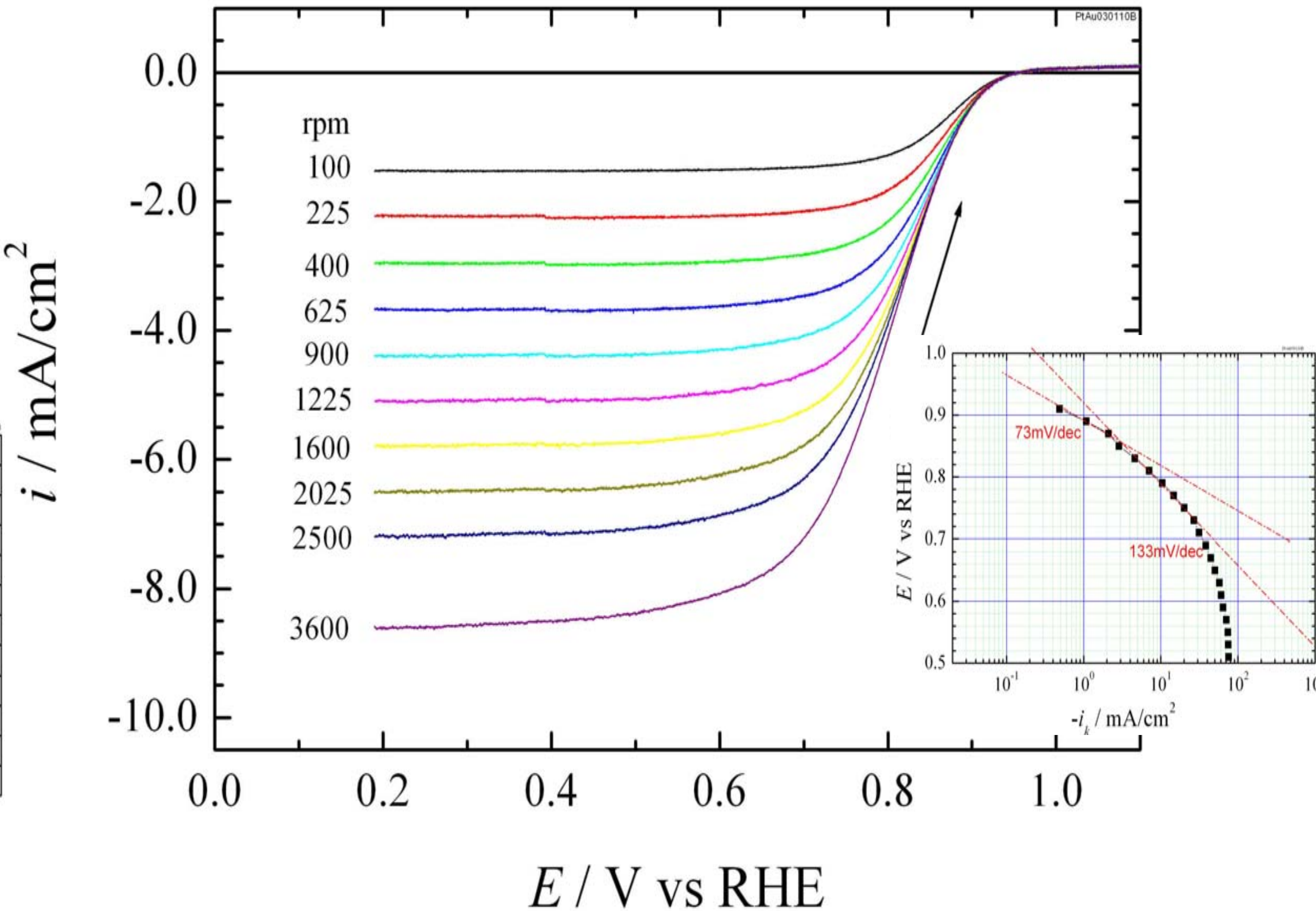
O_2 REDUCTION ON Pt/Au/C

Stripping Cu from Au nanoparticles

0.1M $HClO_4$; 10mV/s **Pt loading ~ 9 μg/cm²**



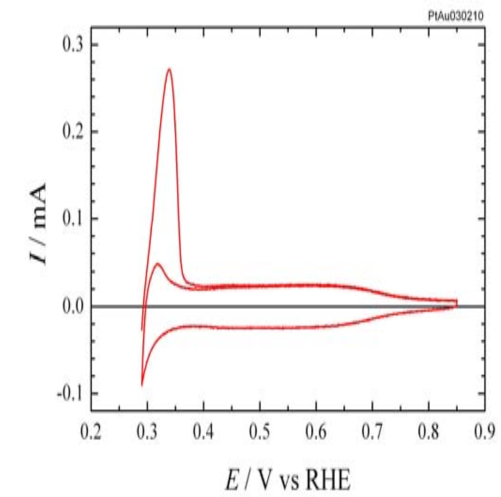


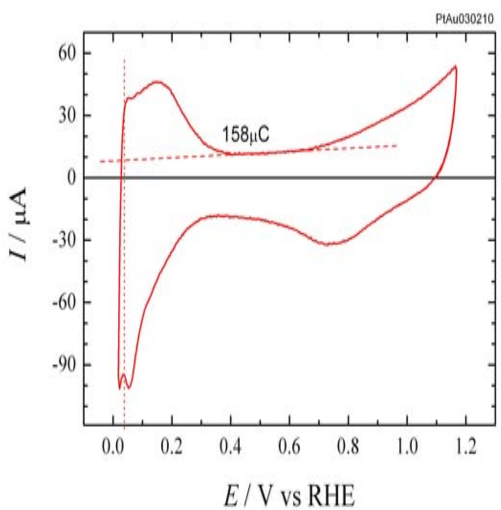


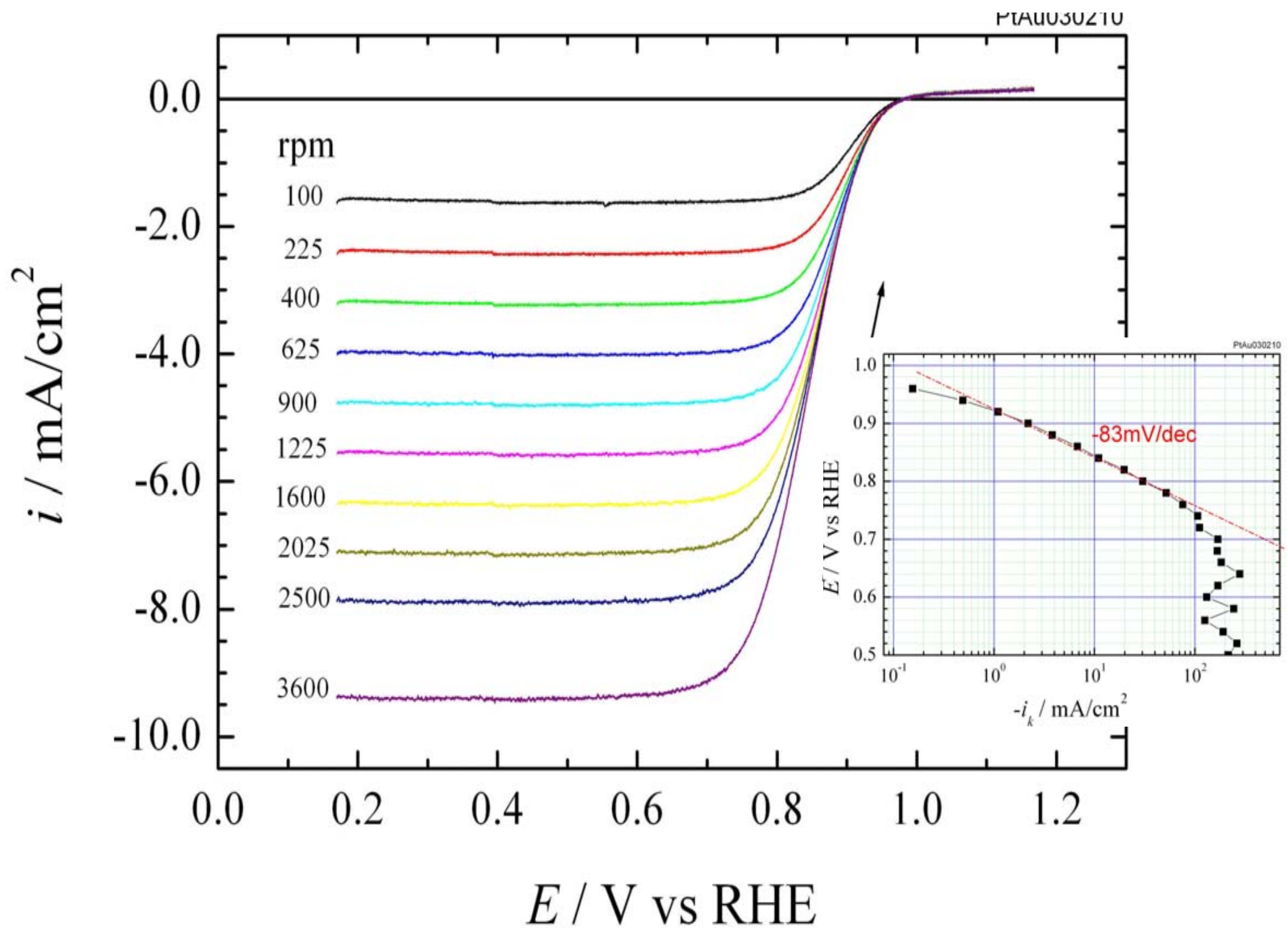
O_2 REDUCTION ON Pt/Au/C

0.1M $HClO_4$ 10mV/s

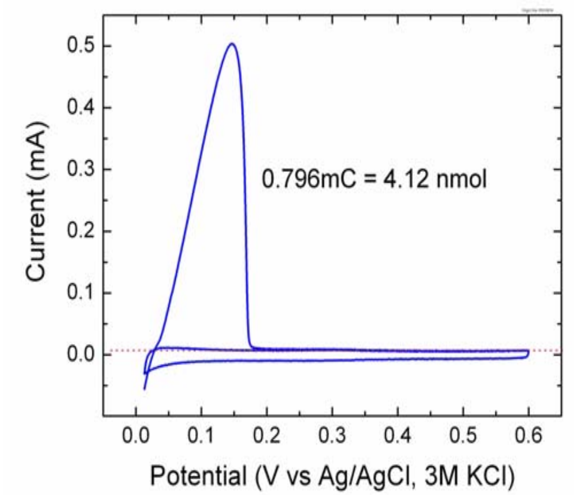
Pt loading ~ 18 μg/cm2

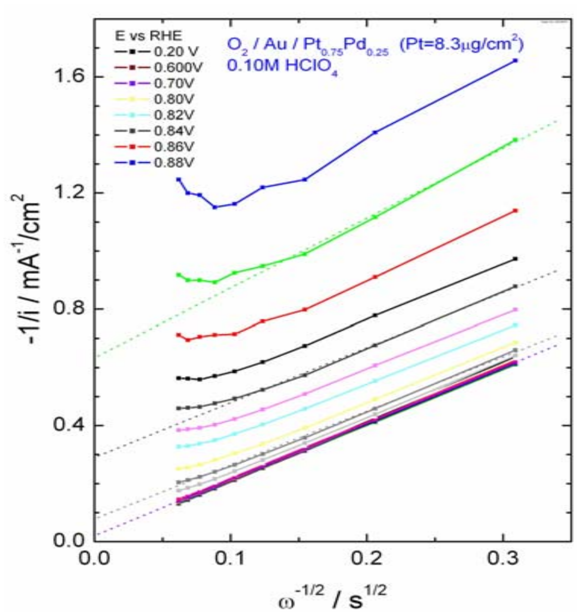


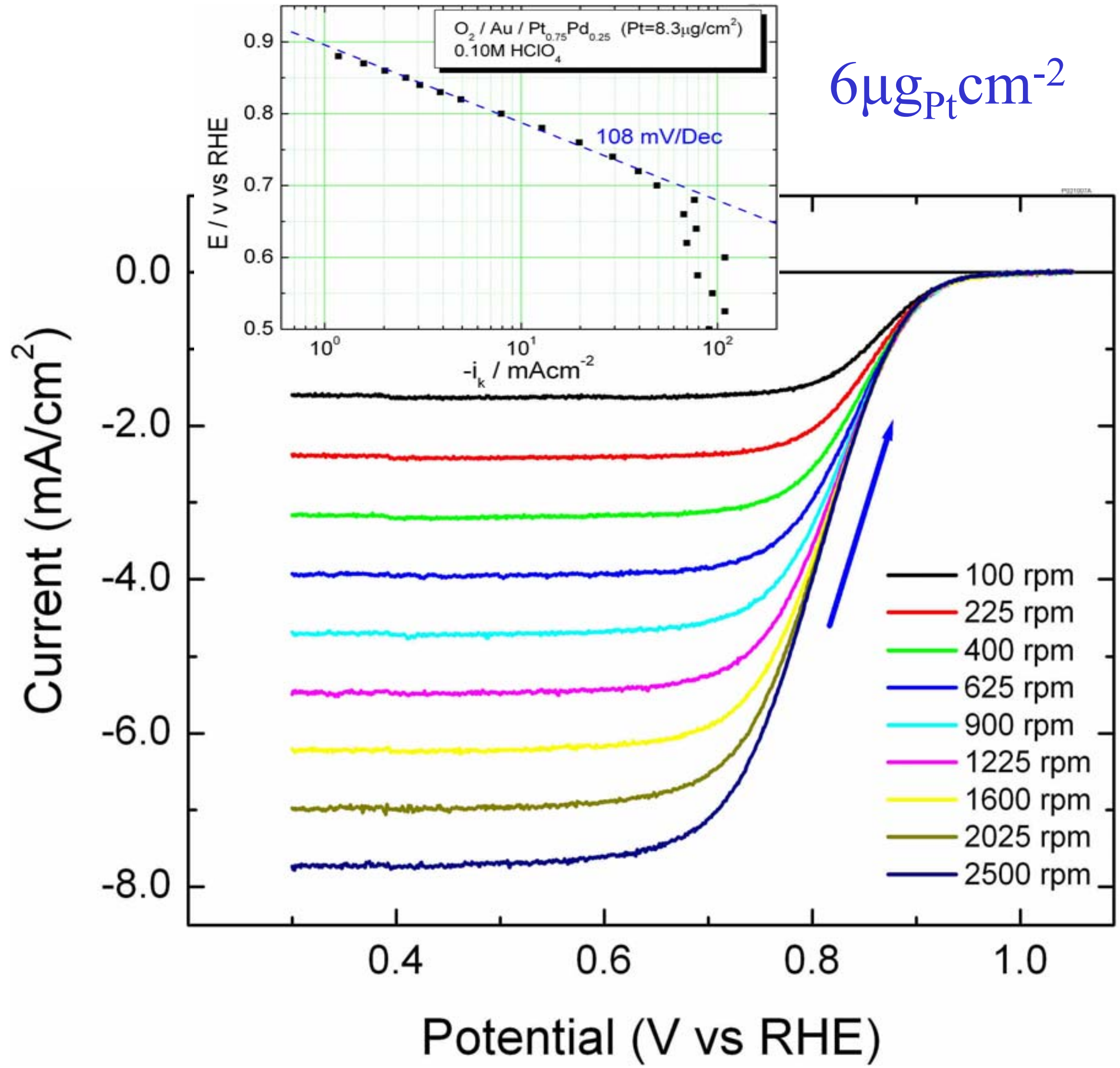




O_2 REDUCTION ON $Pt_{0.75}Pd_{0.25}$/Au/C





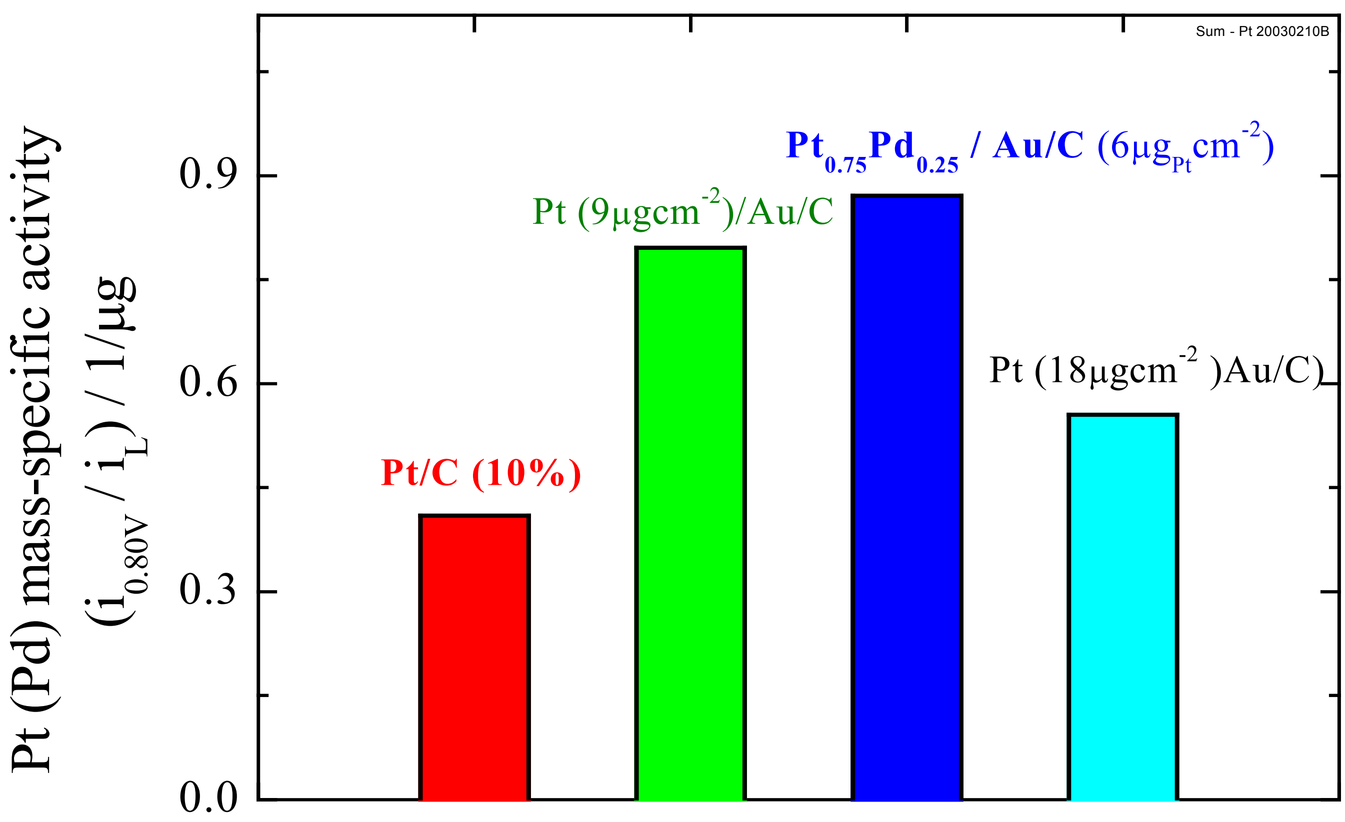


Tafel slopes and half-wave potentials for O_2 reduction on Pt adlayer electrocatalysts

Electrocatalyst/electrode	Tafel slopes / mv(dec)$^{-1}$		$E_{½}$ / V
	l.c.d	h.c.d.	
$Pt_{0.5}$ML/Au(111)	80	188	0.780
Pt_{1ML}/Au(111)	67	126	0.830
Pt(10%)/C	63	122	0.820
Pt_1/Au/C	71	133	0.820
$Pt_{0.75}Pd_{0.25}$/Au/C	65	88	0.817
Pt/Pd/Au/C	54	86	0.853
Pt_2/ Au/C	83	-	0.863
Pt(111) (Markovic et al.)	85	120	0.830

1-(9μgcm-2); 2-(18μgcm-2)

MASS-SPECIFIC ACTIVITIES OF SEVERAL ELECTROCATALYSTS



Interaction with Catalysts Manufacturers :

FCC & I Inc., and Plug Power; renewed contacts with E-TEK

Other Collaboration:

Los Alamos National Laboratory

Answers to the previous review:

Sintering of nanoparticles, stability, rearrangement of Pt?

Sintering is expected to be a lesser problem for Pt(1%)/Ru(10%) (a predominantly Ru particle) than for PtRu (1:1) alloy nanoparticles.

A Pt on Ru system is a strongly segregated case and Pt is expected to remain on a Ru nanoparticle surface. Entropy factors that favor mixing should be small for small nanoparticles.

Reactivation at positive potentials after prolonged tests indicates that Pt dissolution is not significant.

O_2 reduction is more important… - research commenced

FUTURE WORK

H_2/CO and H_2 oxidation

1. Optimization of a Pt/Ru electrocatalyst and final tests at LANL and industrial laboratories.

2. Pt or PtRu on W (W has a d-band vacancy smaller than other valve metals and the Pt/W system is strongly segregated). A 3D growth of Pt has to be suppressed.

O_2 reduction

1. Further development of Pt/Au/C electrocatalyst. Tests at LANL.
2. Investigations of Au-nonoble metal alloy nanoparticles as support for Pt.
3. Pt/Pd/C (initial results very good).