New Electrocatalysts For Fuel Cells

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Project ID
#FC10

Overview

Budget

- Total project funding
  - DOE share 100 %
- Funding received in FY04 : $ 450 K
- Funding for FY05 : $ 500 K

Barriers

- DOE Technical Barriers for Fuel Cell Components
  - Q. Electrode Performance

Partners

- Interactions/ collaborations
  General Motors Alternative Power Center (GAPC)
  3M

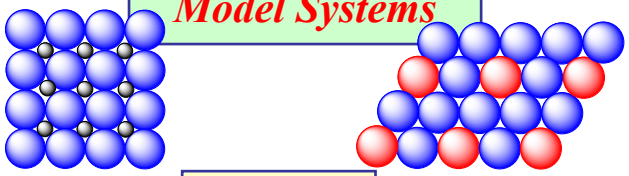
Objectives

- Reduce cost by reduction of precious metal loading (long term)
- Improve catalyst durability (long term)
- Re-examine “crystallite size effect” for oxygen reduction on carbon-supported Pt (FY2004-5)
- Determine effect of temperature of production of peroxide during oxygen reduction on Pt

  (FY2005)

LBNL *Materials-by-Design Approach*

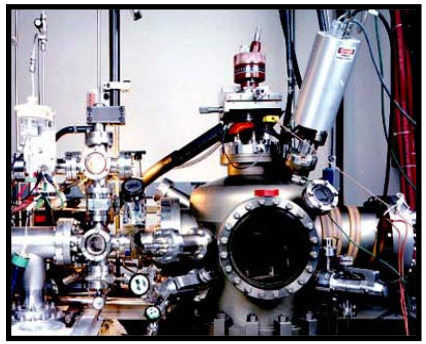
Model Systems



Ex-Situ

XPS

AES

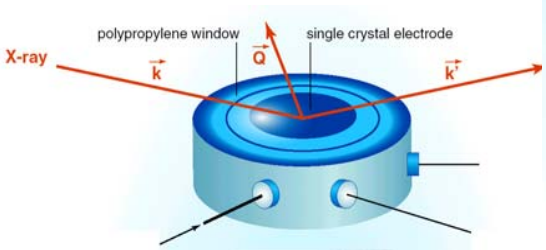


LEIS

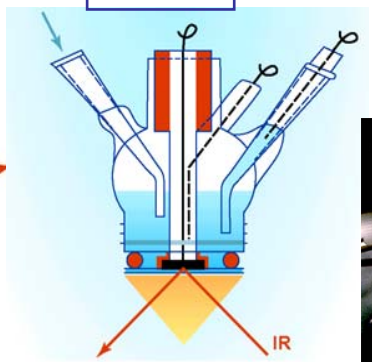
LEED

In-Situ

SXS

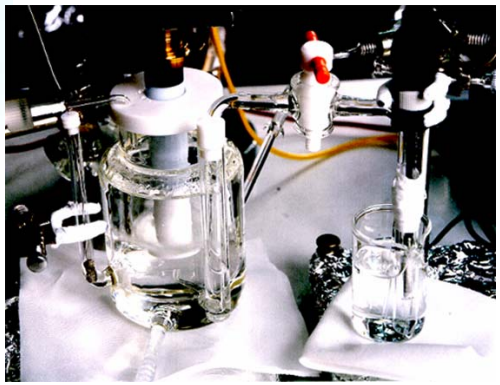


FTIR

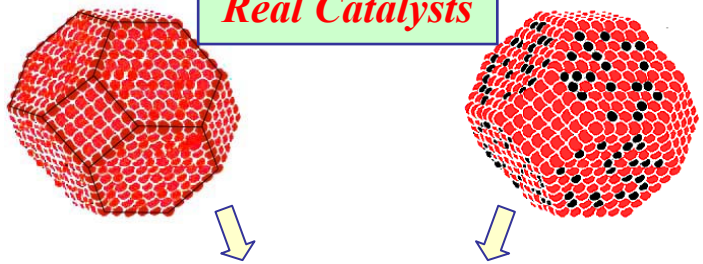


RRDE

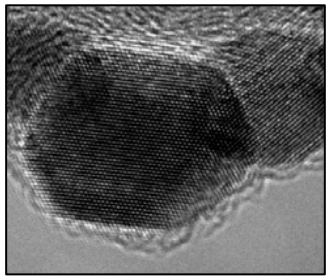
Kinetics

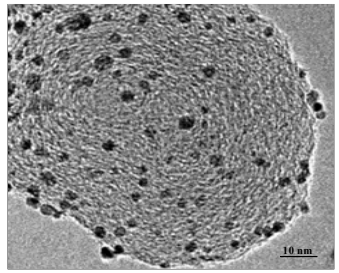


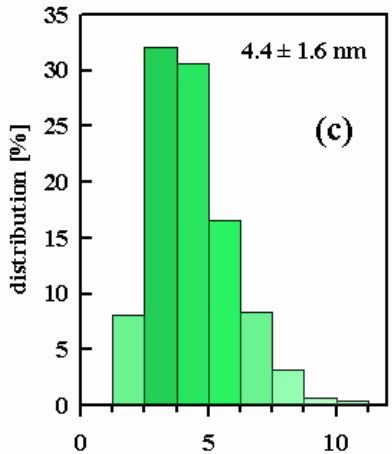
Real Catalysts



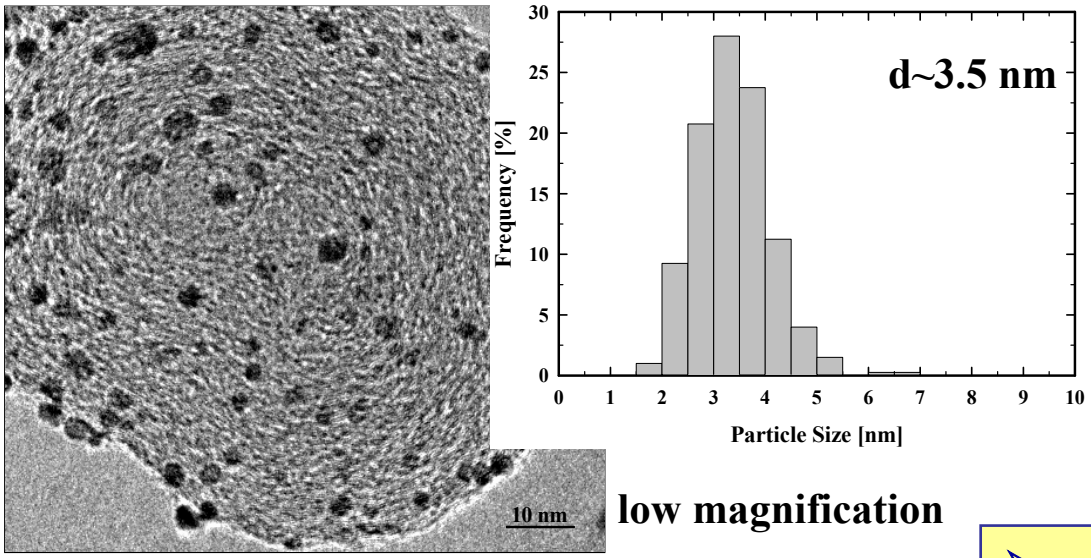
TEM





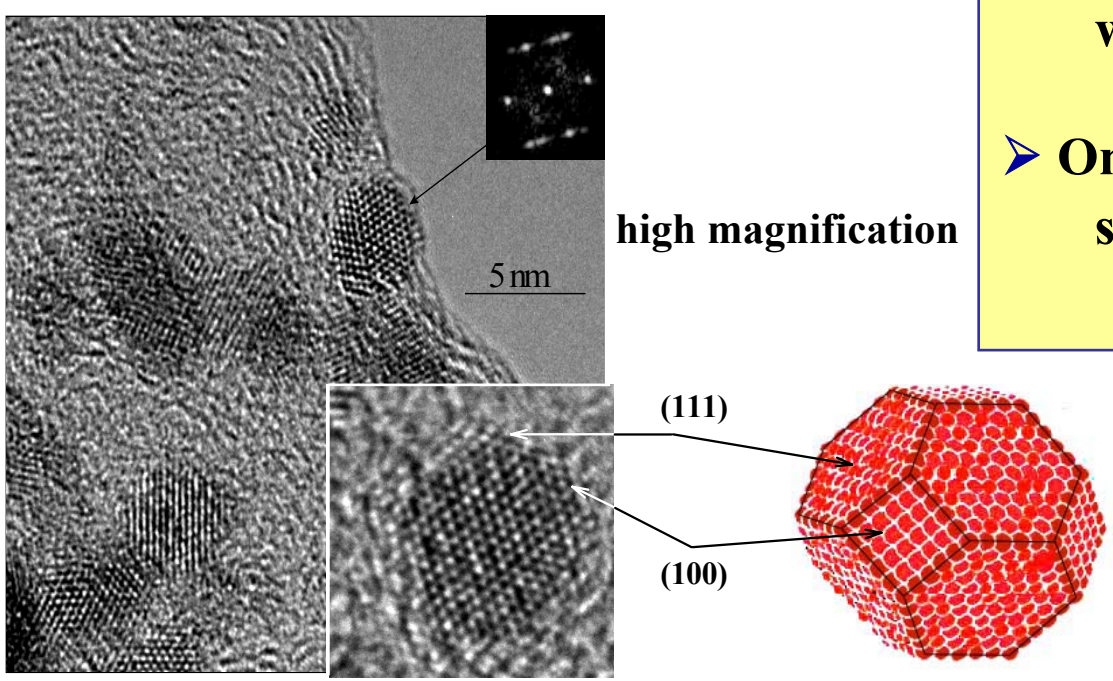


Characterization of Current PEMFC Pt Electrocatalyst



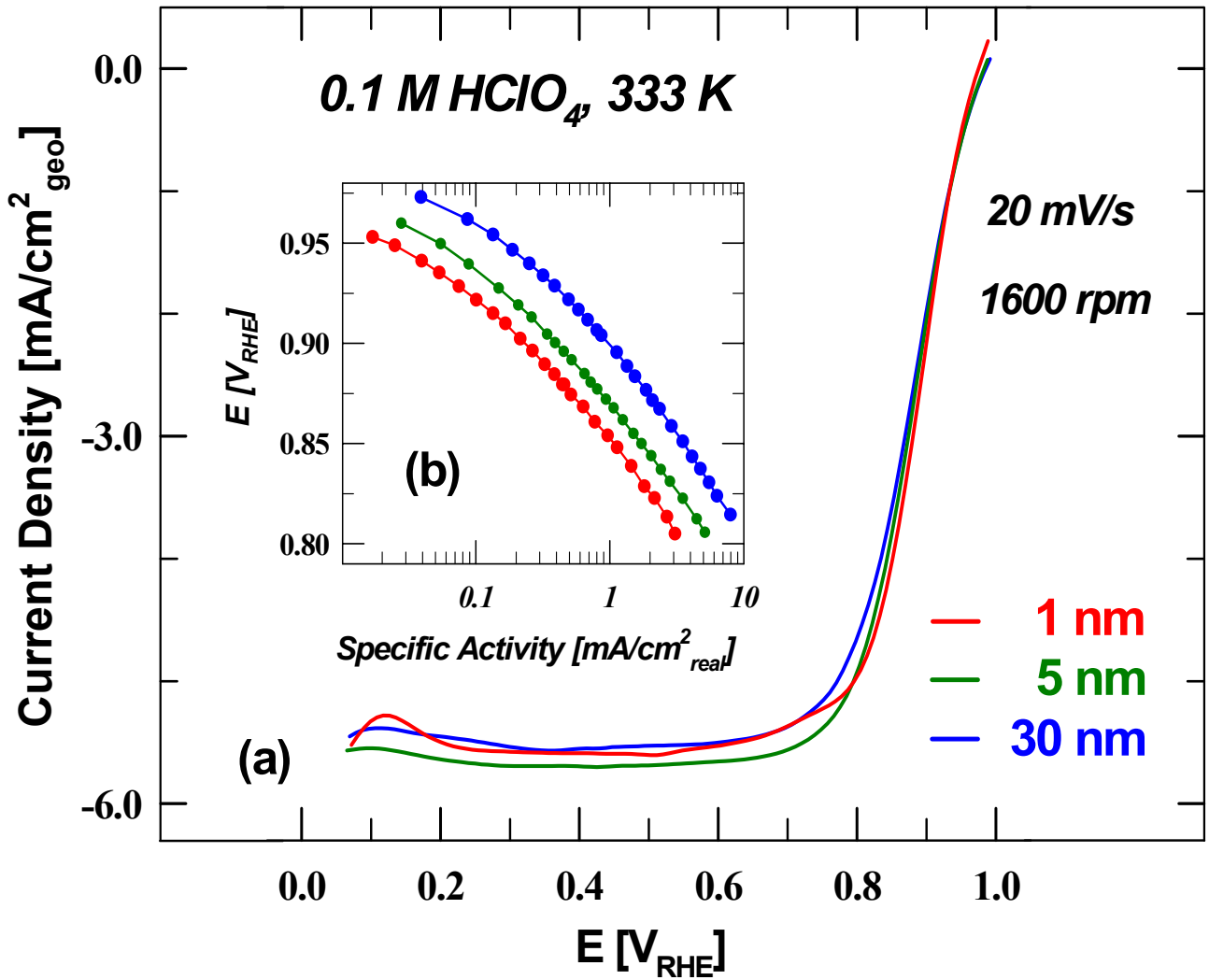
low magnification

Transmission electron microscopy

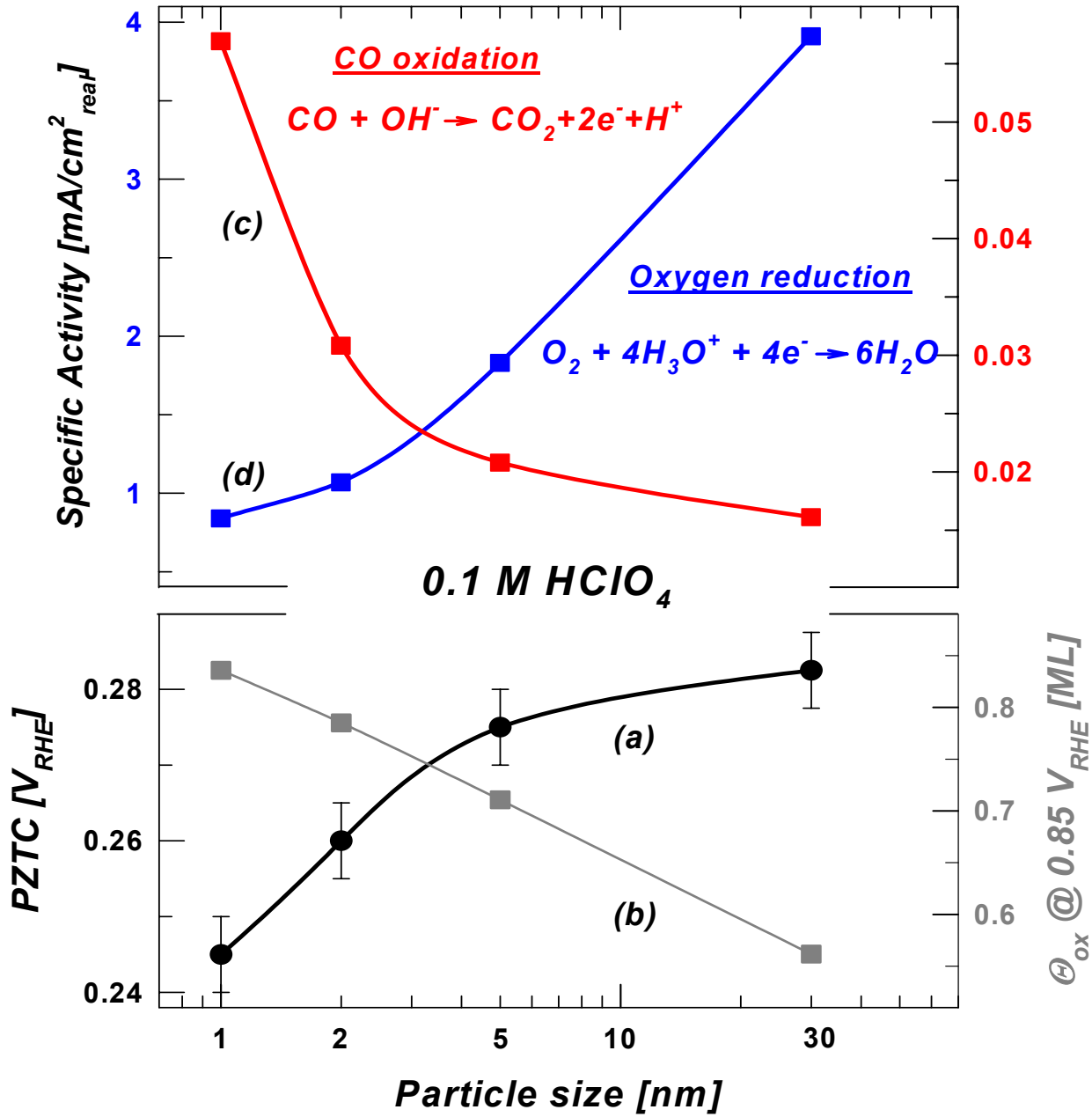


high magnification

- Mainly cubo-octahedral particles with {111} and {100} facets
- Only 25 % of Pt atoms are on the surface ⇒ 75 % are "buried"



(a) Comparison of the oxygen reduction reaction on the 1nm, 5nm and 30nm catalyst (the 2nm catalyst is not shown for clarity) (b) the potential is depicted against the specific activity (Tafel plot). Specific activity varies approximately as 1/d, where d is the average particle size.



Comparison of the results for CO(g) oxidation and O_2 reduction reaction on carbon supported Pt catalysts depending on the particle size and showing a correlation to coverage by OH and its impact on the kinetics of each reaction

Science Behind the Correlation

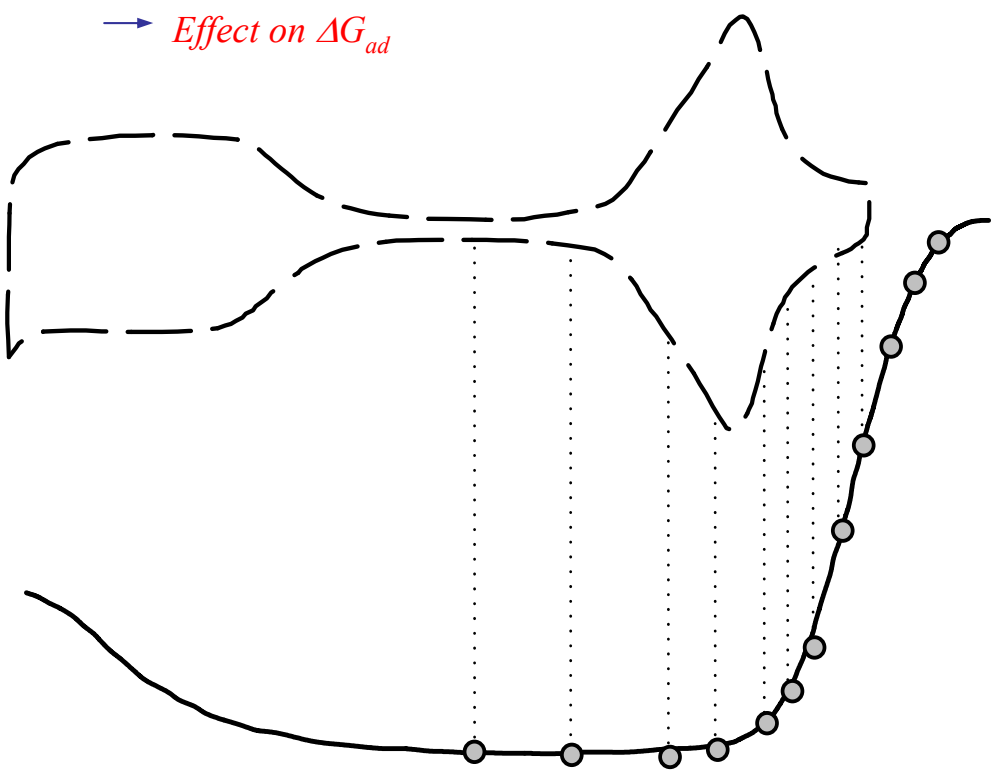
$$i = nFKc_{O_2}(1-\Theta_{ad})^x \exp(-\beta FE/RT)\exp(-\Delta G^*_{\Theta}/RT)$$

$(1-\Theta_{ad})$ term

Θ_{ad} is mostly OH_{ad} and A_{ad}, not $(O_2^-)_{ad}$

→ *Effect on availability of metal sites*

→ *Effect on ΔG_{ad}*



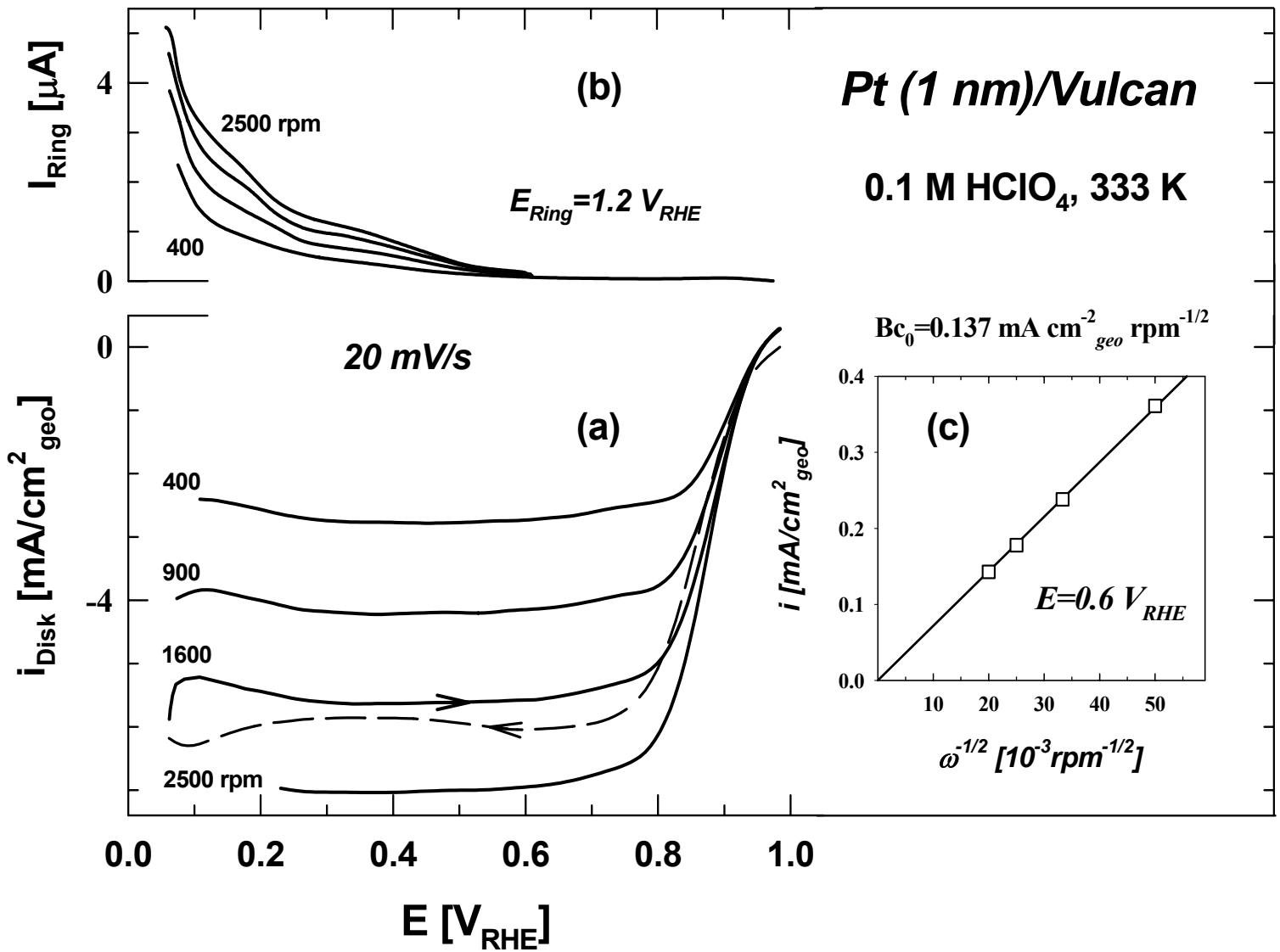
ΔG_{ad} term

O_2 *adsorption strength is uniquely related to the electronic properties of the electrode material*

$Pt - O_2^-$: $\Delta G_{ad} = -0.87$ eV

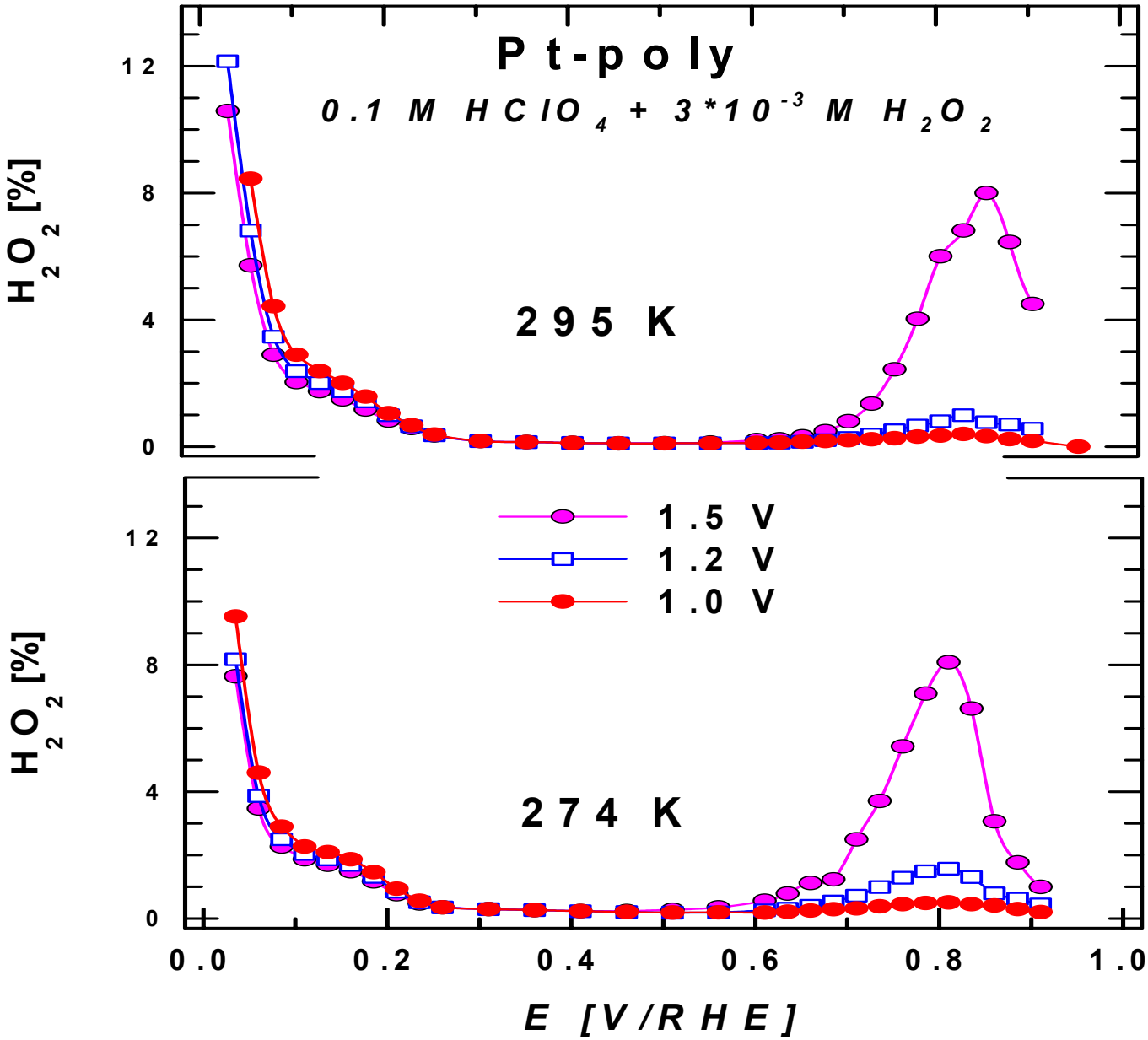
$Au - O_2^-$: $\Delta G_{ad} = +0.24$ eV

Is Peroxide Yield Higher on Pt Nanoparticles ?



Polarization curves for the oxygen reduction reaction (a) and the peroxide detection at the ring (b) for the 1nm catalyst at different rotation speeds. Experiments were conducted in 0.1M perchloric acid at 333K, with a scan rate of 20mV/sec. Insert (b) shows the Levich-Koutecky plot at 0.6V (diffusion-limited region).

Is Peroxide Yield Increased at Low Temperature ?



Conclusions Concerning Peroxide

Operation at 274 K does not produce any more peroxide at either electrode than operation at higher temperatures

Primary source of peroxide is at the hydrogen electrode from reduction of oxygen permeating through the membrane

Supported Pt catalyst does not produce more peroxide than unsupported Pt except at potentials below 0.4 V. Differences are still small and probably not of practical importance.

Anticipated Gains with Pt Bimetallic Nanoparticles

- **Substitution of Pt atoms "buried" in interior of particle with atoms of non-Pt group element atoms**

- **Possibly higher activity for Pt surface atoms by electronic modification from intermetallic bonding (alloying effect)**
  - **Norskov and Hammer theory correlates the position of d-band center to H_{ad} and O_{ad} adsorption energies**

- **Pt loading reduced (without any loss of performance) by a factor of 4 –5 seems possible**

Bimetallic Catalysts

Model Systems

Monolayer

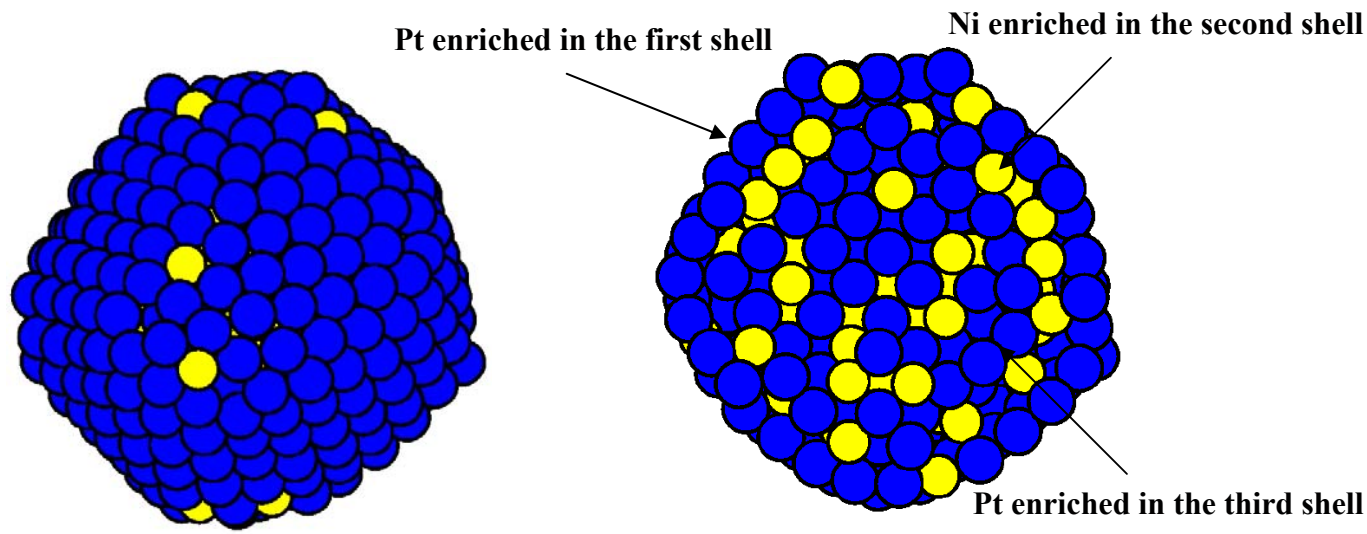
Ni, Pd, Pt	*surface*
bcc(110) fcc(111) hcp(0001)	*substrate*

Nb, Ta, Mo, W, Re,
Ru, Ir, Os, Ni and Pt

Sandwich

Pt	*surface*
3*d*-TM	*subsurface*
Pt(111)	*substrate*

Model



$Pt_{75}Ni_{25}$ fcc cubo-octahedral nanoparticle

Discussion

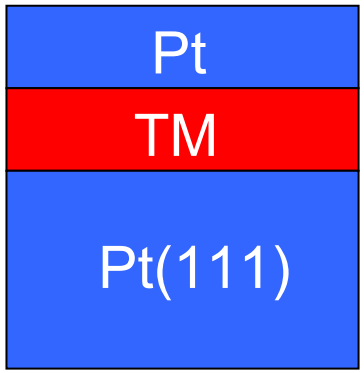
A. Upon annealing the sputtered alloy surfaces, the DOS at Fermi level is reduced, and the center of d-band moves away from the Fermi level.

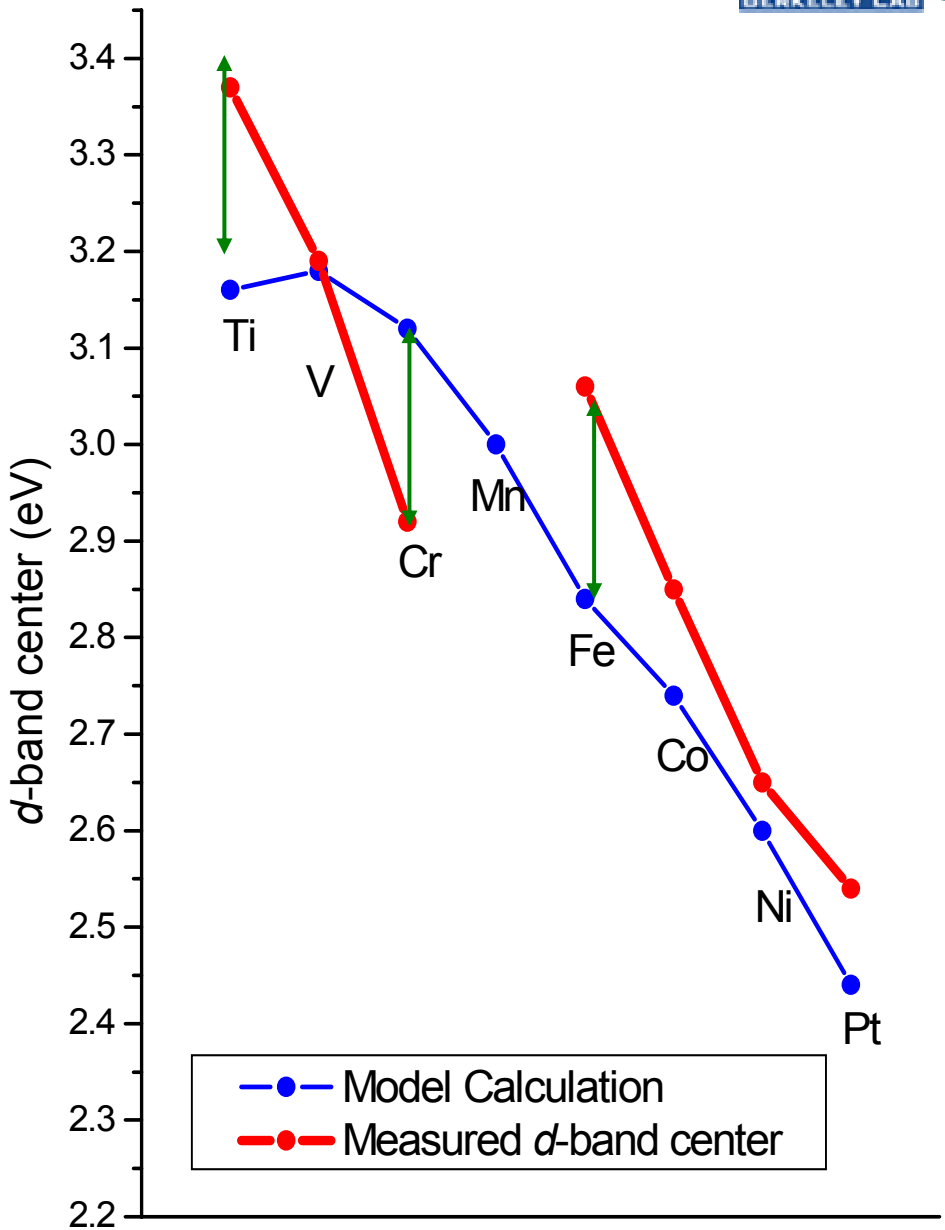
B. Overall, the slope of d-band center gives good qualitative agreement with theoretical model.

C. The deviations on Ti, Cr, and Fe suggest possible different structure from theoretical model, I.e. not having surface sandwich In fact, theory suggests strong anti-segregation for all these 3d-TM on Pt surface (A. Ruban, Phys. Rev. B 59 15990)

D. The theory is based on Pt (111) substrate while the measured samples are polycrystalline. In experiment, contribution from other crystal planes is present (could increase shift).

Sandwich

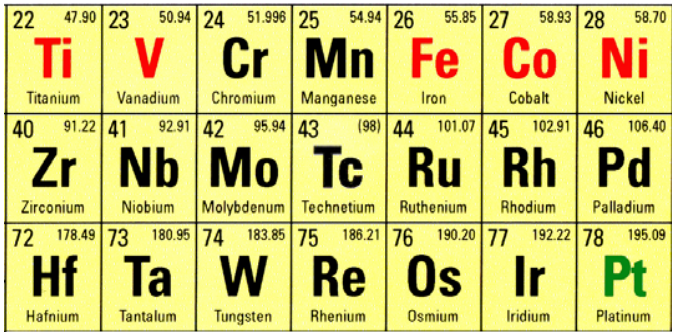


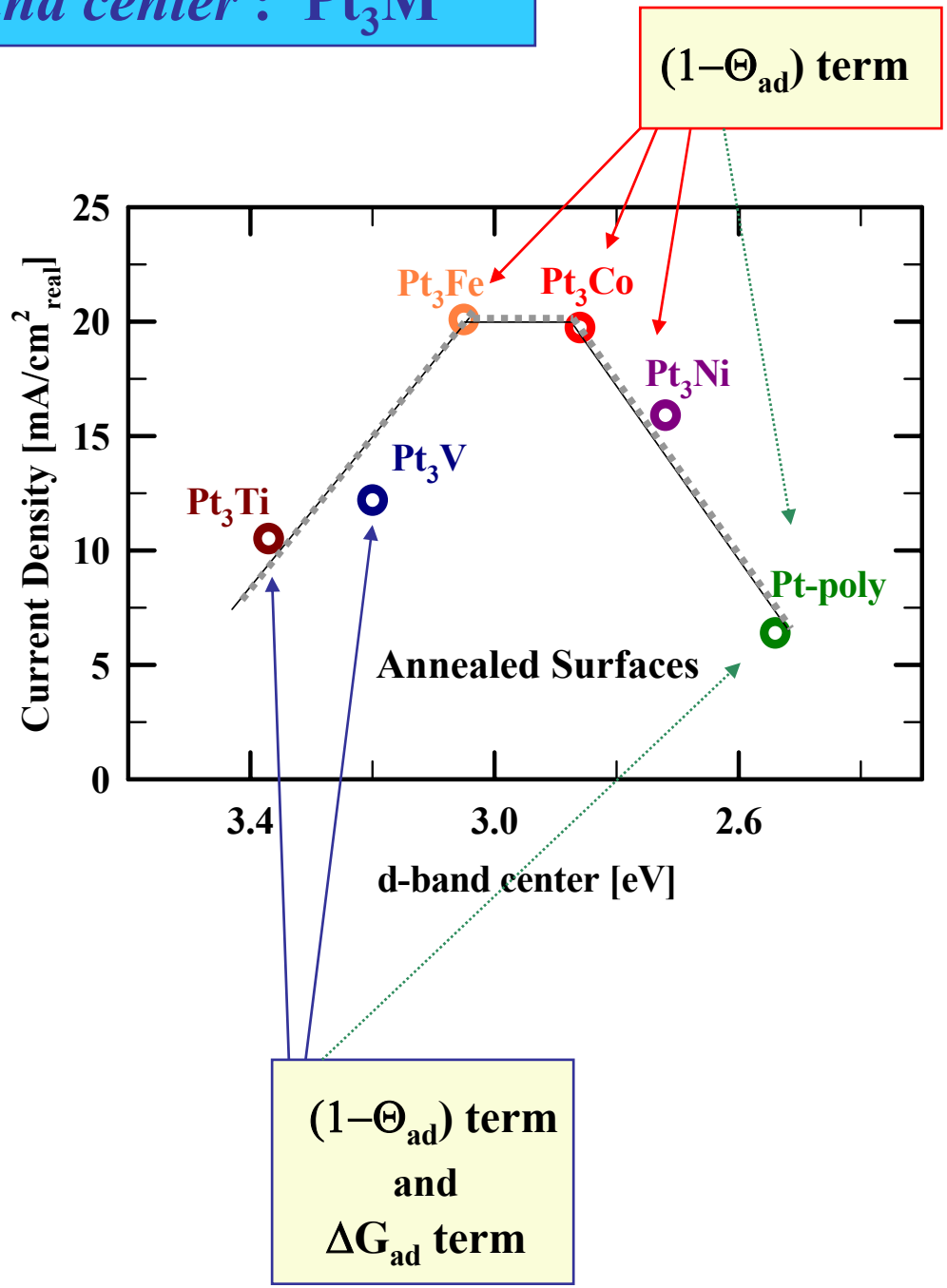


Periodic table of 3d transition metal

J. R. Kitchin, J. K. Nørskov, J. G. Chen, and M. A. Barteau, *J. Chem. Phys. 120, 10240 (2004)*

ORR activity vs. d-band center : Pt_3M





- Pt_3Co model catalysts project a five-fold increase in activity
- Nanoparticle Pt_3Co catalyst show a two to three fold increase vs pure Pt nanoparticles of same size
- Pt_3M have different structure sensitivity for ORR than pure Pt (i.e. the Devil is in the details)

d-Band DOS of $Pt_3Ni(hkl)$

- Shift in d-band center between Pt(hkl) and $Pt_3Ni(hkl)$ varies strongly with hkl
- Shift decreases with decreasing surface coordination number
- Suggests electronic effect of the surface sandwich structure in bulk alloy is diminished in nanoparticles (consistent with experiment)
- Optimized catalyst has both controlled particle size and **shape**

	Pt (100)	Pt3Ni(100)
d-band center	2.90 eV	3.14 eV
d-band width	3.59 eV	3.77 eV

	Pt (110)	Pt3Ni(110)
d-band center	2.70 eV	2.53 eV
d-band width	3.49 eV	3.27 eV

	Pt (111)	Pt3Ni(111)
d-band center	2.76 eV	3.09 eV
d-band width	3.42 eV	3.74 eV

Future Plans

<u>Balance of FY2005</u>
Complete development of chemistry for synthesis of carbon-supported Pt-Re nanoparticles (3 – 5 nm)

<u>FY2006</u>
Pursue bimetallic catalysts with controlled particle size and shape
- Thin films on non-carbon fibers
- Non-carbon support material with strong metal-support interaction (induces raft or disc shapes)

<u>FY2007</u>
P.I. Retires from Berkeley Lab and program in its present form concludes

Publications and Presentations

Journal Publications

Stamenkovic V, Grgur BN, Ross PN, et al "Oxygen reduction reaction on Pt and bimetallic Pt electrodes covered by adsorbed CO- Mechanism of air bleed effect with reformate", *Journal of the Electrochemical Society* **152** (2): A277-A282 (2005)

Arenz M, Stamenkovic V, Ross PN, et al. "Surface electrochemistry on Pt(111) modified by a pseudomorphic Pd monolayer", *Surface Science* **573** (1): 57-66 (2004)

Presentations

N.M. Markovic, Keynote Address, "Electrocatalysis at the Atomic and Molecular Levels", International Society of Electrochemistry (ISE), Thesseloniki, Greece, September 2004

P.N. Ross, "Effect of Temperature on Reduction of Oxygen to Peroxide on Pt Electrodes", Workshop on Freezing of PEM Fuel Cells, Phoenix AZ, February 2005.