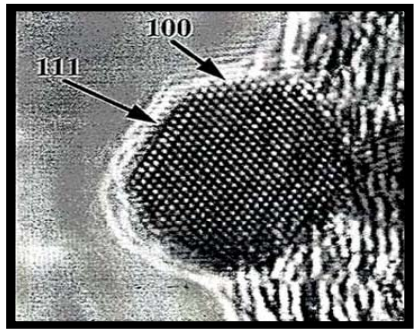
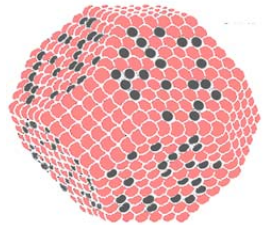
New Electrocatalysts For Fuel Cells





Objective: Reduction of precious metal loading

Principal Investigator: Philip N. Ross, Jr.

Staff Scientist: Nenad M. Markovic

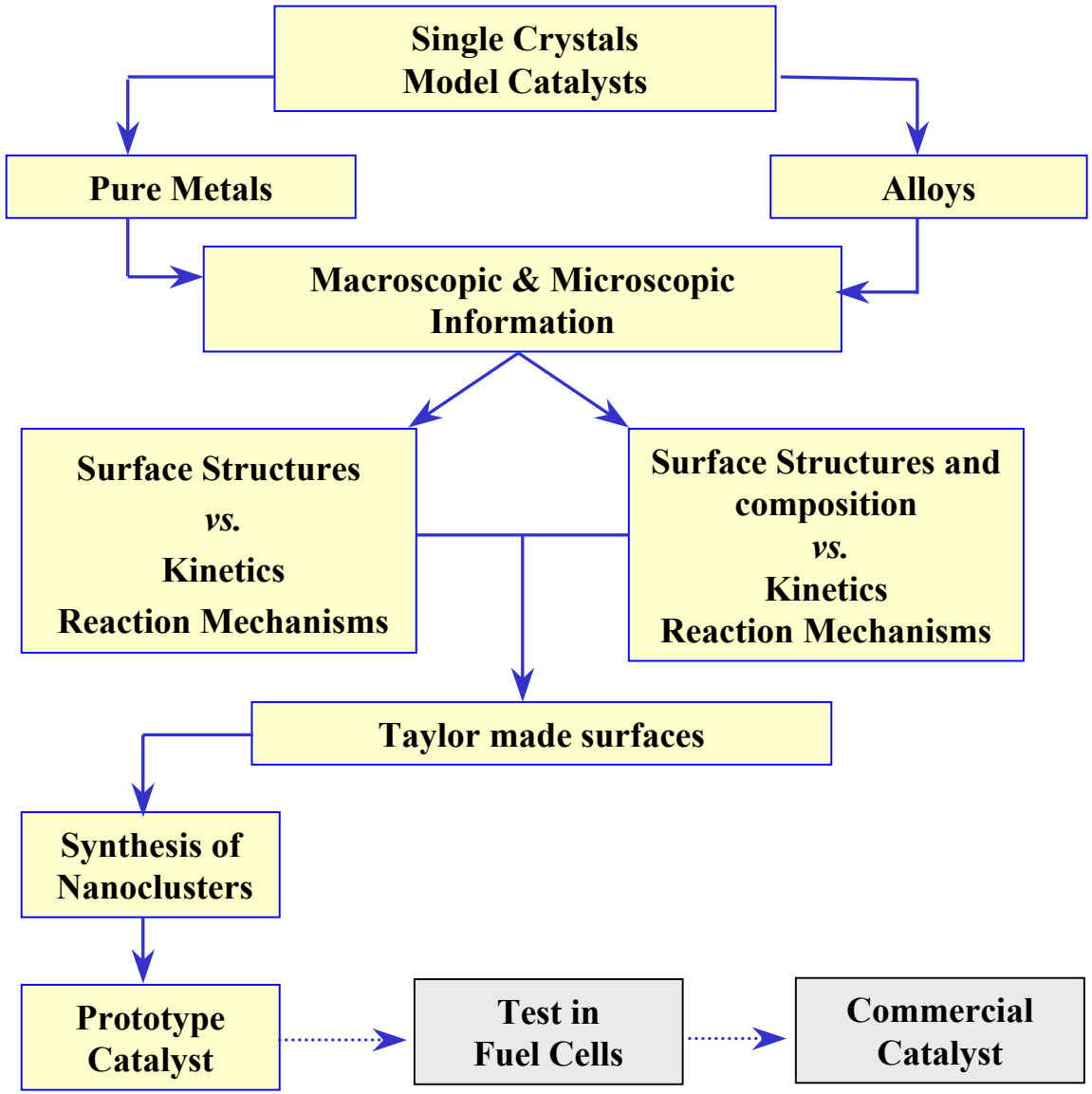
Post Doctoral Fellow: Vojislav Stamenkovic

Visiting Scientists: Matthias Arenz (Humboldt Fellow)

Berislav Blizanac (Belgrade)

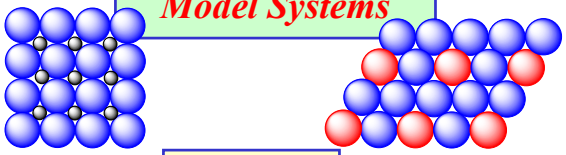
A research program conducted at the Lawrence Berkeley National Laboratory for the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Advanced Transportation Technologies of the U.S. Department of Energy under contract No. DE-AC03-76SF00098

LBNL *Materials-by-Design Approach*



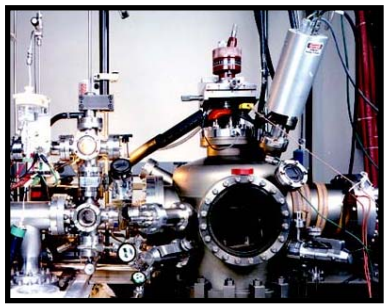
Methodologies

Model Systems



Real Catalysts

Ex-Situ



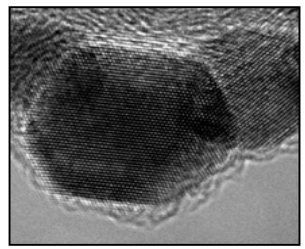
XPS

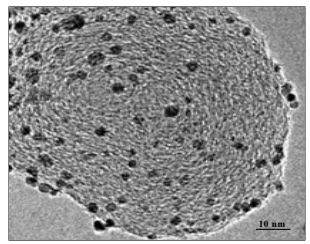
AES

LEIS

LEED

TEM



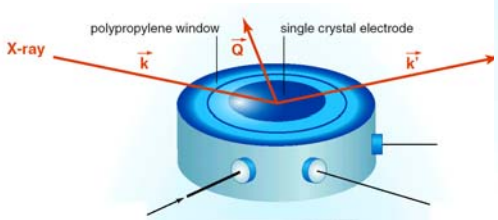


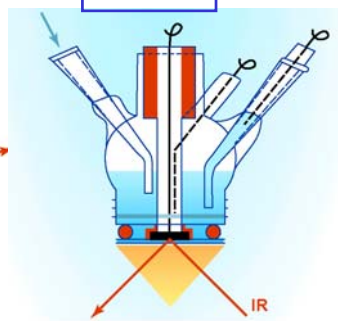
In-Situ

RRDE

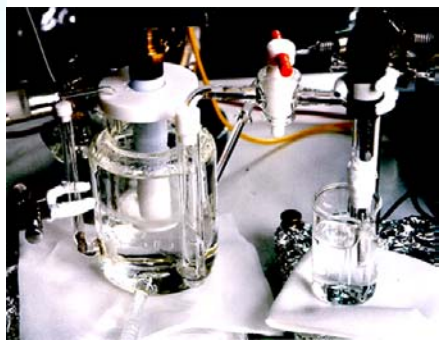
FTIR

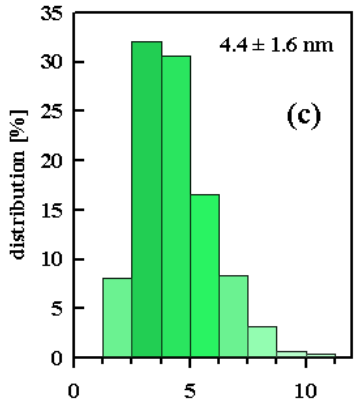
SXS





Kinetics

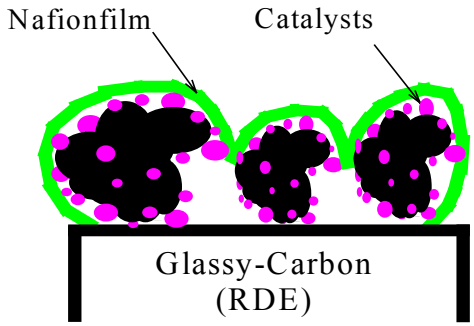




Collaborations

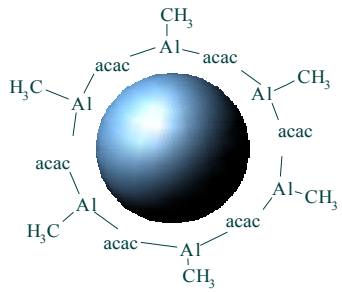
Industry

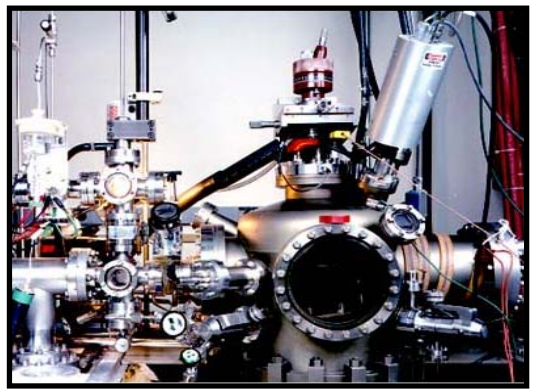
- GM, Rochester, NY, USA
- IFC, South Windsor, CT, USA
- 3M, Minneapolis, MN, USA



Universities and Institutes

- Max-Planck-Institut fuer Kohlenforschung, Muelheim/Ruhr, Germany
- Texas Tech University, Lubbock, TX, USA
- University of Eindhoven, Holland
- University of Wales, UK
- University of Bonn, Germany
- University of Liverpool, UK





Publications (Since 10/2001)

Refereed Journals and Refereed Conference Proceedings:

1. U.A. Paulus, A. Wokaun, G.G. Scherer, T.J. Schmidt, V. Stamenkovic, V. Radmilovic, N.M. Markovic, and P.N. Ross, "Oxygen Reduction on Carbon Supported Pt-Ni and Pt-Co Alloy Catalysts", *J. Phys. Chem. B* 106 (2002) 4181.
2. Stamenkovic V. Schmidt TJ. Ross PN. Markovic NM. "Surface composition effects in electrocatalysis: Kinetics of oxygen reduction on well-defined PtNi and PtCo alloy surfaces." *Journal of Physical Chemistry B*. 106(46):11970-11979, 2002 Nov 21.
3. Tripkovic AV. Popovic KD. Grgur BN. Blizanac B. Ross PN. Markovic NM. "Methanol electrooxidation on supported Pt and PtRu catalysts in acid and alkaline solutions." *Electrochimica Acta*. 47(22-23):3707-3714, 2002 Aug 30.
4. Schmidt TJ. Stamenkovic V. Arenz M. Markovic NM. Ross PN. "Oxygen electrocatalysis in alkaline electrolyte: Pt(hkl), Au(hkl) and the effect of Pd-modification." *Electrochimica Acta*. 47(22-23):3765-3776, 2002 Aug 30.
5. Paulus UA. Wokaun A. Scherer GG. Schmidt TJ. Stamenkovic V. Markovic NM. Ross PN. "Oxygen reduction on high surface area Pt-based alloy catalysts in comparison to well defined smooth bulk alloy electrodes." *Electrochimica Acta*. 47(22-23):3787-3798, 2002 Aug 30.
6. Schmidt TJ. Markovic NM. Stamenkovic V. Ross PN. "Surface characterization and electrochemical behavior of well-defined Pt-Pd{111} single-crystal surfaces: A comparative study using Pt{111} and palladium-modified Pt{111} electrodes." *Langmuir*. 18(18):6969-6975, 2002 Sep 3.
7. Schmidt TJ. Ross PN. Markovic NM. "Temperature dependent surface electrochemistry on Pt single crystals in alkaline electrolytes Part 2. The hydrogen evolution/oxidation reaction." *Journal of Electroanalytical Chemistry*. 524(Special Issue):252-260, 2002 May 3.
8. Arenz M. Stamenkovic V. Schmidt TJ. Wandelt K. Ross PN. Markovic NM. "CO adsorption and kinetics on well-characterized Pd films on Pt(111) in alkaline solutions." *Surface Science*. 506(3):287-296, 2002 May 20.
9. Paulus UA. Wokaun A. Scherer GG. Schmidt TJ. Stamenkovic V. Radmilovic V. Markovic NM. Ross PN. "Oxygen reduction on carbon-supported Pt-Ni and Pt-Co alloy catalysts." *Journal of Physical Chemistry B*. 106(16):4181-4191, 2002 Apr 25.
10. Schmidt TJ. Ross PN. Markovic NM. "Temperature-dependent surface electrochemistry on Pt single crystals in alkaline electrolyte: Part 1: CO oxidation." *Journal of Physical Chemistry B*. 105(48):12082-12086, 2001 Dec 6.
11. Schmidt TJ. Stamenkovic V. Attard GA. Markovic NM. Ross PN. "On the behavior of Pt(111)-Bi in acid and alkaline electrolytes." *Langmuir*.17(24):7613-7619, 2001 Nov 27.

Research Plan: 2002

- **Unified concept for both anode and cathode catalysts utilizing PGM-based bimetallic nanoparticles with "grape" structure (PGM skin with base metal core)**

  Choice of skin and core metals different for anode and cathode
  PGM/base metal combinations selected based on existing electronic theory and synthesized in UHV

- **Pursue new synthetic chemistry to synthesize nanoparticles with the "grape" structure**

  Currently focusing on Re as metal core with Pt and Pd as PGM

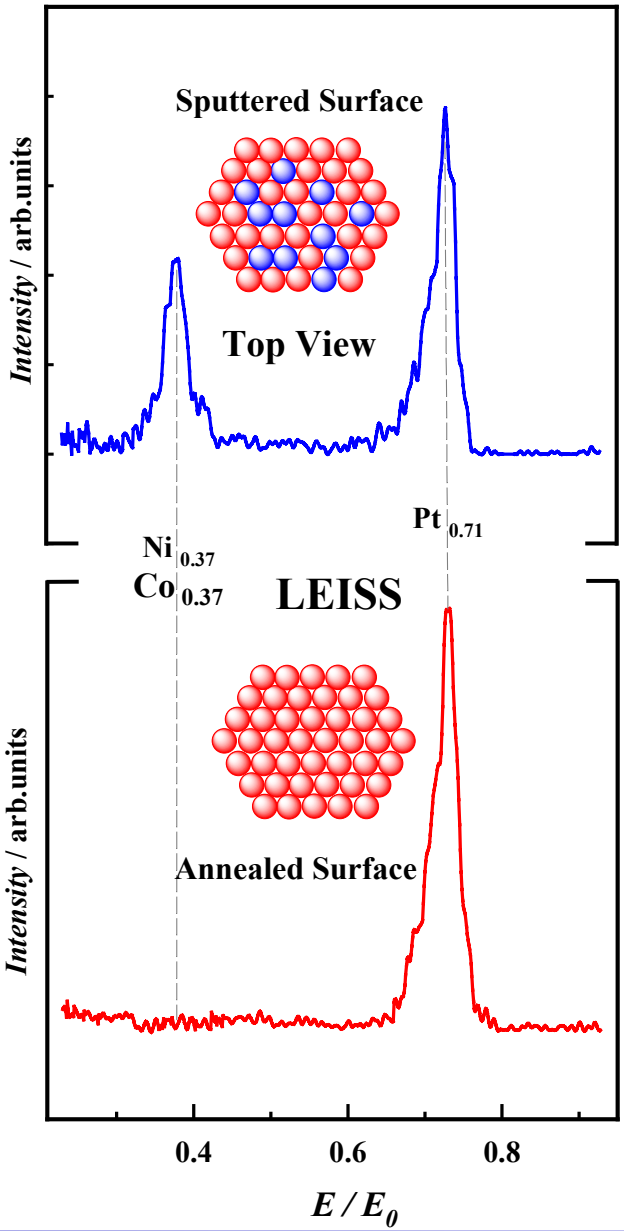
  Pt and Pd monolayers on Re(0001) model system

  Re colloidal chemistry

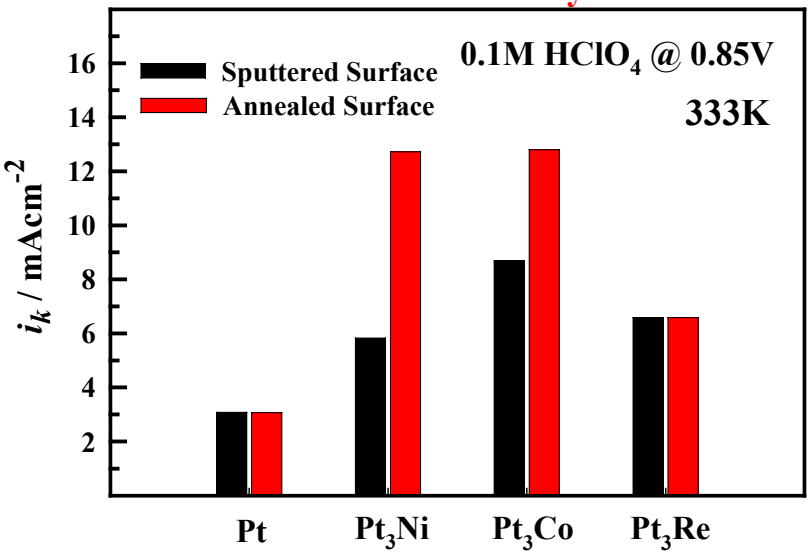
- **Optimization of AuPd anode catalyst for HT membranes**

- **Computational screening of non-PGM catalyst concepts using newly developed (under BES funding) *ab initio* theory of the ORR**

Segregation Effect: Platinum Skin vs. Bulk Alloy Surfaces

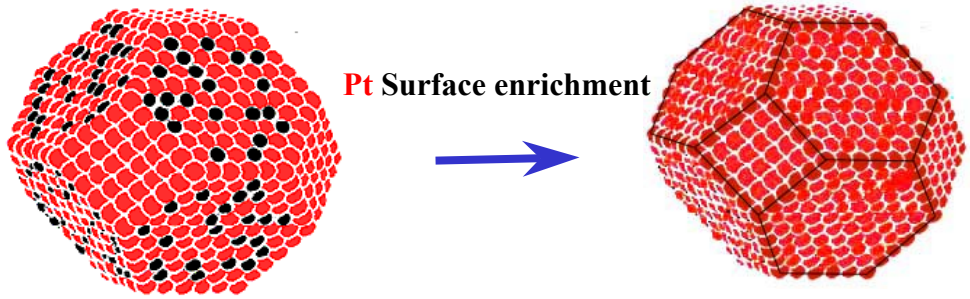


ORR activity



Platinum Skin Effect: Bimetallic Nanoparticle

- Higher intrinsic activity (per unit area)
- Substitution of "buried" Pt atoms in particle core by base metal atoms



Stability: Pt_3Co and Pt_3Ni Surfaces

Experimental Procedure

Pt_3Co ; Pt_3Ni
Sputtered Surfaces

298K

CV stability
Before Treatment
0.0<E<1.0V

ORR : stability
activity
Before Treatment
0.0<E<1.0V

Hold @ 1.0V; 30 min

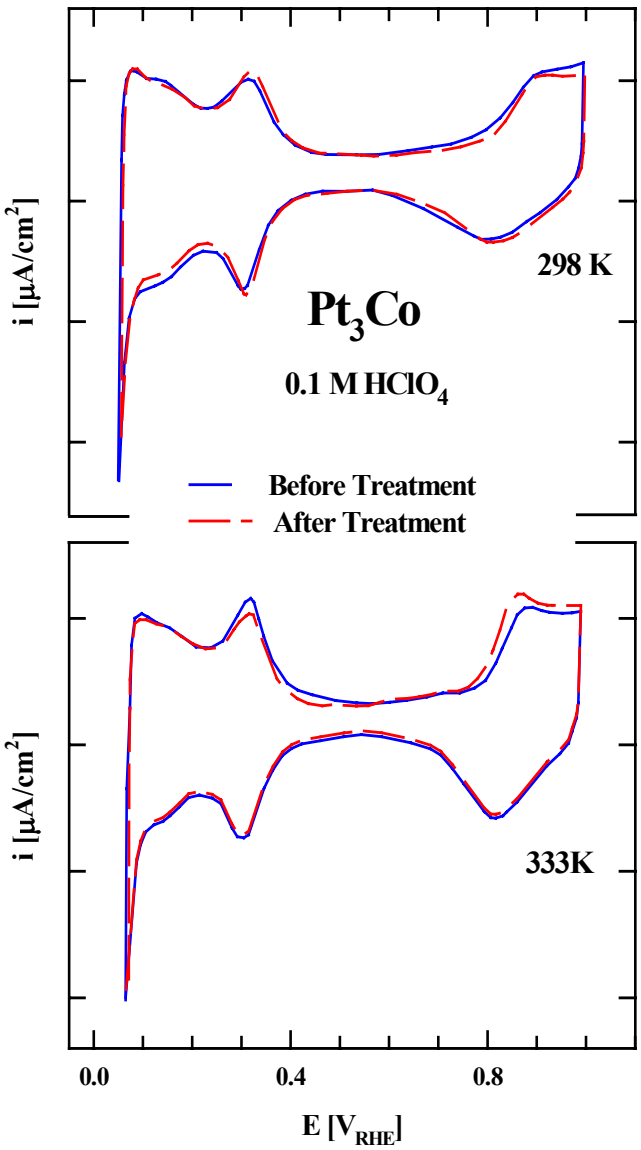
ORR : stability
activity
0.0<E<1.0V

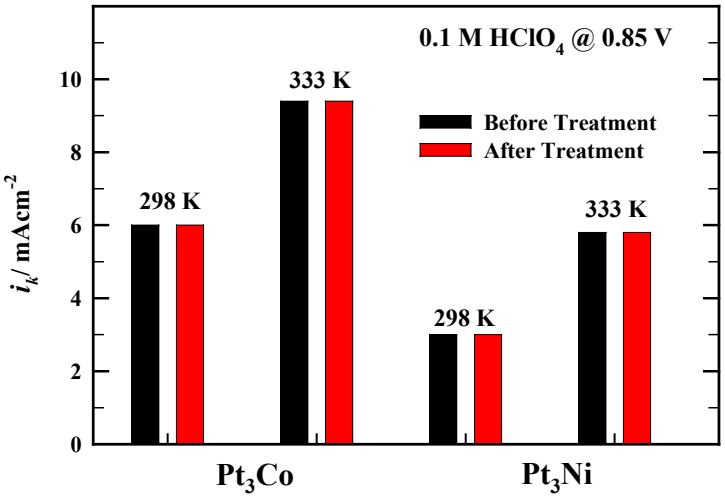
Hold @ 1.2V; 60 min

ORR : stability
activity
After Treatment
0.0<E<1.2V

CV stability
After Treatment
0.0<E<1.2V

333K



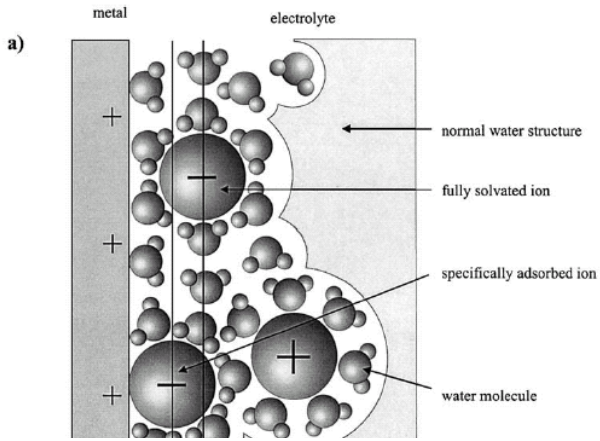


Conclusions

Surface composition is stable between 0.0 < E< 1.2 V !

ORR activity remains the same between 0.0 < E< 1.2 V !

Mechanism of the ORR at metal electrodes



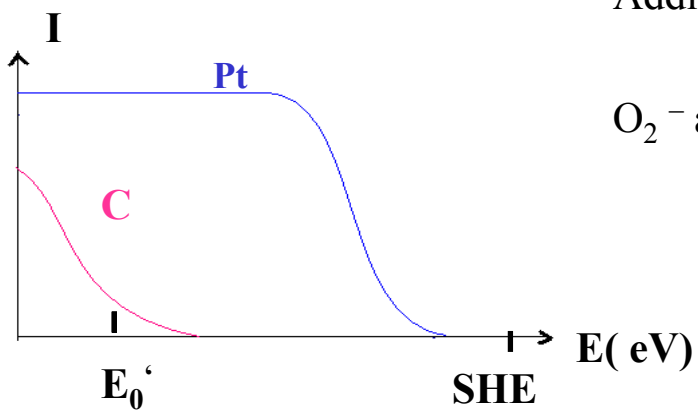
Rate limiting step in electrochemical reduction of O_2 is 1st electron transfer

$O_2 + 1\ e^- \rightarrow (O_2^-)_{sol}$ Outer Sphere ($\mathbf{E_0' = -0.3\ V}$)

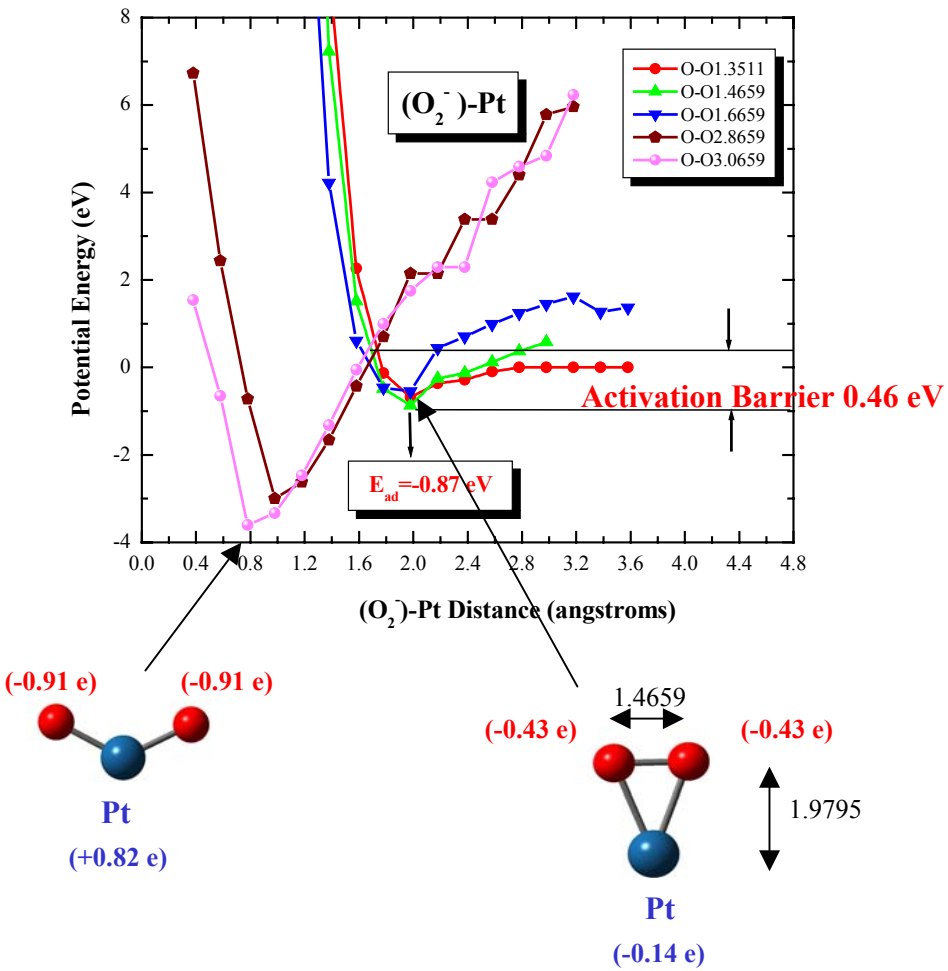
$O_2 + 1\ e^- \rightarrow (O_2^-)_{ads}$ Inner Sphere ($\mathbf{E_0' + \Delta G_{ad}/F}$)

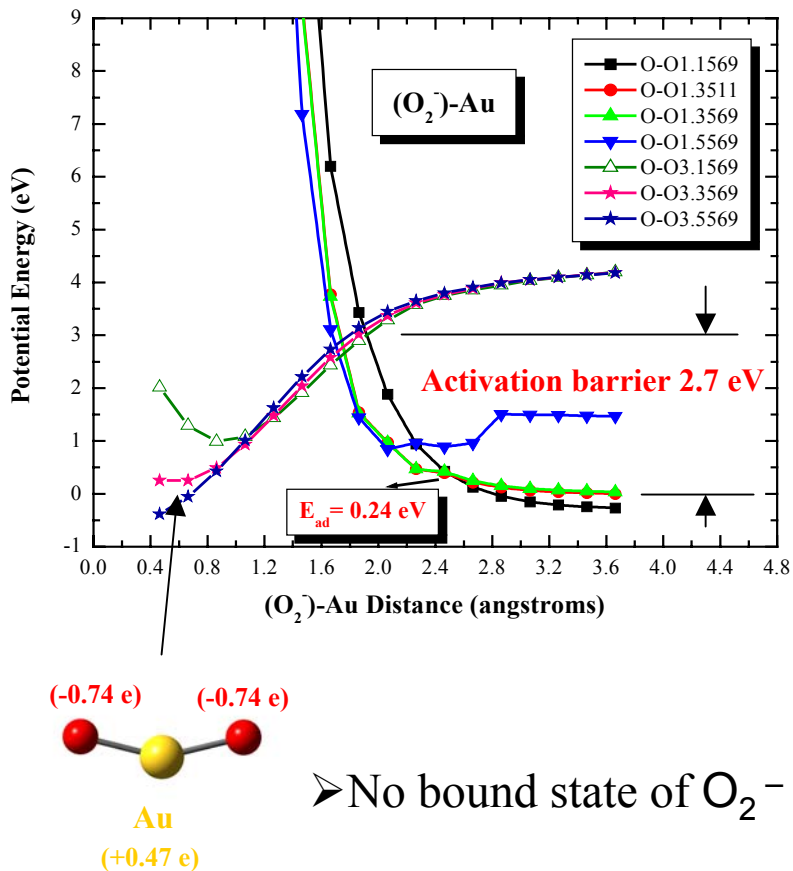
Addition of first electron needed to break O-O bond

O_2^- adsorption strength related to the electronic properties of the electrode material



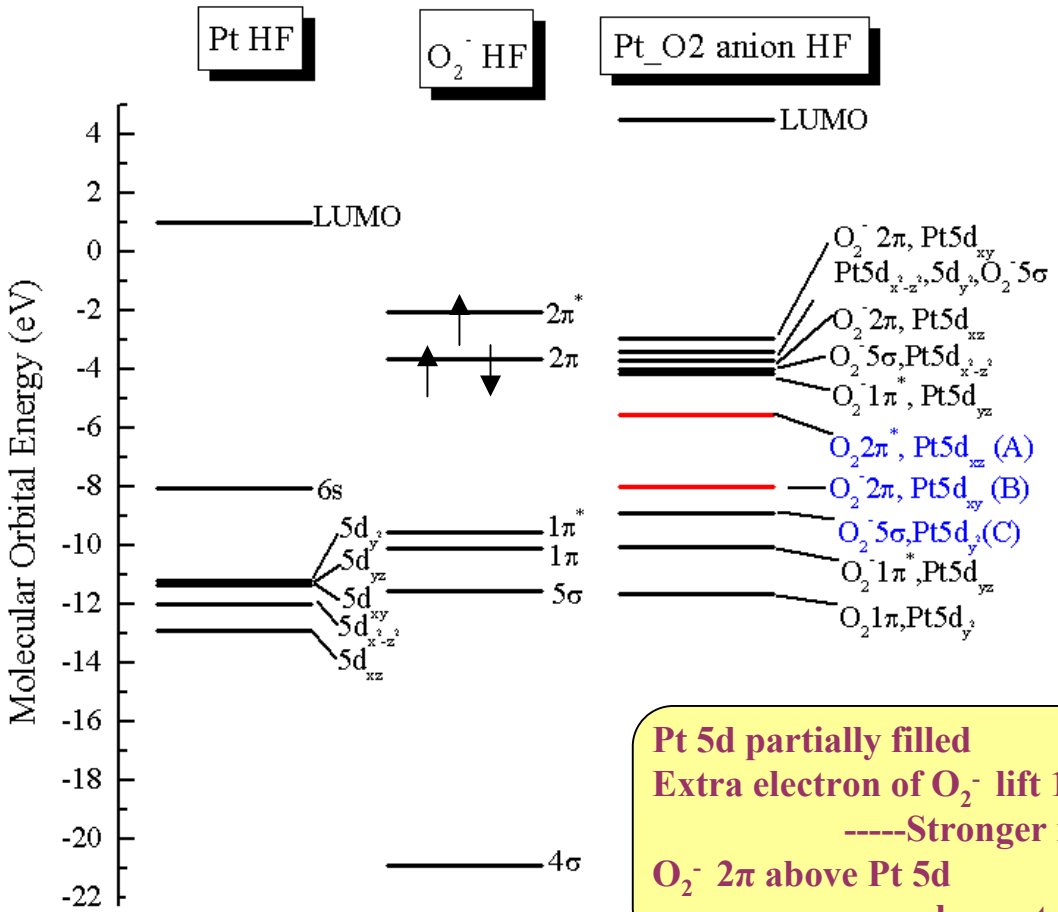
(O_2^-)–Me Potential Energy Curves vs. O-O bond length





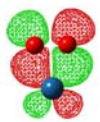
➢No bound state of O_2^-

Correlation Diagram of the Molecular Orbitals of (O_2^-)-Pt



Pt $5d_{xz}$, O_2^- $2\pi^*$

A



Pt $5d_{xy}$, O_2^- 2π

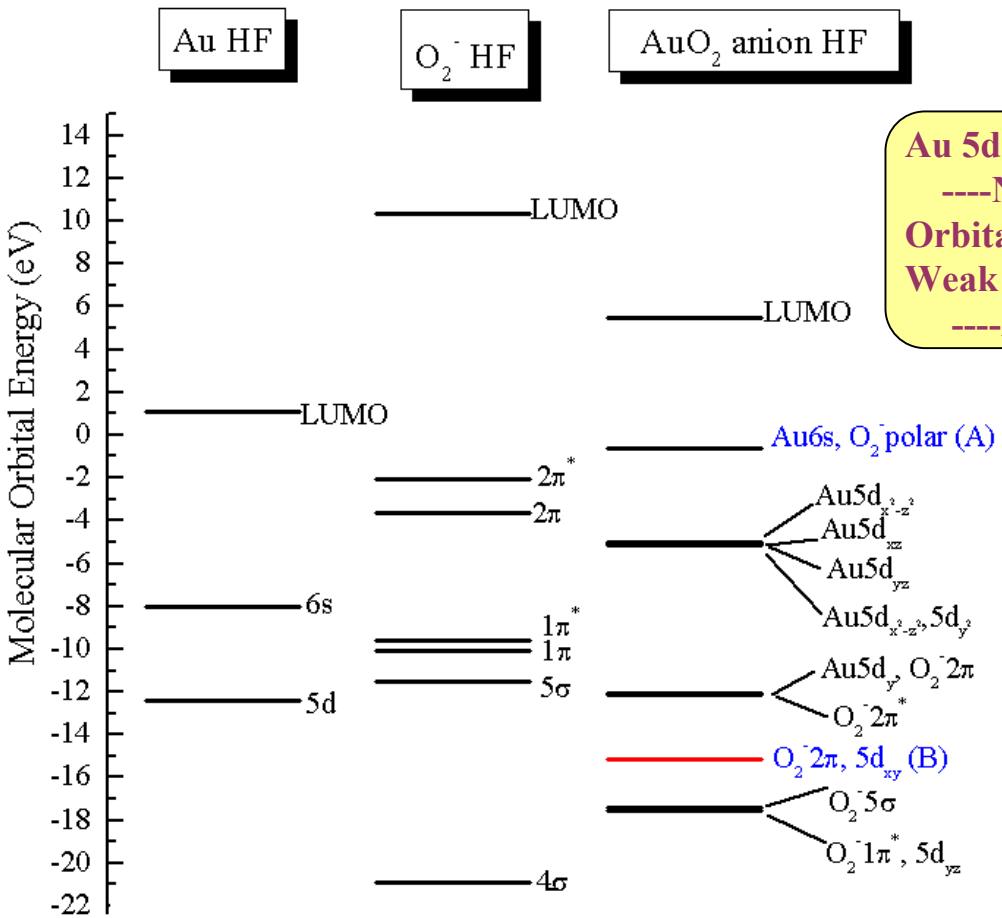
B

Pt $5d_{y2}$, O_2^- 5σ

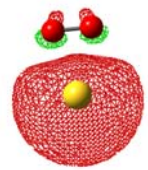
C

Pt 5d partially filled
Extra electron of O_2^- lift 1π close to Pt 5d
-----Stronger interaction
O_2^- 2π above Pt 5d
------charge transfer to Pt

Correlation Diagram of Molecular Orbitals of (O_2^-)-Au



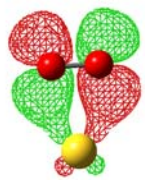
Au 5d completely filled
----No charge transfer between Pt and (O_2^-)
Orbital with different symmetry do not interact
Weak Interaction due to polarization
----Au6s and (O_2^-) π levels



A

Au 6s, O_2^- 2π

Polarization effect

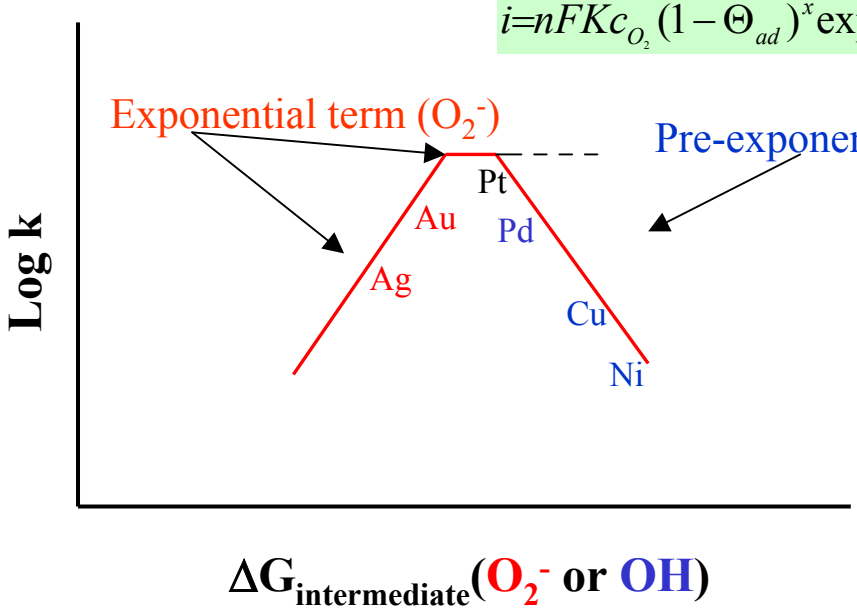


B

Au $5d_{xy}$, O_2^- 2π

The Volcano Relation in ORR Kinetics

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



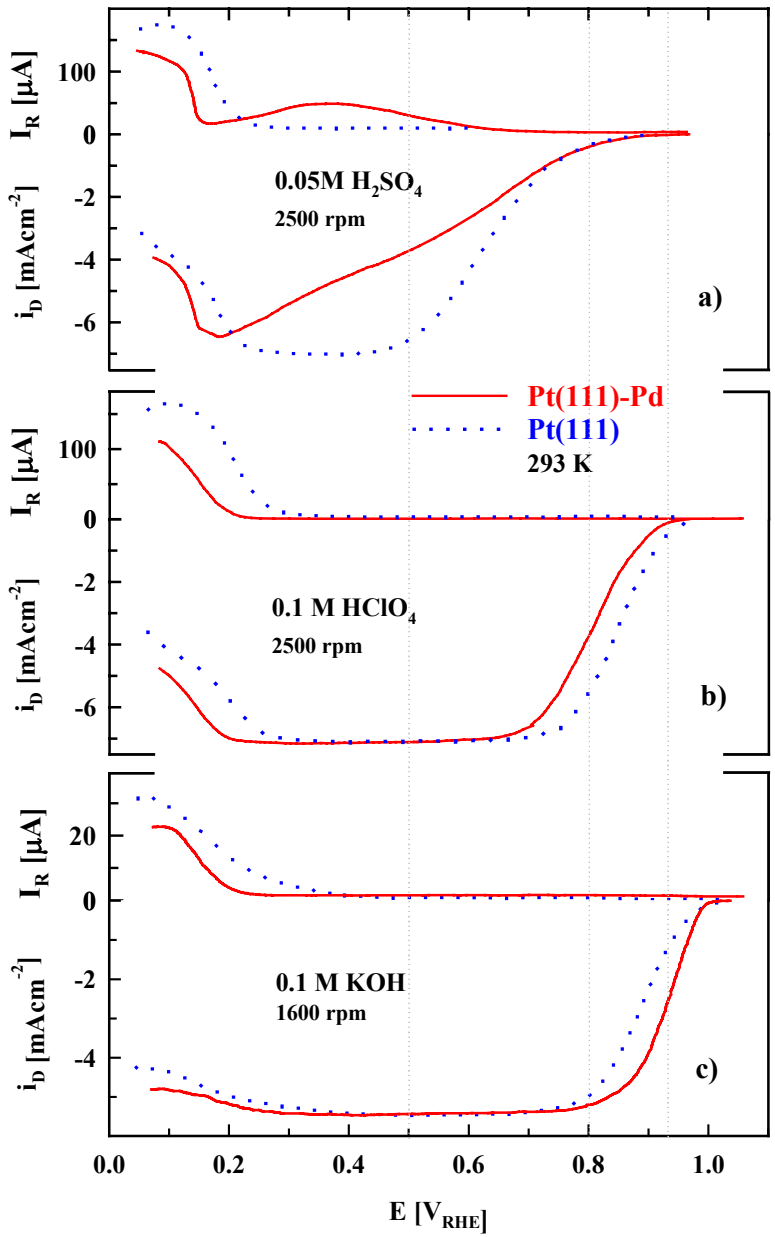
Θ_{ad} is mostly OH_{ad} not $(O_2^-)_{ad}$

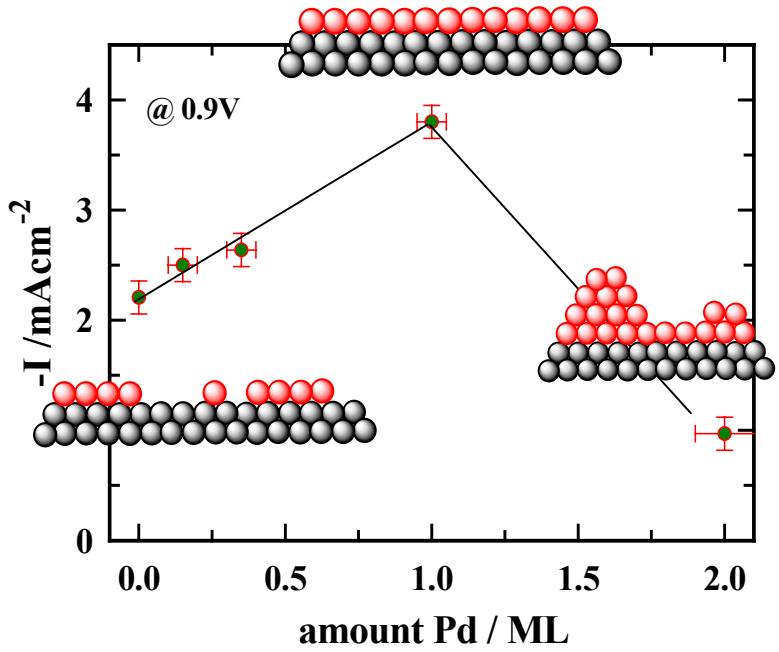
$H_2O = OH_{ad} + H^+ + e^-$
or
$O_2^- + 2\,H^+ + e^- = 2\,OH_{ad}$

Pt at the Top of the Volcano

- **Interaction of the electrode with O_2^- requires partially filled d-orbitals with large radial extent**
  - **Group 1B, 2B, 3B etc. metals have closed d-shells**
  - **Of Group VIII metals, d-orbitals in first row ($3d^{9-n}$)**
    - **do not have sufficient radial extent**
  - **The $5d^{9-n}$ orbitals are the best for forming long bonds**
- **Interaction of the electrode with OH_{ad} must be relatively weak of the Group VII metals, Pt has the weakest interaction with OH_{ad}**

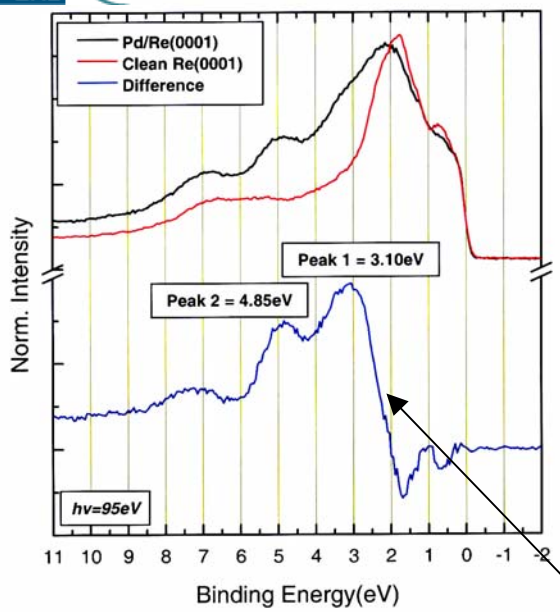
ORR: Pt(111)-Pd

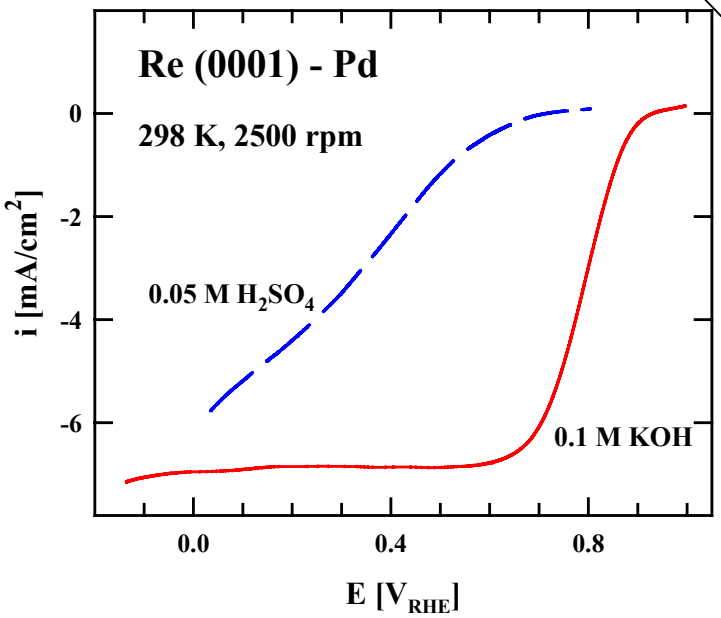


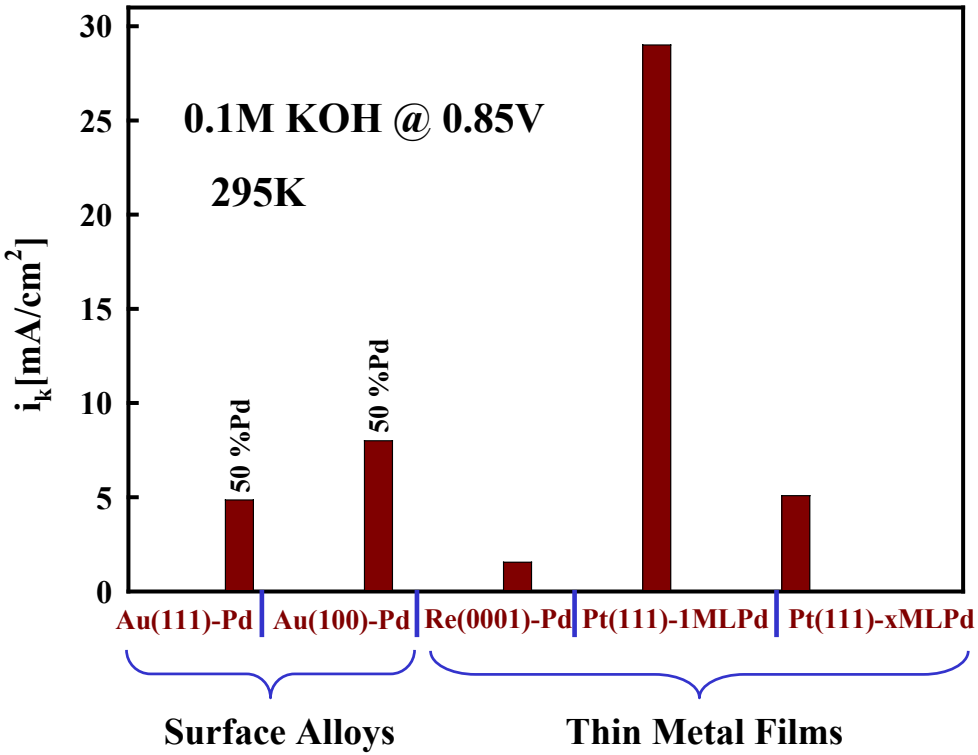


- "Vulcano Plot"
- Electronic Effect

ORR: Re(0001)-Pd





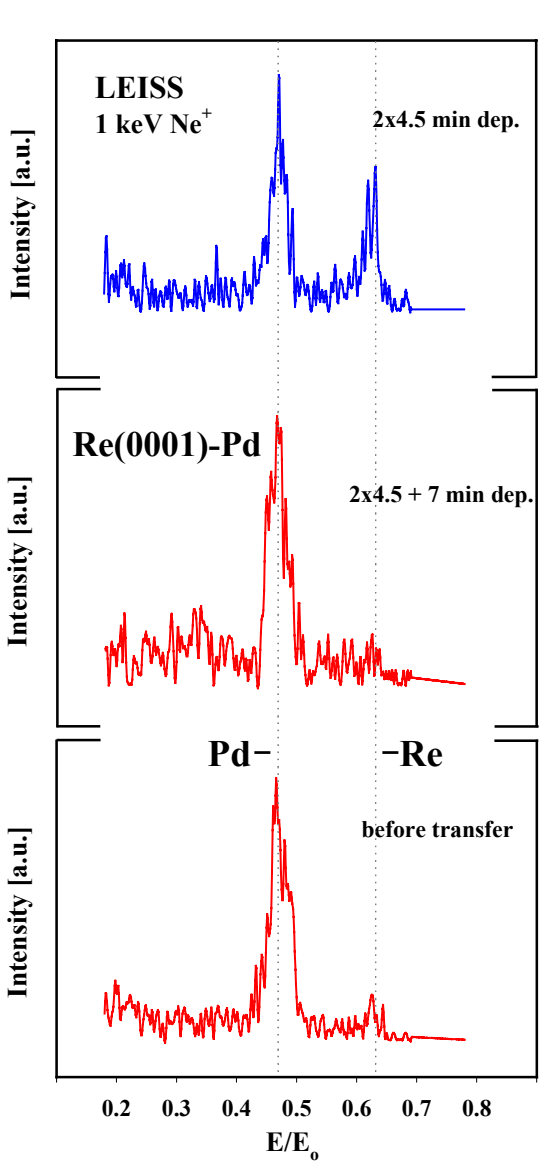


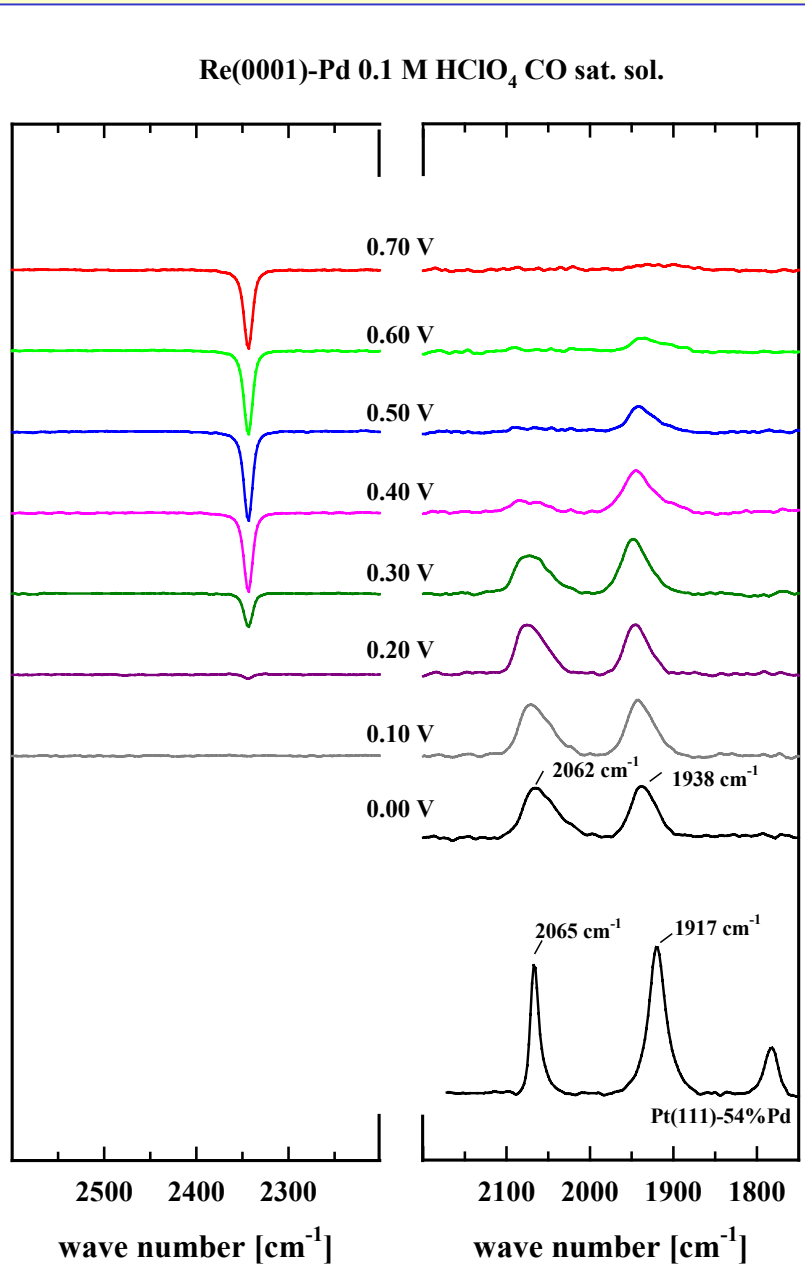
Pd ML film on Re(0001) has Ag-like d-band Density of States (DOS)

and

Activity for ORR is shifted towards that for Ag(111)

CO oxidation: Pt(111)-Pd vs. Re(0001)-Pd





In situ FTIR:

- two adsorption bands
- electronic modification shifts frequency
- preferential oxidation of high frequency band
- electronic modification shifts oxidation potential by ca. – 0.2 V

Research Plan: 2003-2004

- **Unified concept for both anode and cathode catalysts utilizing PGM-based bimetallic nanoparticles with "grape" structure (PGM skin with base metal core)**

  Choice of skin and core metals different for anode and cathode PGM/base metal combinations selected based on existing electronic theory and synthesized in UHV

- **Pursue new synthetic chemistry to synthesize nanoparticles with the "grape" structure**

  Continue focus on Re as metal core with Pt and Pd as PGM

  Pt and Pd monolayers on Re(0001) as model systems

  Begin evaluation of Re-rich supported Pt-Re catalyst for ORR (if stable this catalyst could reduce Pt loading by a factor of 4)

- **Optimization of AuPd anode catalyst for HT membranes**

- **Computational screening of non-PGM catalyst concepts using newly developed (under BES funding) *ab initio* theory of the ORR**