Argonne NATIONAL LABORATORY

ELECTROCATALYSIS:

the role of atomic and electronic structures in nanocatalysts engineering

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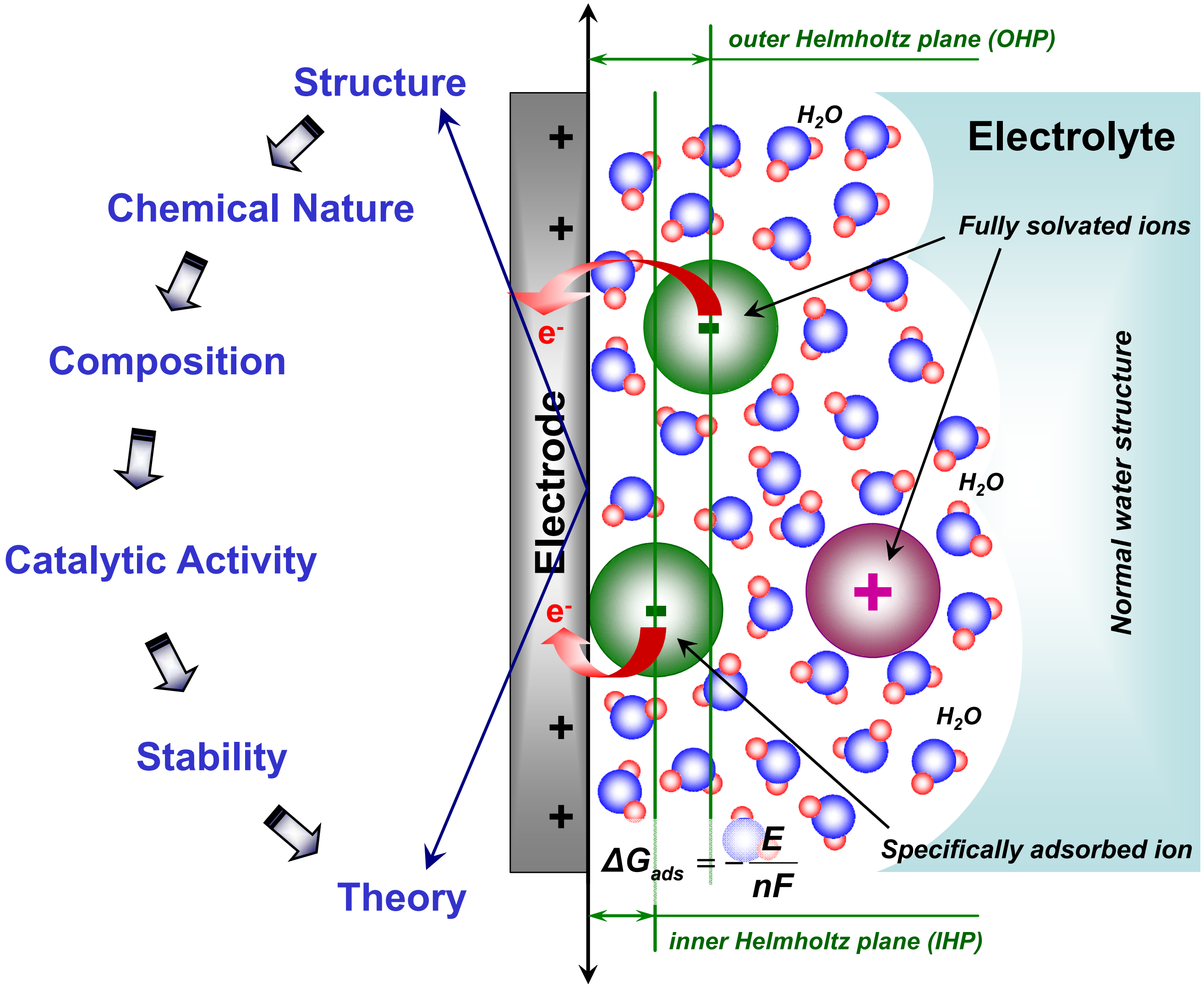
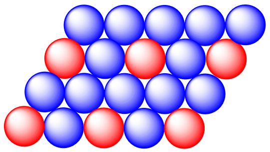
Thanks to: V. Stamenkovic, D. Strmcnik, D. Tripkovic, D. Van der Vliet, C. Lucas, General Motors and DOE

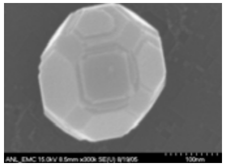
Understanding the surface electrochemistry



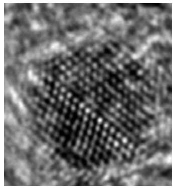
Approach



SINGLE CRYSTALS

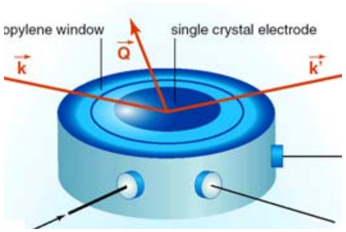


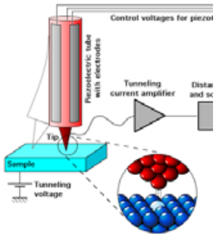
MODEL NANOPARTICLES

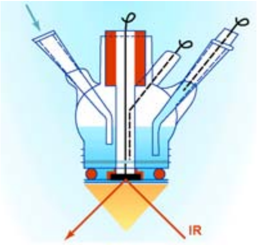


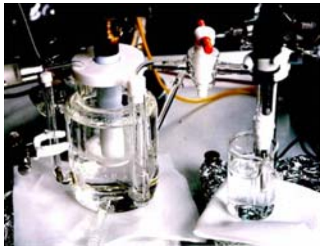
REAL NANOPARTICLES

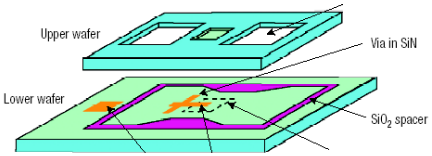
Use and develop state-of-the-art surface sensitive probes, spectroscopes and EC

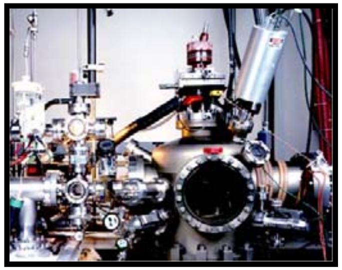












- ✓ *Atomic/molecular structures*
- ✓ *Electronic structures*
- ✓ *Chemical nature*
- ✓ *Composition*
- ✓ *Size and shape*
- ✓ *Kinetics*

STRUCTURE/FUNCTION RELATIONSHIPS AND STABILITY

Cathode reaction in PEMFC

1. Single crystal surfaces

- ➢ Monometallic surfaces: structure sensitivity
  - ✓ *Adsorption of spectator species on Pt(hkl)*
  - ✓ *ORR on Pt(hkl)*
- ➢ Bimetallic surfaces:

  Polycrystalline Pt_3M (M = Ni, Co, Fe, Mn, Cr, V, T)
  - ✓ *Electrocatalytic trends*
  - ✓ *Stability*

  Single crystal Pt_3Ni(hkl) surfaces
  - ✓ *Electronic (ligand) effects*
  - ✓ *Geometric effects*

2. High surface area catalysts

- ➢ Monometallic surfaces: particle size effects
  - ✓ *ORR on Pt*
- ➢ Bimetallic surfaces

  Tailoring catalytic properties

Oxygen Reduction Reaction

ΔG_{ad} term

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

Pt – O_2^- : ΔG_{ad}= -0.87 eV

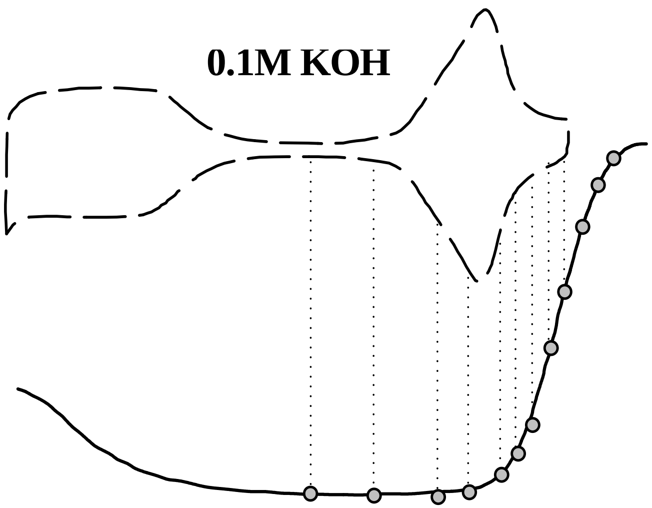
Au - O_2^- : ΔG_{ad}= 0.24 eV

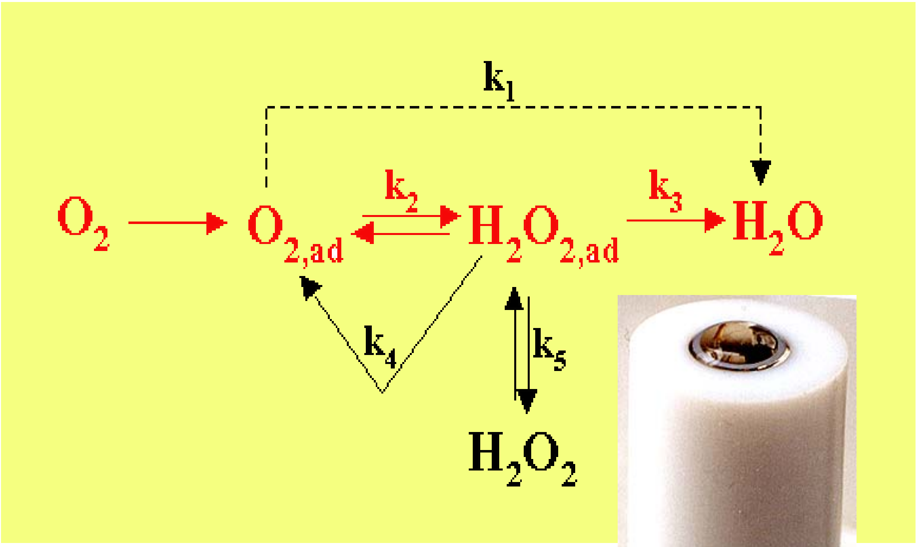
$(1-\Theta_{ad})$ term

Θ_{ad} is mostly spectators, not O_{2ad}

→ *Effects availability of metal sites*

→ *and ΔG_a*

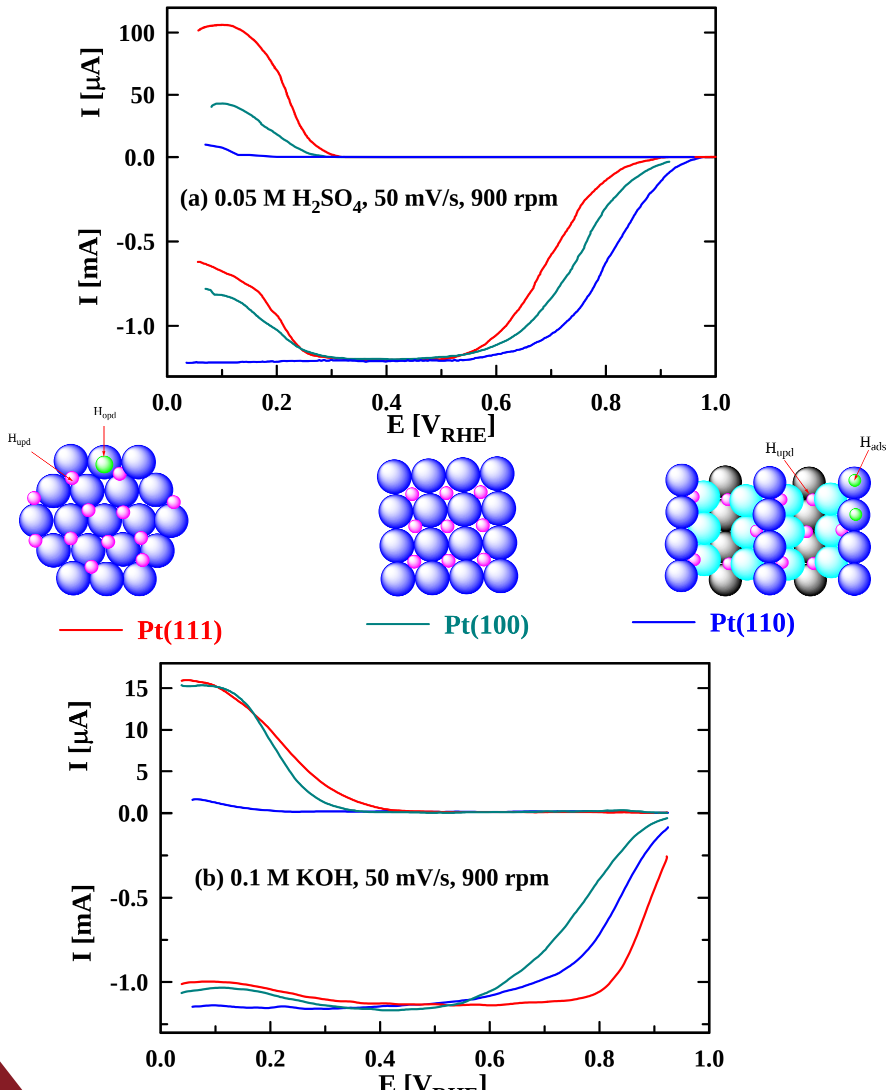




Rotating ring disk method

$$i = n F k (1-\Theta) \exp(-\gamma \Delta G/RT)$$

Structure sensitivity



- **Structure sensitive kinetics due to structure sensitive adsorption of H_{upd} , OH_{ad} and anions**

- **“Serial” reaction pathway:**

$$O_2 \longrightarrow O_{2,ad} \overset{k_2}{\rightleftarrows} H_2O_{2,ad} \xrightarrow{k_3} H_2O \qquad (O_{2,ad} \xrightarrow{k_1} H_2O)$$

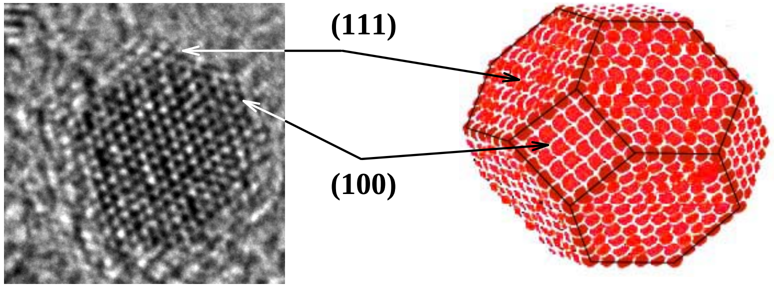
$$i = n\,F\,k\,(1-\Theta)\,\exp\,(-\Delta G/RT)$$

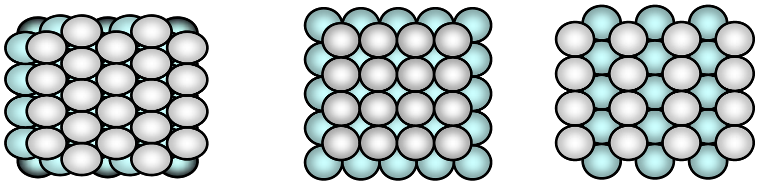
- **Activation energy (@E_r : ΔG~40 kJ/mol) is independent of pH and surface structure**

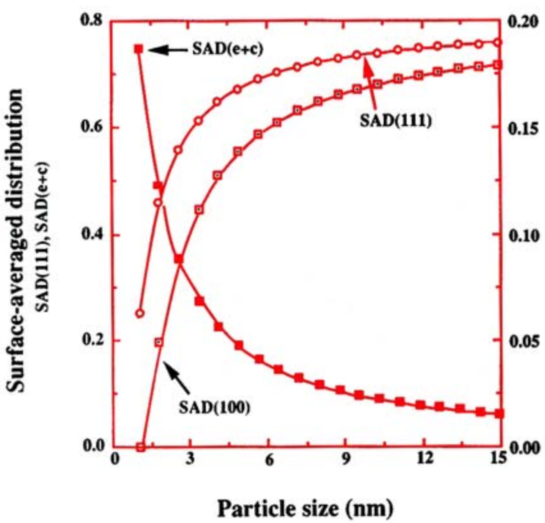
- **ORR kinetics on Pt(hkl) is mainly determined by the $(1-\Theta_{ad})$ term**

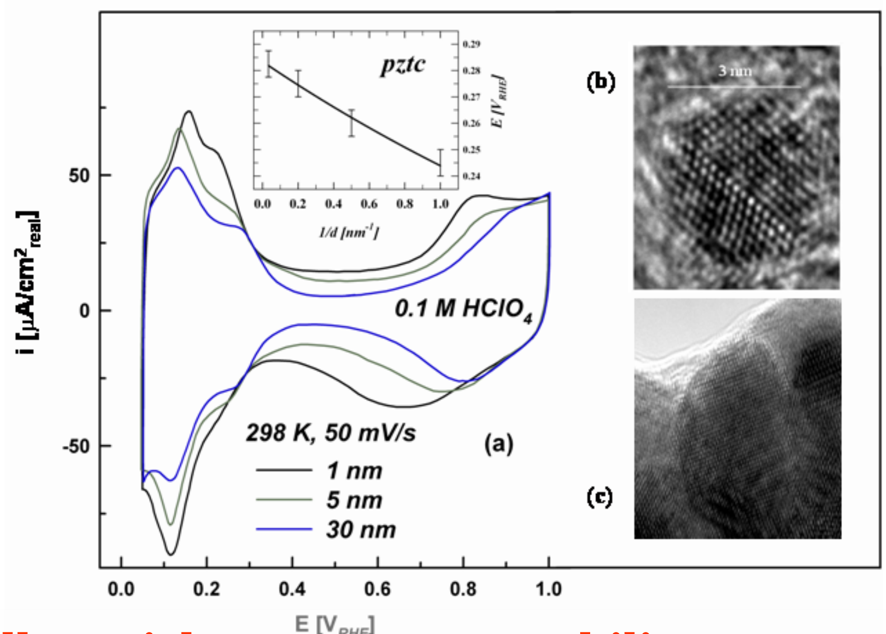
Surface Science Reports 45 (2002) 117

Particle size effect





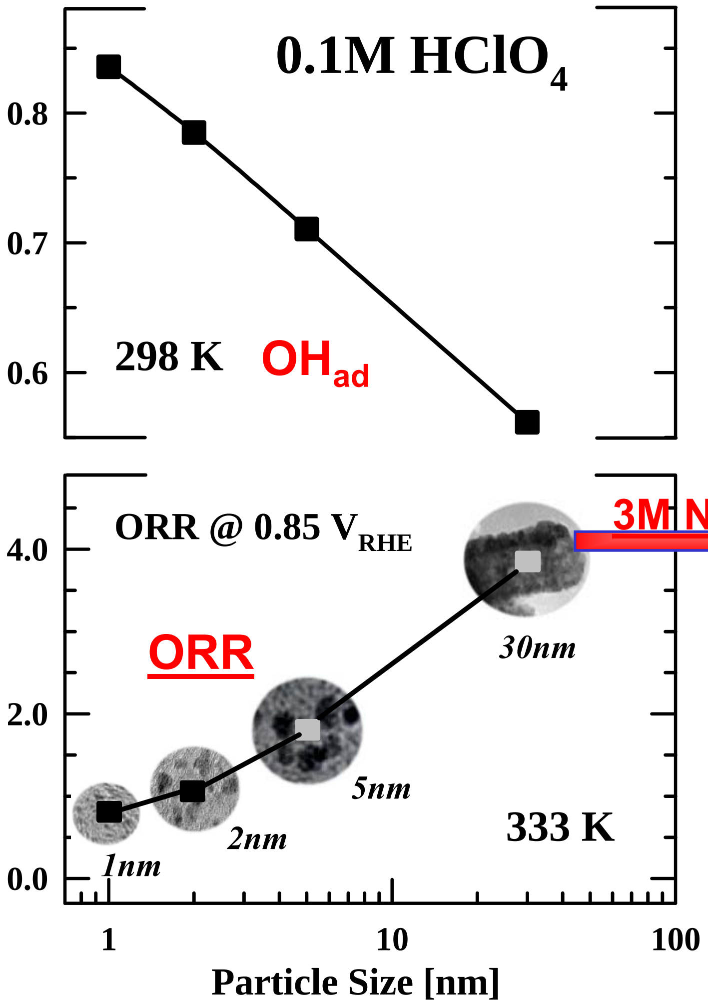


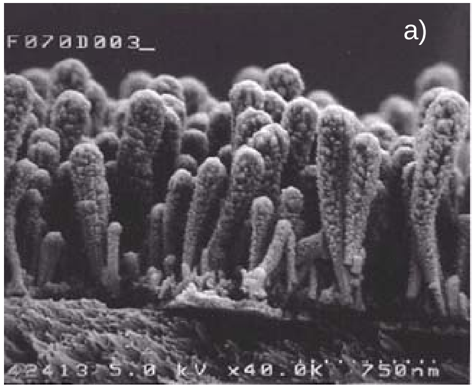


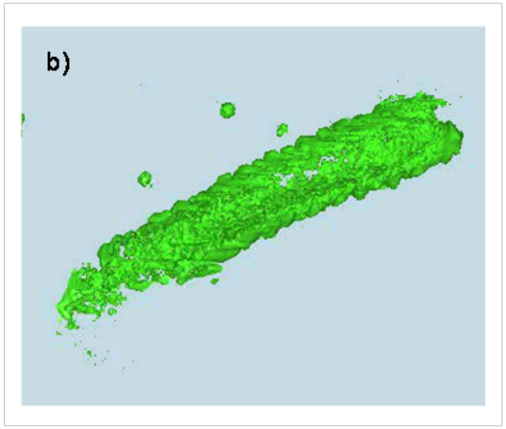
- Small particles are more oxophilic
- pztc increases by increasing the particle size

JECS 127 (2005) 6819

Reactivity





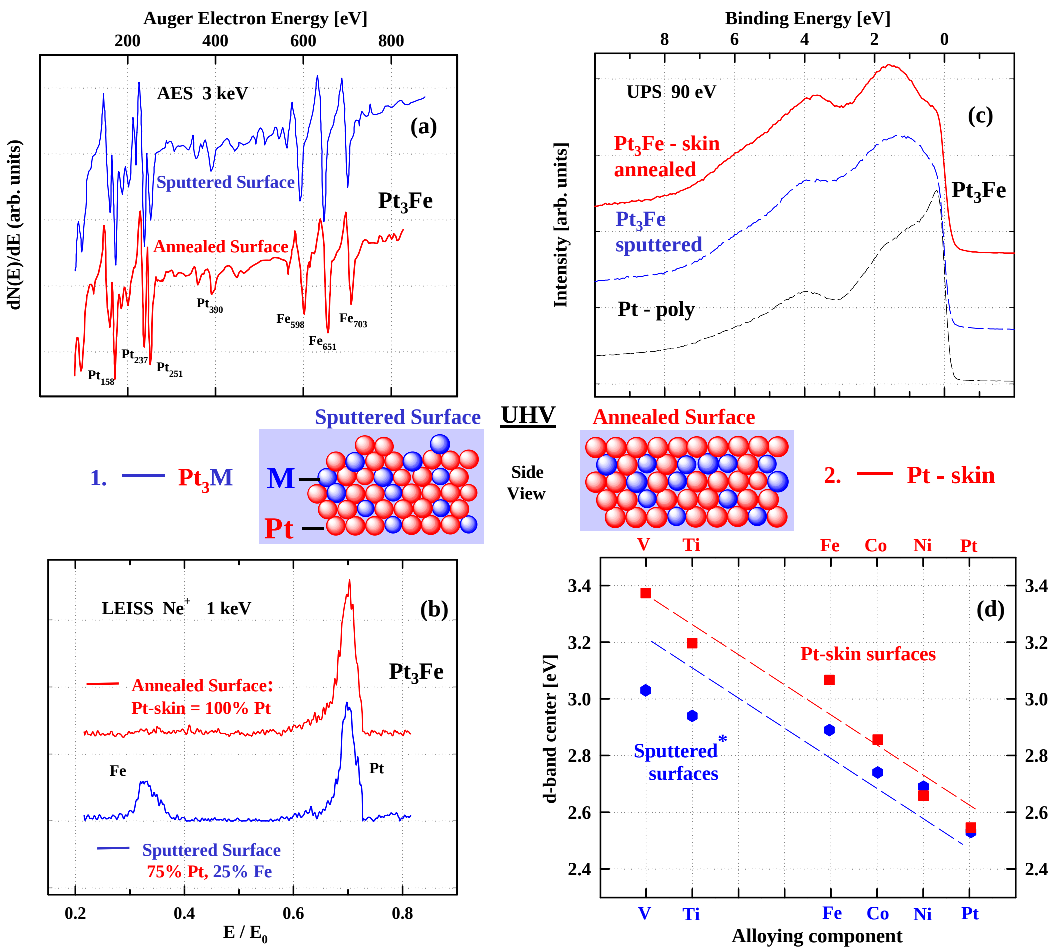


3M NSTF catalysts

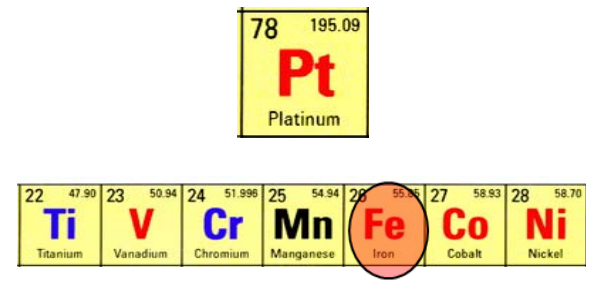
$$i = n F k (1-\Theta) \exp(-\gamma \Delta G/RT)$$

J.Phys.Chem. B 109 (2005)14433

Pt_3M alloys: UHV characterization



SURFACE PROPERTIES



✓ ***Chemical nature***

O and C free surfaces

✓ ***Composition***

annealing; pure Pt ("Pt-skin")

spattering: bulk terminated

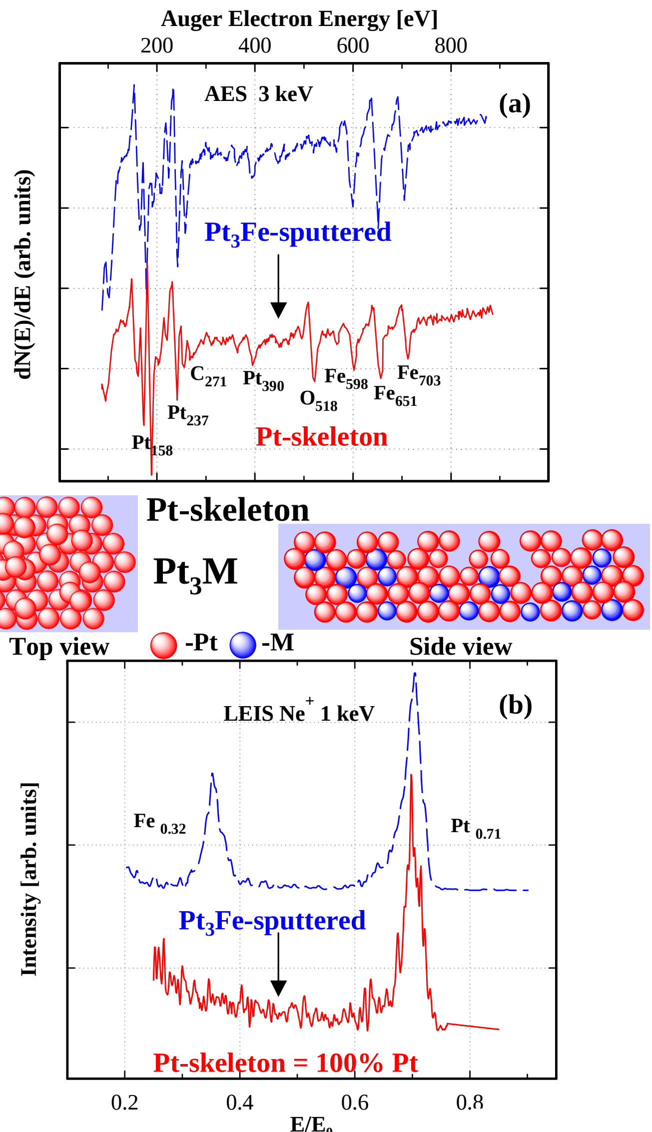
✓ ***Electronic structure***

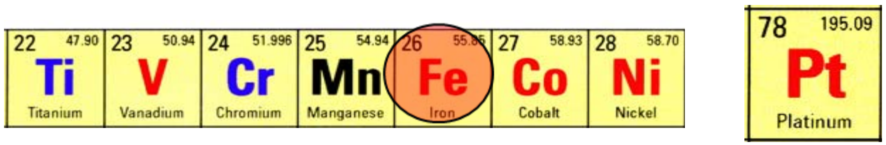
Pt < bulk term. < Pt-skin

ε_d vs. M linear

JECS 128 (2006) 8813

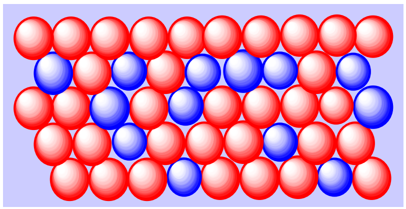
Stability





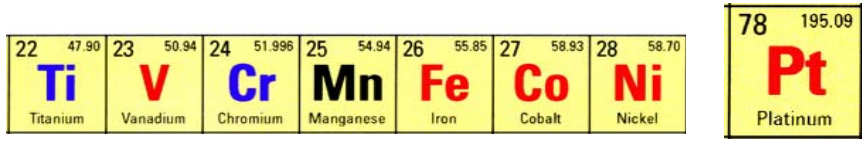
✓ **Annealed surface (Pt-skin) is stable:**
oscillatory segregation profile ?????

Pt-skin

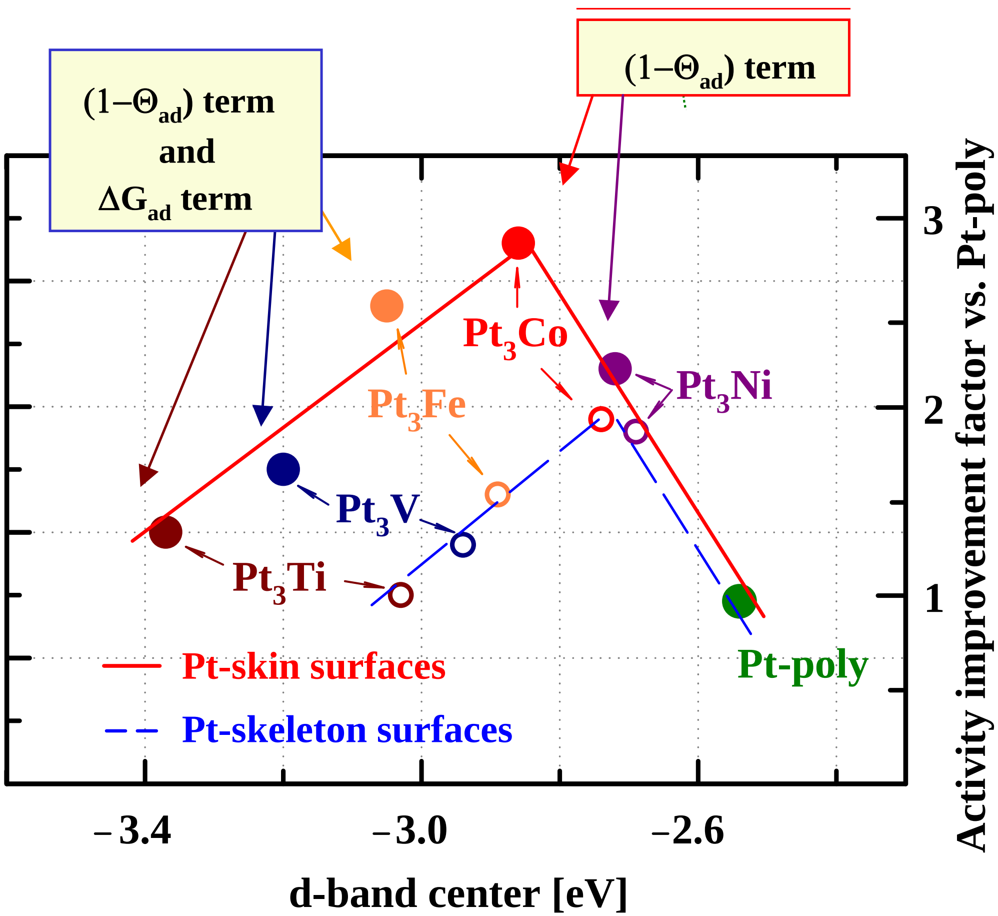


✓ **Sputtered surface is unstable: "Pt-skeleton"**
bulk terminated concentration profile
"rough" surface

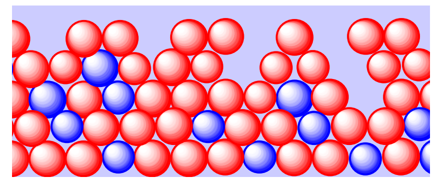
Nature Materials 6 (2007) 214



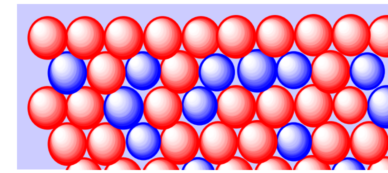
$$i = n F k (1-\Theta) exp(-\gamma \Delta G/RT)$$

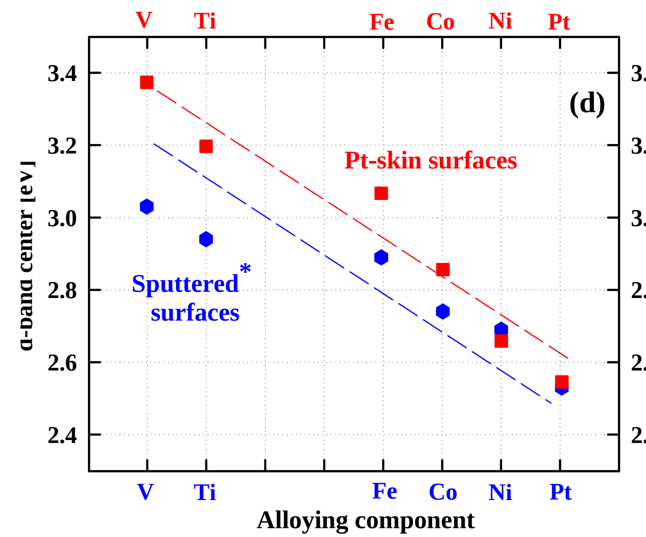


Pt-skeleton



Pt-skin



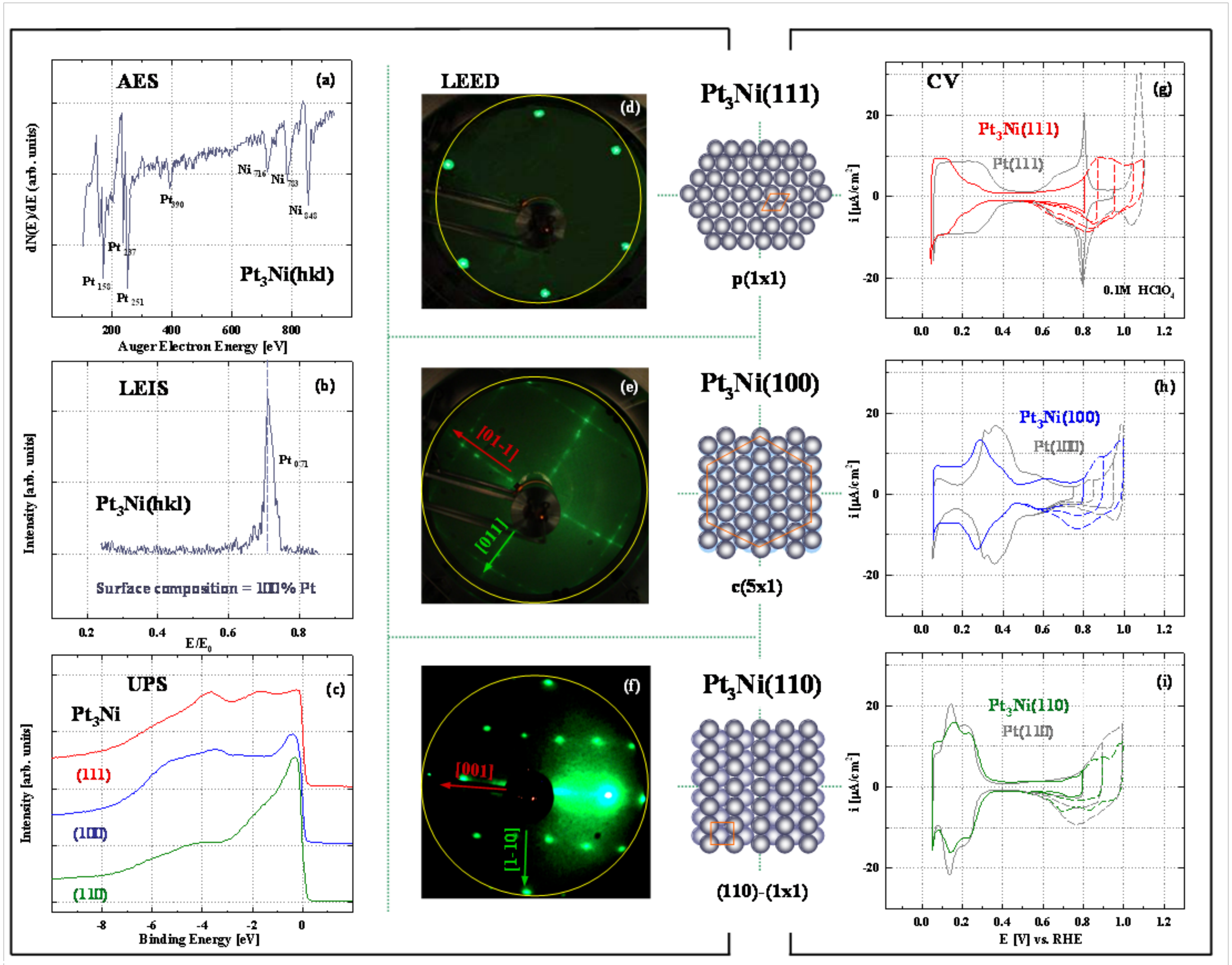


J. Chem Phys. 123 (2005) 204717

Nature Materials 6 (2007) 214

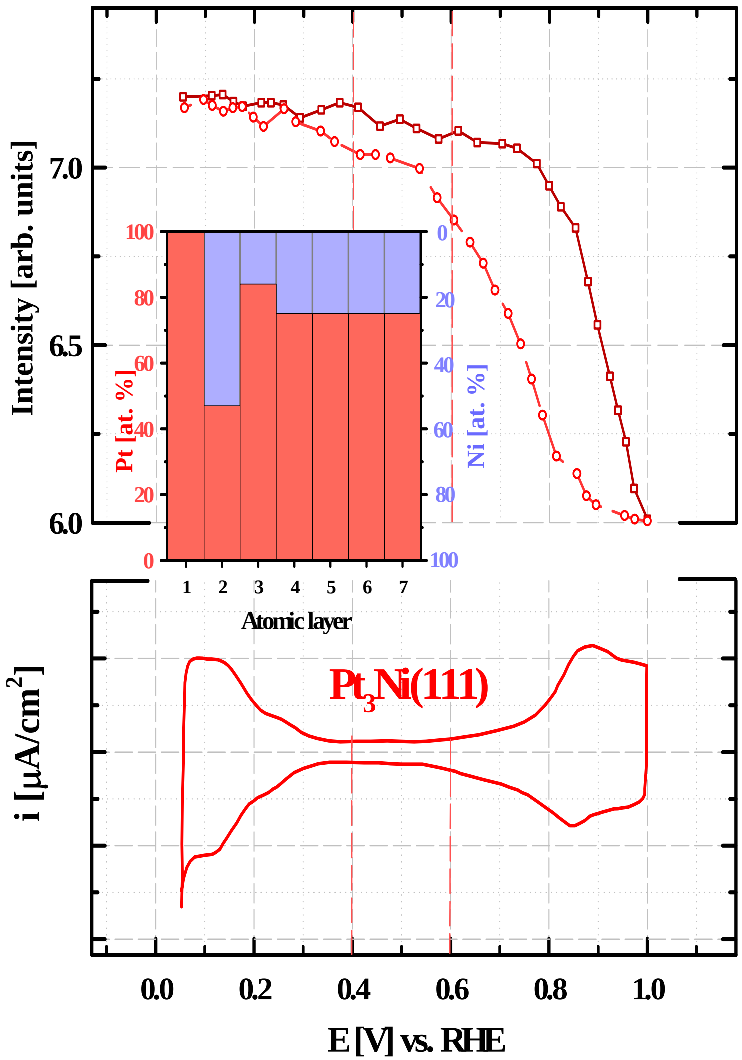
Angew.Chem 45 (2006) 2897 (in colaboration with Norskov's group)

$Pt_3Ni(hkl)$- Ex-situ



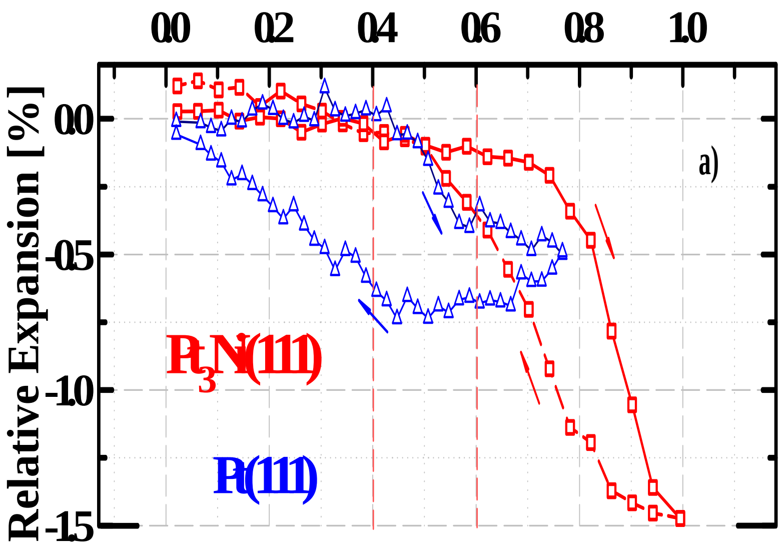
Science 315 (2007) 493

$Pt_3Ni(111)$- In-situ

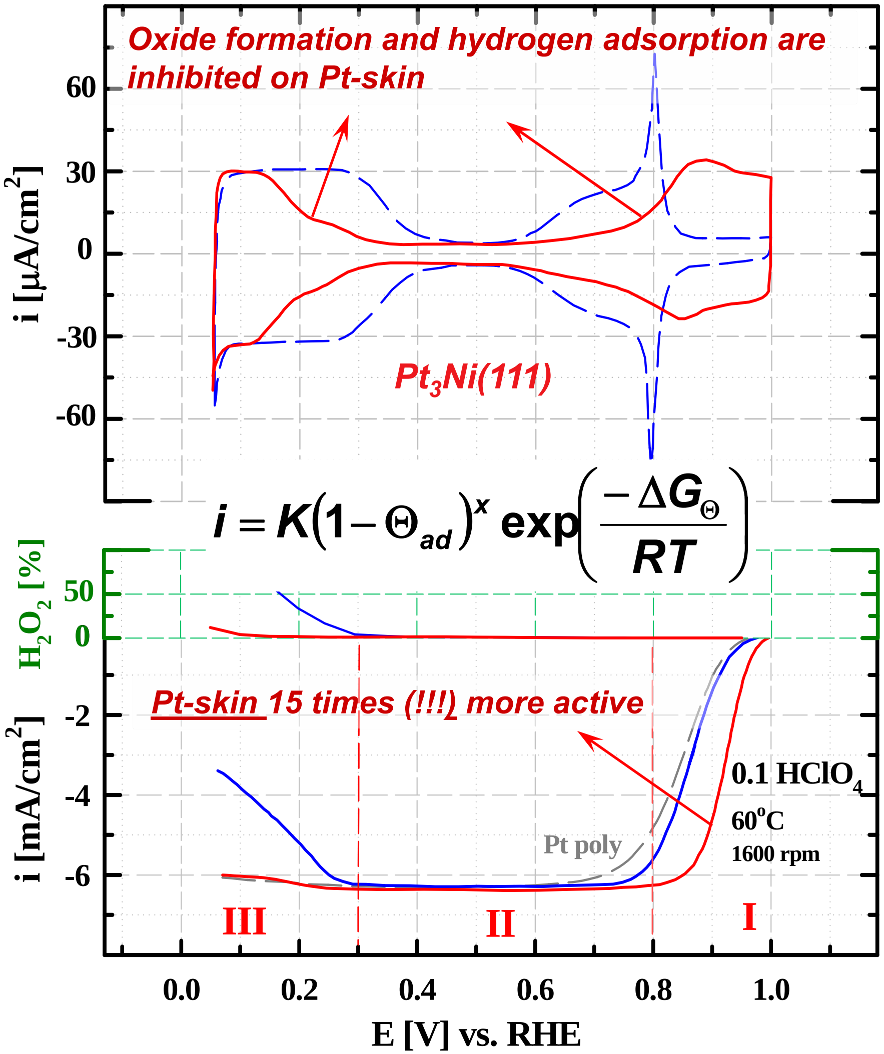


$Pt_3Ni(111)$

- ***Atomic structure: (1x1)***
- ***Segregation oscillatory profile: "Pt-skin"***

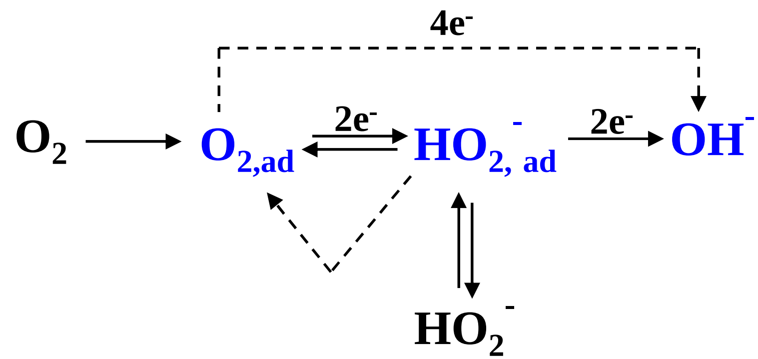


$Pt_3(111)$ system: ORR



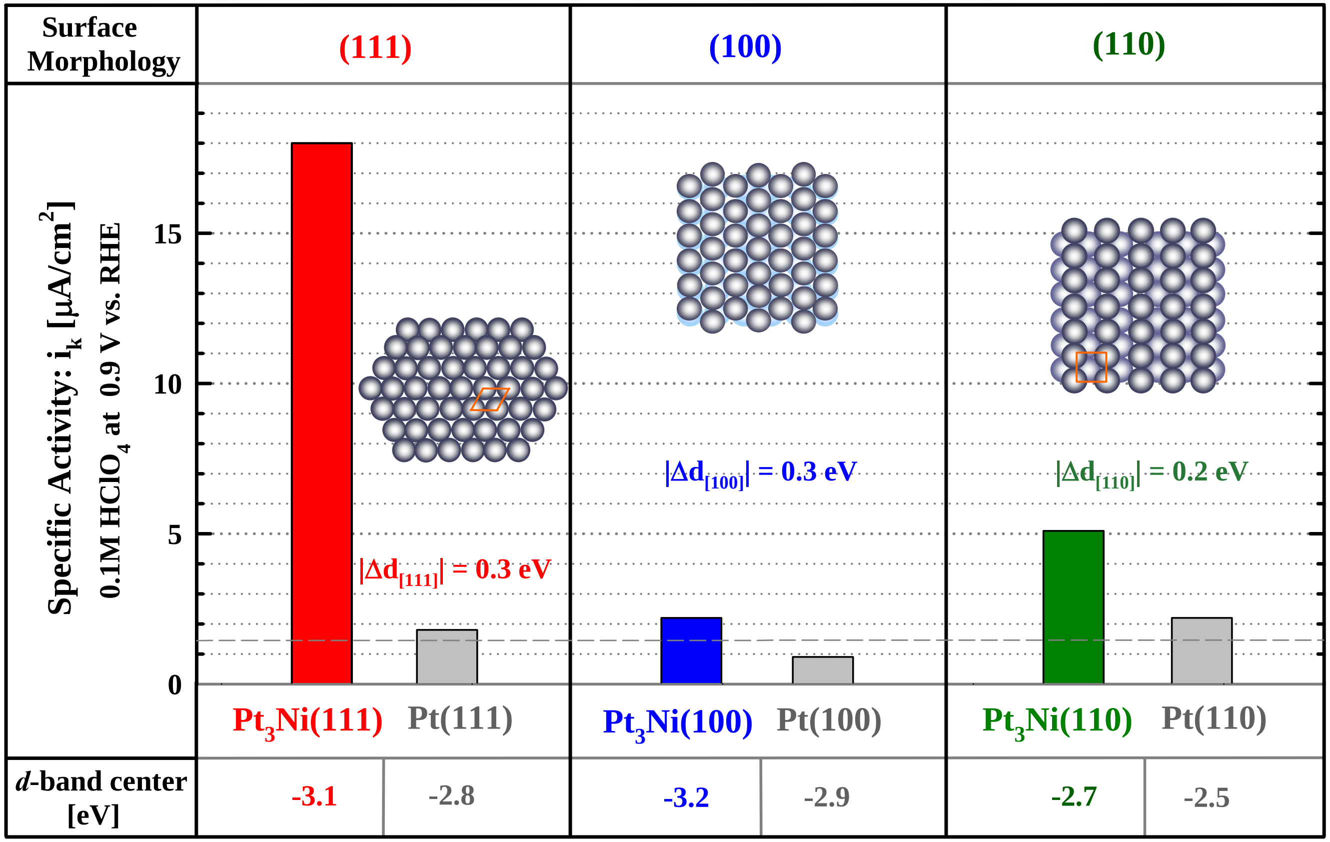
$$i = K(1-\Theta_{ad})^x \exp\left(\frac{-\Delta G_\Theta}{RT}\right)$$

- ε_d : $Pt_3Ni(111) < Pt(111)$
- Θ_{OH}: $Pt_3Ni(111) < Pt(111)$



$$i = n F k (1-\Theta) \exp(-\gamma \Delta G/RT)$$

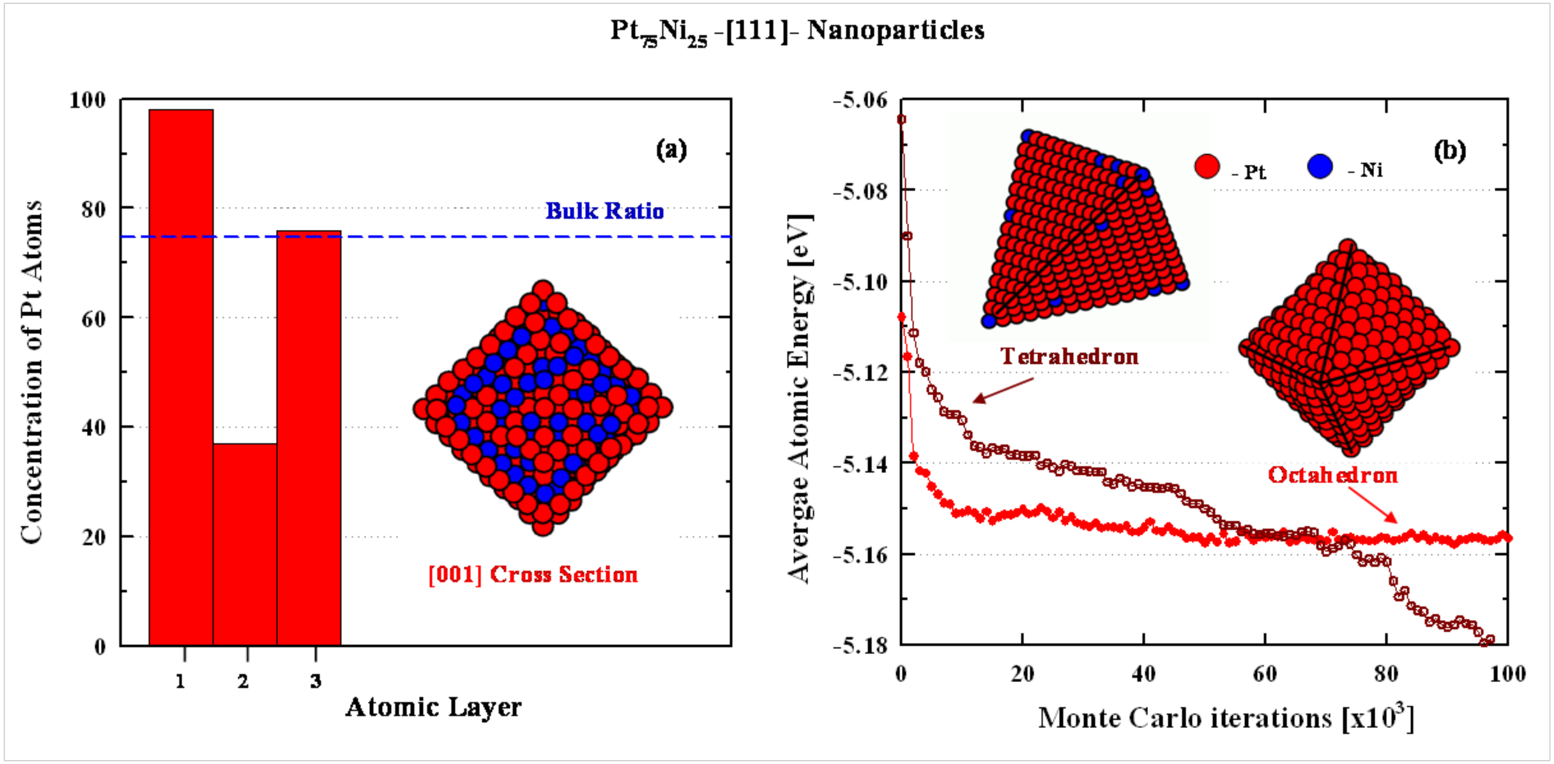
Pt_3(hkl) systems: ORR



✓ ORR on $Pt_3Ni(111)$ is the highest that has ever been observed on cathode catalysts !

Science 315 (2007) 493

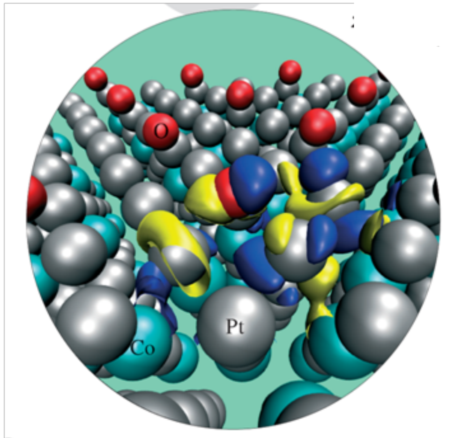
Pt-skin octahedral nanoparticles: Monte Carlo

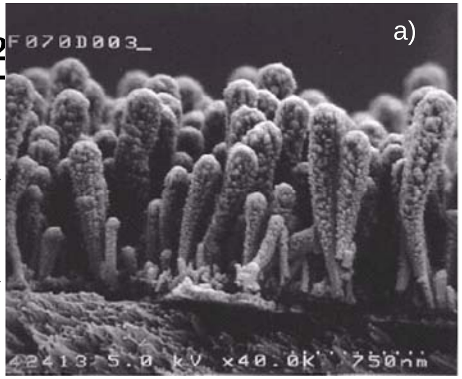


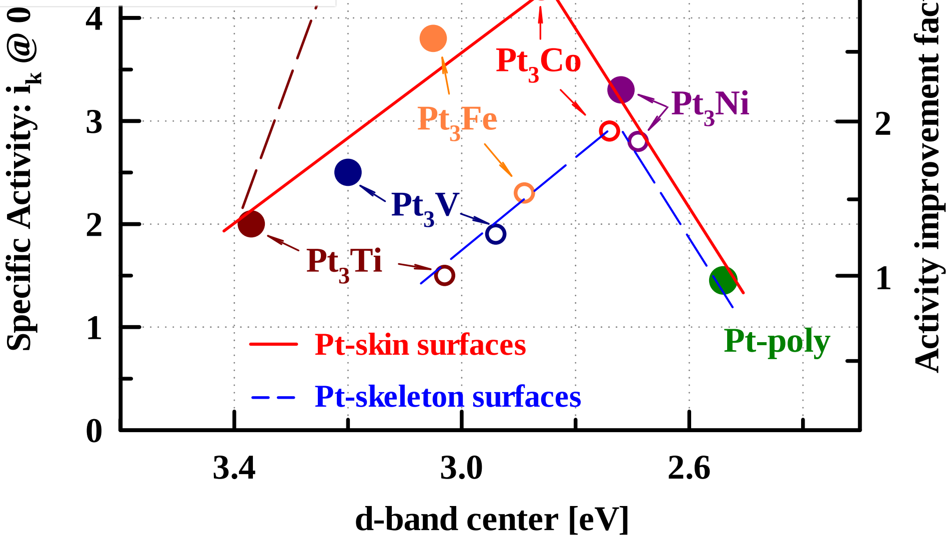
✓ Segregation profile obtained from MC simulation

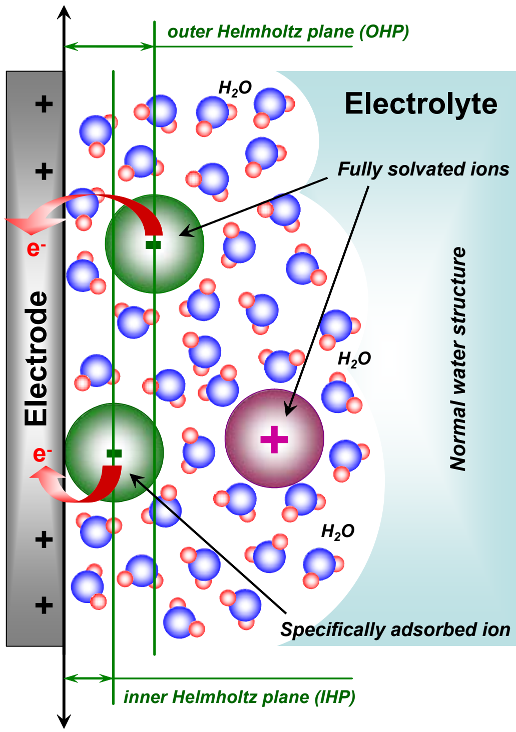
✓ Octahedral particles are thermodynamically stable

Summary and Targets









- ✓ 10-fold higher of Pt(111) and 90-fold higher of state-of-the art Pt/C
- ✓ 3 m^2/g_{Pt} will exceed 4xPt mass activity target

“ARGONNE” INTERFACE