Near-Surface Alloys for Improved Catalysis

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Acknowledgements

- Ratko Adzic (BNL)
- J. Chen (U of Delaware)
- Jeff Greeley, Ye Xu, Anand Nilekar
- Jens Nørskov and colleagues @ CAMP – Denmark

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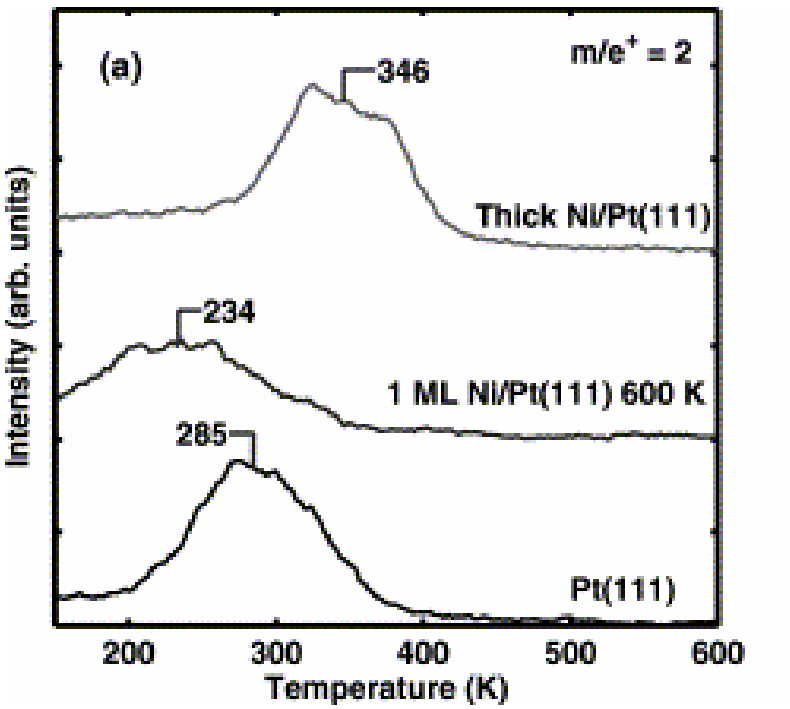
- NPACI, DOE-NERSC, PNNL (supercomputing resources)

Outline

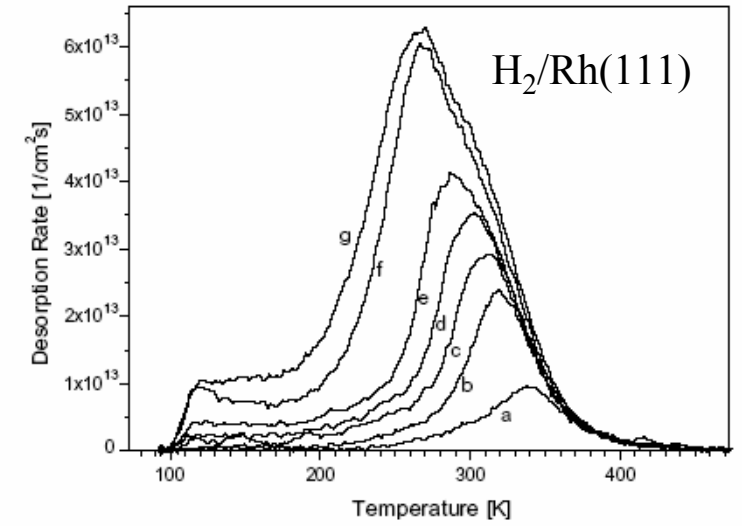
- H_2 catalytic chemistry:
  - Identifying Promising Catalysts from 1st Principles:
    H_2 and H on Bimetallic Near Surface Alloys (NSAs)

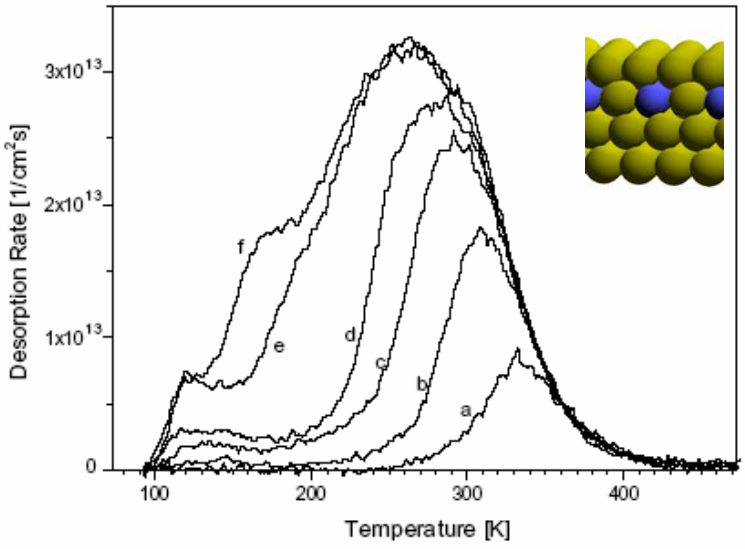
- Oxygen Reduction Reaction (ORR)
  - Improved catalysts with ML structures
  - Further improvements with mixed-metal ML structures

Hydrogen on NSA's



[1]Ni/Pt(111)





[2]V/Rh(111)

1. J. Kitchen, N. Khan, M. Barteau, J. Chen, B. Yashhinskiy, and T. Madey, Surf. Sci. **544** (2003) 295

2. R. Schennach, G. Krenn, B. Klötzer, K. Rendulic, Surf. Sci. **540** (2003) 237

Methods

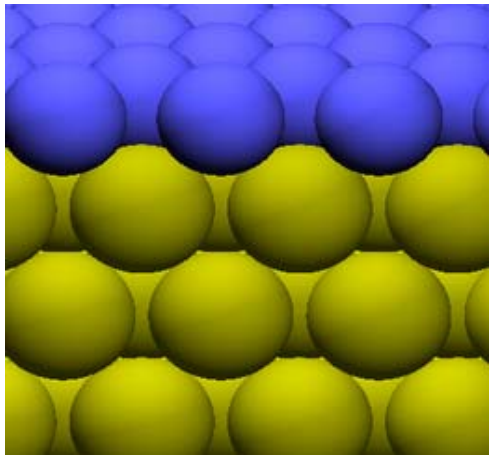
- Density Functional Theory – DACAPO total energy code [1,2]
- Periodic self-consistent PW91-GGA [3]
- Ultra-soft Vanderbilt pseudo-potentials [4]
- Plane wave basis sets with 25-Ry kinetic energy cut-off
- Spin polarization as needed
- Four-metal-layer slabs; (2x2) unit cell; top two layers relaxed
- First Brillouin zone sampled at 18 *k*-points
- Nudged Elastic Band method for reaction paths [5]

1. B. Hammer, L. B. Hansen, J. K. Nørskov, *Phys. Rev. B* 59, **1999**, 7413.
2. J. Greeley, J. K. Nørskov, M. Mavrikakis, *Annu. Rev. Phys. Chem.* 53, **2002**, 319.
3. J. P. Perdew *et al.*, *Phys. Rev. B* 46, **1992**, 6671.
4. D. H. Vanderbilt, *Phys. Rev. B* 41, **1990**, 7892.
5. G. Henkelman, H. Jónsson, *J. Chem. Phys.* 113, **2000**, 9978.

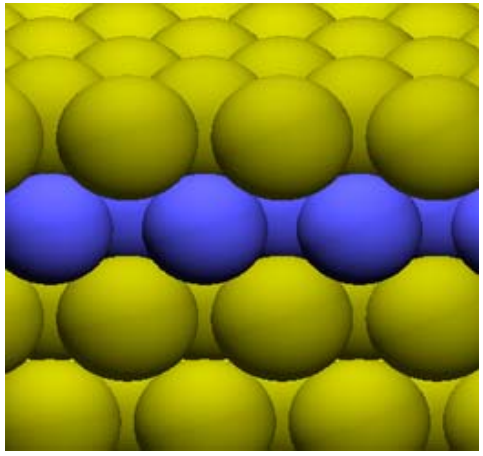
Ideal Bimetallic Near Surface Alloys

- Segregation properties of two metals are critical
- Consider two special classes:
  - Overlayers
  - Subsurface Alloys

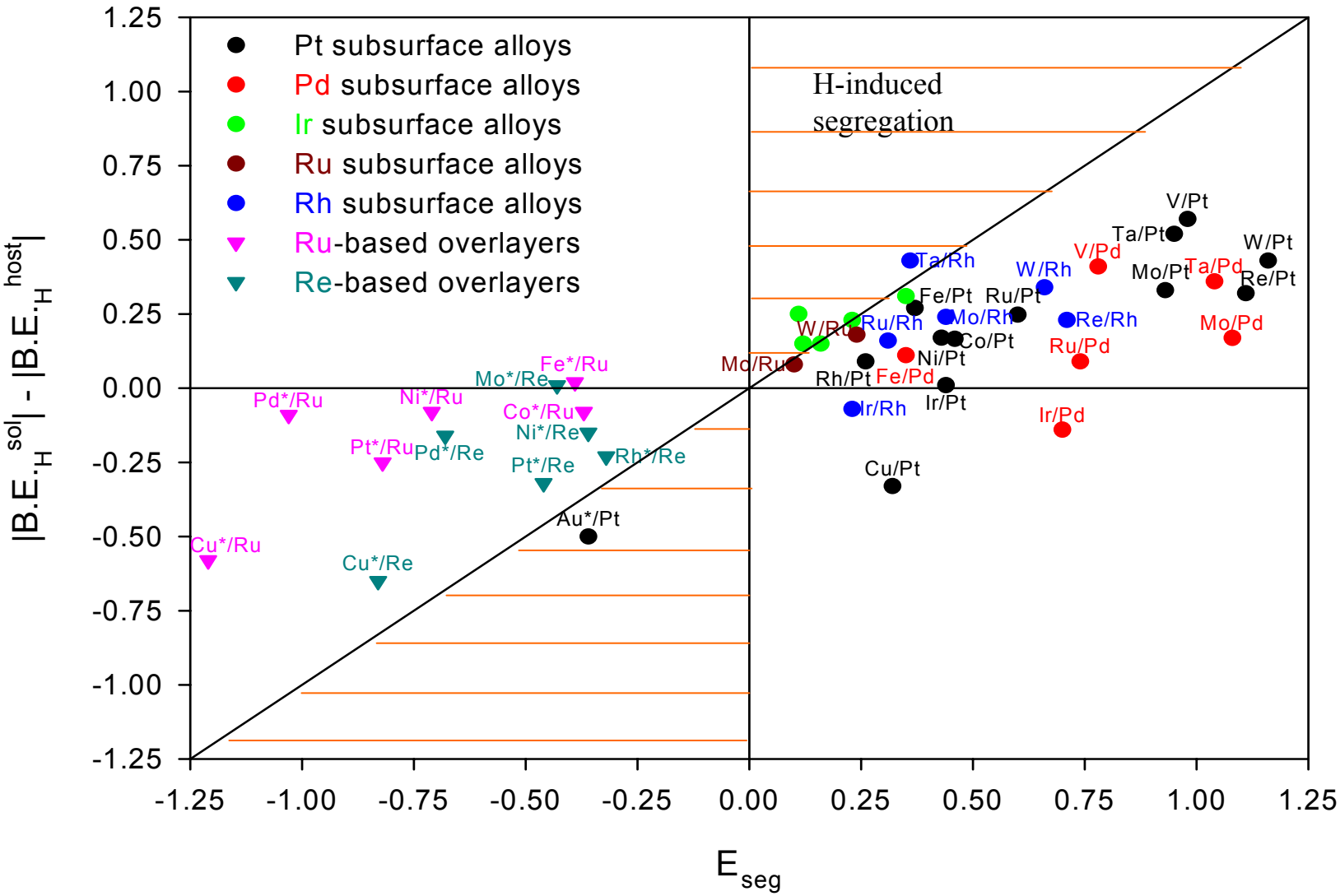
Overlayers*



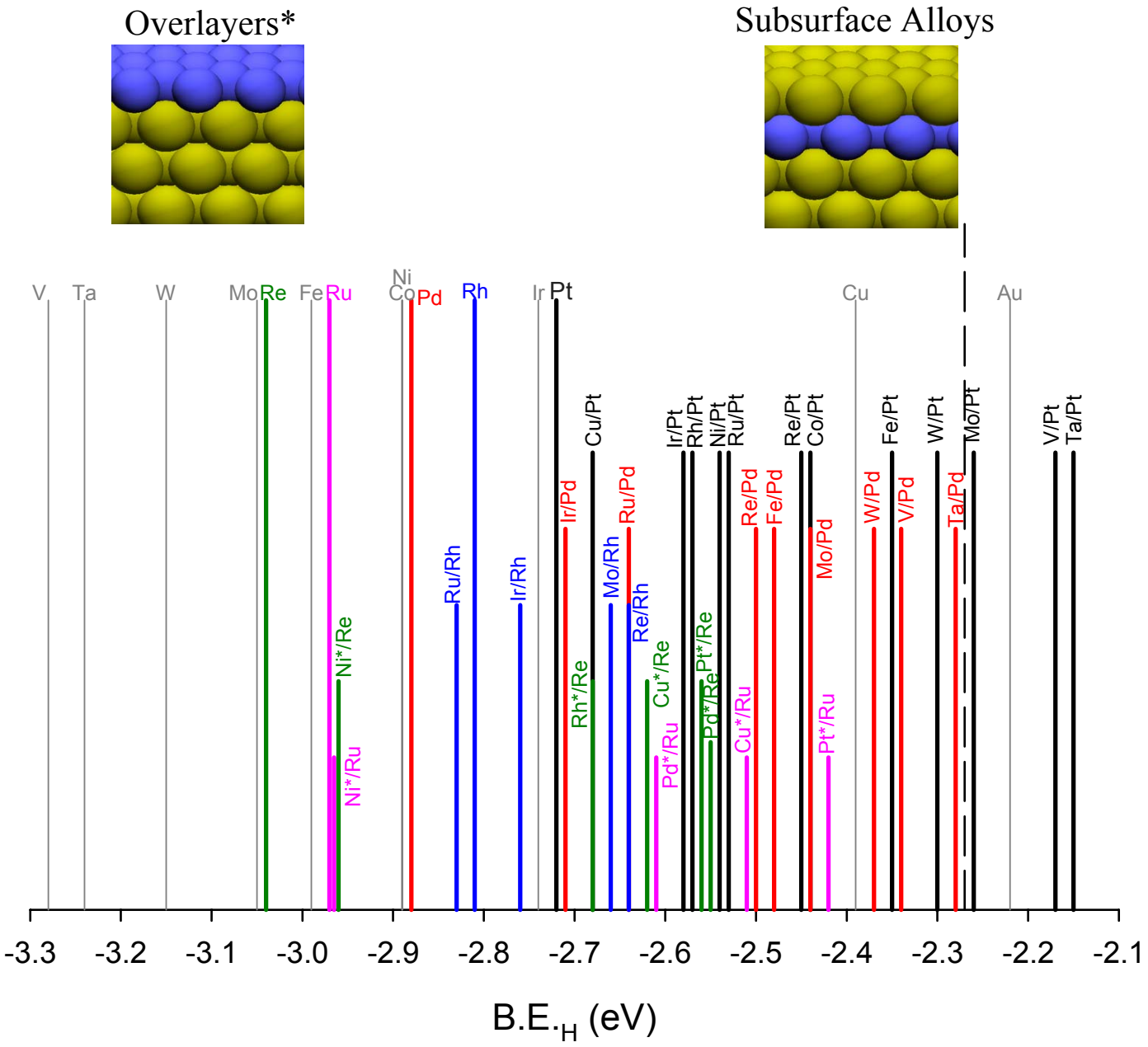
Subsurface Alloys



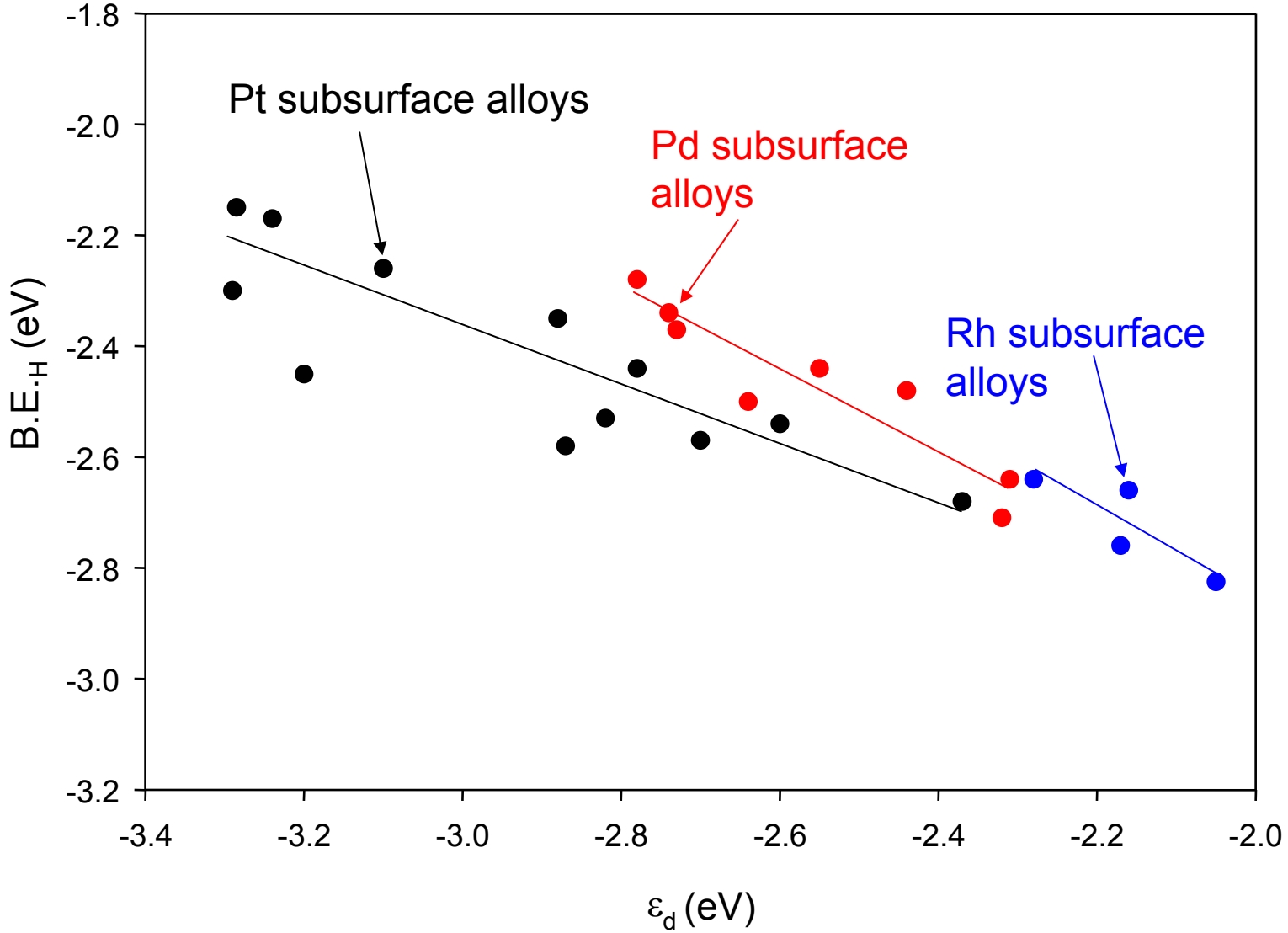
Stability of NSA's with Respect to Hydrogen-induced Segregation



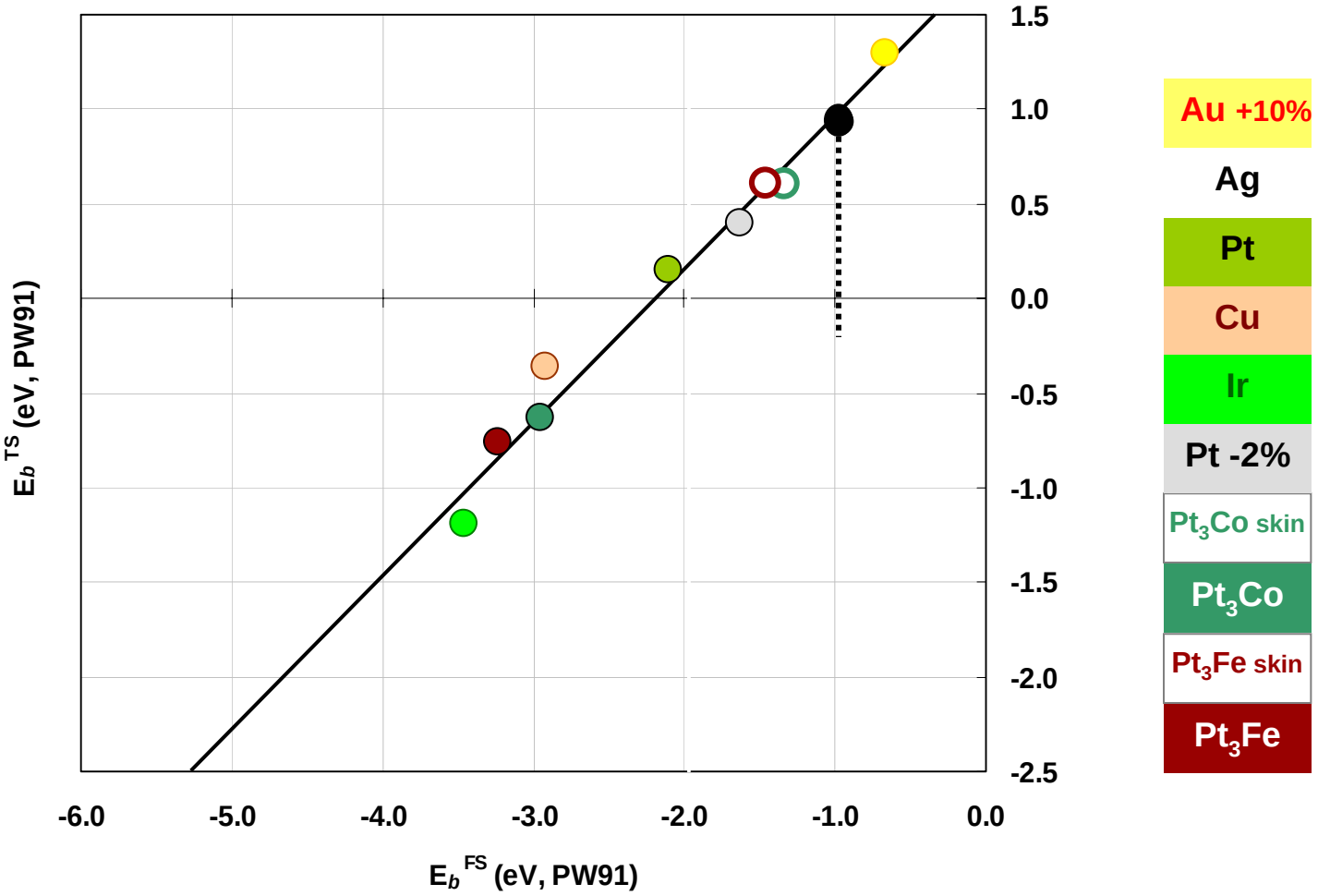
$B.E._H$ on Close-Packed Metal Surfaces



Correlation of $B.E._H$ with Clean Surface Properties



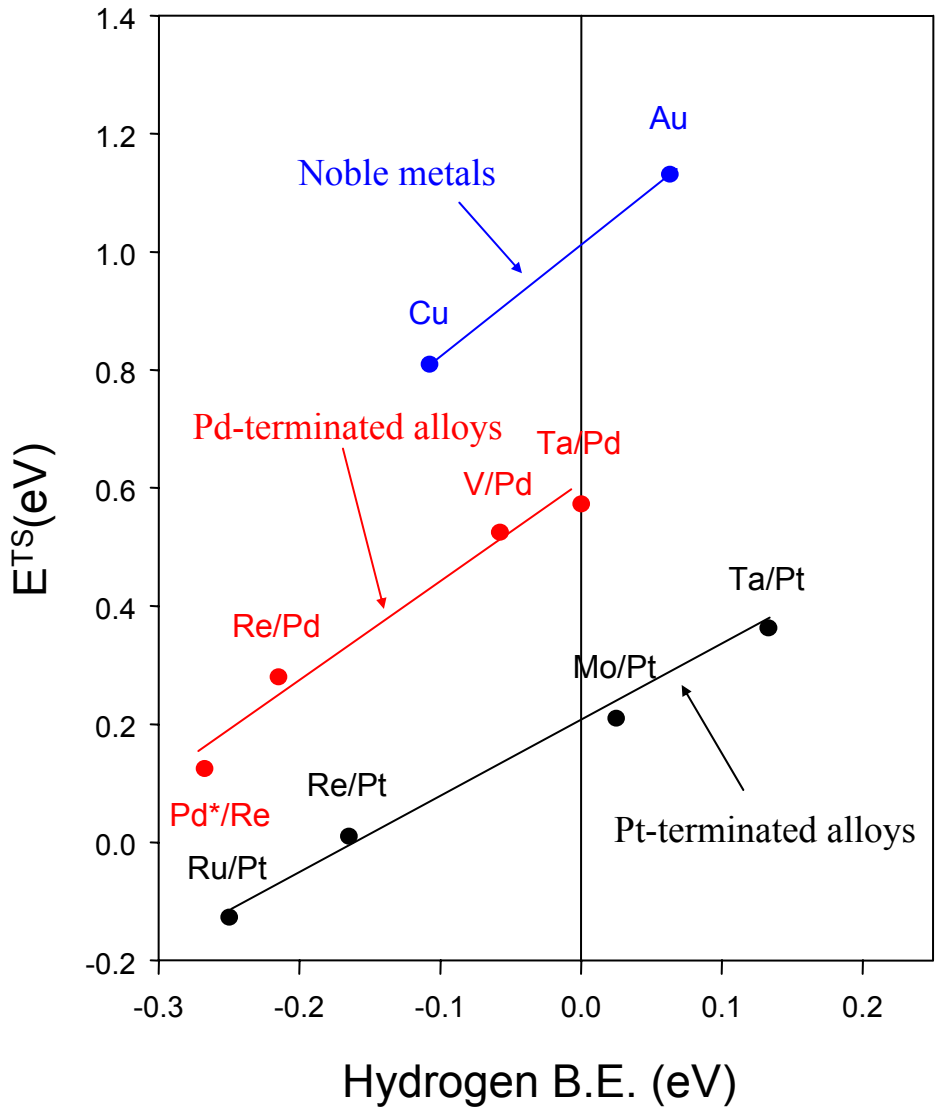
O_2 dissociation: Does E_b^{TS} follow E_b^{FS}?



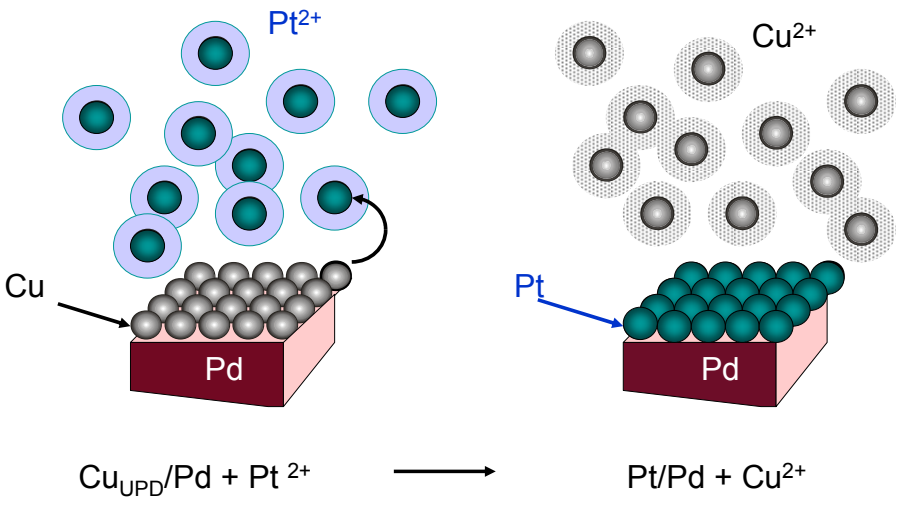
Y. Xu, A. V. Ruban, M. Mavrikakis, *JACS* 126, 4717 (2004).

BEP Plot for H_2 Dissociation onNSA's

J. Greeley, M. Mavrikakis, *Nature Materials* 3, 810 (2004)



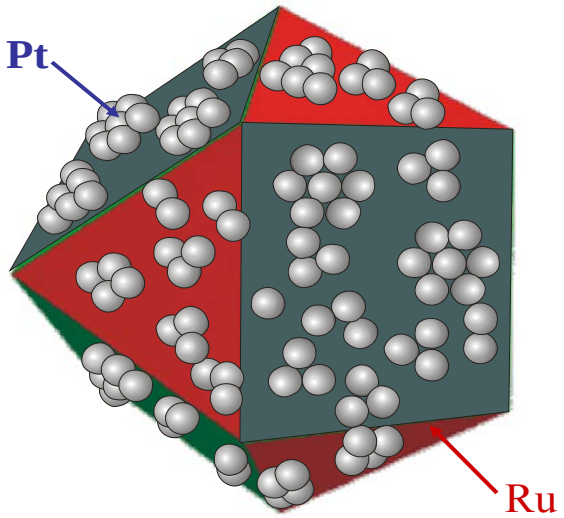
Metal monolayer deposition by galvanic displacement of a less noble metal monolayer deposited at underpotentials



Brankovic, S. R.; Wang, J. X.; Adzic, R. R. *Surf. Sci.* **2001**, *474*, L173

Zhang, J.; Vukmirovic, M.; Xu, Y.; Mavrikakis, M.; Adzic, R. R. *Angew. Chem. Int. Ed.* **2005**, *44*, 2132

Electroless (spontaneous) deposition of one metal on another metal

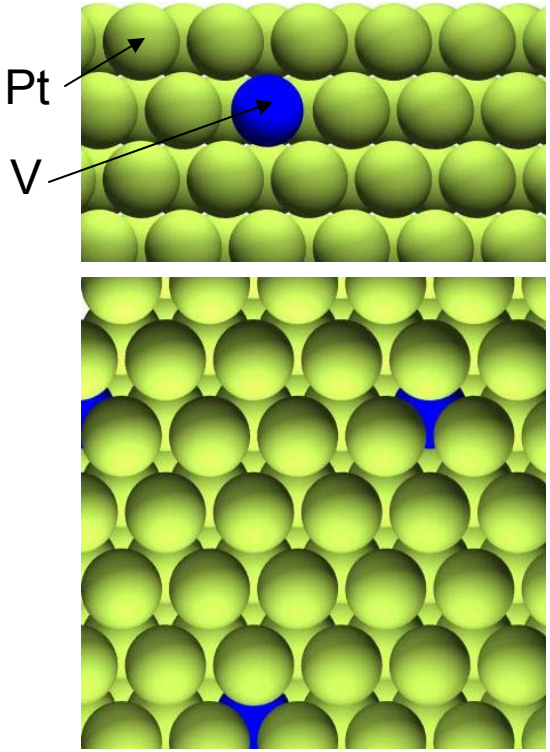


Brankovic, S. R.; McBreen, J.; Adzic, R. R. *J. Electroanal. Chem.* **2001**, *503*, 99

Sasaki, K.; Wang, J. X.; Balasubramanian, M.; McBreen, J.; Uribe, F.; Adzic, R. R. *Electrochim. Acta* **2004**, *49*, 3873

A new kind of Minority/Defect site for TM Catalysis

J. Greeley, M. Mavrikakis, *Catalysis Today* 111, 52 (2006)



Isolated metal hetero-atoms near metal surfaces can be viewed as generating an alternative type of "defect/minority" surface sites, associated with a different kind of near-surface "impurity".

These sites could be more poison-resistant and possess better catalytic kinetics than the rest of the surface sites.

NSA's - Summary

- First-Principles Methods can help with identifying promising bimetallic NSAs with interesting catalytic properties

- Example:

  1. H and H_2 on NSA's: Fine-tuning BE_H is possible
  2. Some NSA's: Activate H_2 easily AND bind atomic H weakly → useful for highly selective low T H-transfer reactions

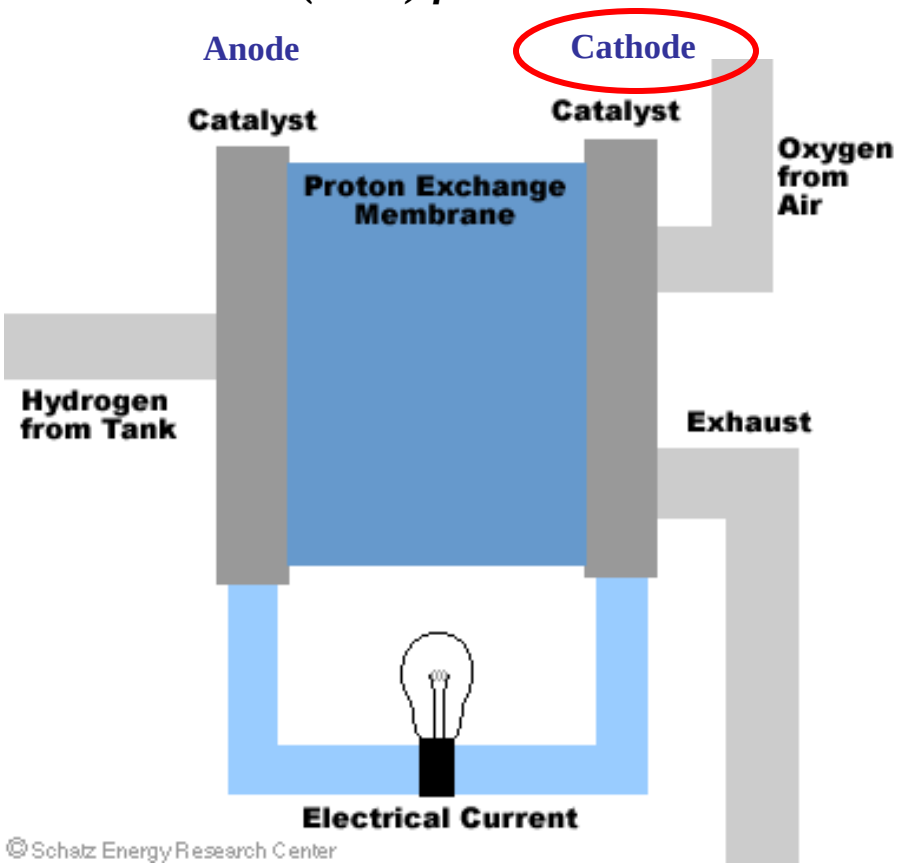
- Developing Catalyst Preparation Techniques with Layer-by-Layer control of metal deposition (ALD-like) is critical for making the desired NSAs

- New type of "NSA" - defect site

Low Temperature Fuel cells

Proton Exchange Membrane

(PEM) fuel cell



Representative Catalysis

Anode:

$$2H_2 \leftrightarrow 4\ H^+ + 4\ e^-$$

Cathode:

$$O_2 \leftrightarrow 2\ O^-$$

$$2O^- + 2H^+ + 2e^- \leftrightarrow 2OH^-$$

$$2OH^- + 2H^+ \leftrightarrow 2H_2O$$

Oxygen Reduction Reaction (ORR)- Very slow kinetics

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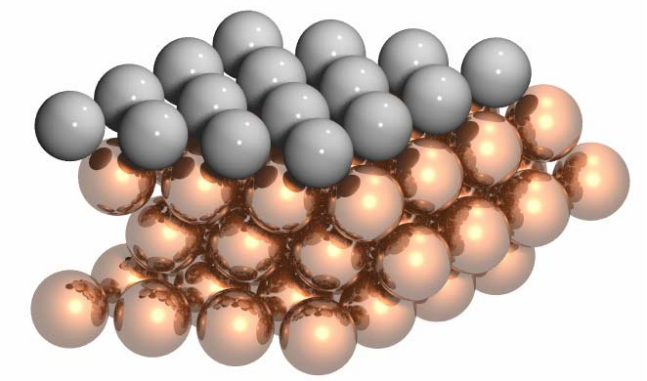
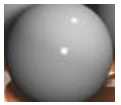
Pt monolayers on transition metals

- Pt monolayers on
  - Ru(0001), Ir(111), Rh(111), Au(111) and Pd(111)
  - Ru(0001), Ir(111) and Rh(111) lead to compression of Pt overlayer
  - Au(111) leads to expansion of Pt overlayer
  - Pd(111) has almost same lattice constant as Pt(111)





Pt monolayer

Substrate

(Ru, Ir, Rh, Pd, Au)

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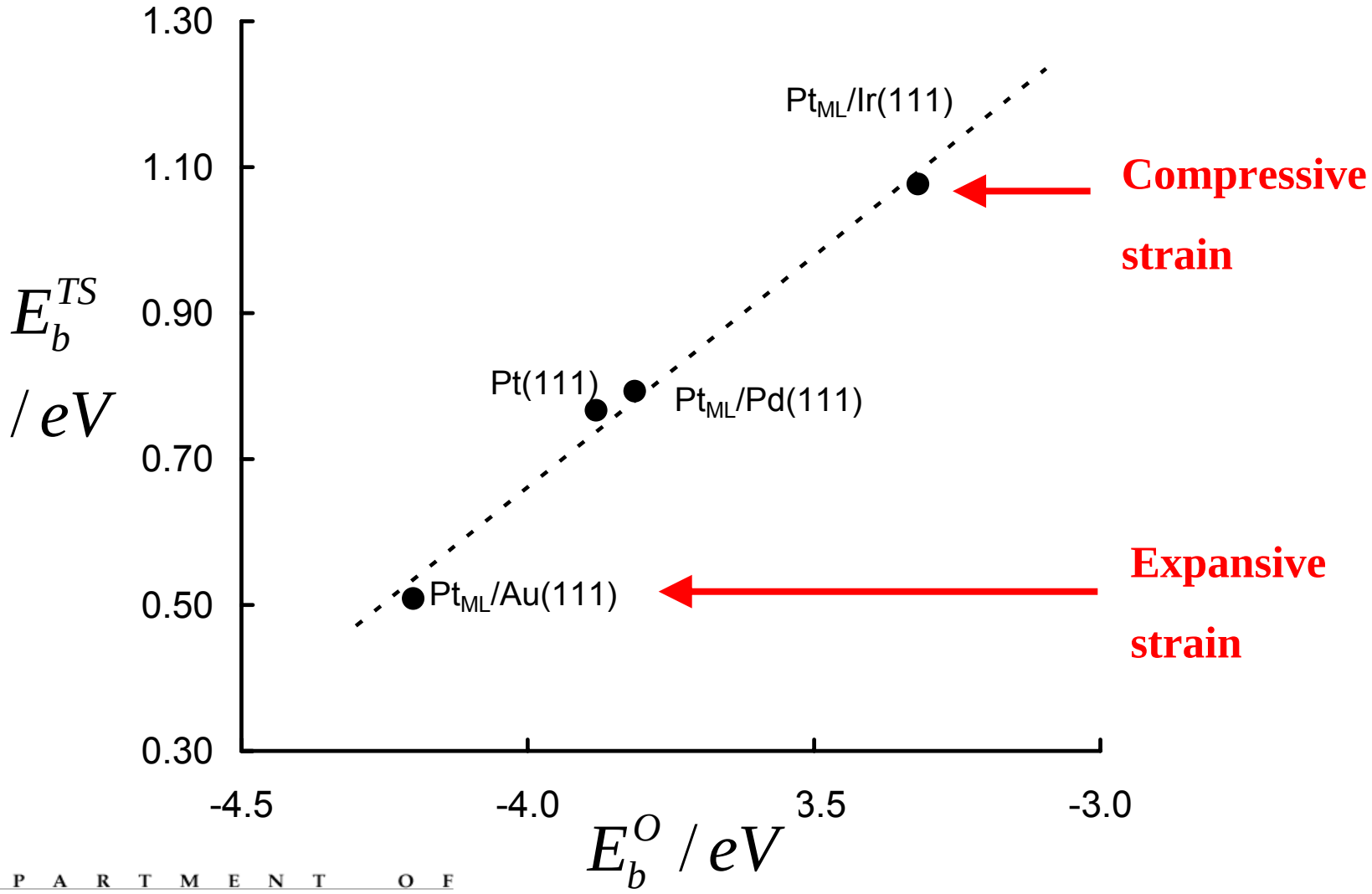
O_2 Dissociation Barrier



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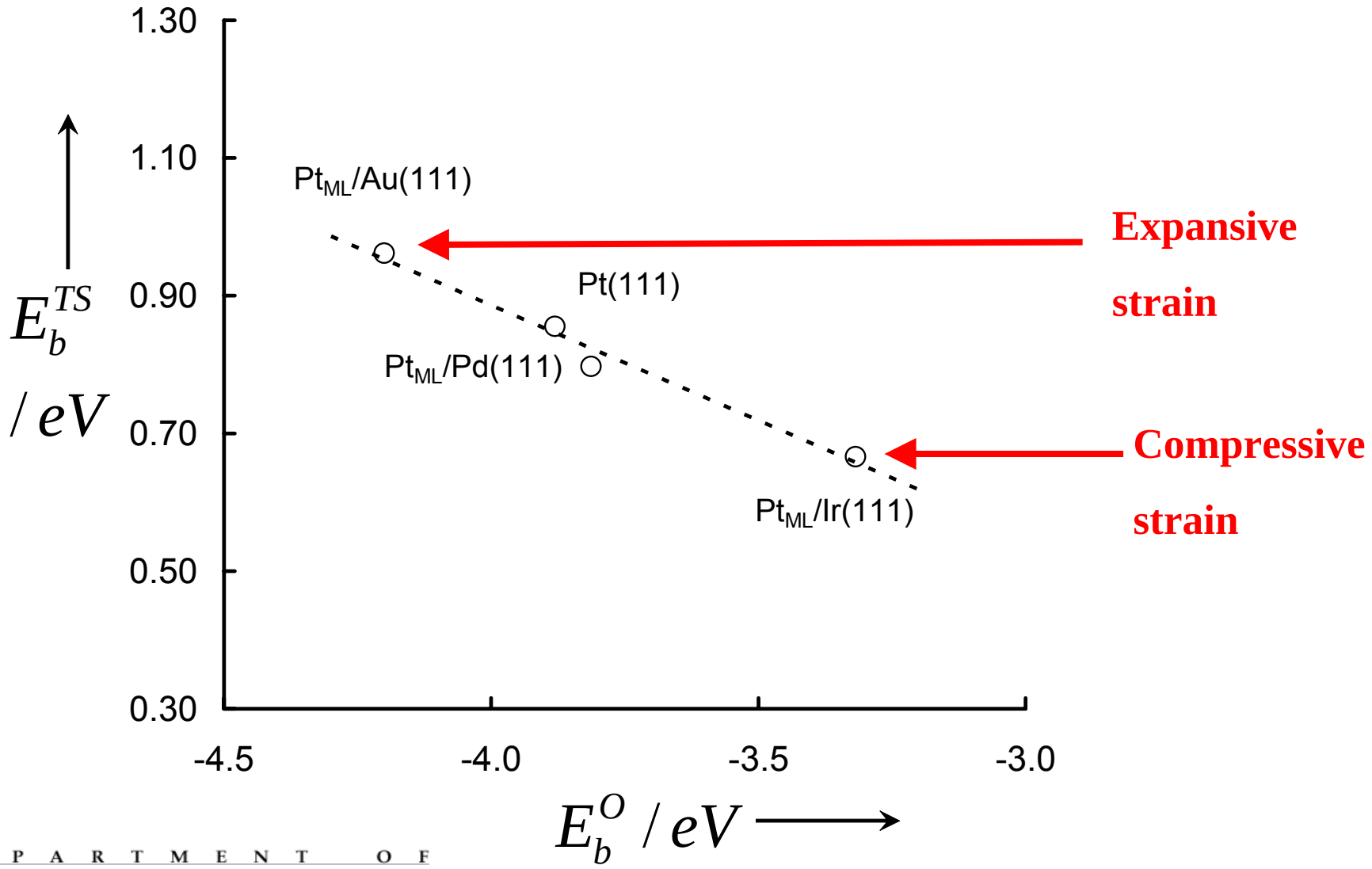
J Zhang, MB Vukmirovic, Y Xu, M Mavrikakis, RR Adzic, Angew. Chemie, Int. Ed., 44, 2132 (2005)

OH Formation Barrier



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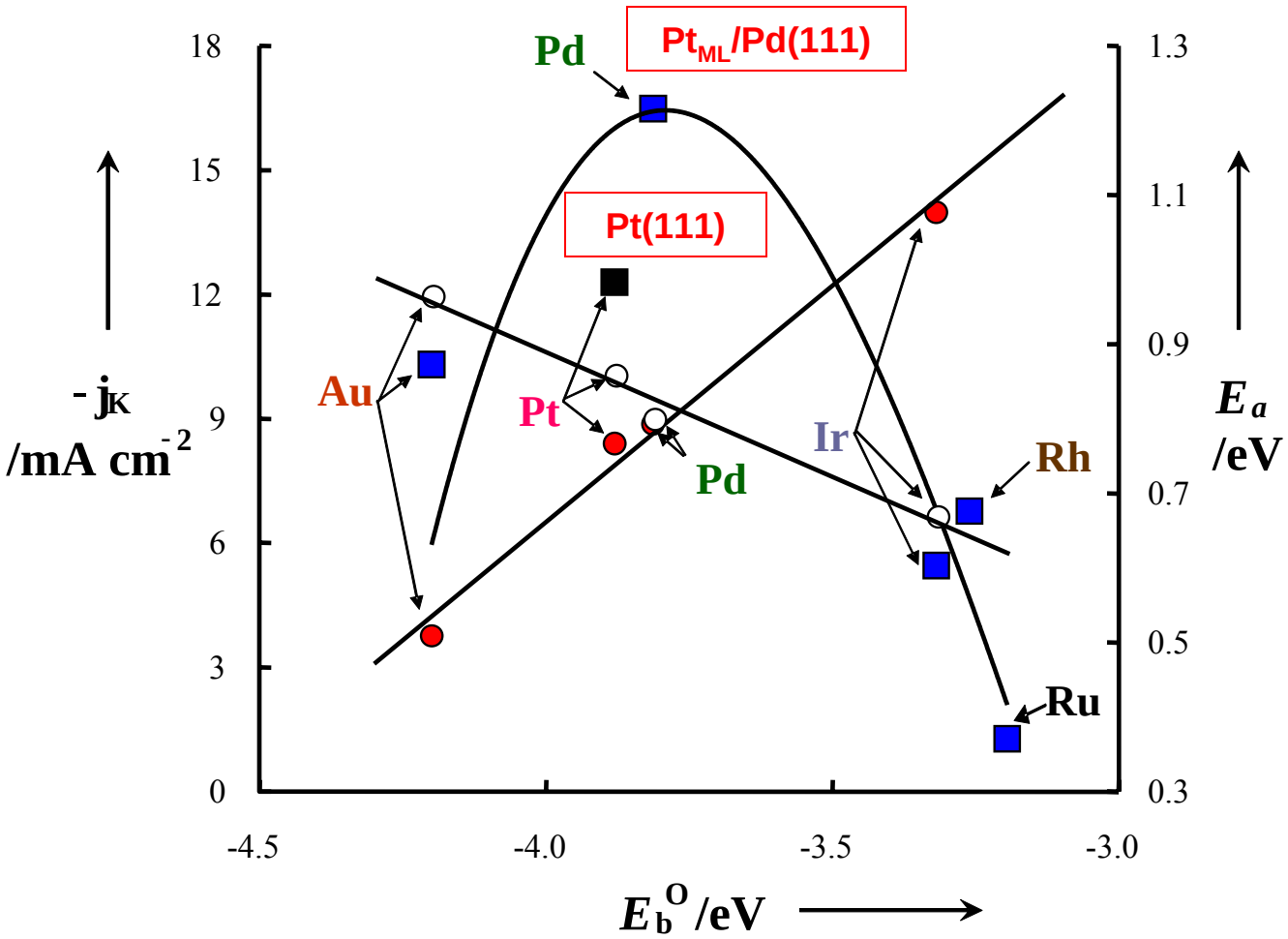
J Zhang, MB Vukmirovic, Y Xu, M Mavrikakis, RR Adzic, Angew. Chemie, Int. Ed., 44, 2132 (2005)

The best catalyst performs a Balancing Act



E_a for O_2 dissociation (filled red circles)

E_a for OH formation (**open** circles)

Kinetic currents (j_K; blue squares)

j_k value for Pt(111) (black square) obtained from Markovic et.al., *J. Electroanal. Chem. 1999, **467**, 157*

1--Pt$_{ML}$/Ru(0001)

2--Pt$_{ML}$/Ir(111)

3--Pt$_{ML}$/Rh(111)

4--Pt$_{ML}$/Au(111)

5--Pt(111)

6--Pt$_{ML}$/Pd(111)

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J Zhang, MB Vukmirovic, Y Xu, M Mavrikakis, RR Adzic, Angew. Chemie, Int. Ed., 44, 2132 (2005)

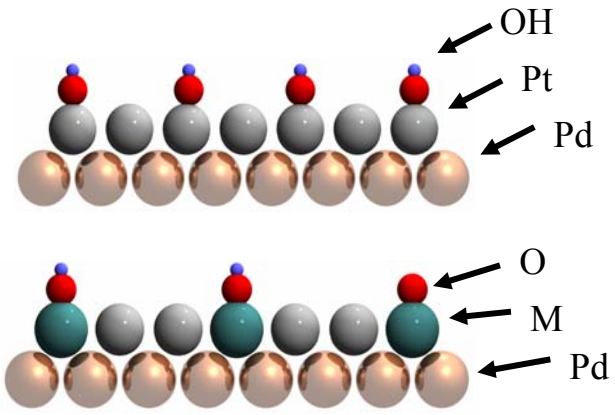
Further Decrease of Pt -loading:

The role of "OH poisoning" in ORR

- Pt binds OH strongly → OH blocks active sites on Pt
- Replace part of the Pt_{ML} on Pd(111) with another transition metal M

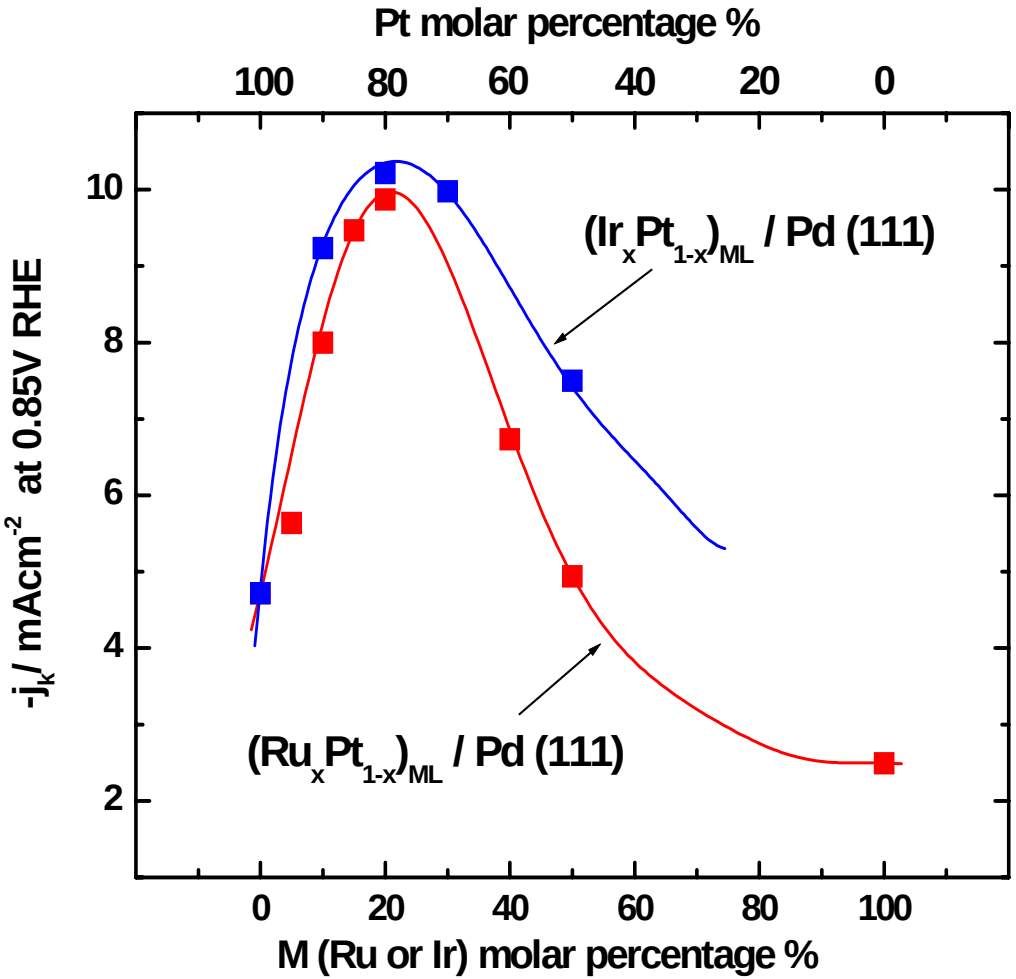
Hypothesis

M will attract initial OH and induce repulsion on neighbouring Pt-OH → decrease OH binding and OH coverage on Pt



ORR Experiments on $(M_xPt_{1-x})_{ML}/Pd(111)$: Current .vs. Surface Composition

- Effect of addition of different amount of M: Ir & Ru in $Pt_{ML}/Pd(111)$
  - Around 20% M gives highest ORR activity



J Zhang, MB Vukmirovic, K. Sasaki, A. U. Nilekar, M Mavrikakis, RR Adzic, JACS, 127, 12480 (2005)

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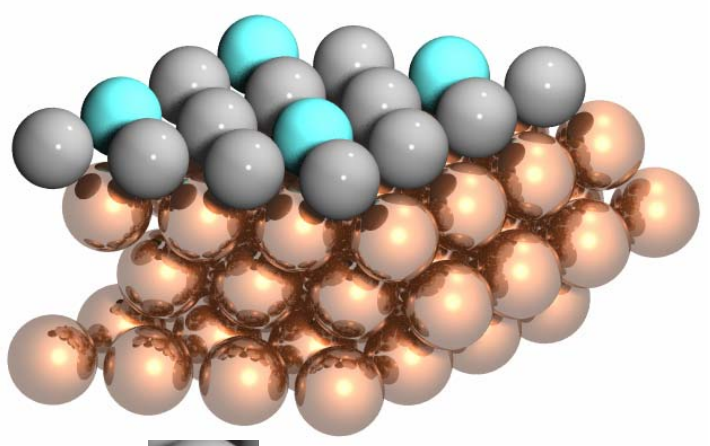
Mixed metal Pt monolayer

- Modeling these systems with DFT:
  - $(Pt_3M)_{ML}$/Pd(111) to get $\theta_M = 0.25$ ML
- Calculate: OH+OH or O+OH repulsion with M being:

Au	Os
Pd	Re
Pt	
Rh	
Ru	



Pt monolayer

Pd Substrate

Other metal (M)

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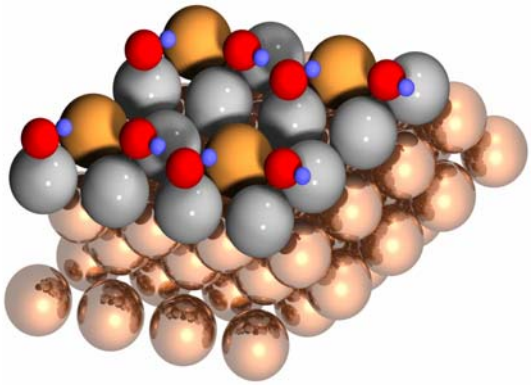
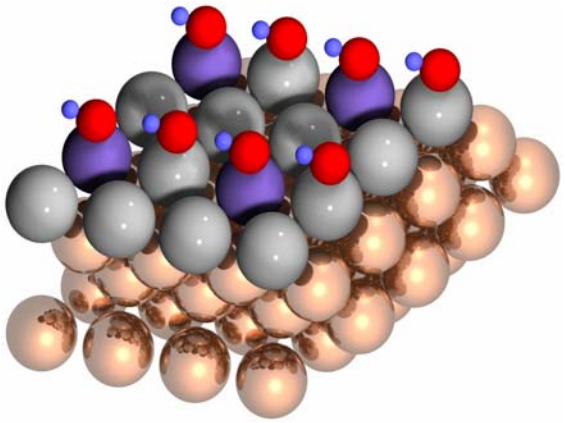
OH+OH or O+OH optimal structures



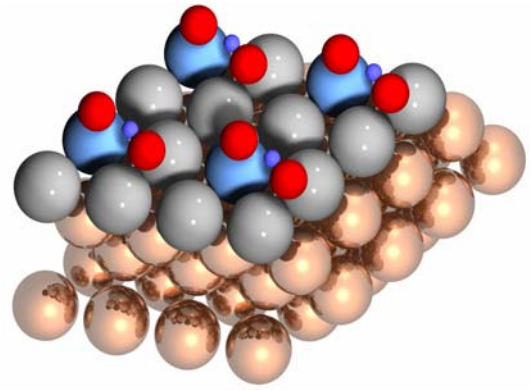
M with reactivity less or equal compared to Pt in Pt_{ML}/Pd(111): Au, Pd, Pt

1st OH on Pt-top and 2nd OH on Pt-Pt-bridge site



M with reactivity higher than Pt in Pt_{ML}/Pd(111): Rh, Ru, Ir

1st OH on M-top and 2nd OH on Pt-top



M with much higher reactivity than Pt in Pt_{ML}/Pd(111): Os, Re (break the OH bond to form H_2O and O)

O on M-top and 1st OH on Pt-Pt-bridge site

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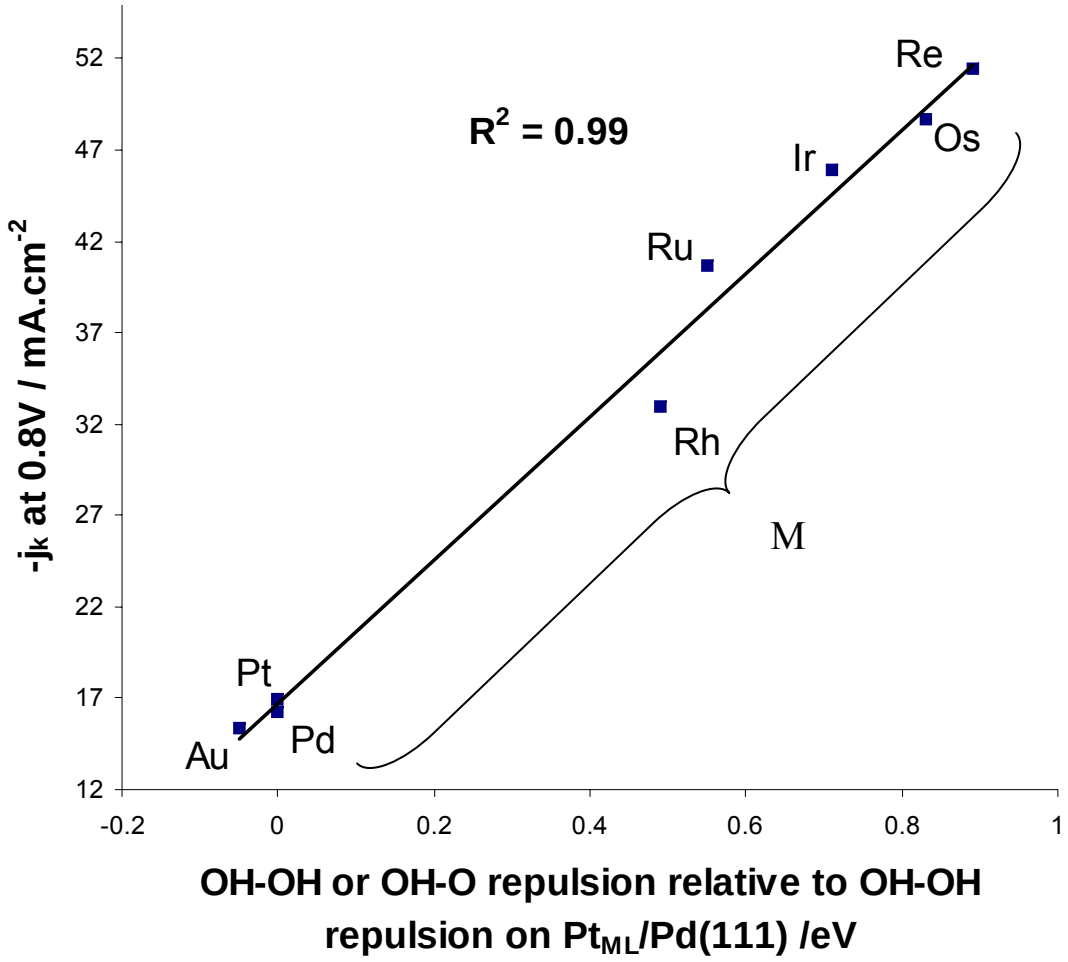
Comparison of theory with experiment



$(Pt_3M)_{ML}/Pd(111)$

400% increase in ORR activity for $(Pt_3Re)_{ML}/Pd(111)$ compared to Pt(111)

J Zhang, MB Vukmirovic, K. Sasaki, A. U. Nilekar, M Mavrikakis, RR Adzic,

JACS, 127, 12480 (2005)

ORR - Summary:

- A combination of first-principles studies with experiments can identify key ORR reactivity descriptors:
  - Kinetics of O-O Bond-breaking
  - Kinetics of O-H Bond-making

  } ← BE_O
  - OH-poisoning
- Use less Pt: $Pt_{ML}/Pd(111)$ → 30% more current [compared to Pt(111)]
- Use even less Pt: $Pt_3M/Pd(111)$ → up to 400% increase in current [compared to Pt(111)]
- First-principles can help with further improvements of ORR catalysts, by identifying materials which are:
  - Cheaper (low Pt loading)
  - More active
  - Increased stability of Pt against oxidation

Dr. Jeff Greeley

Dr. Ye Xu

CAMP
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Computational Surface Science and Catalysis Group

Department of Chemical and Biological Engineering

University of Wisconsin-Madison

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NPACI

Anand Nilekar

Acknowledgements

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- NSF - CTS
- NPACI, DOE-NERSC, PNNL (supercomputing resources)