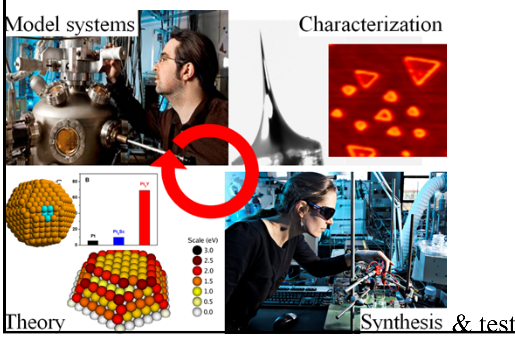
# Catalysis for sustainable energy:

## The challenge of harvesting and converting energy

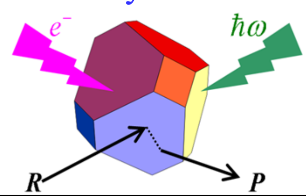
Tokyo, Japan 22 November 2011

I. Chorkendorff

The common denominator is surface science where the functionality of nanoparticles plays an essential role for catalysis in energy harvesting, conversion and environmental protection.



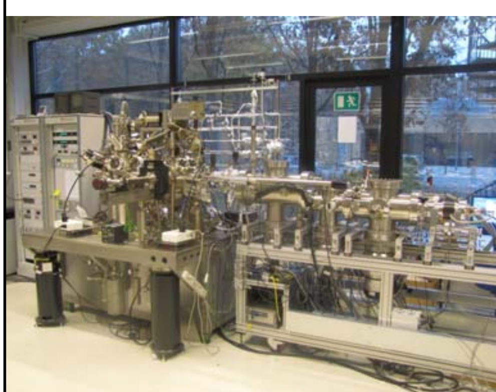

- Heterogeneous Catalysis
- Electrocatalysis
- Photocatalysis



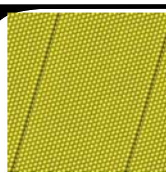

# Steam reforming and methanation

**Strongly Endothermic** $CH_4 + H_2O \xrightleftharpoons{\text{Ni, 1000 °C}} CO + 3H_2$

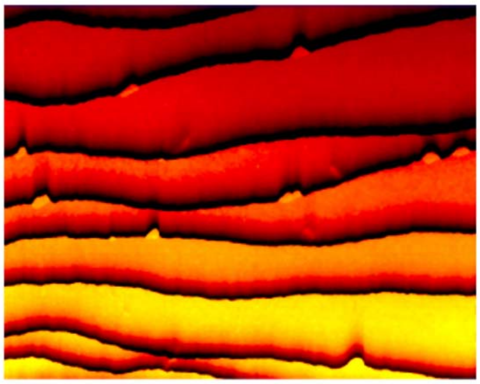
**Exothermic** $CO + H_2O \xrightleftharpoons{\text{Cu, 200 °C}} CO_2 + H_2$

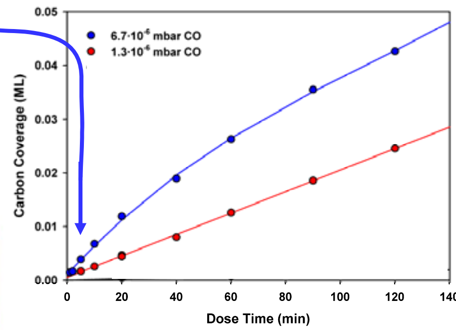


# Deposition at 500K on Ni(14 13 13) only B5 sites

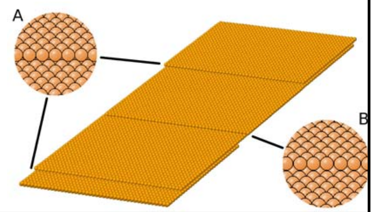


240L CO at 500K





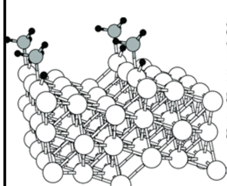

The barrier fro CO dissociation is measured experimentally to be 1.5-1.6 eV

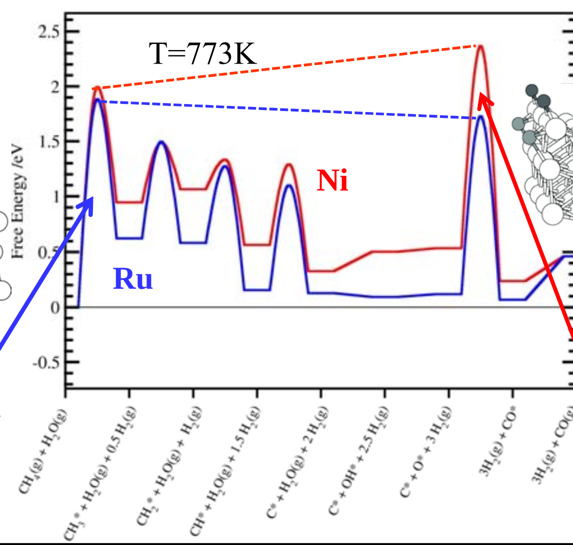


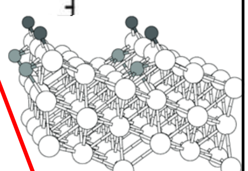

# The Steam Reforming

Steam reforming → $CH_4 + H_2O \leftrightarrow CO + 3H_2$ ← Methanation

Ru slightly better than Ni





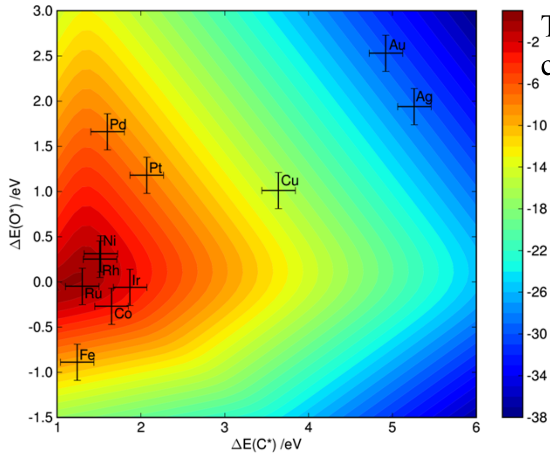



Major entropy loss involved in going from gas phase to adsorbed state

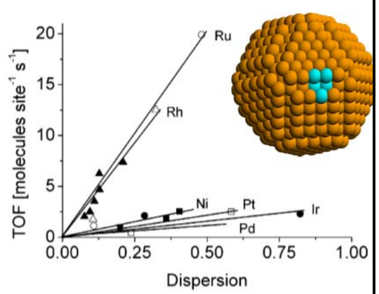
Methane becomes RLSfor Nickel at High T

## Two-dimensional volcano-curve of rate for steam reforming

Based on micro kinetic model using scaling laws (BEP)



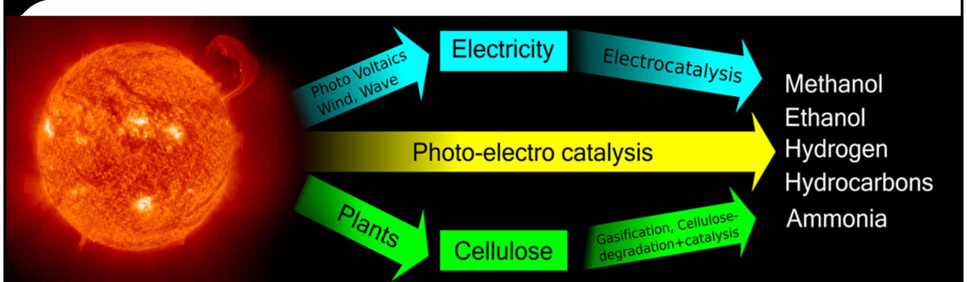

T = 773K, P = 1 bar; 10% conversion 0.2 eV error bars



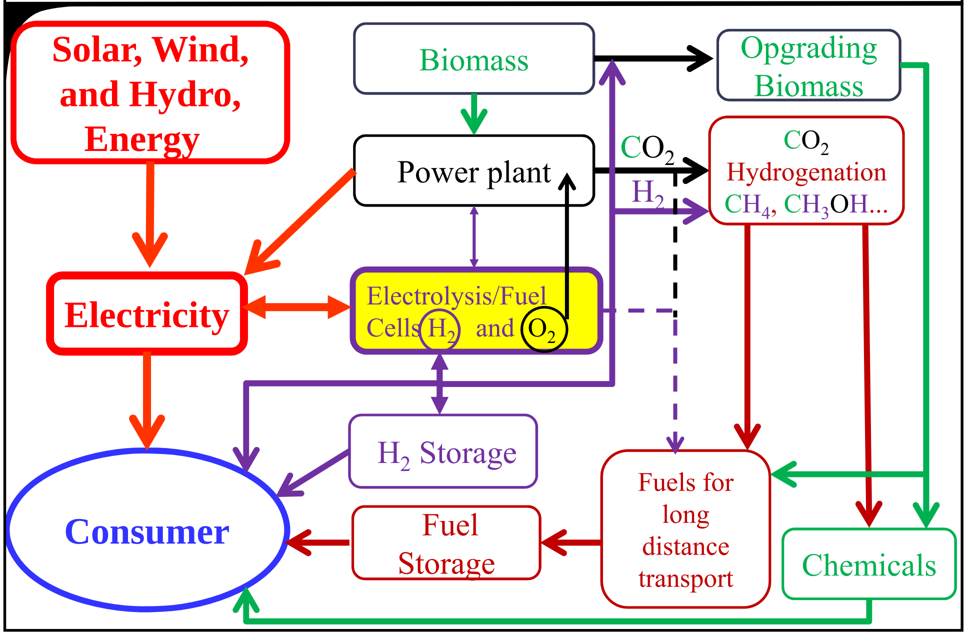

Ru, Rh, Ni are equally good. Pt poor

G. Jones, J. G. Jakobsen, S. S. Shim, J. Kleis, M. P. Andersson, J. Rossmeisl, F. Abild-Pedersen, T. Bligaard, S. Helveg, B. Hinnemann, J. R. Rostrup-Nielsen, I. Chorkendorff, J. Sehested, and J. K. Nørskov, **J. Catal. 259 (2008) 147.**

## Catalysis for sustainable Energy (CASE)



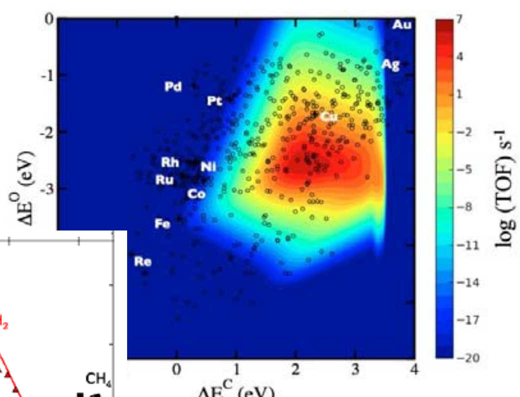

# Electrifying seems to be the future

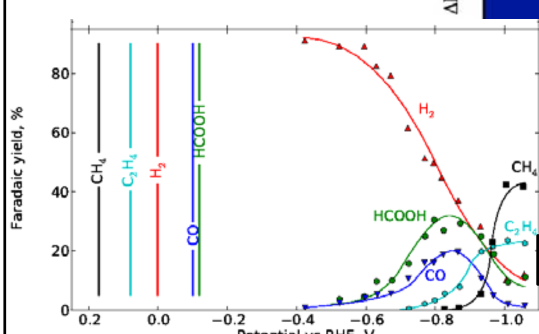



# Possible Solar Fuels

$4H_2 + CO_2 = CH_4 + 2H_2O$

$3H_2 + CO_2 = CH_3OH + H_2O$

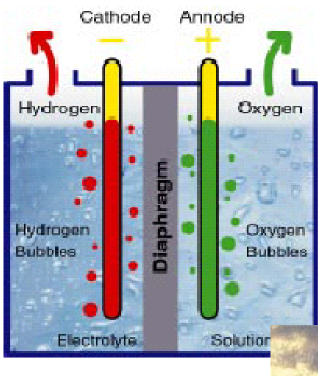



$8H^+ + CO_2 + 8e^- = C_2H_4 + 2H_2O$

Y. Hori, *Modern Aspects of Electrochemistry*, vol. 42, pp. 89-189 2008.

## Averaging renewal energy sources




Cathode: $2(H^+ + e^-) \rightarrow H_2$

Anode: $H_2O \rightarrow \frac{1}{2} O_2 + 2 H^+$

Total: $H_2O \rightarrow \frac{1}{2} O_2 + H_2$

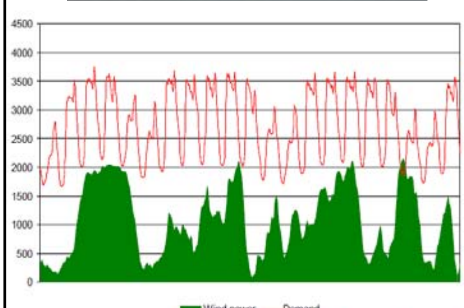
$\Delta G^0 = 2.46$ eV (1.23 eV/electron)

Could be a route for averaging out sustainable energy production i.e. from wind

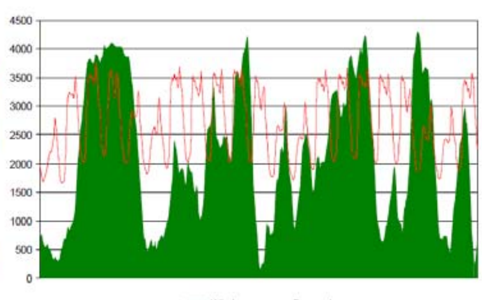

In DK ~ 21% power from wind alone

~3 % of total energy consumption

## Electricity is good but it comes with temporal variations



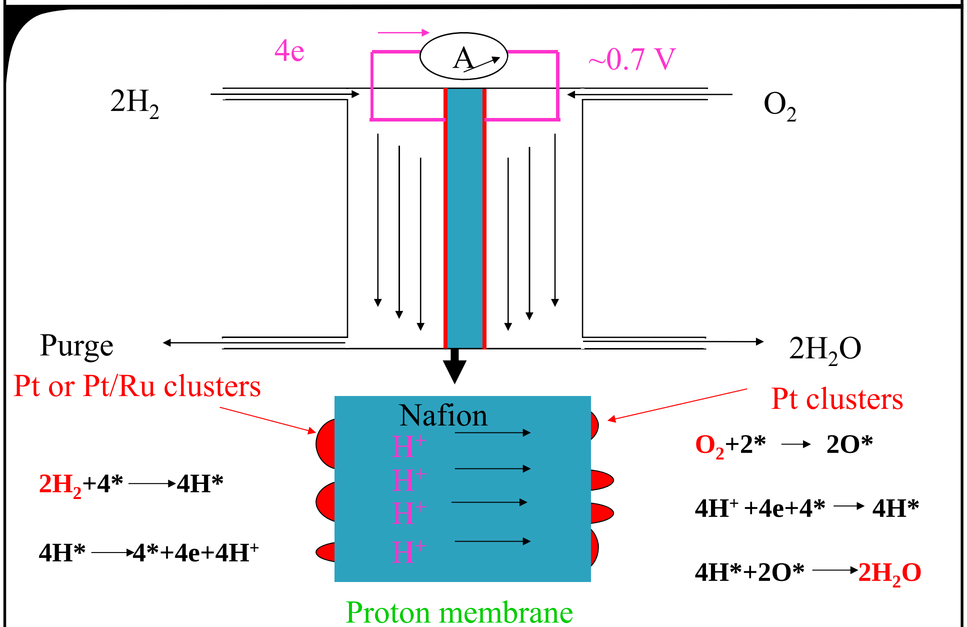

DK West January 2008




Demand and Wind power

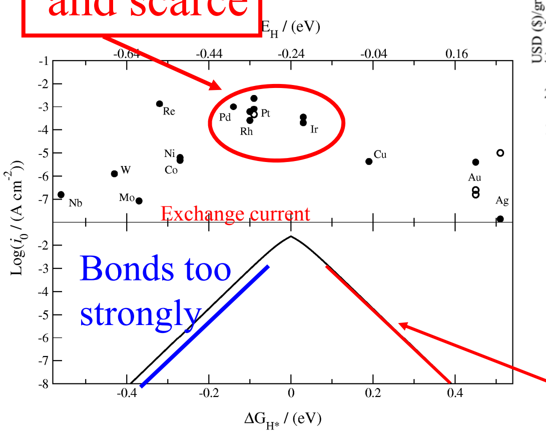
January 2008 + 3,000 MW

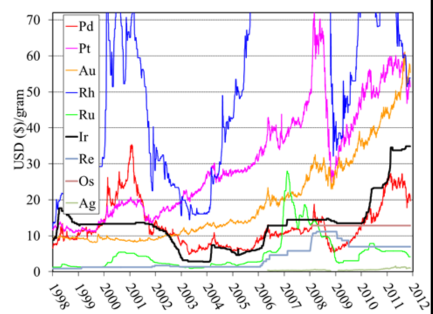
## Working Principles PEM fuel cell




## Trends for Hydrogen Production

Expensive and scarce



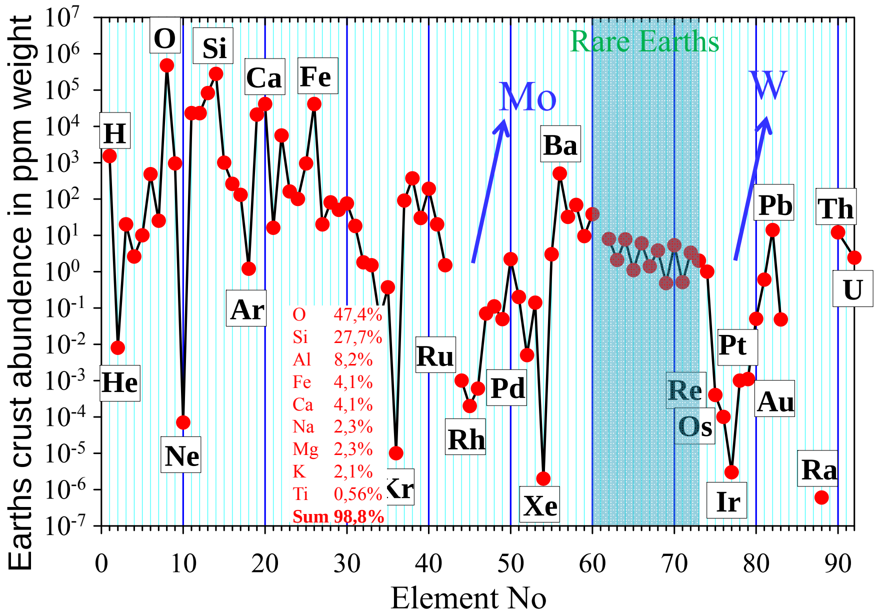

Some 200 Ton Pt a year
Today: 1g Pt per kW or
4 million cars per year!

Barrier for dissociation

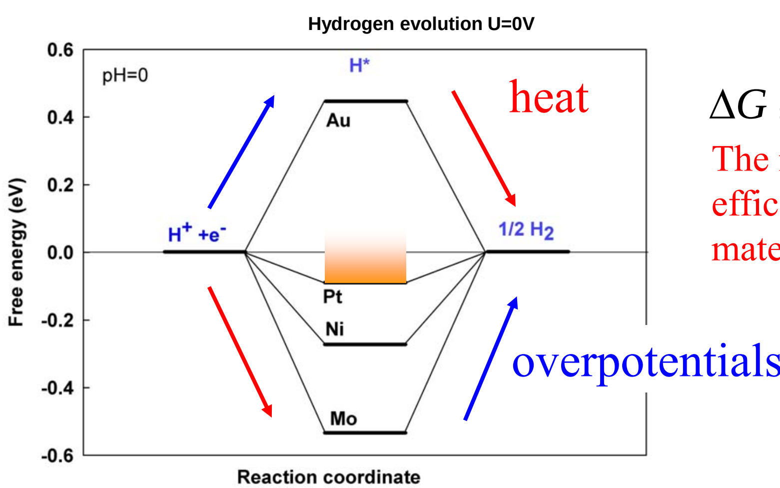
*J.K. Nørskov, T. Bligaard, Á. Logadóttir, J.R. Kitchin, J.G. Chen, Pandelov, and U. Stimming: J. Electrochem. Soc. 152, J23, (2005)*

R. Parson 1957

## Composition of Earths Crust




## The hydrogen evolution process



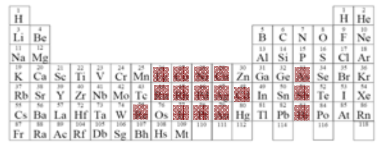

$\Delta G \cong 0$

The most efficient materials

# The criteria

A $(\sqrt{3}x\sqrt{3})R30^{\circ}$ H-coverage on 3-layer slap with 16 different metals :
Fe, Co, Ni, Cu, As, Ru, Rh, Pd, Ag, Cd, Sb, Re, Ir, Pt, Au, and Bi

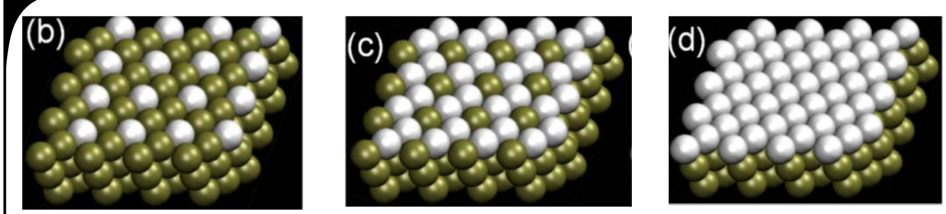
| | |
|---|---|
| pure metal | 16 |
| pure metal overlayer | 240 |
| 1/3 surface alloy | 240 |
| 2/3 surface alloy | 240 |
| Leading to a total of | **736** surface alloys |



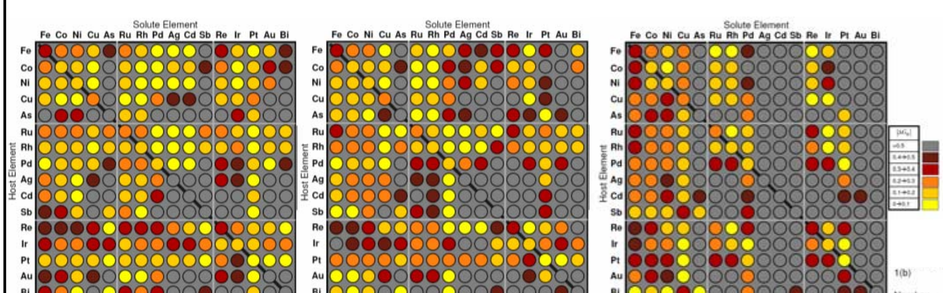
- $\Delta G \sim 0$ - No kinetics i.e. no barriers are considered
- $\Delta G$ for surface segregation (stability of the overlayer)
- $\Delta G$ for intra-surface transformations (island formation, de-alloying)
- $\Delta G$ oxygen poisoning of the surface (Water splitting/oxide formation)
- $\Delta G$ for corrosion the free energy for dissolution

J. Greeley, T. Jaramillo, J. Bonde, I. Chorkendorff, and J. K. Nørskov,
Nature Materials 5 (2006) 909.

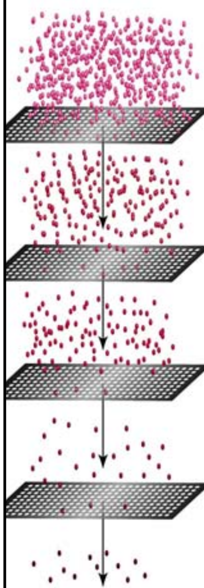
# Screening results on $(\sqrt{3} \times \sqrt{3})R30^{o}$ 3-layer slabs




1/3 ML | 2/3 ML | 1 ML

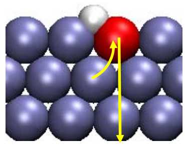


# Stability Criteria

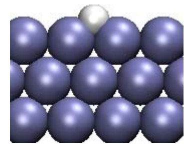


180 binary surface alloys have good predicted activity

Check for surface-bulk segregation effects:

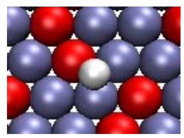



Reject all alloys where $\Delta\Omega_{seg} < 0$

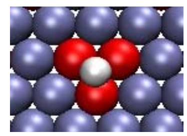


~105 alloys remain

Check for intrasurface rearrangements and islanding:




Reject all alloys where $\Delta\Omega_{surface} < 0$



~45 alloys remain

Check for electrochemical stripping effects: pH=0

$$M(s) \rightarrow M^{n+} + ne^{-}$$

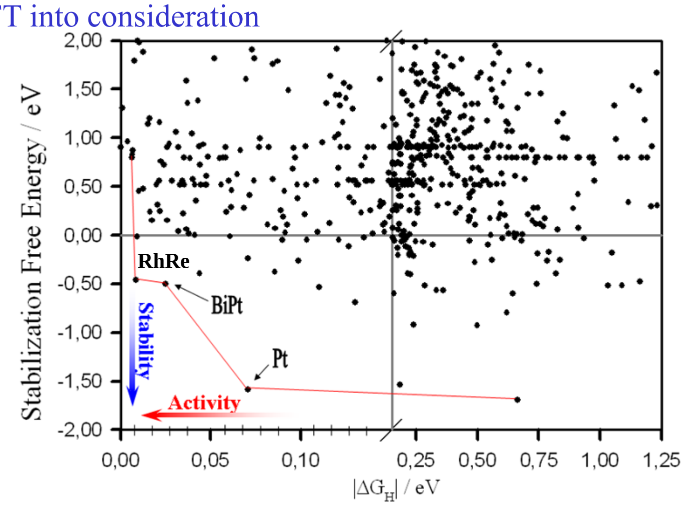
~25 alloys remain

Check for adsorption of oxygen:

~15 alloys remain

# Pareto-optimal plot

The knees are always the point of interst i.e. PtBi taking uncertanity of DFT into consideration

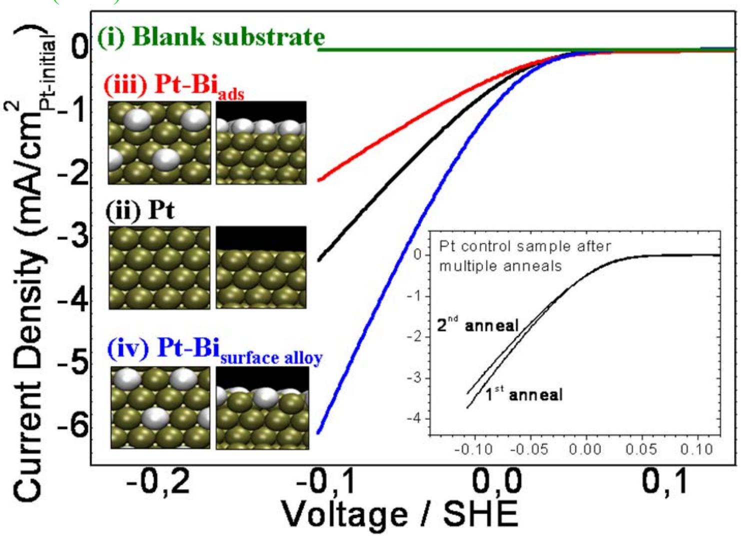



J. Greeley, T. Jaramillo, J. Bonde, I. Chorkendorff, and J. K. Nørskov, Nature Materials 5 (2006) 909.

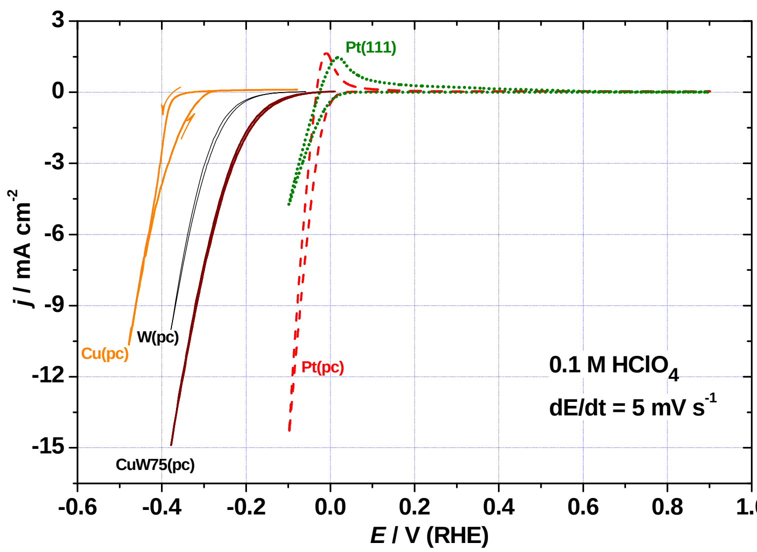
## Test of $PtBi_{surface\ alloy}$ HER

J. Greeley, T. Jaramillo, J. Bonde, I. Chorkendorff, and J. K. Nørskov, Nature Materials 5 (2006) 909.

The surface alloy shows enhanced activity

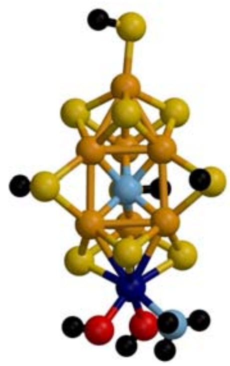


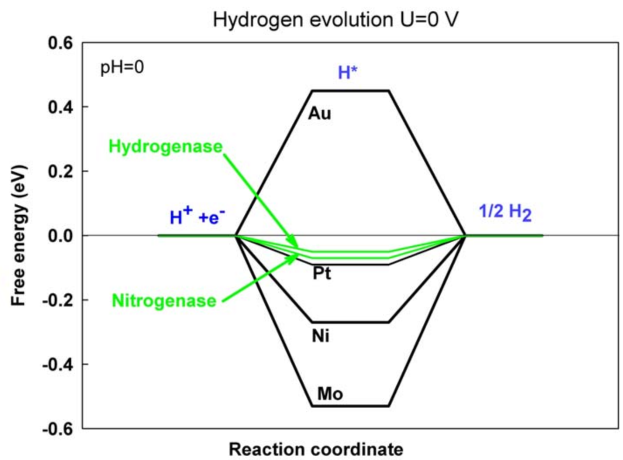

## Standard bulk alloys of CuW




# How does nature do it ?

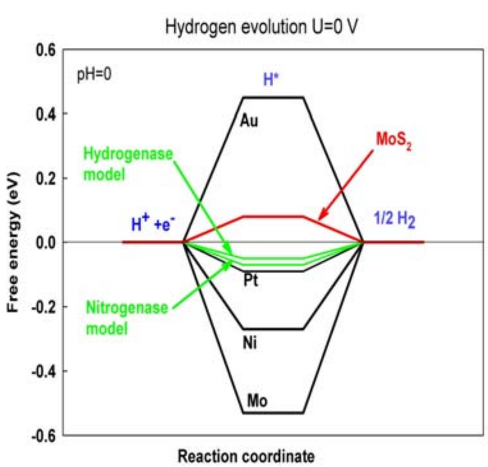
Nitrogenase:

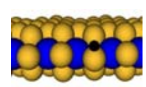
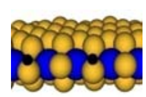
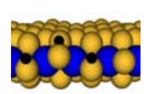
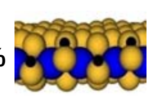





B. Hinnemann and J.K Nørskov, *J. Am. Chem. Soc.* 126, 3920 (2004)
Hydrogenase: Per Siegbahn, Adv. Inorg. Chem. 56, 101 (2004).

# $MoS_2$ as a catalyst for hydrogen evolution

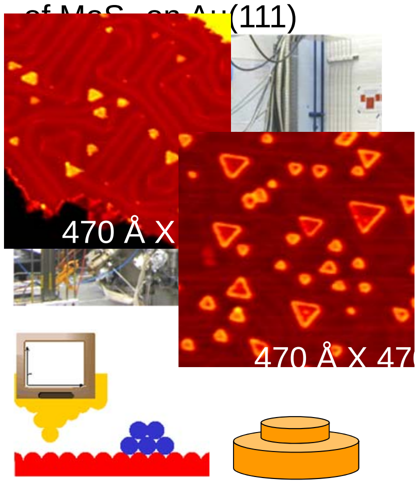



| | Model with four rows | Differential free energy (eV) |
|---|---|---|
| 25% |  | -0.33 |
| 50% |  | 0.08 |
| 75% |  | 0.76 |
| 100% |  | 0.79 |

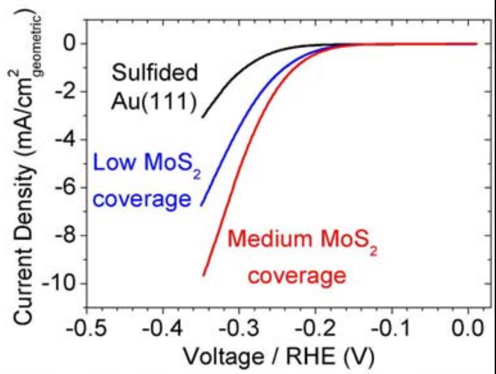
- The coverage cannot be changed continuously.
- Probably only coverage changes between 25% and 50% contribute.

# Combining surface science and electrochemistry

1) Synthesis and STM of MoS on Au(111)

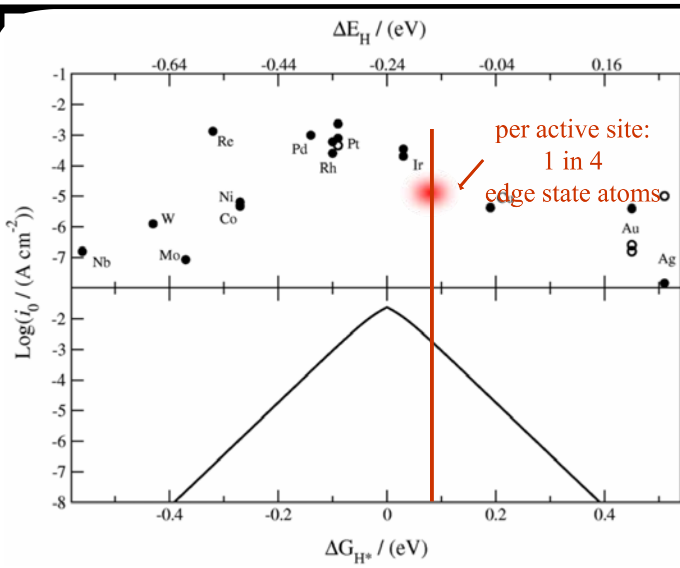



2) Measure electrochemical activity of the MoS just




T.F. Jaramillo, K.P. Jørgensen, J. Bonde, J.H. Nielsen, S. Horch, I. Chorkendorff, Science 137 (2007) 100

# $MoS_2$ on the volcano

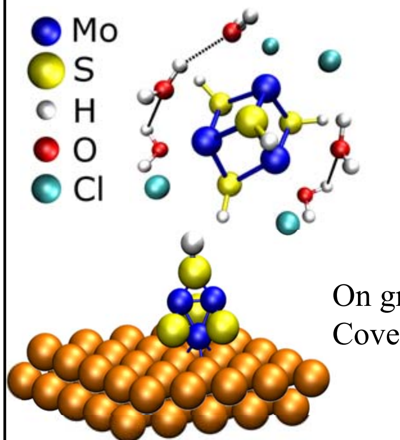


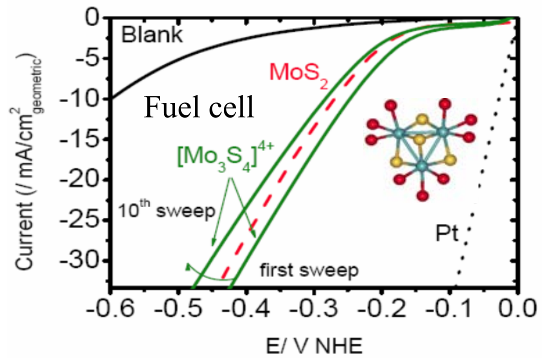

We now know exactly where to look for improvement: Increase the hydrogen bonding to the edge!

T.F. Jaramillo, K.P. Jørgensen, J. Bonde, J.H. Nielsen, S. Horch, I. Chorkendorff, Science 137 (2007) 100

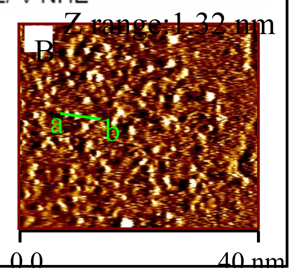
# $Mo_3S_4$ going small

The smallest entity of the active site of $MoS_2$ ?




On graphite HOPG
Coverage $1*10^{13}$ $cm^{-2}$~1%

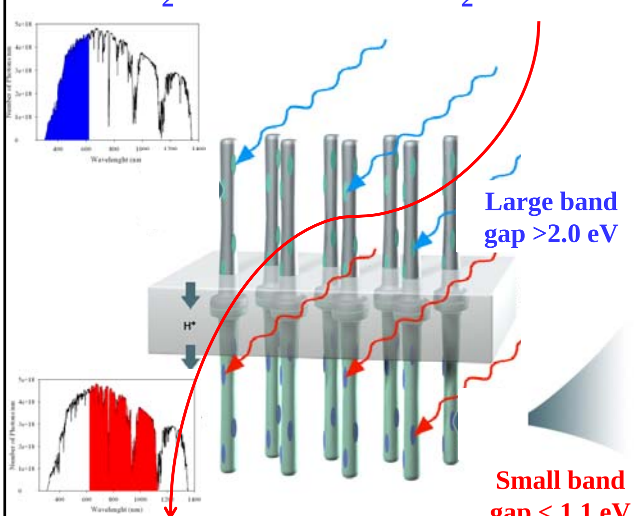


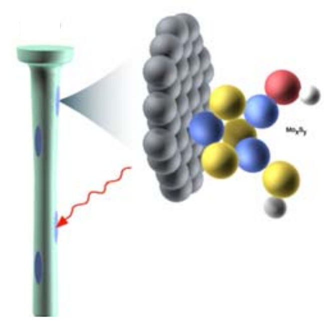

T. F. Jaramillo, J. Zhang, B. Lean Ooi, J. Bonde, K. Andersson, J. Ulstrup, I. Chorkendorff, J. Phys. Chem. 112 (2008) 17492.

# The dream device

$H_2O + 4h^+ \longrightarrow O_2 + 4H^+$

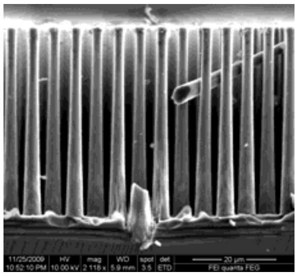
**The Helios concep (Nate Lewis)**

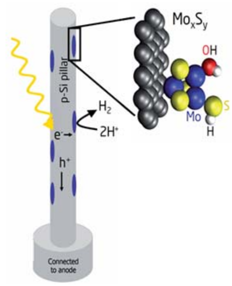


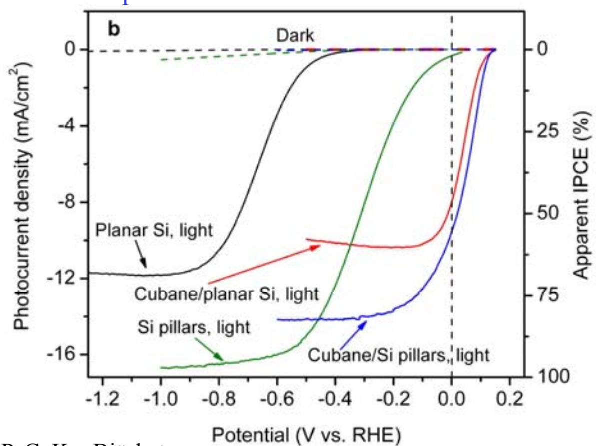
$4H^+ + 4e^- \longrightarrow 2H_2$

# Measurements on pillared structures

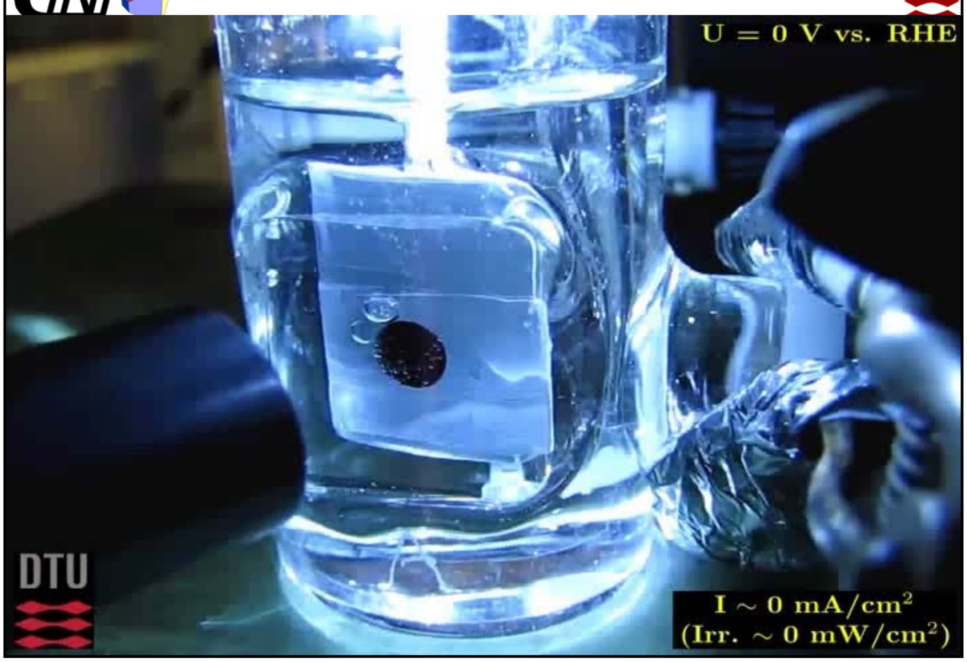





- UV-lithography and dry-etching of silicon
- 3 μm diameter circular w 6 μm spacing
- Hexagonal pattern and 60 μm long
- 32000 pillars/mm$^2$ increased area of ~15

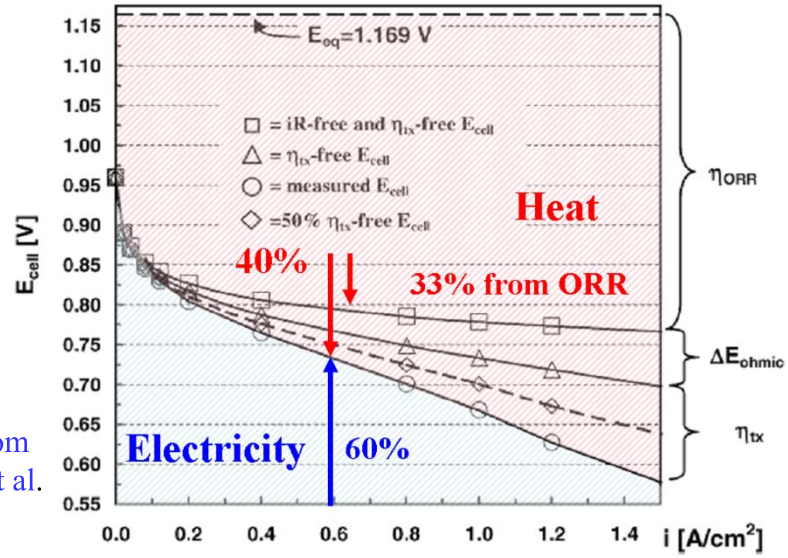



Hou Y. D., Abrams, B. L., Vesborg, P. C. K., Björketun, M. E., Herbst, K. *et al.*, *Nature materials*, **10**, 434-438 (2011).



# The Major loss in ORR and OER

The anode reaction in a fuel cell: $O_2 + 4H^+ + 4e^- = 2H_2O$

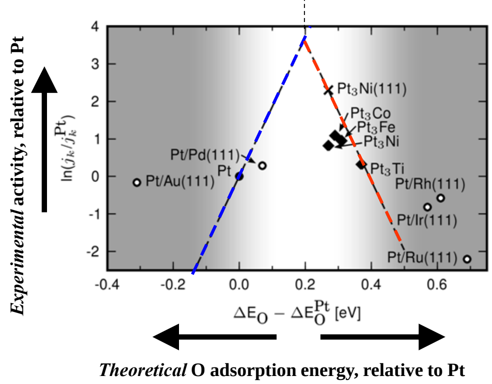



Adapted from Gasteiger et al.

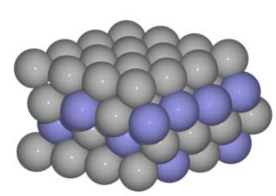
# Theoretical trends for oxygen reduction

**Using $\Delta E_O$ as a 'descriptor' for Pt alloys**

**O binds too strongly:** | **O binds too weakly:**




**All catalysts with 'Pt-skin' overlayers**



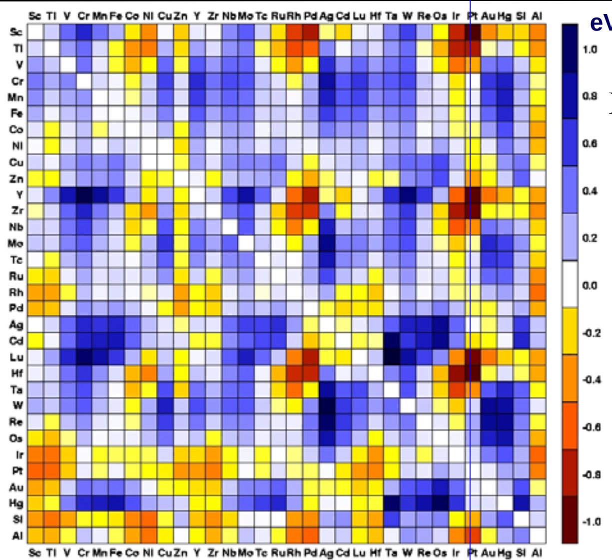
**Need to search for new Pt-alloy catalyst with**

$$\Delta E_O - \Delta E_O^{Pt} \sim 0.2 \text{ eV}$$

Experimental data from: Zhang et al Angew. Chem. Int. Ed., 2005; Stamenkovic et al, Angew. Chem, Int. Ed 2006; Stamenkovic et al. Science, 2007

# Structural stability of ordered alloys

25 %




75 %

Pt

Formation energy of the $L1_2$ binary alloy structures with respect to pure metals

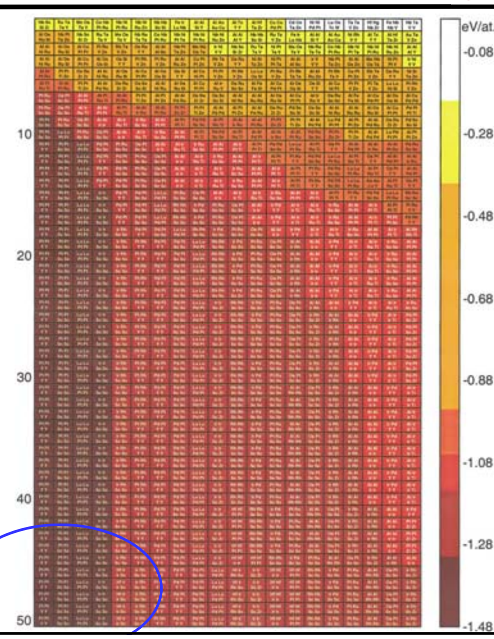
LMTO-GGA calculations

Johannessen, Bligaard, Ruban, Skriver, Jacobsen, Nørskov, PRL 88 (2002) 255506

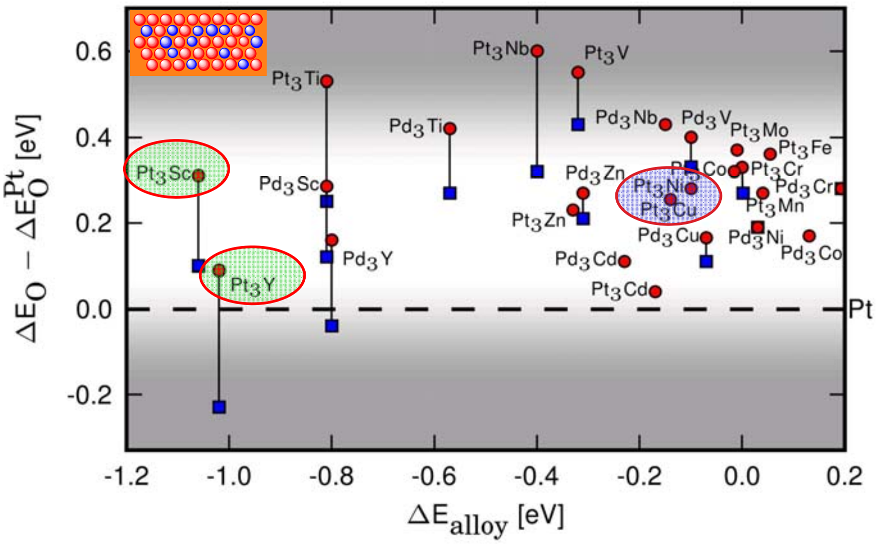
# Evolutionary Search Approach

192.016 possible fcc and bcc alloys that can be constructed out of 32 different metals.

| | ΔH (eV) |
|---|---|
| $Pt_2Y_2$ | -1.48 |
| $Pt_2Sc_2$ | -1.47 |
| $Lu_2Pt_2$ | -1.41 |
| $Ir_2Sc_2$ | -1.35 |
| $HfIr_2Sc$ | -1.30 |
| | . |
| | . |
| | . |
| $Pt_3Sc$ | -1.06 |
| $HfPt_3$ | -1.03 |
| $Pt_3Y$ | -1.02 |

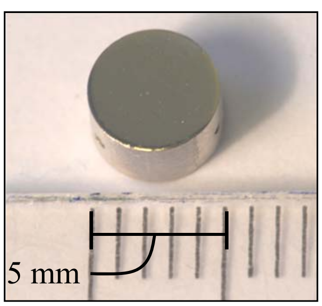


## Screening of $Pt_3X$ and $Pd_3X$ alloys




Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo, Rossmeisl, Chorkendorff, Nørskov (2009) Nature Chemistry 1 (2009) 522

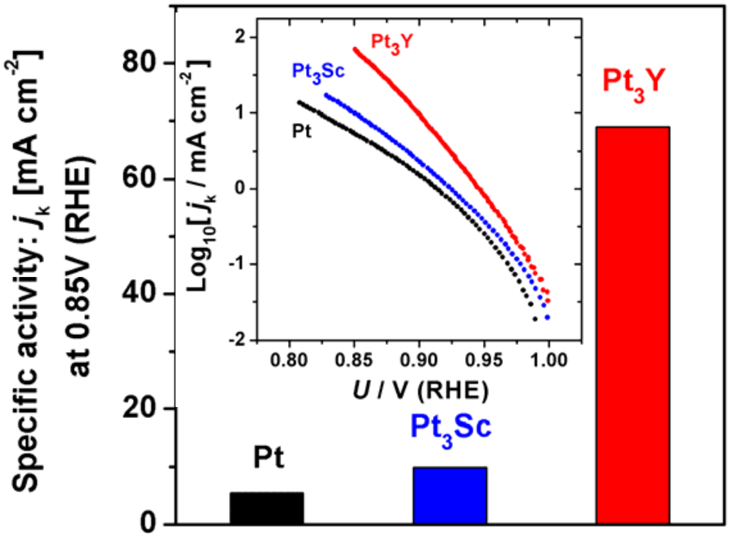
## Experimental verification of theory: Activity measurements of Pt(111)




Polycrystalline Pt or Pt(111) disc electrodes cleaned and characterised under ultra high vacuum conditions.

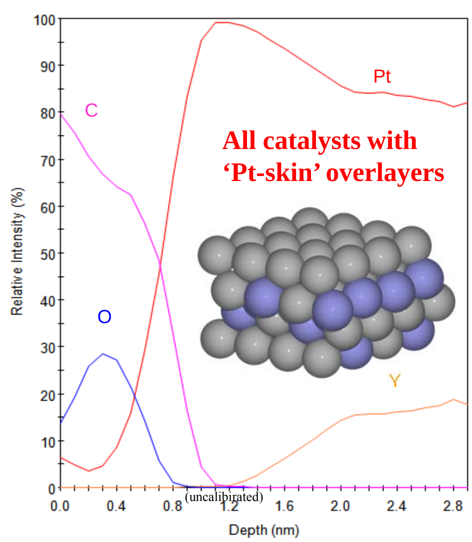
Rotating disc electrode (RDE) measurements in liquid cell with $O_2$-saturated 0.1 M $HClO_4$ solution, at room temperature.

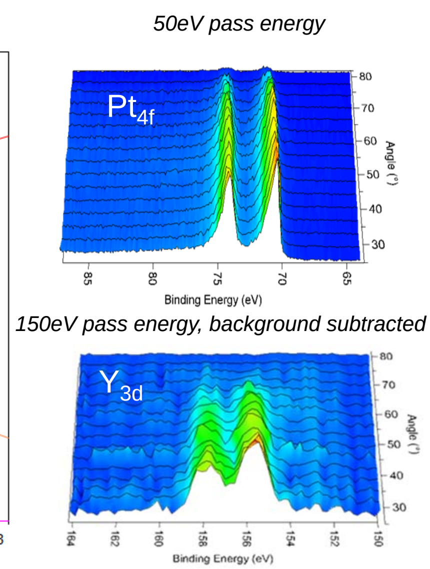
# Kinetic rates



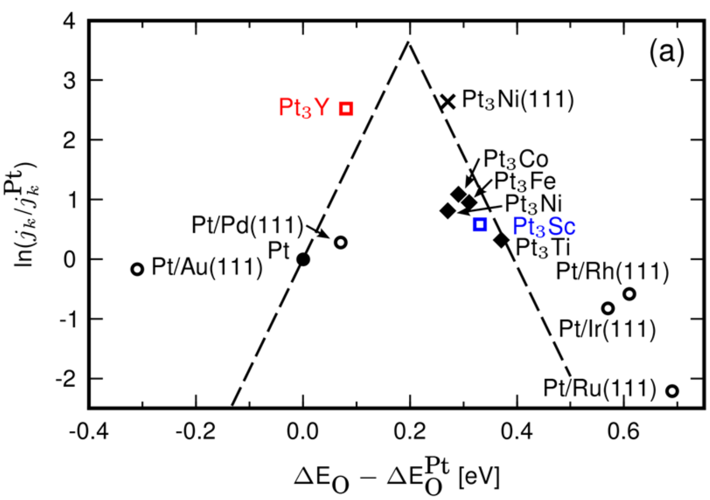

Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo,
Rossmeisl, Chorkendorff, Nørskov (2009) Nature Chemistry 1 (2009) 522

# Proof of Pt skin?
# Angle resolved XPS depth profile



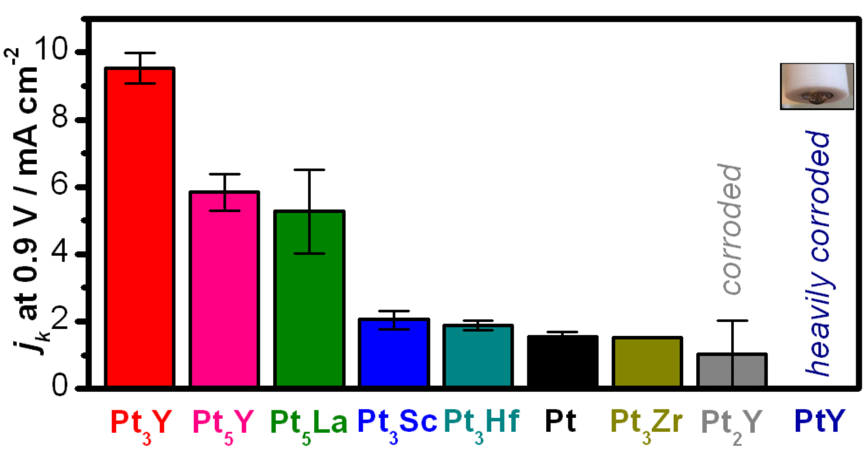



# The ORR volcano II



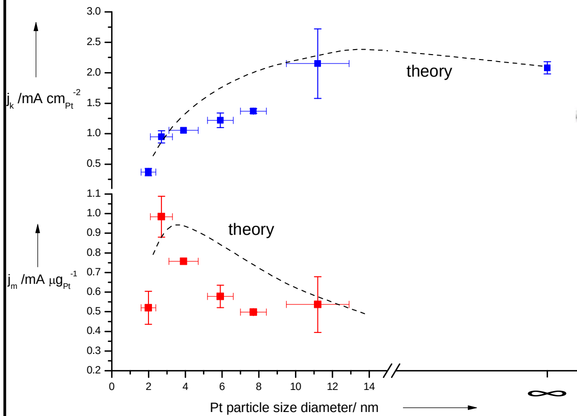

Greeley, Stephens, Bondarenko, Johansson, Hansen, Jaramillo, Rossmeisl, Chorkendorff, Nørskov (2009) Nature Chemistry 1 (2009) 522

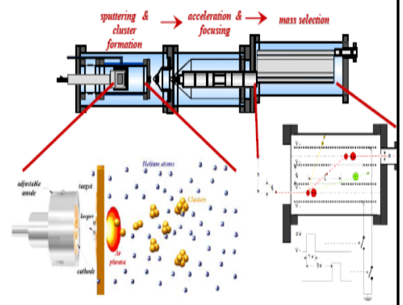
# Alloys invested so far

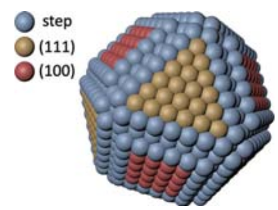



Stephens, Bondarenko,Johansson, Rossmeisl, Chorkendorff, ChemCatChem (2011)

## Specific and mass activity versus Size



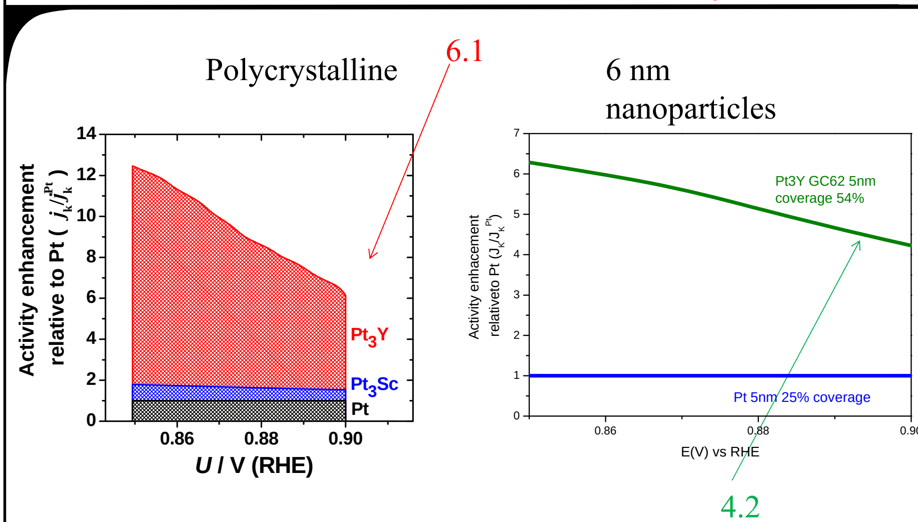




F.J. Perez-Alonso, D.N. McCarthy, A. Nierhoff, C. Strebel, I. E. L. Stephens, J.H. Nielsen, and I. Chorkendorff. Submitted (2011)

## Enhancement of activity

Polycrystalline

6 nm nanoparticles



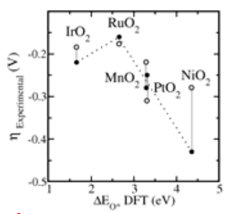

Pt-Y Nanoparticles can be made and they are stable on a 24 h test.

F.J. Perez-Alonso, D.N. McCarthy, A. Nierhoff, C. Strebel, I. E. L. Stephens, J.H. Nielsen, and I. Chorkendorff. In preparation (2011)

# Summary

**Designing new materials with specific requirements by defining decisive factors such as:**
- Band gap of semi conductors
- Binding energy of Hydrogen
- Binding energy of Oxygen
- Binding energy of specific intermediates
- Determining rate limiting steps (RLS)

**Conversion of energy:**
- Electrolysis (Pt, $IrO_2$, $RuO_2$)
- Fuel Cells (Pt, Ru)
- Synthesis of Solar Fuels (Ru, Pt,…?)




**Harvesting energy:** Photo electro catalysis PEC (same as above plus semiconductor)