New Electrocatalysts For Fuel Cells

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May 25, 2004

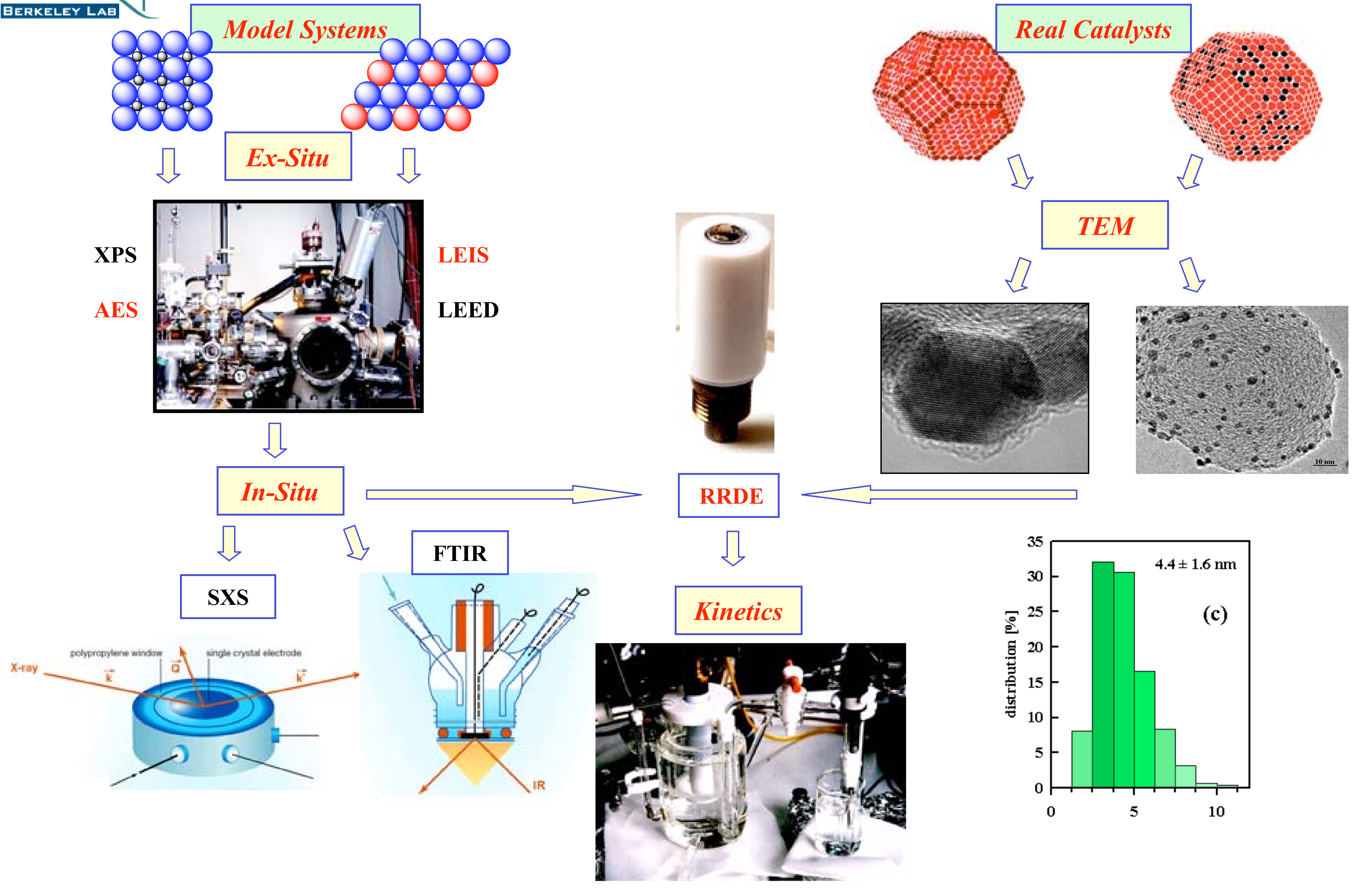
- Objective: Reduction of precious metal loading
- DOE Technical Barriers for Fuel Cell Components
  - Q. Electrode Performance
- Budget: FY2003: $ 400 K
  FY2004: $ 450 K

Staff Scientist: Nenad M. Markovic

Post Doctoral Fellow: Vojislav Stamenkovic

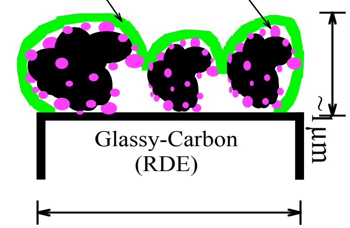
Graduate Students: Berislav Blizanac (Belgrade)
Karl Mayrhofer (Vienna Tech. Univ.)

LBNL *Materials-by-Design Approach*



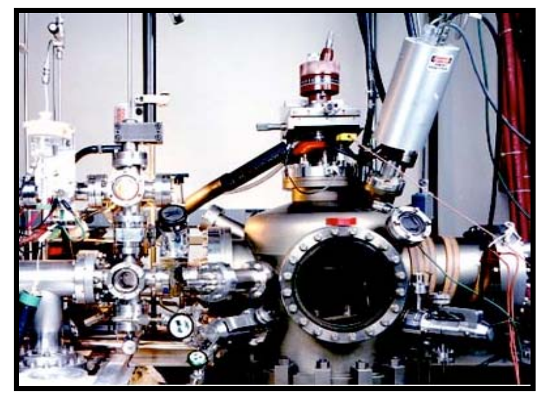
Collaborations

Industries



Characterization and testing of new catalysts for developers

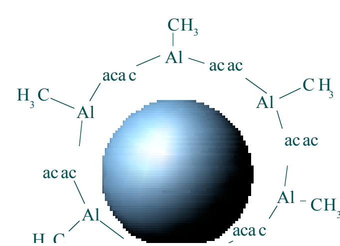
- **GM , Rochester, NY, USA**
- **IFC, South Windsor, CT, USA**
- **3M, Minneapolis, MN, USA**



Universities and Institutes

Synthesis of metallic nanoclusters

- **Max-Planck-Institut fuer Kohlenforschung, Muelheim/Ruhr, Germany**
- **University of Liverpool, UK**



Research Plan: 2003-2004

New catalysts for both anodes and cathodes being developed following a unified concept of PGM-based bimetallic nanoparticles with a “grape” structure (a PGM “skin” with base metal core)

- **Choice of PGM and core metals different for anode and cathode**
- **PGM/base metal combinations based on computational screening of PGM core-shell nanostructures using newly developed (under BES funding) Monte Carlo simulations**

Fundamental studies of the crystallite size effect for the oxygen reduction reaction in acidic electrolytes on carbon supported Pt and Pt alloy nanoparticles

Pursue new synthetic chemistry to synthesize nanoparticles with a “grape” structure

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

Optimization of AuPd as alternative to Pt in anodes

Publications (Since 10/2002)

Refereed Journals and Refereed Conference Proceedings

1. Schmidt TJ. Stamenkovic V. Markovic NM. Ross PN. "Electrooxidation of H_2, CO and H_2/CO on well-characterized Au(111)-Pd surface alloys." *Electrochimica Acta*. 48, 3823-3828, 2003 Nov 15.
2. Arenz M. Stamenkovic V. Schmidt TJ. Wandelt K. Ross PN. Markovic NM. "The electro-oxidation of formic acid on Pt-Pd single crystal bimetallic surfaces." *Physical Chemistry Chemical Physics*. 5, 4242-4251, 2003 Oct 1.
3. Stamenkovic V. Schmidt TJ. Ross PN. Markovic NM. "Surface segregation effects in electrocatalysis: kinetics of oxygen reduction reaction on polycrystalline Pt_3Ni alloy surfaces." *Journal of Electroanalytical Chemistry* 554,191-199, 2003 Sep 15.
4. Arenz M. Schmidt TJ. Wandelt K. Ross PN. Markovic NM. "The oxygen reduction reaction on thin palladium films supported on a Pt(111) electrode." *Journal of Physical Chemistry B* 107(36), 9813-9819, 2003 Sep 11.
5. Arenz M. Stamenkovic V. Ross PN. Markovic NM. "Preferential oxidation of carbon monoxide adsorbed on Pd submonolayer films deposited on Pt(100)." *Electrochemistry Communications* 5(9), 809-813, 2003 Sep.
6. Arenz M. Stamenkovic V. Schmidt TJ. Wandelt K. Ross PN. Markovic NM. "The effect of specific chloride adsorption on the electrochemical behavior of ultrathin Pd films deposited on Pt(111) in acid solution." *Surface Science* 523, 199-209, 2003 Jan 10.
7. Schmidt TJ. Stamenkovic V. Ross PN. Markovic NM. "Temperature dependent surface electrochemistry on Pt single crystals in alkaline electrolyte - Part 3.The oxygen reduction reaction." *Physical Chemistry Chemical Physics* 5, 400-406, 2003.
8. Stamenkovic V. Schmidt TJ. Ross PN. Markovic NM. "Surface composition effects in electrocatalysis: Kinetics of oxygen reduction on well-defined Pt_3Ni and Pt_3Co alloy surfaces." *Journal of Physical Chemistry B* 106, 11970-11979, 2002 Nov 21.

Books and Book Chapters

1. Markovic NM. Radmilovic V. Ross PN. "Physical and Electrochemical Characterization of Bimetallic Nanoparticle Electrocatalysts", in *Catalysis and Electrocatalysis at Nanoparticle Surfaces*, Ed. Wieckowski A. Savinova ER. Vayenas CG., Marcel Dekker, New York and Basel, 2003, Chapter 9, pp. 311-342.
2. Ross, PN. "Oxygen Reduction Reaction on Single Crystal Electrodes", in *Handbook of Fuel Cells: Fundamentals, Technology and Applications, Volume 2, Electrocatalysis*, Ed. Viestich W. Lamm A. Gasteiger H., John Wiley & Sons Ltd., Chichester, 2003, pp. 465-481.

Accomplishments Outline

- Results of Monte-Carlo Simulations of Microstructure in Pt_3Ni and Pt_3Re Nanoparticles
  (DOE/BES sponsored research)

- High precision activity measurements for well-characterized Pt alloys (i.e. what is the most active alloy and what activity enhancement could we expect)
  (GM sponsored research)

- Definitively determined the leaching out of the transition metal in all Pt_3M alloys in acid electrolyte and its consequences

- Correlated enhanced specific activity of Pt3Co alloy catalyst for ORR to electronic state of Pt skin with Co-enriched second layer

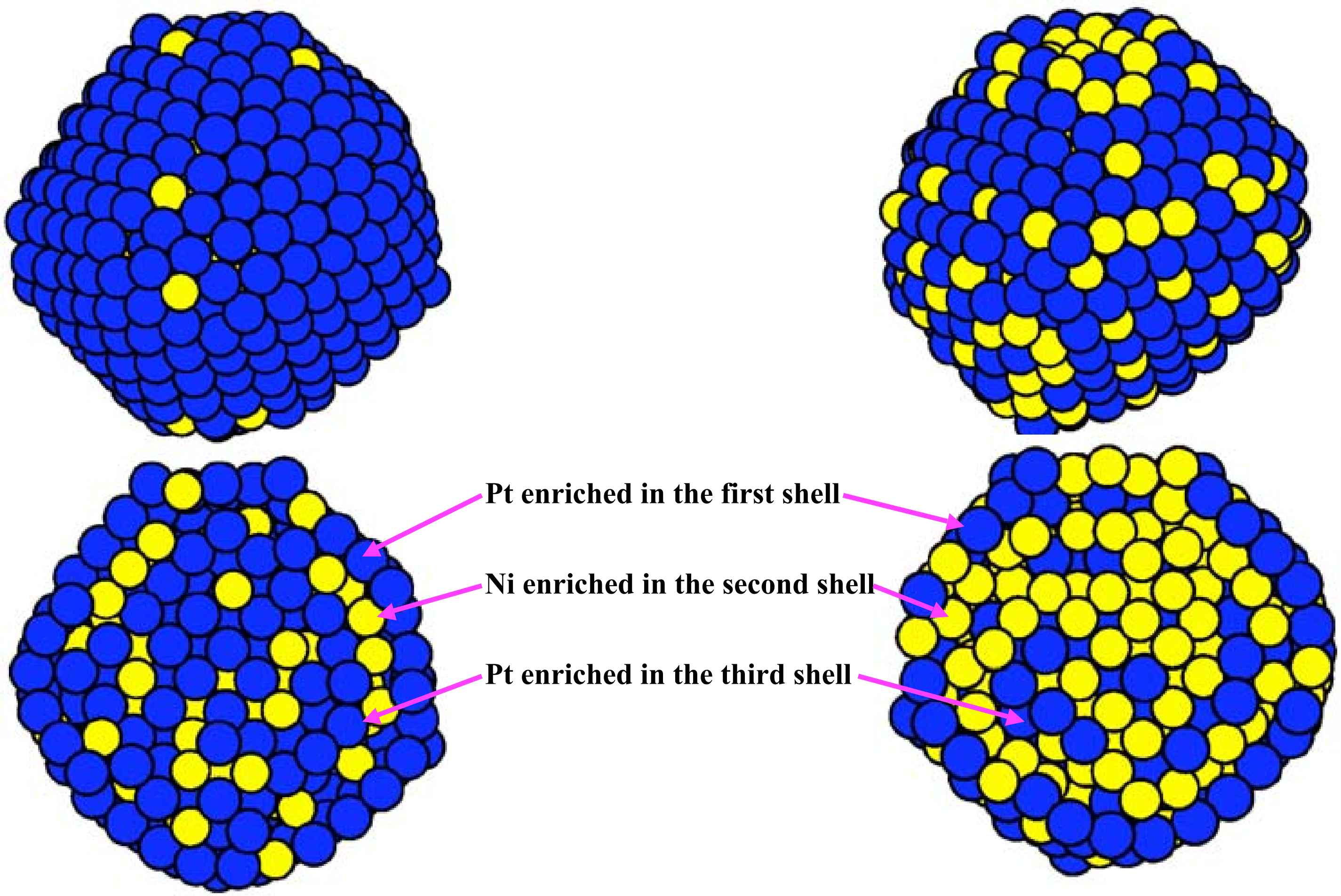
- Re-examined the "crystallite size effect" for the oxygen reduction reaction on carbon supported Pt nanoparticles

- Measured surface area and activity of 3M "nanostructured" (NS) catalysts and benchmarked against conventional carbon supported Pt catalyst

Surface-sandwich Structures of Pt-Ni Nanoparticles

$Pt_{75}Ni_{25}$ fcc cubo-octahedral nanoparticle (snapshot and [001] cross-section)

$Pt_{50}Ni_{50}$ fcc cubo-octahedral nanoparticle (snapshot and [001] cross-section)

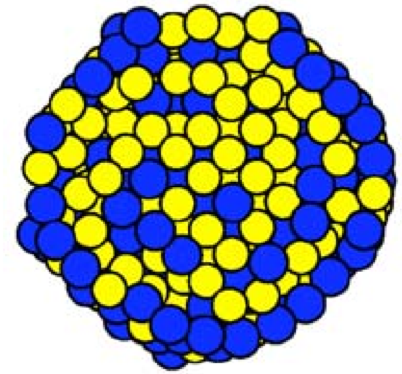


Nanoparticle Structures and Order-Disorder Transitions

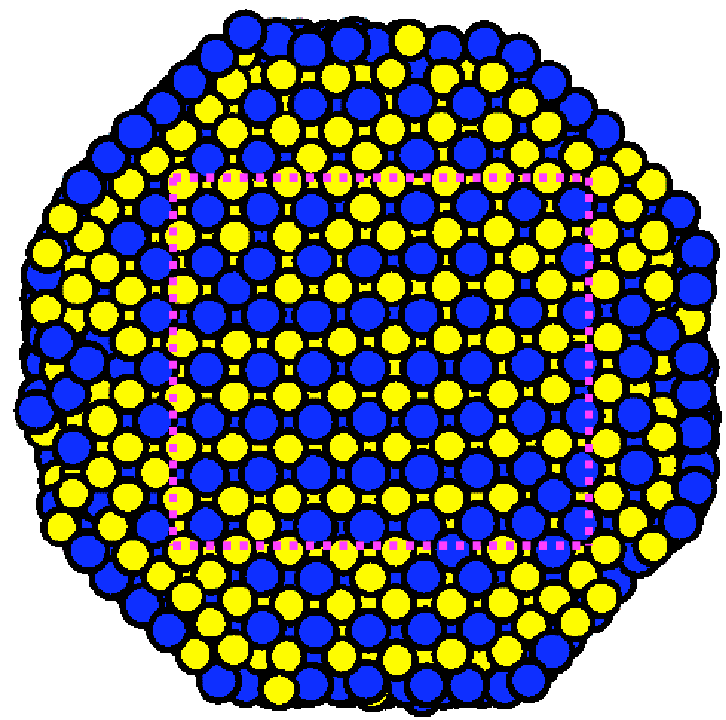
Segregation profiles (in atomic concentrations of Pt atoms) of equilibrium cubo-octahedral $Pt_{50}Ni_{50}$ nanoparticles simulated at T=600K

N	C_1	C_2	C_3	C_{core}
586	70	27	44	35
1289	74	31	43	35
2406	79	36	38	37
4033	81	37	41	39

Surface-sandwich structure with a disordered core for smaller nanoparticles



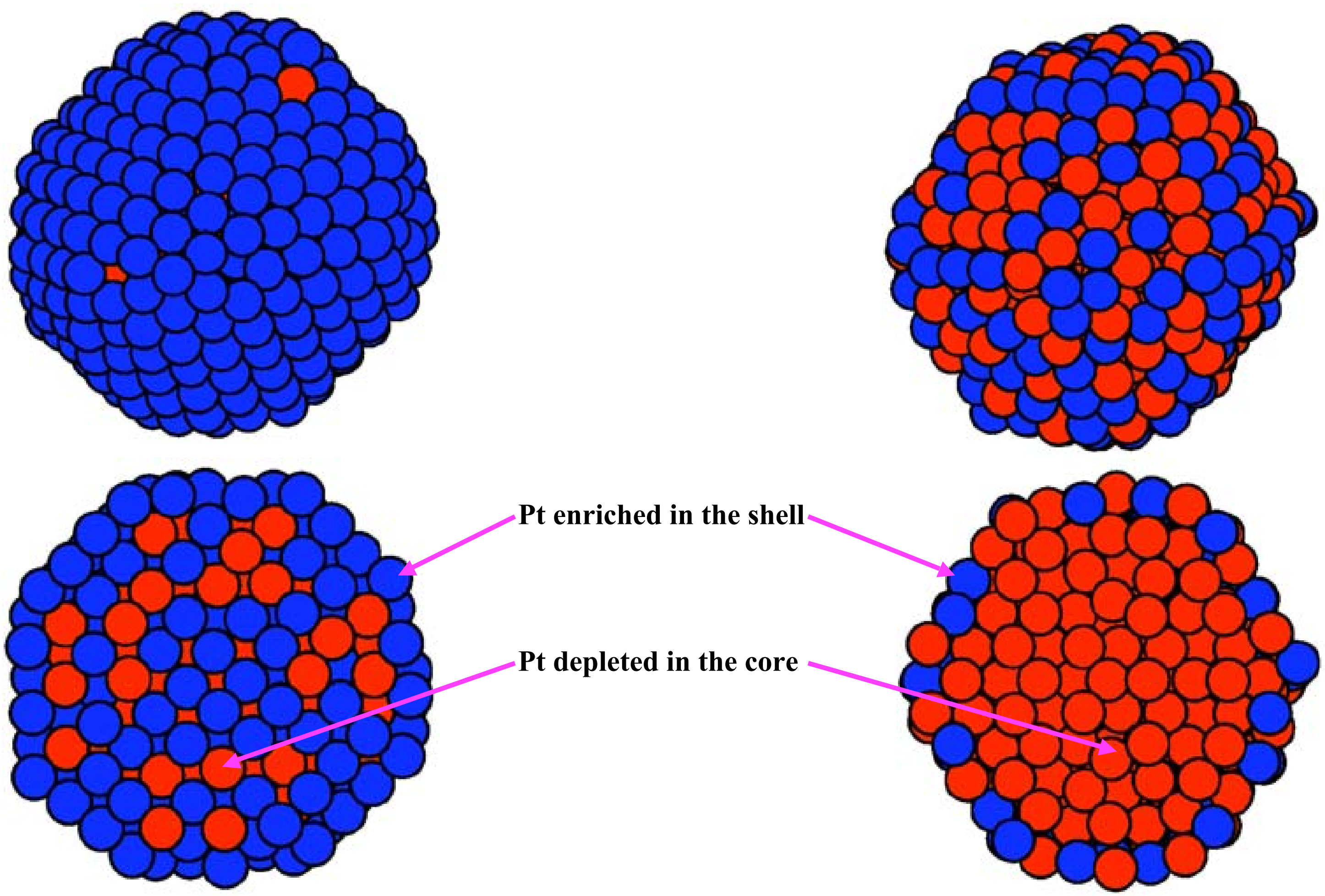
Core-shell structure with an ordered core for larger nanoparticles



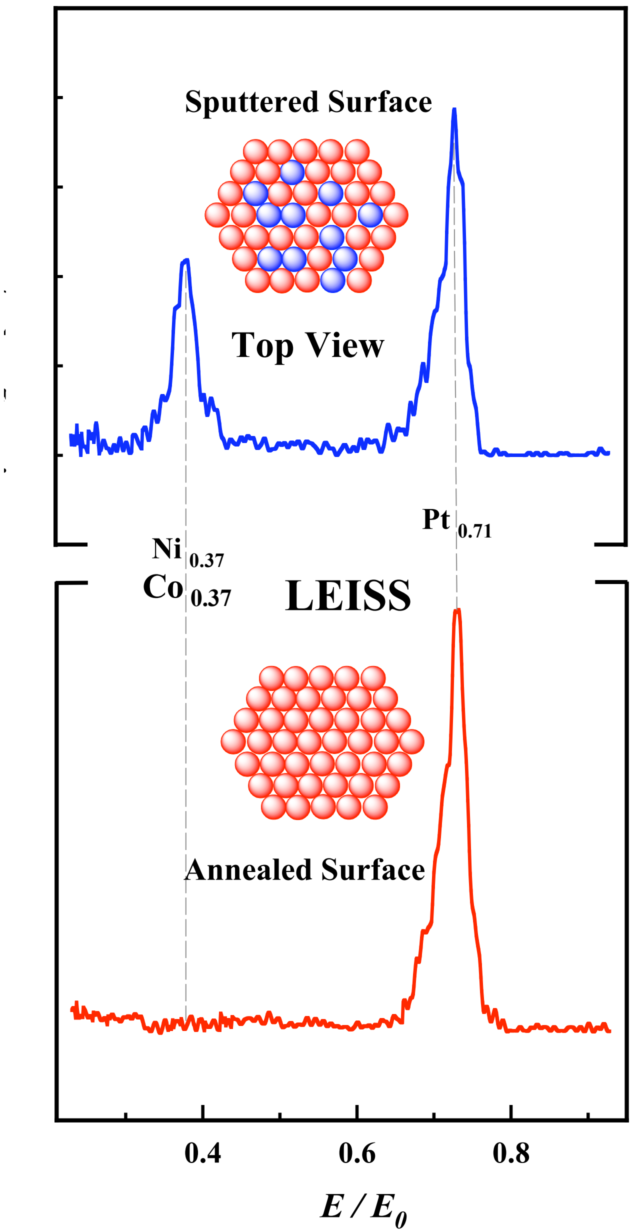
Core-shell Structures of Pt-Re Nanoparticles

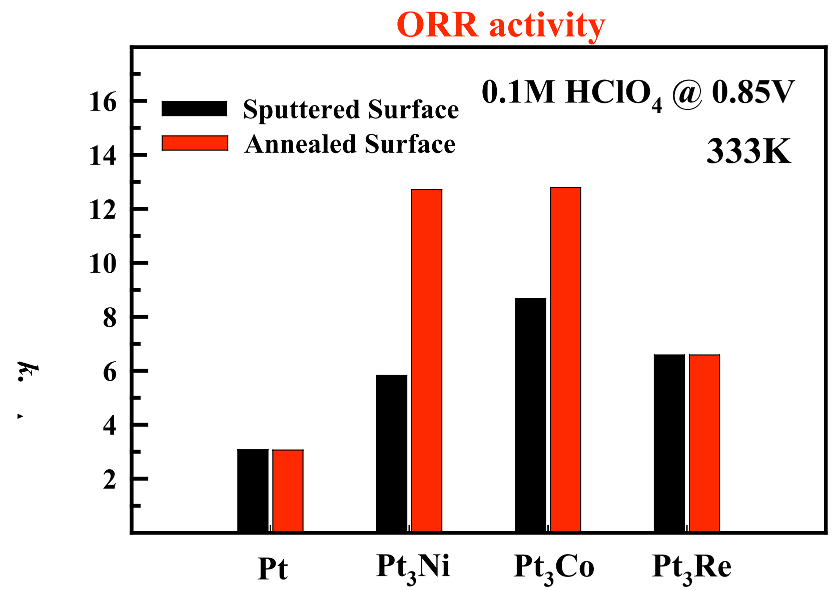
$Pt_{75}Re_{25}$ fcc cubo-octahedral nanoparticle (snapshot and [001] cross-section)

$Pt_{25}Re_{75}$ hcp truncated hexagonal bipyramidal nanoparticle (snapshot and $[11\bar{2}0]$ cross-section)



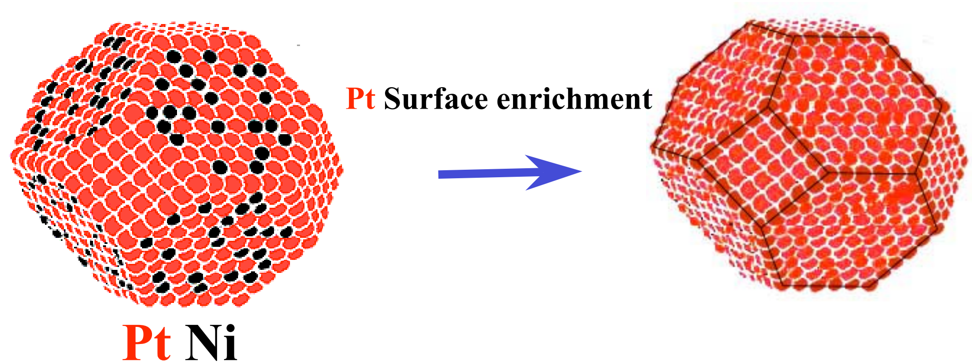
Segregation Effect: Platinum Skin vs. Bulk Alloy Surfaces





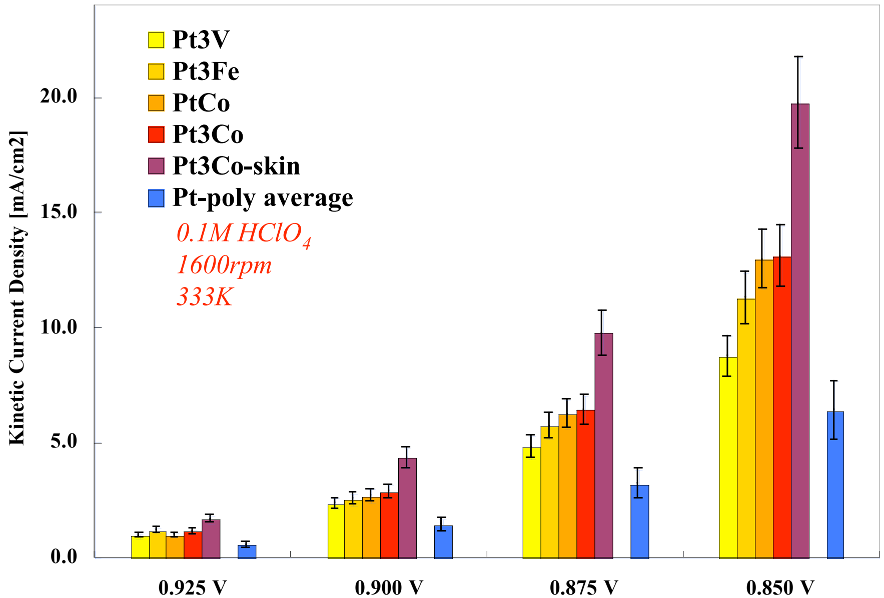
Platinum Skin Effect: Bimetallic Nanoparticle

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



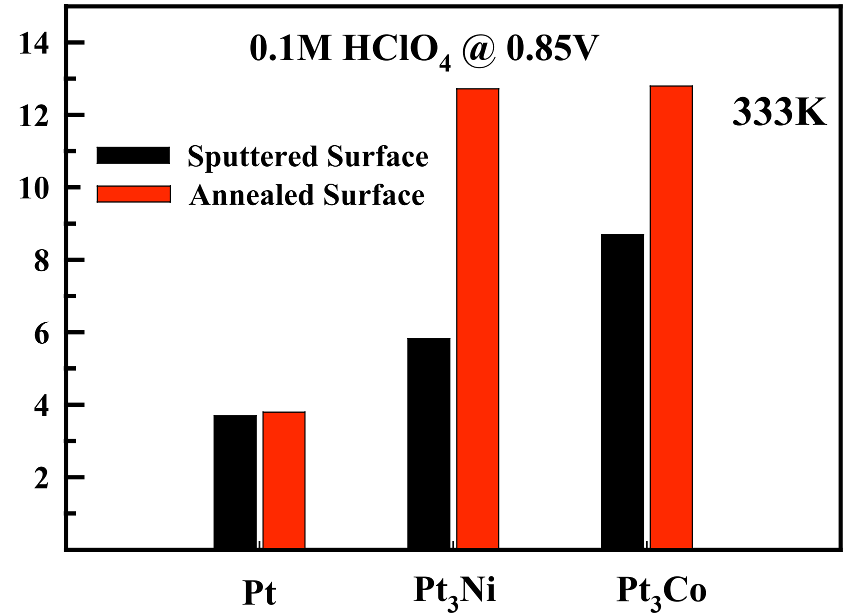
Activity Factors

New results



Pt_3V	Pt_3Fe	PtCo	Pt_3Co	Pt_3Co skin
1.4 1.0-1.8	**1.8** 1.4-2.4	**2.0** 1.5-2.7	**2.0** 1.5-2.7	**3.1** 2.3-4.2

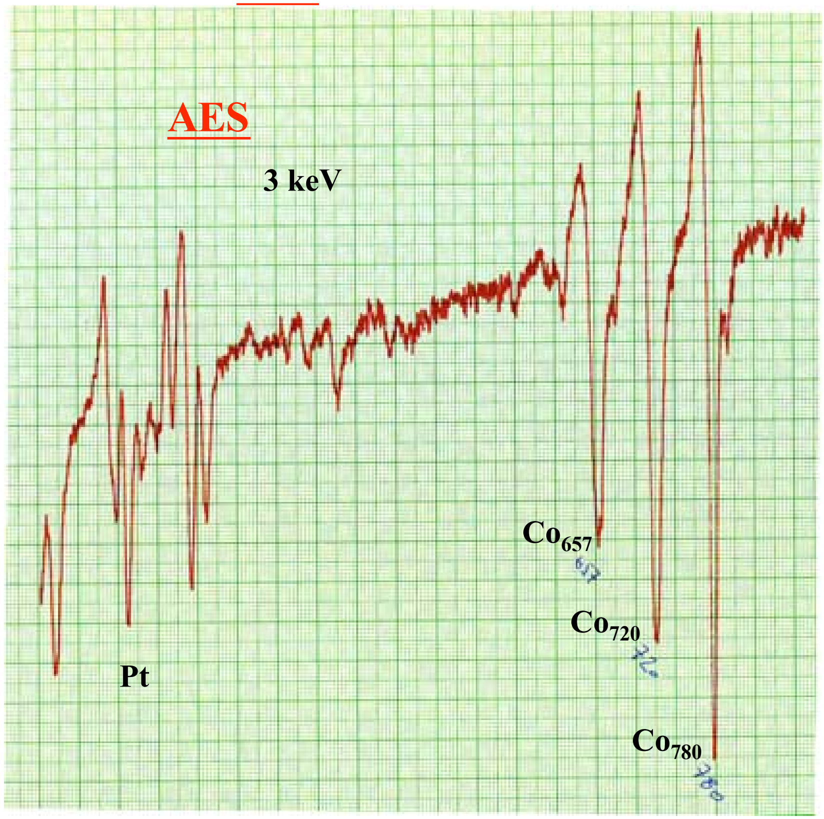
Published results



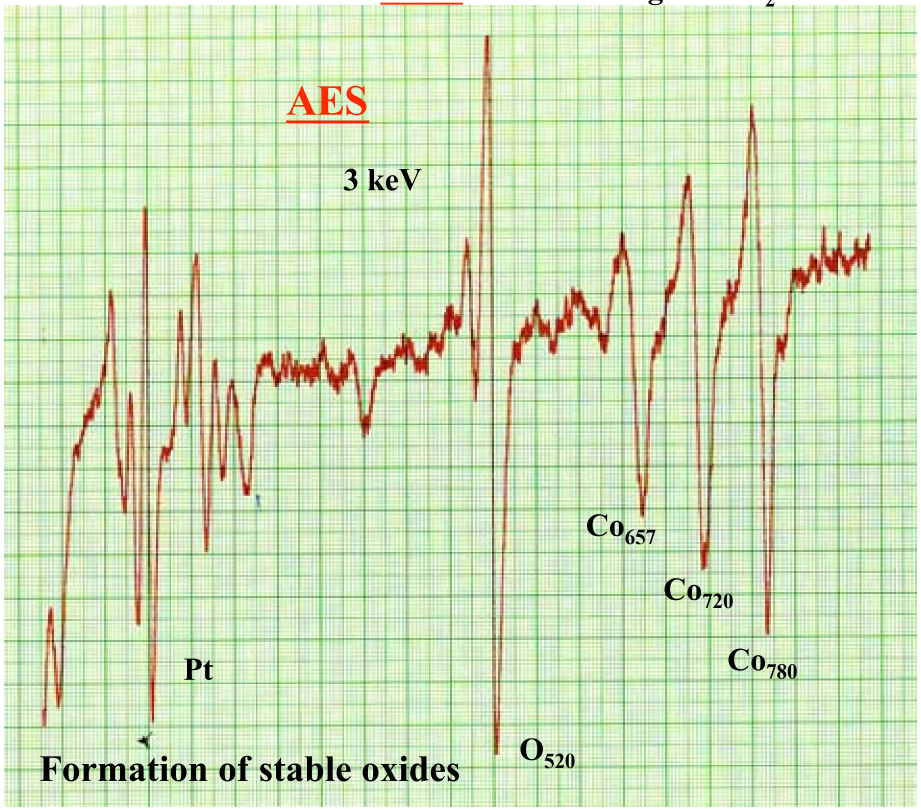
Pt poly	Pt_3Ni	Pt_3Co	Pt_3 Ni skin	Pt_3Co skin
-	**1.6**	**2.3**	**3.2**	**3.4**

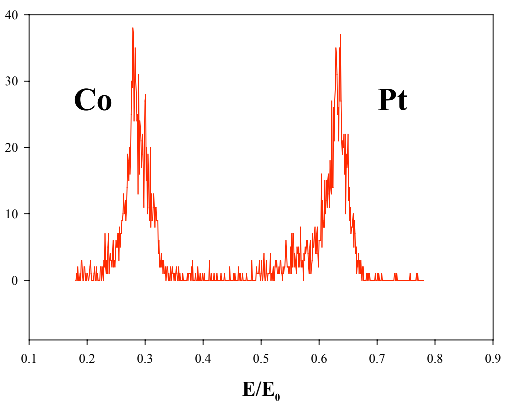
Surface Chemistry of PtCo

UHV: Before Transfer



UHV: After Rinsing with H_2O

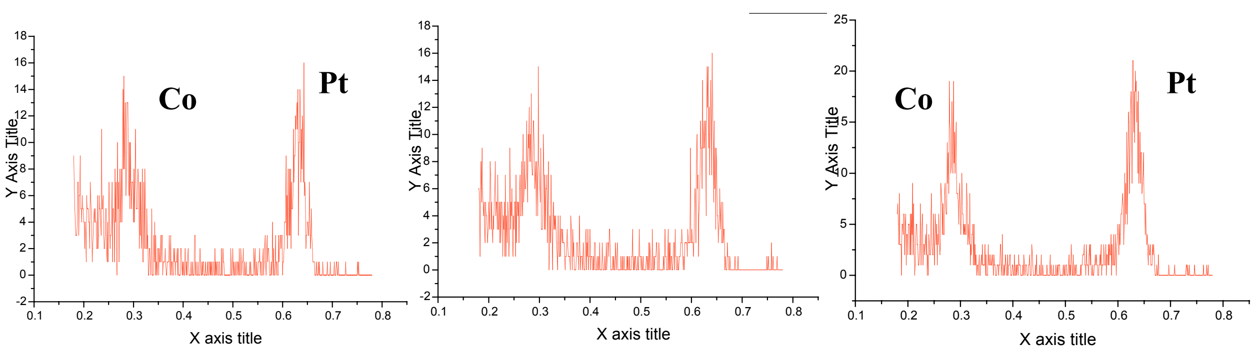




LEIS

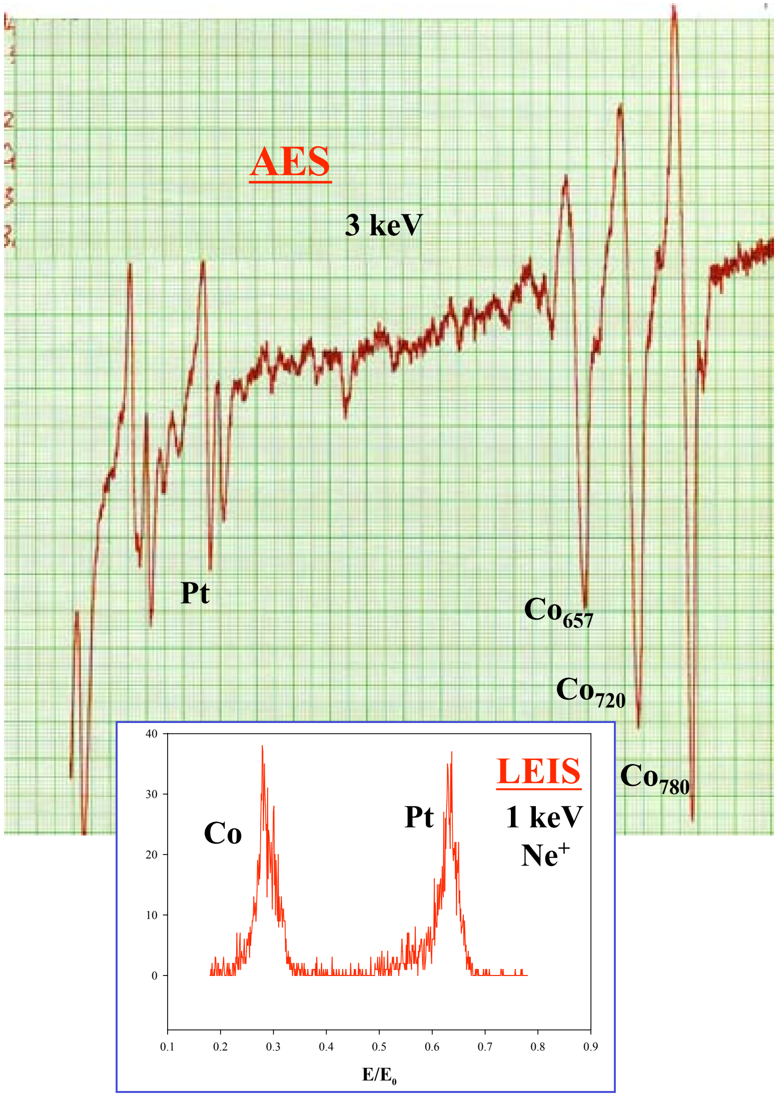
1 keV

Ne^+

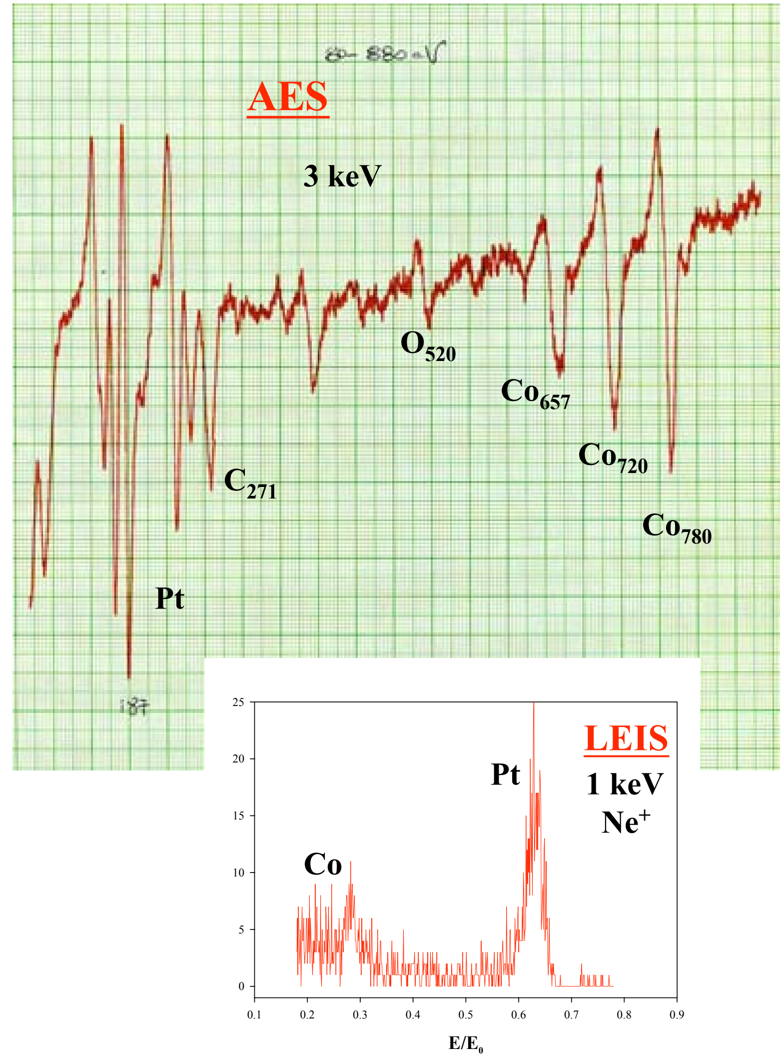


Surface Chemistry of PtCo

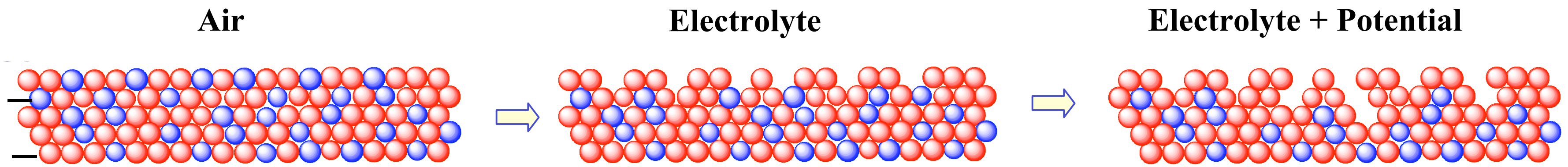
UHV: **Before Transfer**



UHV: **After Electrochemistry and/or After rinsing with 0.1M $HClO_4$**



Effect of Dissolution of Alloying Metal



Could active surface area (Pt sites) be higher vs. Pt-poly due to dissolution of alloying components?

H_{upd} charge as measure of Pt site density

Pt_3Ni	Pt_3V	Pt_3Fe	PtCo	Pt_3Co	Pt_3Co_{skin}	Pt
~170	xxx	~160	~190	~180	~180	~200

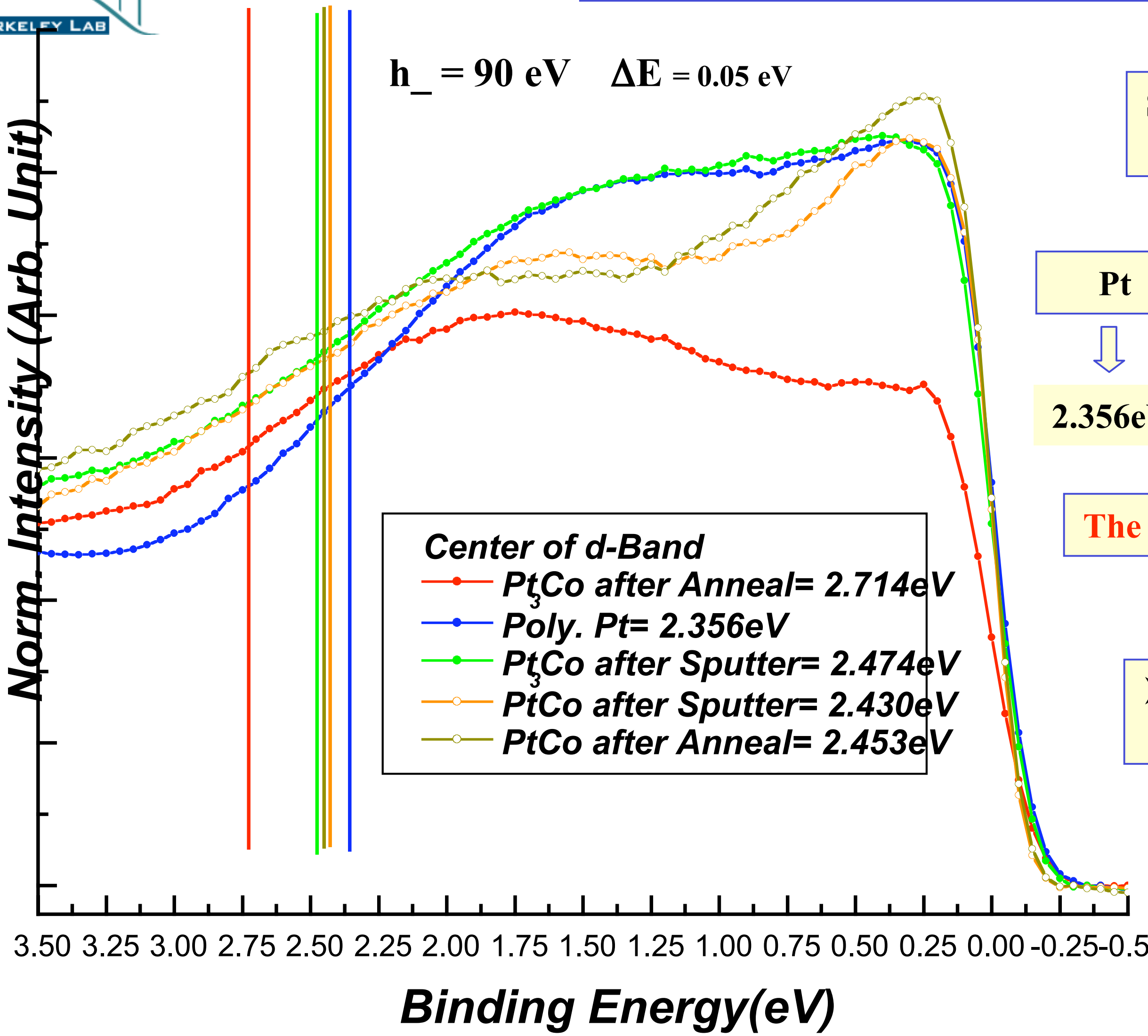
⇩

H_{upd} charge is lower but activity for ORR is higher

⇩

➢Possible electronic effect of alloying component on Pt skin

Electronic properties of Pt Alloys vs. Pt



Systematic shift of d-band center relative to the Fermi level

⇩

Pt	PtCo	Pt_3Co	Pt_3Co "skin"
⇩	⇩	⇩	⇩
2.356eV	2.430eV	2.474eV	2.714eV

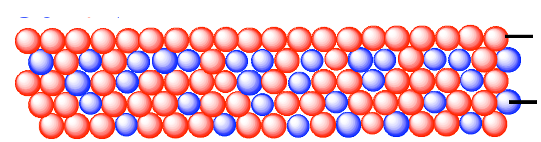
The same order applies for ORR activity

⇩

- **Alloying component is changing the electronic properties of the Pt**

⇩

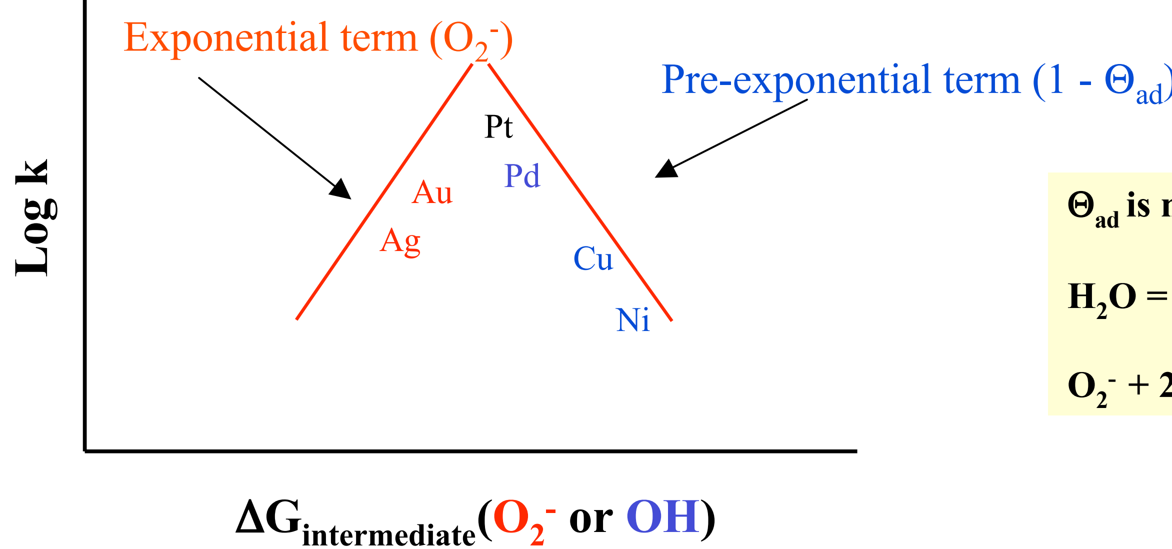
- **The electronic effect is strongest for a Pt skin on a Co - enriched second layer**



Norskov and Hammer theory correlates the position of d-band center to H_{ad} and O_{ad} adsorption energies

The Volcano Relation in ORR Kinetics

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



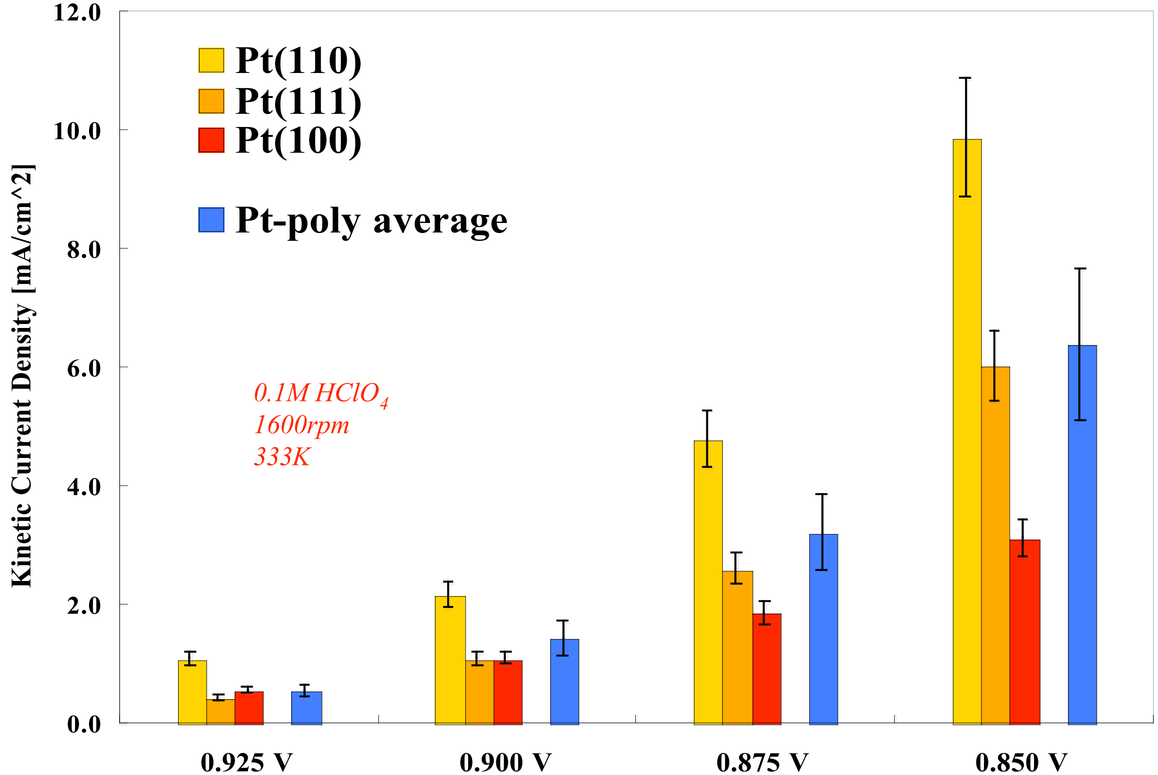
Θ_{ad} is mostly OH_{ad} not $(O_2^-)_{ad}$

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

Pt alloys at the Top of the Volcano

- **Interaction of the electrode with O_2^- requires partially filled d-orbitals with large radial extent**
  - **Only Group VIII metals satisfy this requirement**
- **Interaction of the electrode with OH_{ad} must be relatively weak**
  - **Of the Group VIII metals, Pt has the weakest interaction with OH_{ad}**
  - **Pt skin on Ni,Co alloy has weaker binding with OH_{ad}**

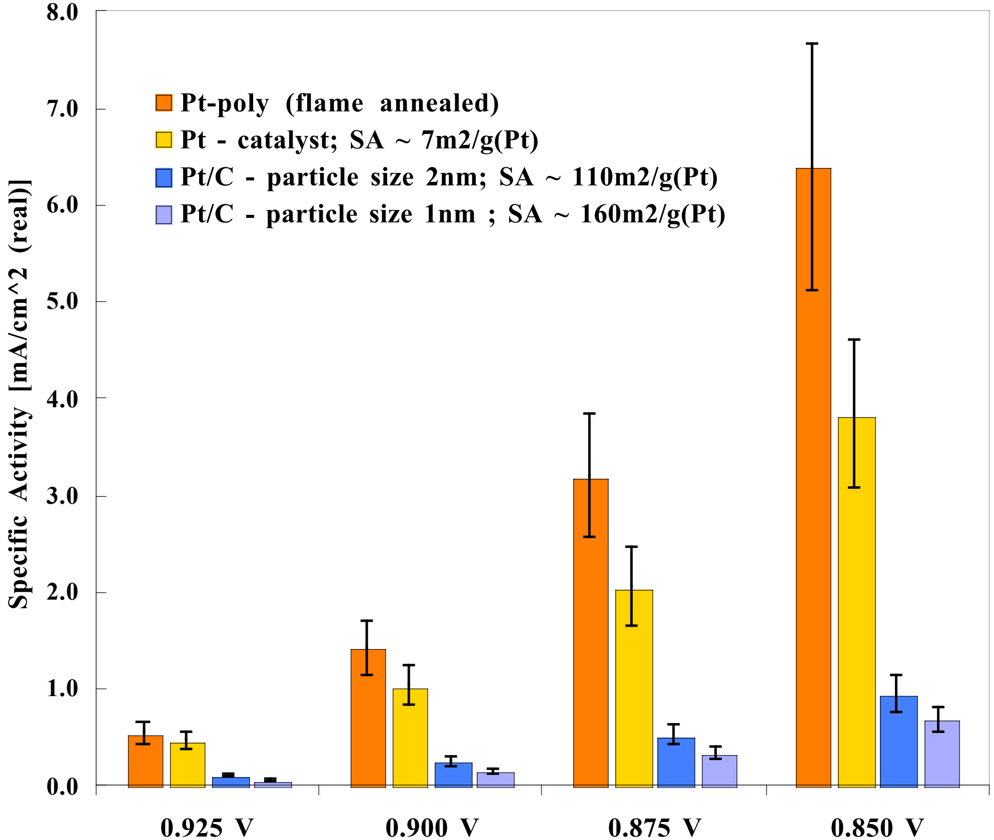
Structure Sensitivity of ORR

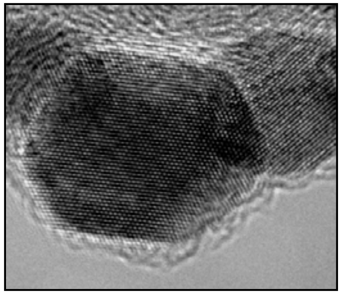


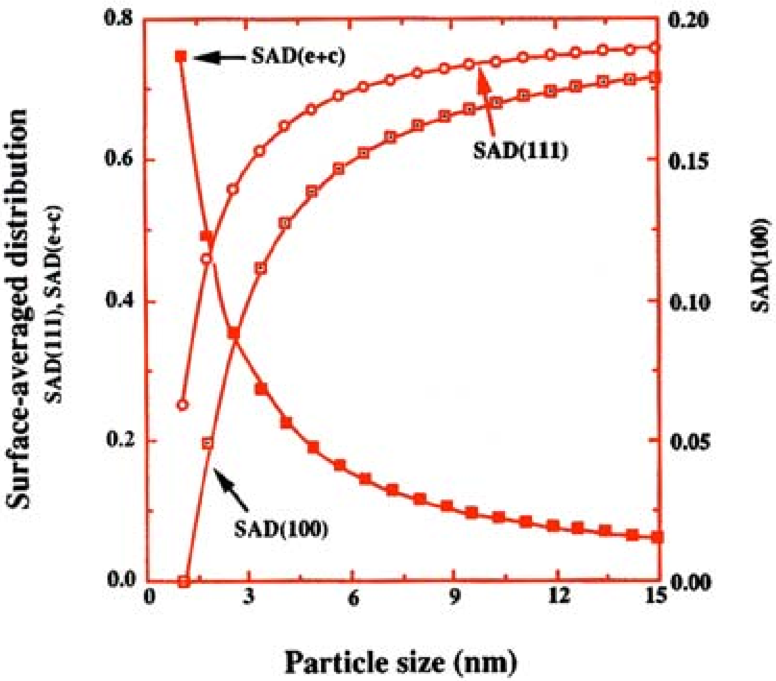
Pt(100) < Pt(111) < Pt(110) **Pt-poly**

	Pt(100)	Pt(111)	Pt(110)	Pt-poly
I_k @ 0.850V :	3.0 ± 0.3	6.0 ± 0.6	10.0 ± 1	6.4 ± 1.2
I_k @ 0.875V :	≈ 1.8	≈ 2.6	≈ 4.8	≈ 3.2
I_k @ 0.900V :	≈ 1.1	≈ 1.1	≈ 2.2	≈ 1.4
I_k @ 0.925V :	≈ 0.5	≈ 0.4	≈ 1.1	≈ 0.5

Specific Activity and Particle Size

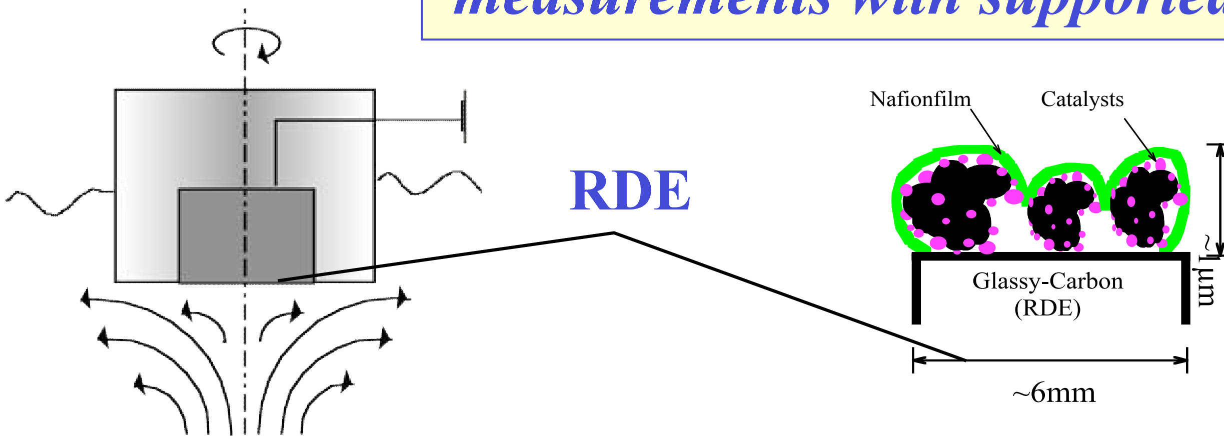




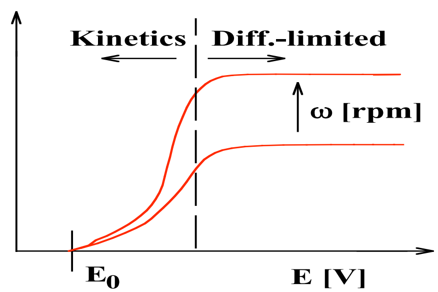


- Cannot reconcile "loss" of specific activity in Pt nanoparticles with structure sensitivity in single crystals
- There is a maximum in mass activity (mA/mg Pt) at about 60 m^2/g (ca. 5 nm particle size)

Thin-film RDE method for kinetic measurements with supported catalysts



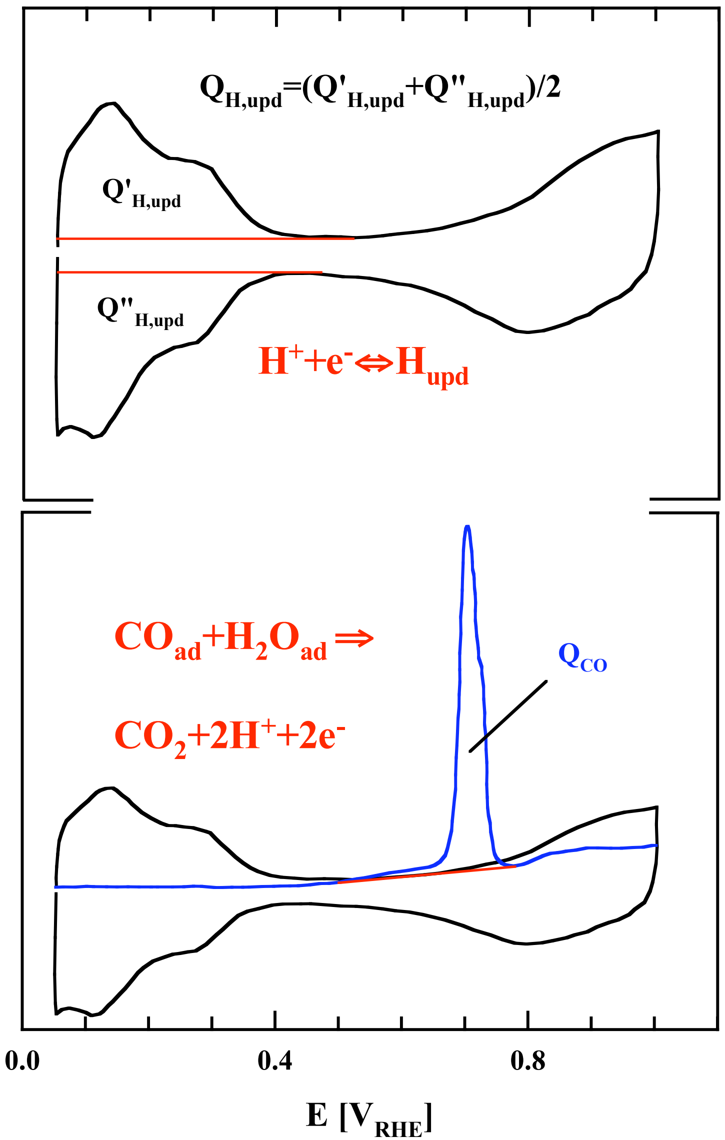
- **No agglomerate diffusion**
  - *thin catalyst layer, < 1μm*
- **Negligible mass transport resistance through Nafion film**
  - *0.1-0.2 μm*
- **Reproducible loading**
  - $\geq 7\mu g_{metal}/cm$_
- **100% wetting/utilization**
- **Fuel cell relevant mass specific current densities**



$$\frac{1}{i} = \frac{1}{i_{kinetic}} + \frac{1}{i_{diff,l}}$$

$$i_{diff,l} = 0.62 nFD^{2/3} \nu^{-1/6} c_{O_2} \omega^{1/2} = Bc_{O_2} \omega^{1/2}$$

Roughness factor and real Pt surface from H_{upd} and CO stripping



- Pt loading is expressed over geometric surface area
- Geometric surface area = 0.283 cm^2
- r_f=1 for $Q_{H,upd}=Q_{CO}/2=0.220\ mC/cm^2$

Roughness factor (r_f) and real Pt surface (A_{Pt}) from H_{upd}:

$$r_f = \frac{Q_{H,upd}}{0.220 mC / cm^2} \left[\frac{cm^2(real)}{cm^2(geo)}\right]$$

$$A_{Pt} = \frac{r_f}{Pt_{loading}} \left[\frac{m^2}{g_{Pt}}\right]$$

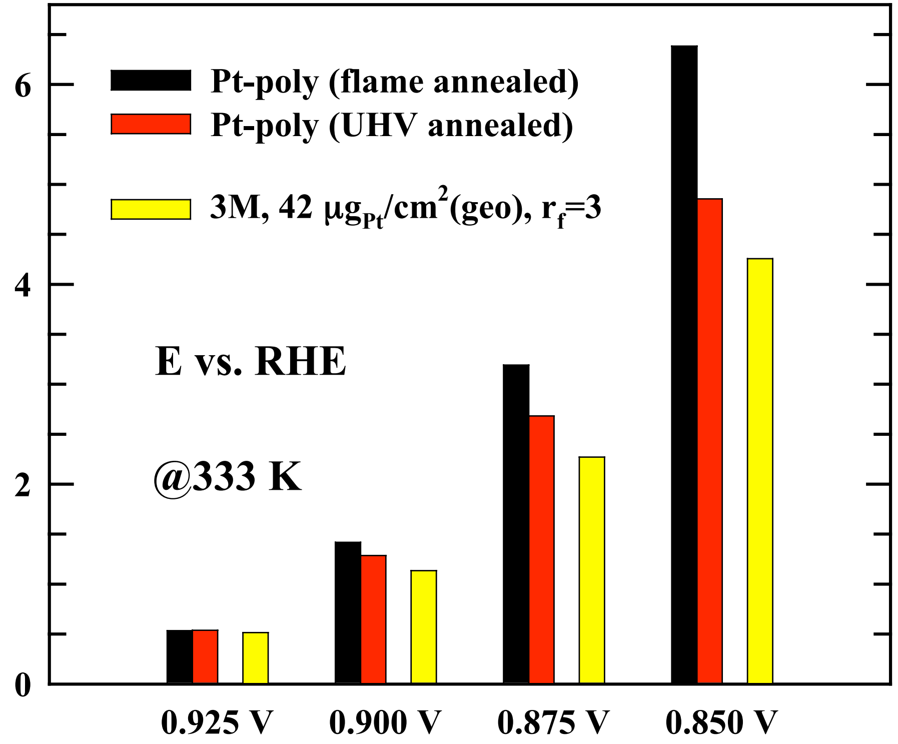
Roughness factor (r_f) and real Pt surface (A_{Pt}) from CO stripping:

$$r_f = \frac{Q_{CO}/2}{0.220 mC / cm^2} \left[\frac{cm^2(real)}{cm^2(geo)}\right]$$

$$A_{Pt} = \frac{r_f}{Pt_{loading}} \left[\frac{m^2}{g_{Pt}}\right]$$

Summary

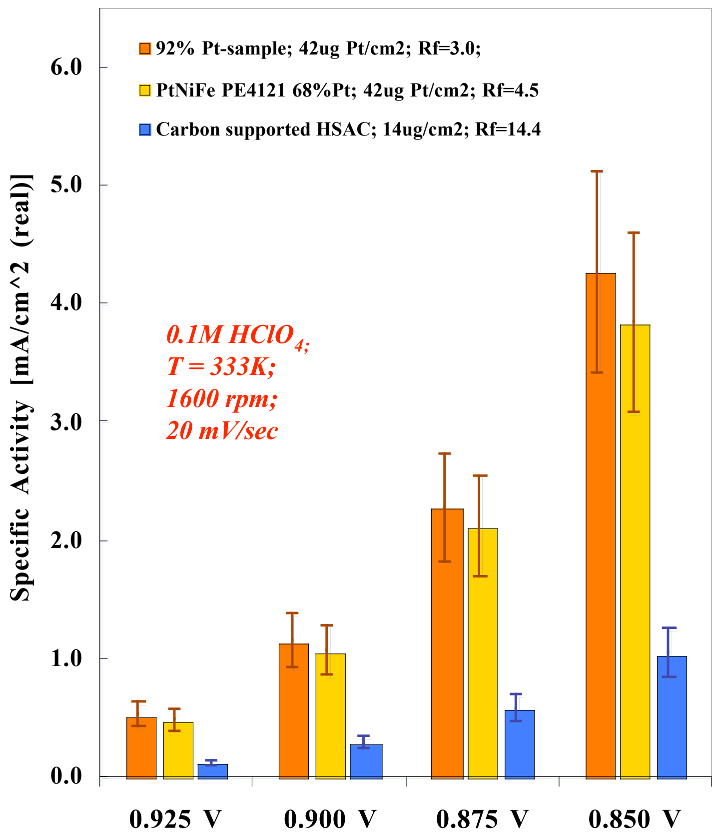
- Thin-film RDE method was optimized for measuring 3M NS Pt catalysts
- Pt real surface area of 7 - 10 m^2/g_{Pt}
- Activity for ORR close to those obtained on polycrystalline Pt



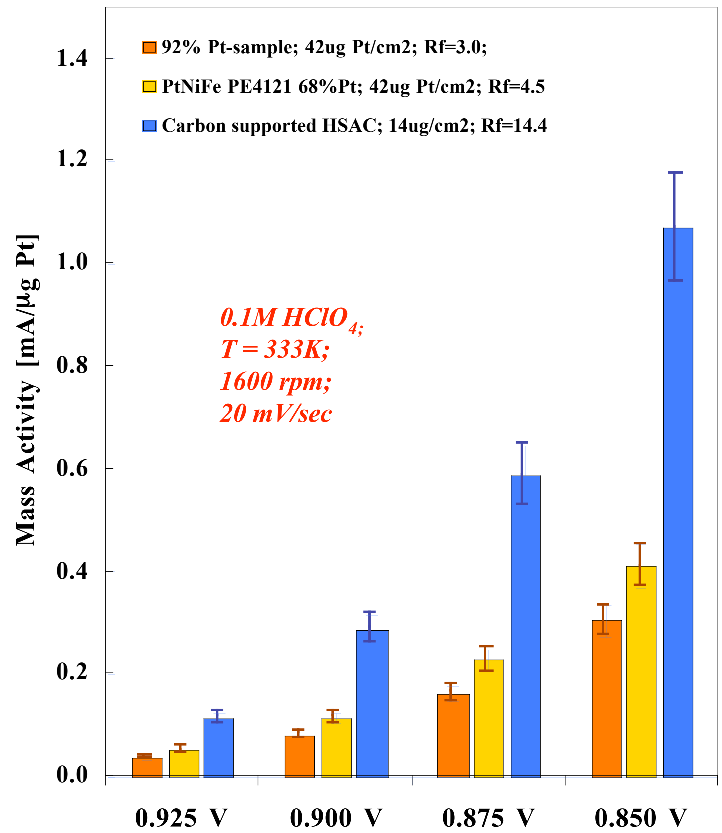
- During ORR no peroxide production in region of mixed kinetic-diffusion control
- Activation energy of ~22 kJ/mol same as for poly Pt

NS Pt Versus Conventional HSAC Supported Pt

(a) Specific Activity [mA/cm^2_{geo}]



(b) Mass Activity [$mA/\mu g_{Pt}$]



- *Pt alloy NS catalyst has approximately the same specific activity as 92% Pt-sample, but because of the significantly higher roughness factor (Rf=4.5 instead of 3.0) mass activity for alloy is ~35% higher.*
- *Compared to a carbon-supported High Surface Area Catalyst (Pt-Loading is 14µg/cm^2) under same experimental conditions, specific activity is ca. 4 times higher for both 3M-NS catalysts, **but** mass activity is 3 to 4 times lower.*