Electrolysis

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Part I:

General intro

- Hydrogen economy
- Electrolysis vs. Fuel cells
- Electrochemistry
- Difficulties and problems

DFT for beginners

Hydrogen formation

- Bioinspired (MoS_2)
- High-throughput screening (BiPt)

Oxygen formation

- Origin of the overpotential
- Trends in catalytic activity
- Finding new materials

Part II:

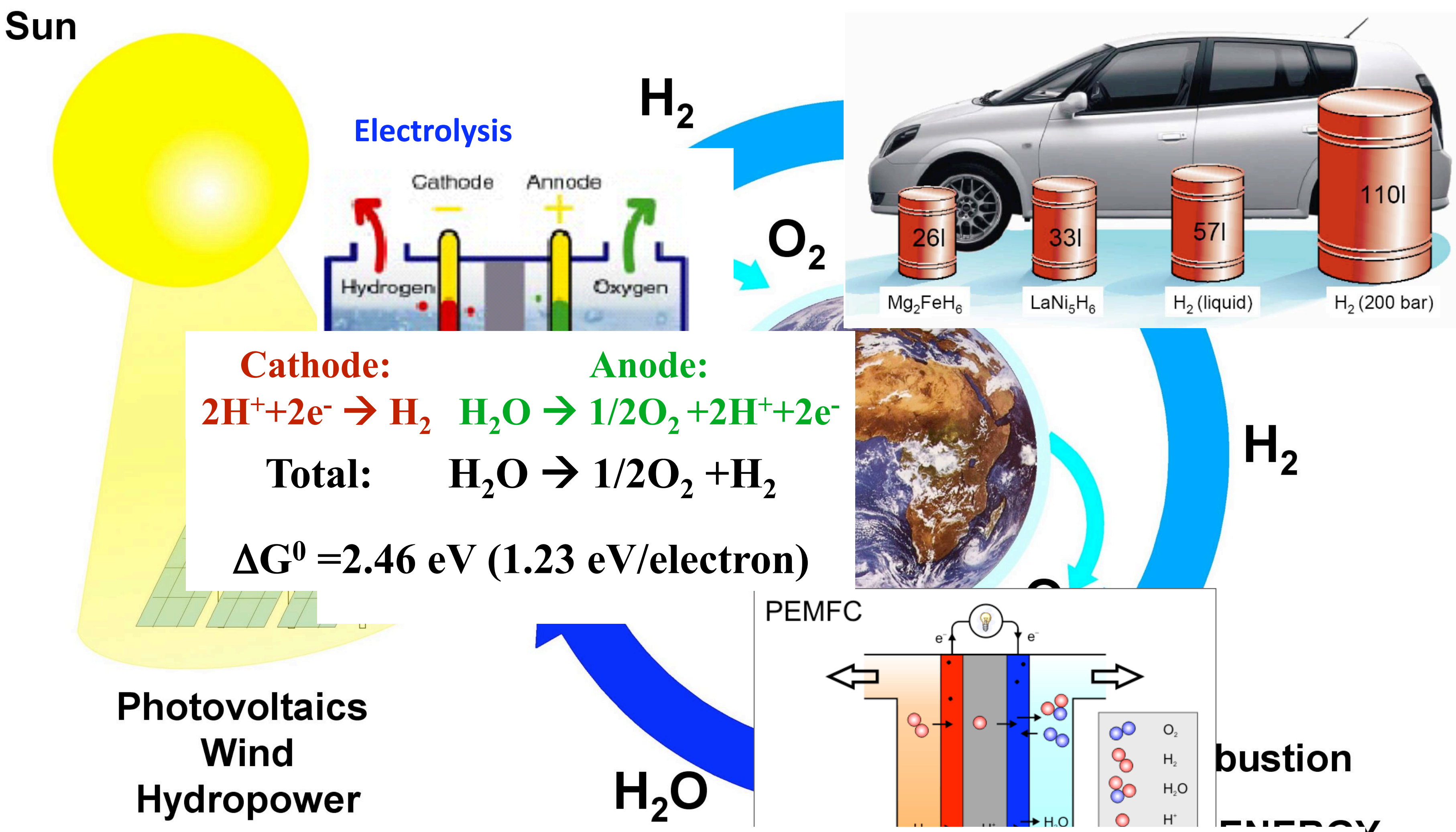
Details of hydrogen formation

- Different reaction mechanisms
- The charge solid-liquied interface
- Various DFT approaches

Results

CAMd
Center for Atomic-scale Materials Design

Towards Hydrogen Economy: Sustainable Hydrogen



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

Anode: $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$

Total: $H_2O \rightarrow 1/2O_2 + H_2$

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

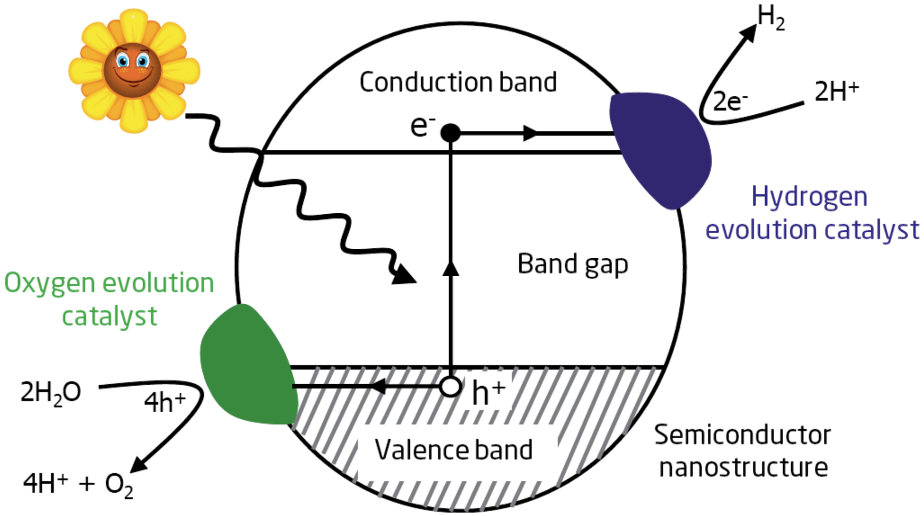
Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

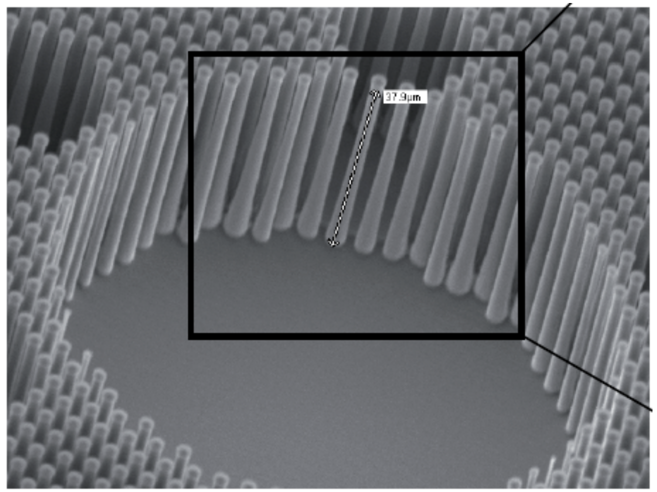
Total: $1/2O_2 + H_2 \rightarrow H_2O$ + electricity

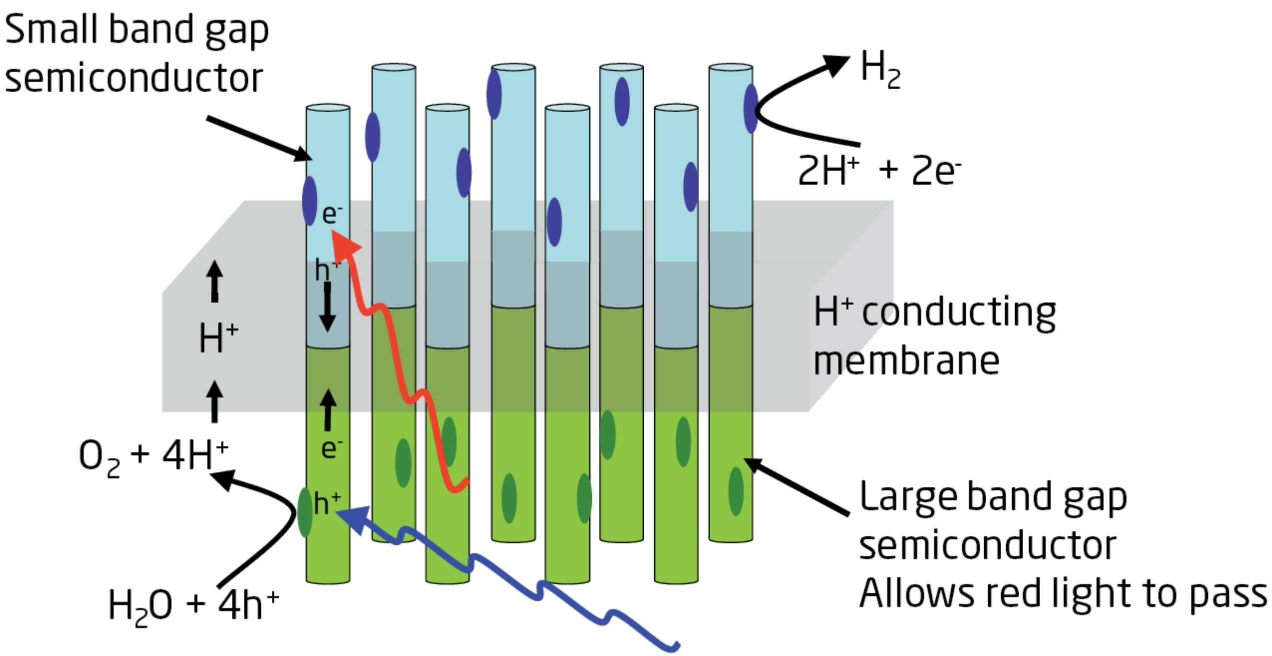
Zuttel, Borgschulte, Schlapback (2008)

Dream Device

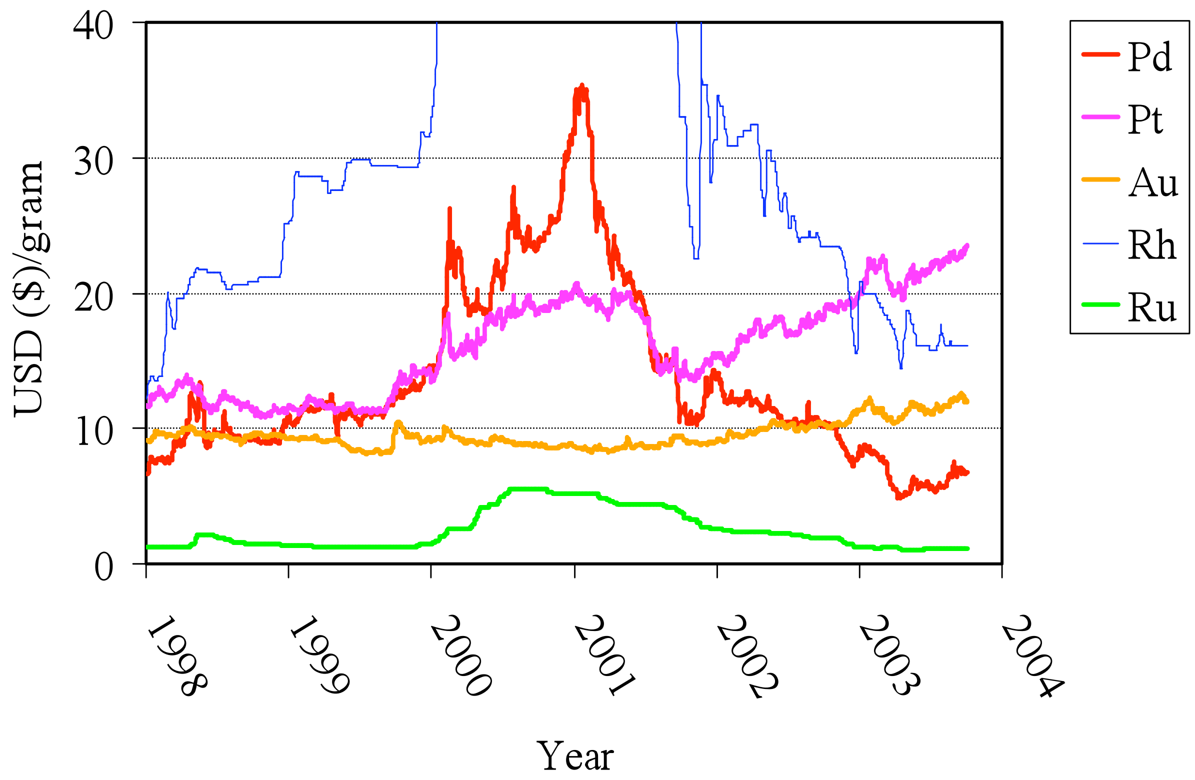


First results:
Billie Abrams, Yidong Hou
and Christian Damsgaard





Why a replacement for Platinum is needed

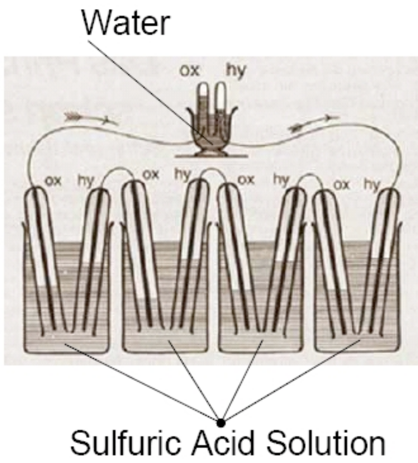


Platinum is at the time being one of the most effective catalyst for use in both fuel cells and electrolysis.

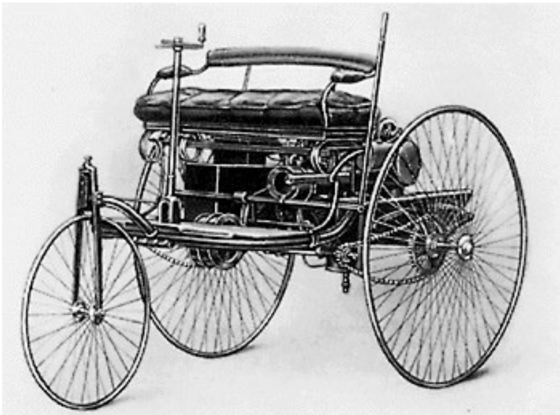
- Only 180 tons of Pt is mined every year and most of it is at the time being used for car catalysts and jewelry.
- Today's state of the art hydrogen cars use app. 100 grams of Pt. Thus only about 1.8 million cars can be made pr. year.

Electrochemistry

… active scientific field in the 19th century



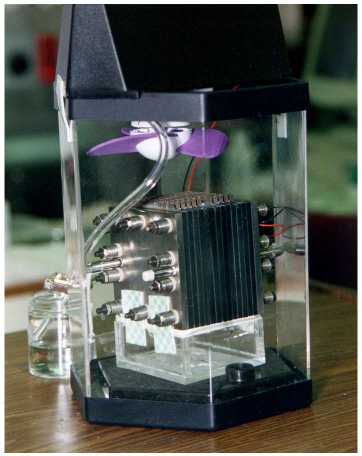
William Grove's 1839 fuel cell

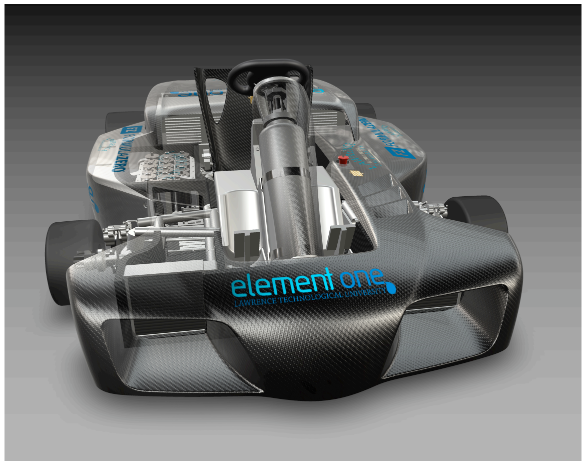


… until the first combustion engine was made and gasoline cars mass produced around 1900

Today - principles still same

Becoming a very active research field again

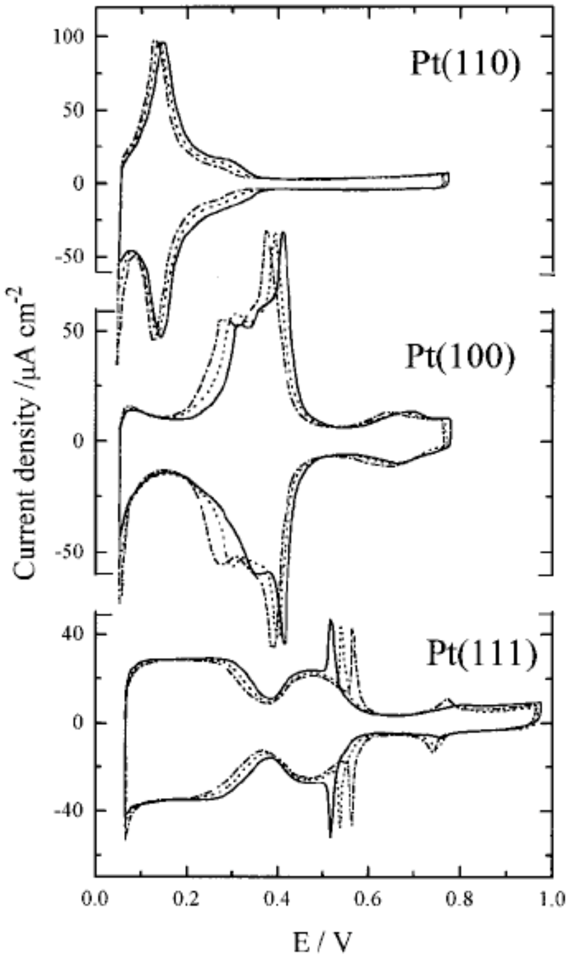




Electrochemistry

Still today:
Macroscopic characterization

Cyclic Voltammetry
H on Pt



Tune the bias, measure the current

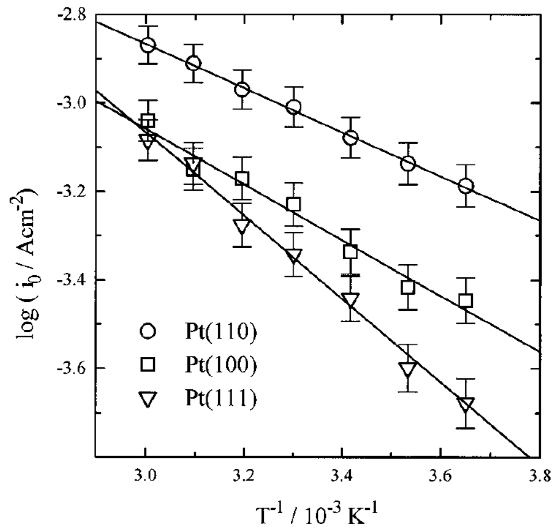
Information:
Amount of adsorbed species

Markovic *et al.*, *J. Phys. Chem. B* **101** (1997)

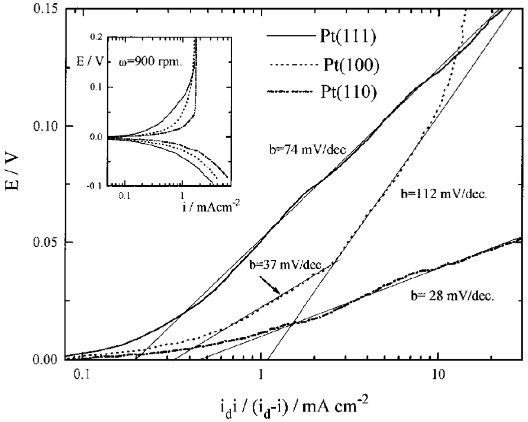
Information:
Activation barrier and prefactor of the rate limiting reaction step

Which step?

Arrhenius plot



Tafel plot



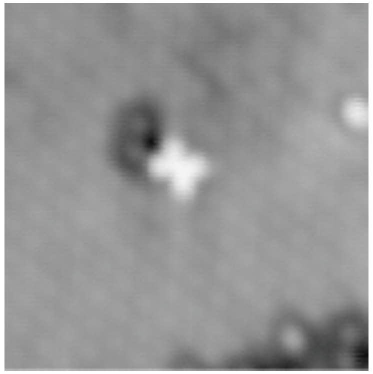
Tune the overpotential and measure the current

The slopes are supposed to give information about the reaction mechanism

Pt(110): $2H^* \rightarrow H_2$ (Tafel)
Pt(100): $H^* + H^+ + e^- \rightarrow H_2$ (Heyrovsky)
Pt(111): ?

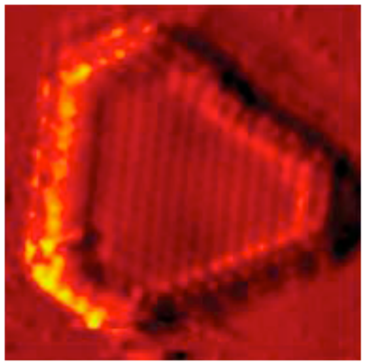
Modern science

STM of π* molecular orbital of O_2 on Pt(111)



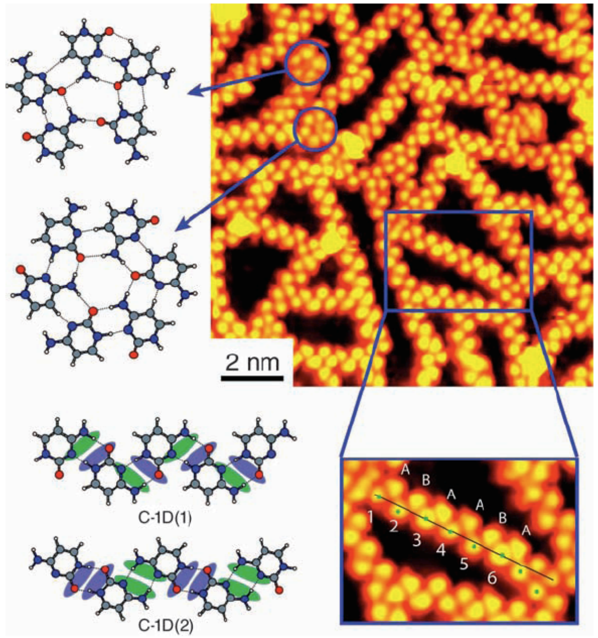
Stipe, Rezaei, Ho, Gao, Persson, Lundqvist, *PRL* **78** (1997)

STM of MoS_2 nanoparticle on Au(111)



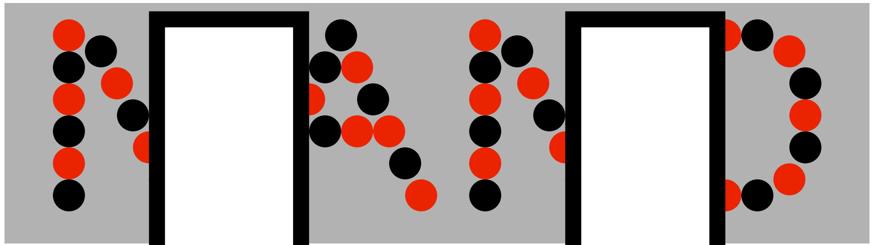
Jaramillo, Jørgensen, Bonde, Nielsen, Horch, Chorkendorff , *Science*, **317** (2007)

STM of the DNA base Cytosine on Au(111)



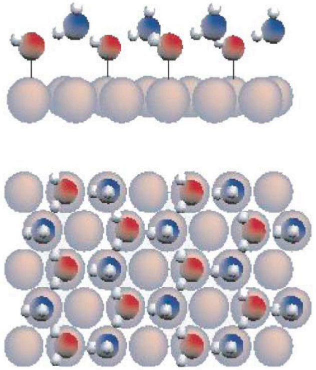
Otero, Lukas, Kelly, Xu, Lægsgaard, Stensgaard Kantorovich, Besenbacher, *Science*, **319** (2008)

Solid-gas interface
@ low pressure (UHV)
-> atomic resolution
via STM & AFM

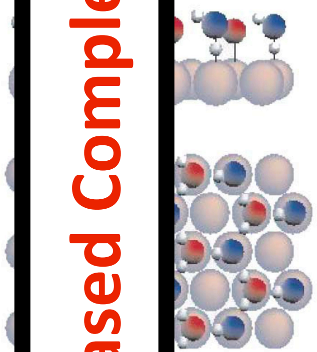


Recently: Bridging the gap to higher pressure

Solid-liquid interface
Spectroscopy @ 150K
DFT @ 0K

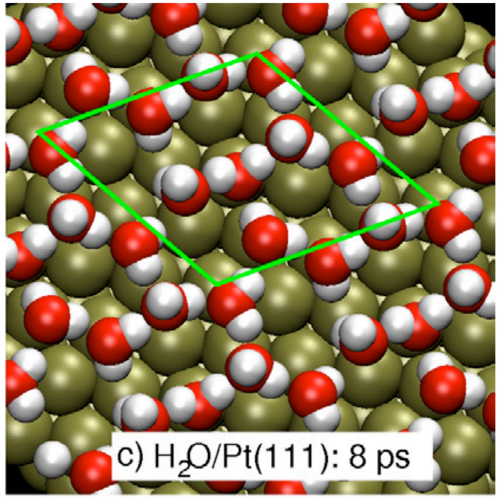


Ogasawara *et al*,
PRL, **89** (2002)



Solid-liq erface
/ 300K

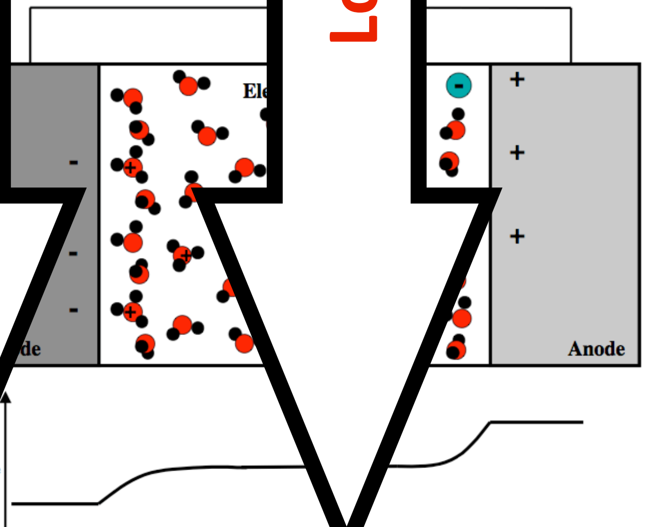
& Groß,
(2009)



Increased Complexity

Lower resolution

<u>Electrochemical interface:</u>
charged solid electrode,
solvated ions in liquid,
applied bias
electric field
charge-transfer during reactio



How can we get microscopic insight?

EC-STM
Spectroscopy
DFT

Helmholtz (1853) Gouy (1910)
Chapman (1913) Stern (1924)
Grahame (1947)

Density Functional Theory (DFT)

A method for solving the many electron Schrödinger equation in principle exact

Input : Atomic configuration

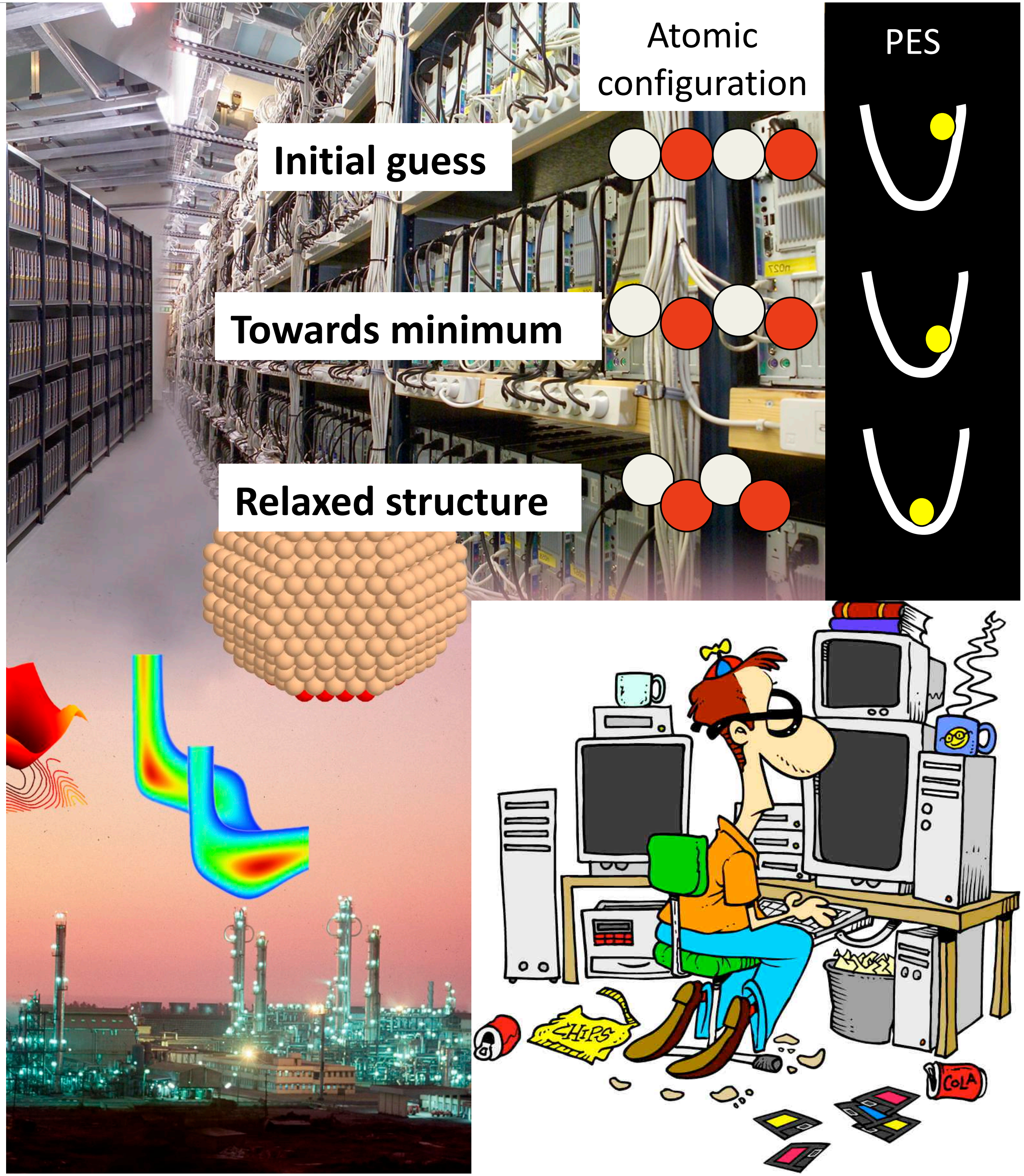
Press ***ENTER***

The atoms start to experience *forces* from each other and move towards an *energy local minimum* (iteratively) until the forces are zero and *ground state* is reached

Output : Ground state electron density and total potential energy

Computational expensive

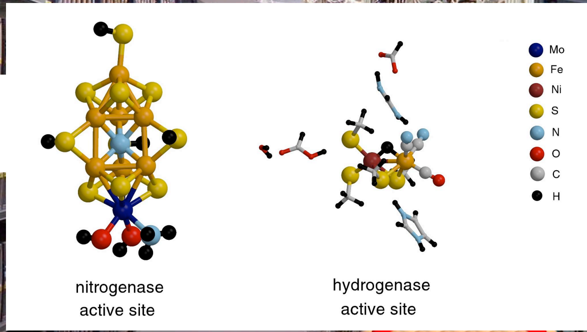
-> systems with ~100 atoms

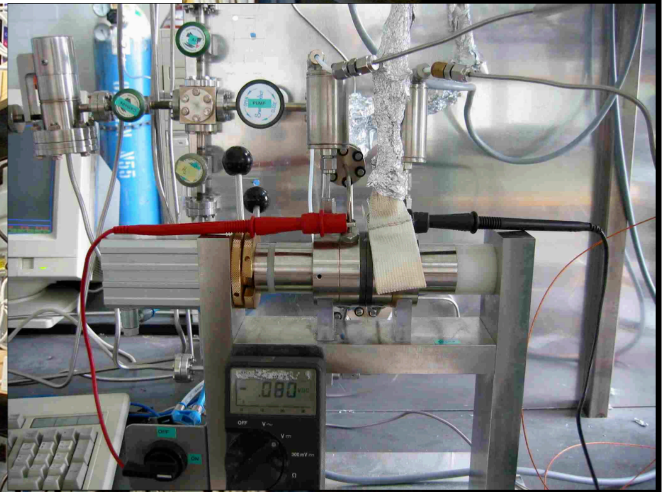


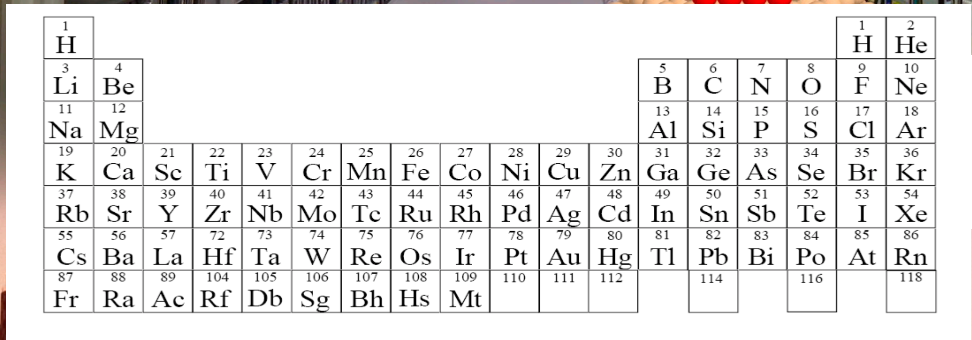
We need a catalyst - What do we do?

Using either simulations or experiments:

1. Learn from nature?



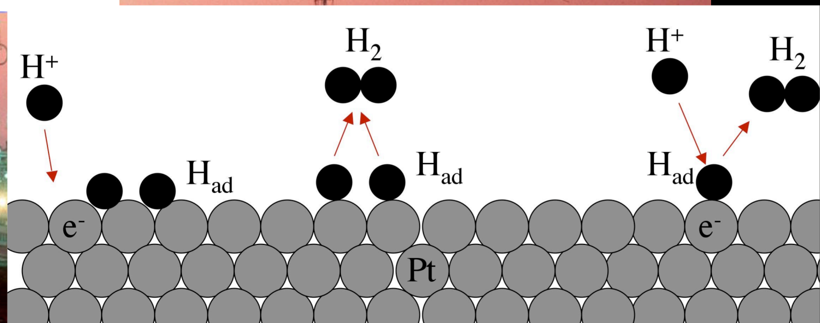




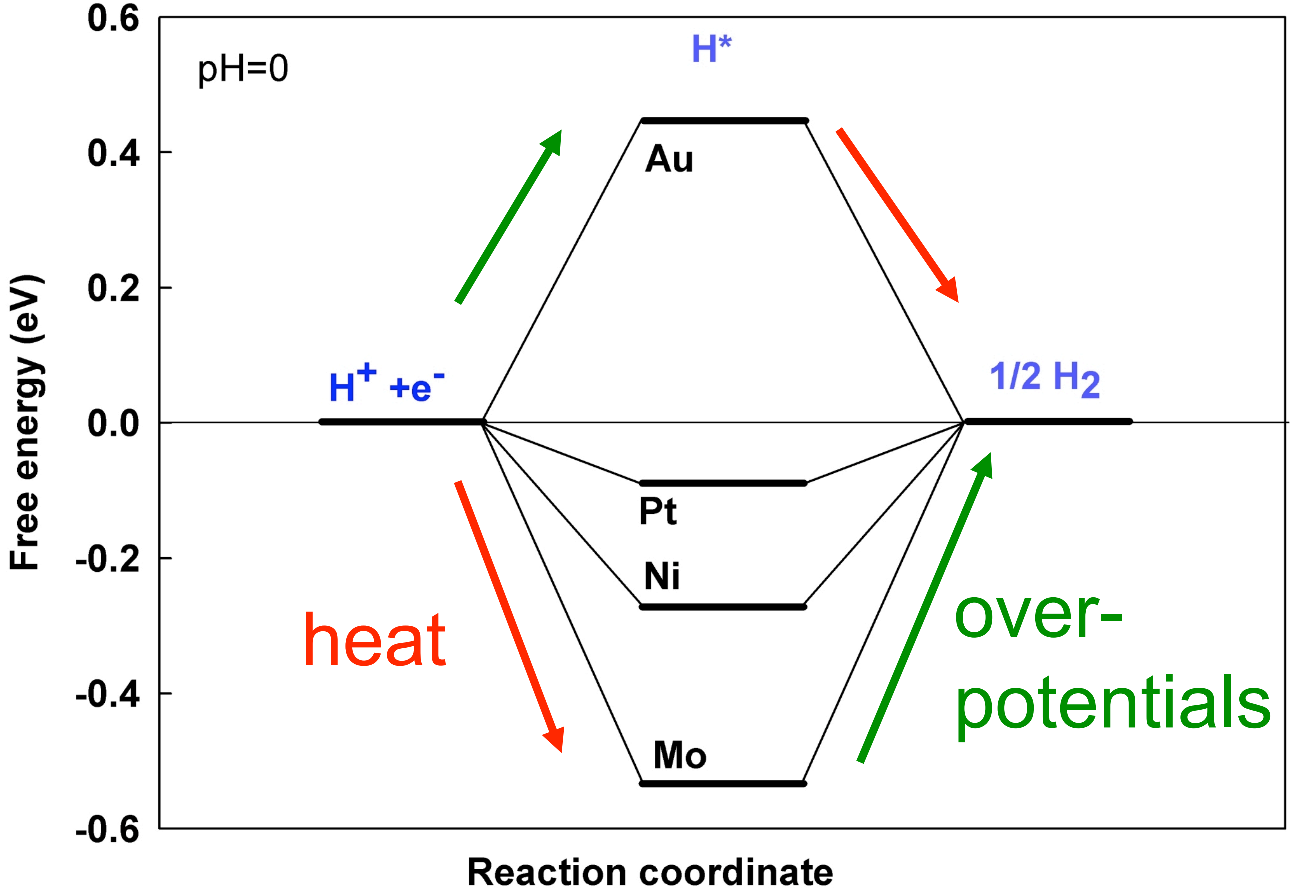
2. High-throughput screening?

3. Understand the atomistic details

Use that knowledge to design a new catalyst



Simple model, calculate ΔG_{Had}

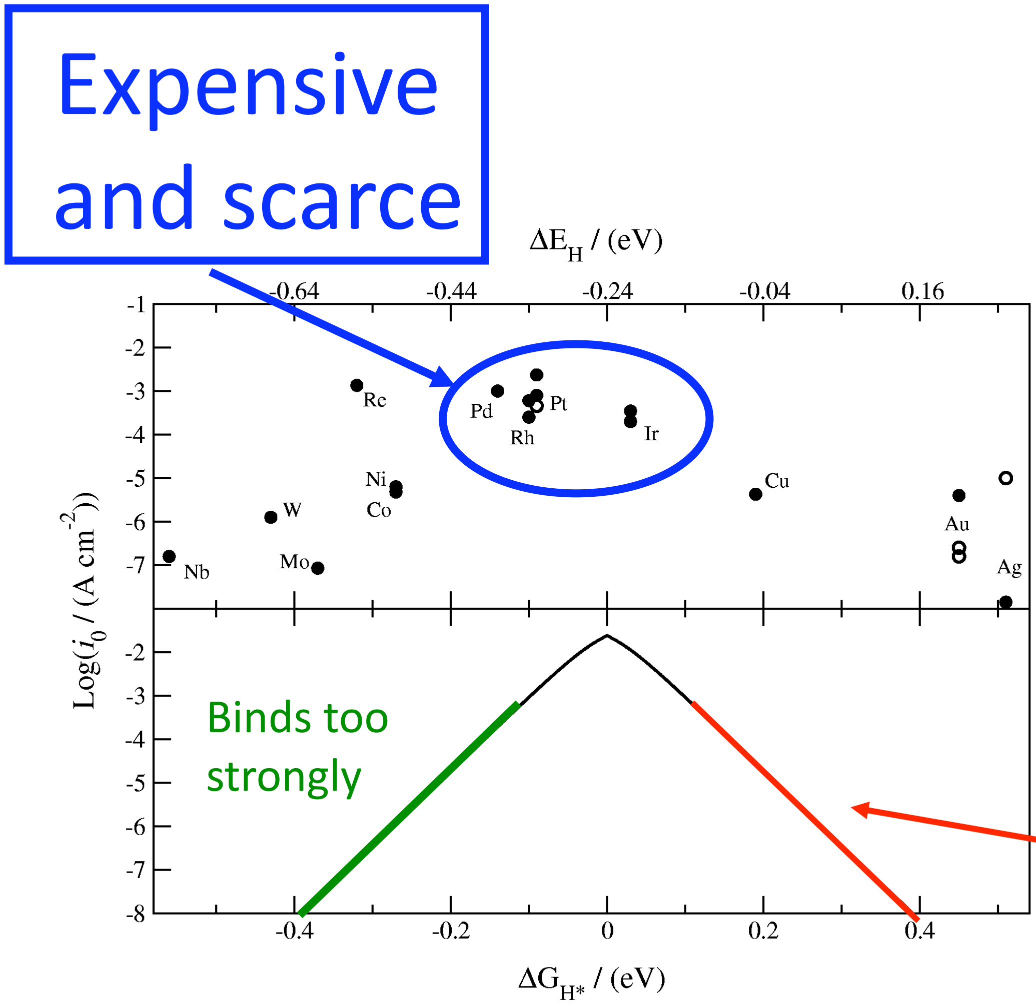


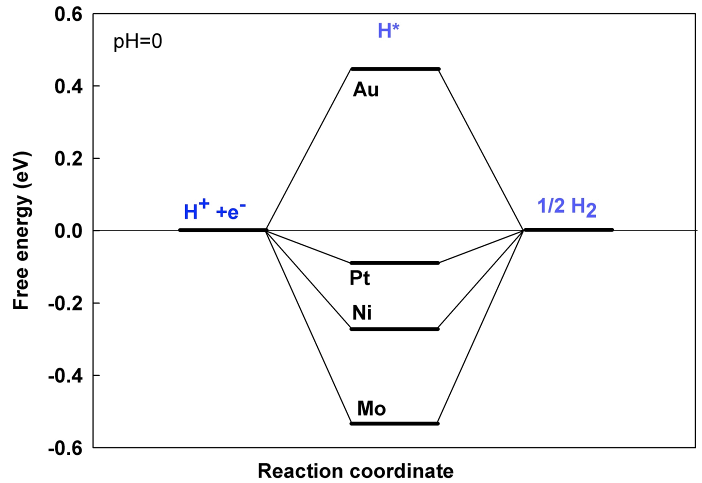
$\Delta G_{Had} \approx 0$

The most efficient materials

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

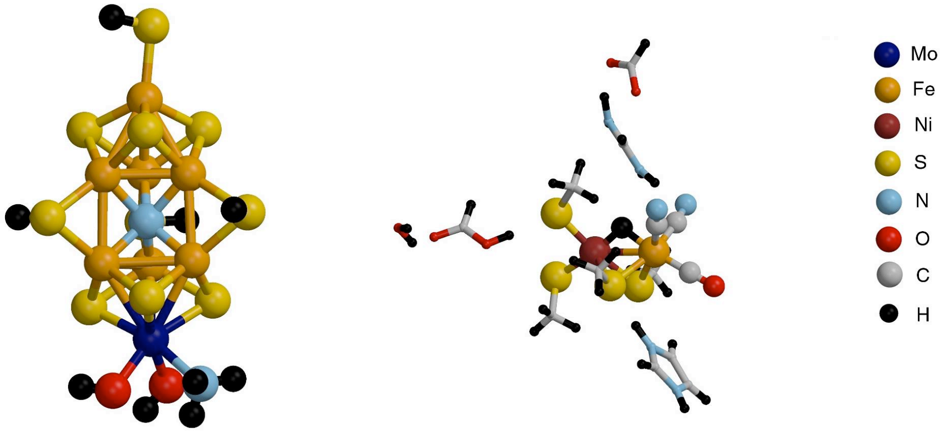
Using DFT energies in volcano



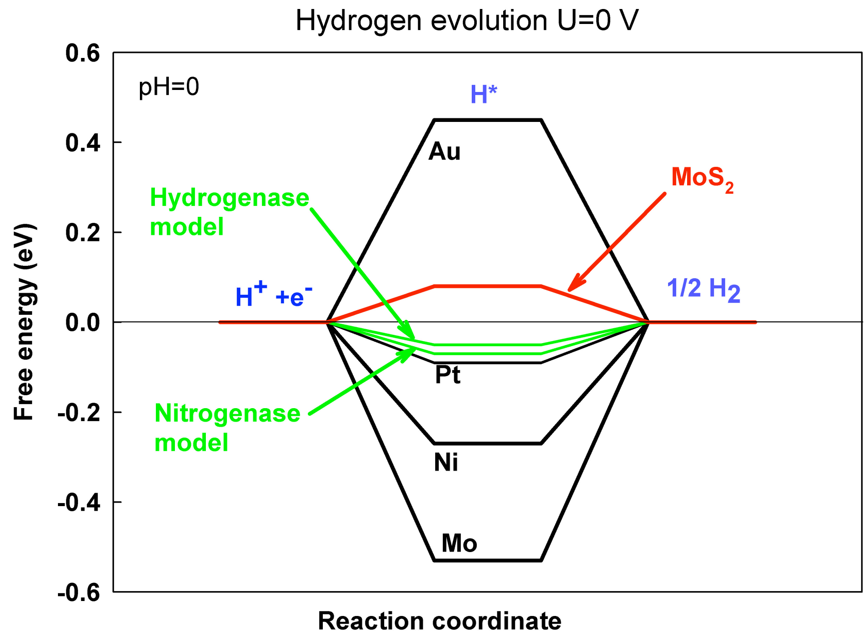


J.K. Nørskov, T. Bligaard, Á. Logadóttir, J.R. Kitchin, J.G. Chen, Pandelov, and U. Stimming, *J. Electrochem. Soc.*, (2005)

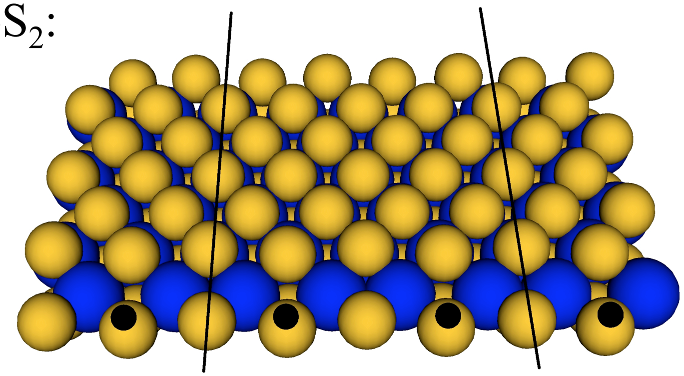
Inspired by Nature



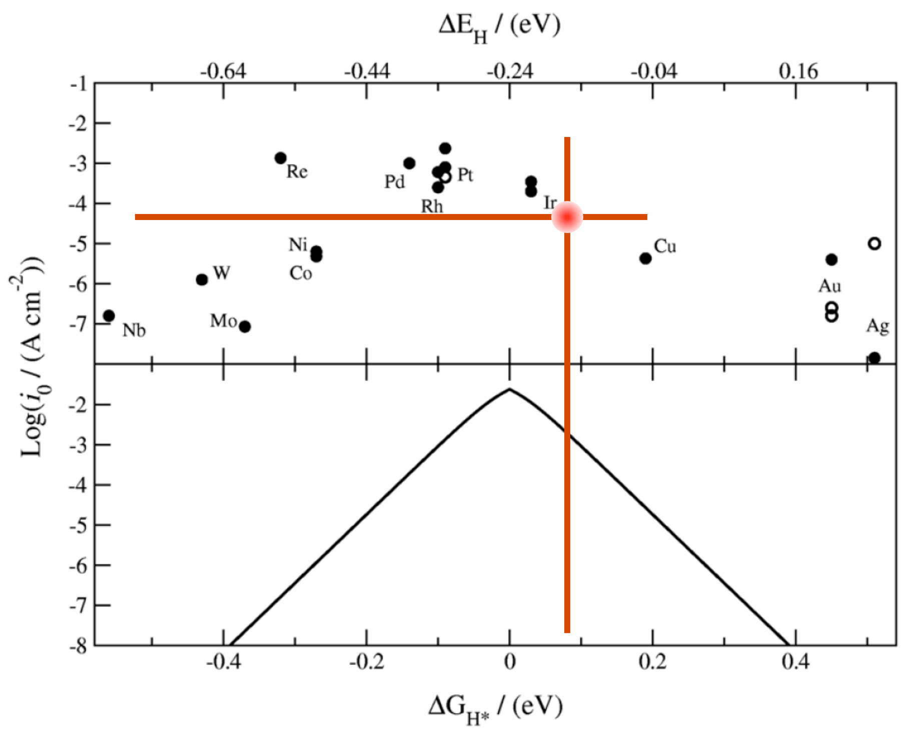
nitrogenase hydrogenase



MoS$_2$:

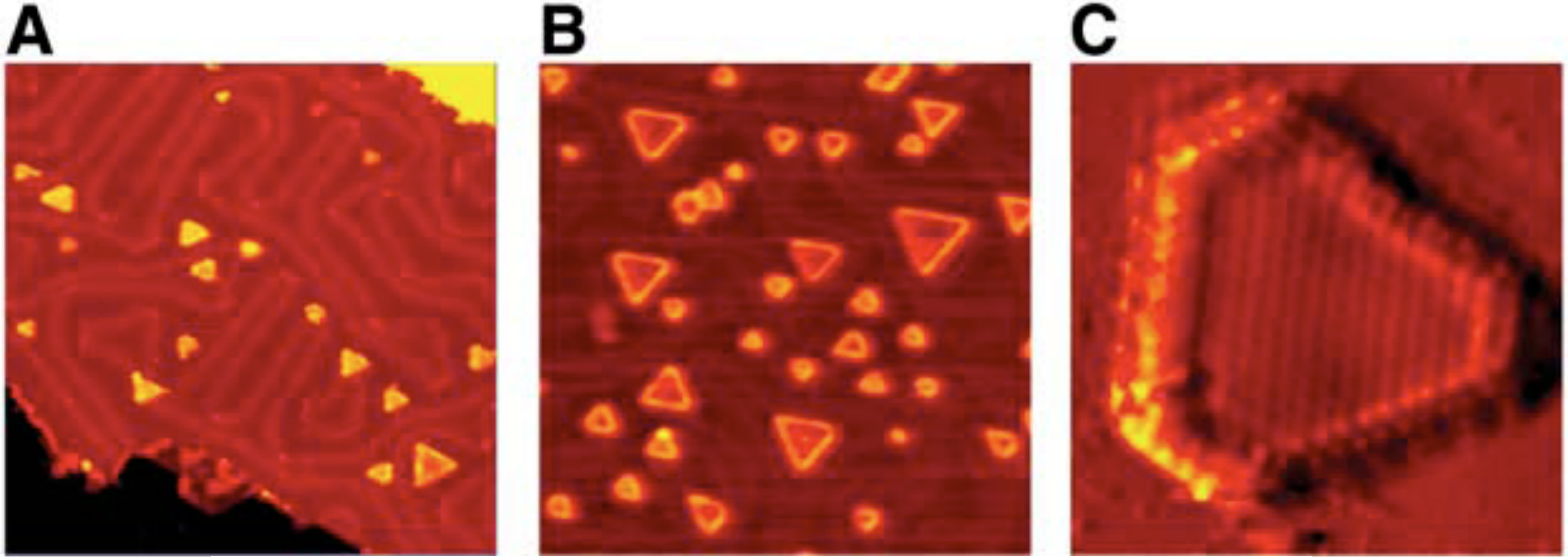


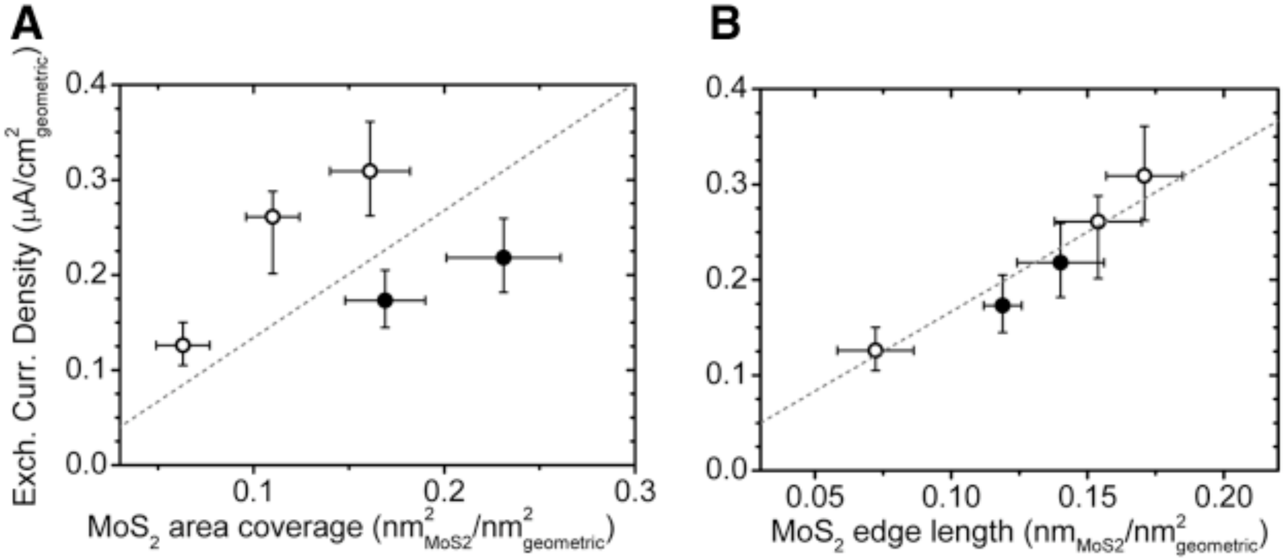
$(10\bar{1}0)$
Mo-edge



Siegbahn, Adv. Inorg. Chem. **56**, 101 (2004)
Hinnemann, Nørskov, JACS **126**, 3920 (2004)
Hinnemann, Bonde, Jørgensen, Nielsen, Horch, Chorkendorff, Nørskov, JACS **127** 5308 (2005)

Combined STM/HER Measurements on MoS_2/Au



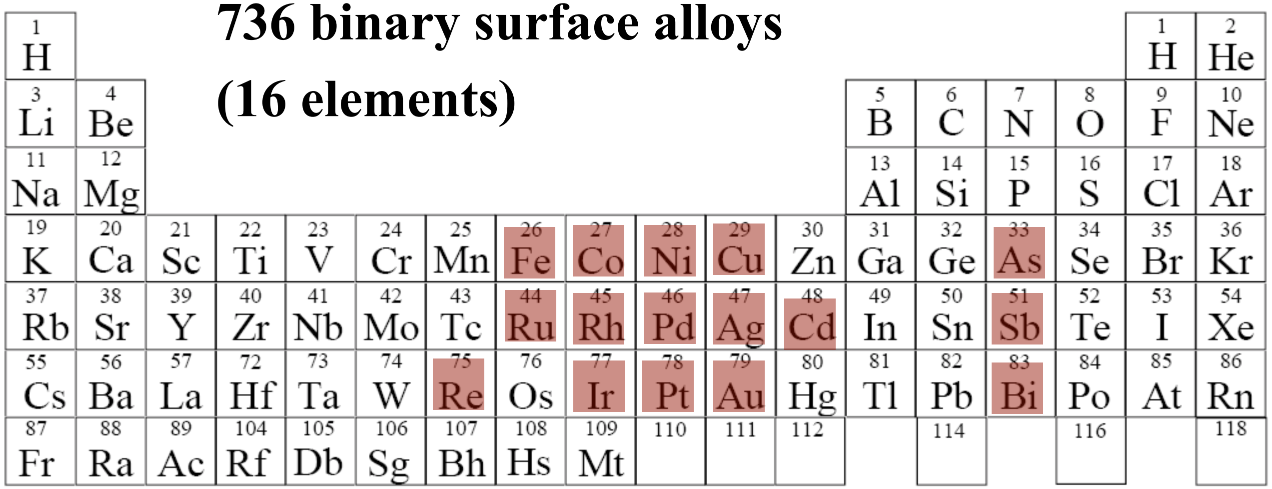


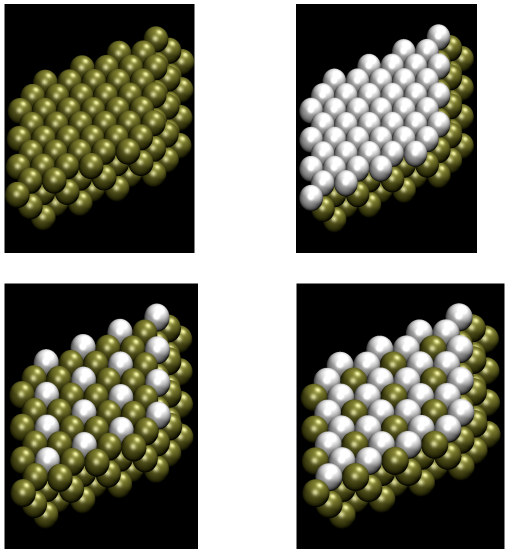
Jaramillo, Jørgensen, Bonde, Nielsen, Horch, Chorkendorff , *Science*, **317** (2007)

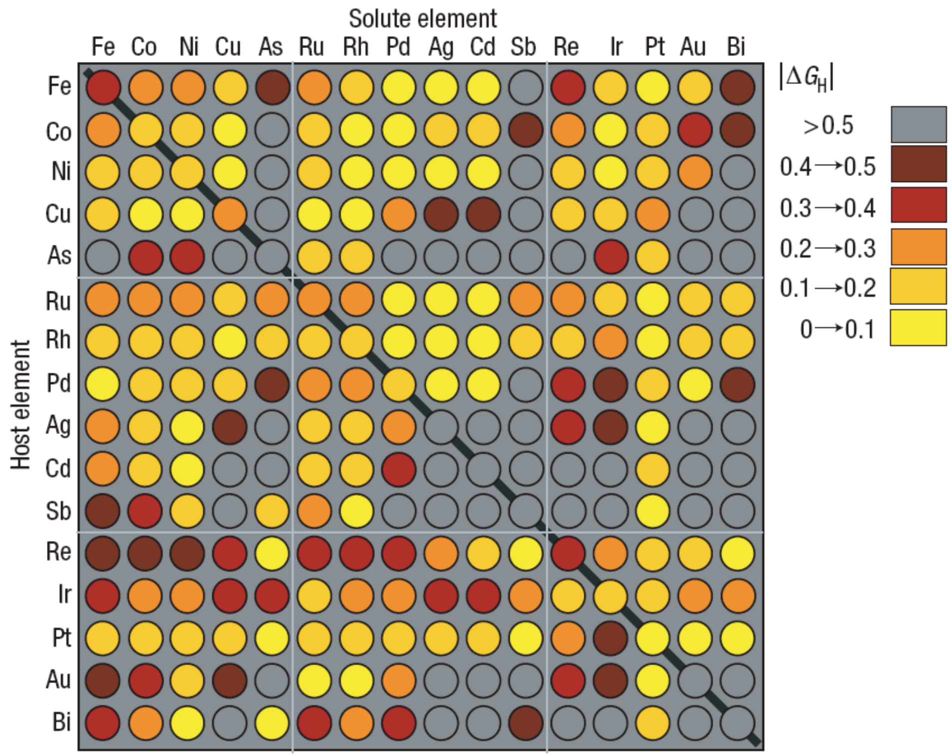
Computational High-throughput Screening

736 binary surface alloys

(16 elements)







Greeley, Jaramillo, Bonde, Chorkendorff, Nørskov, *Nature Materials* (2006)

The criteria

High activity

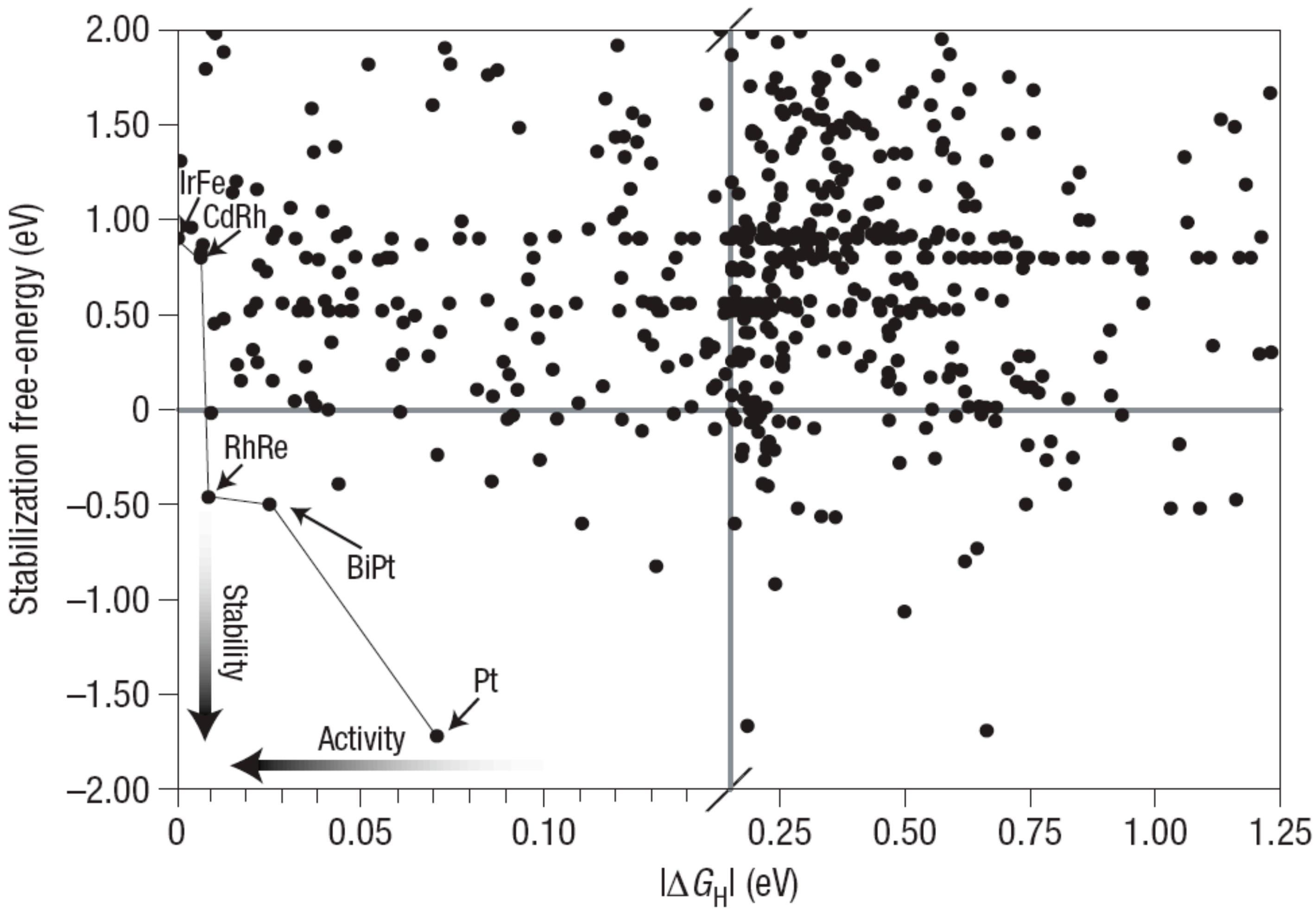
- $\Delta G \sim 0$ - no kinetics i.e. no barriers are considered

Stability criteria

- stable against surface segregation (stability of the overlayer)
- stable against intra-surface transformations (island formation)
- stable against oxygen poisoning of the surface (water splitting)
- stable against corrosion (the free energy for dissolution)

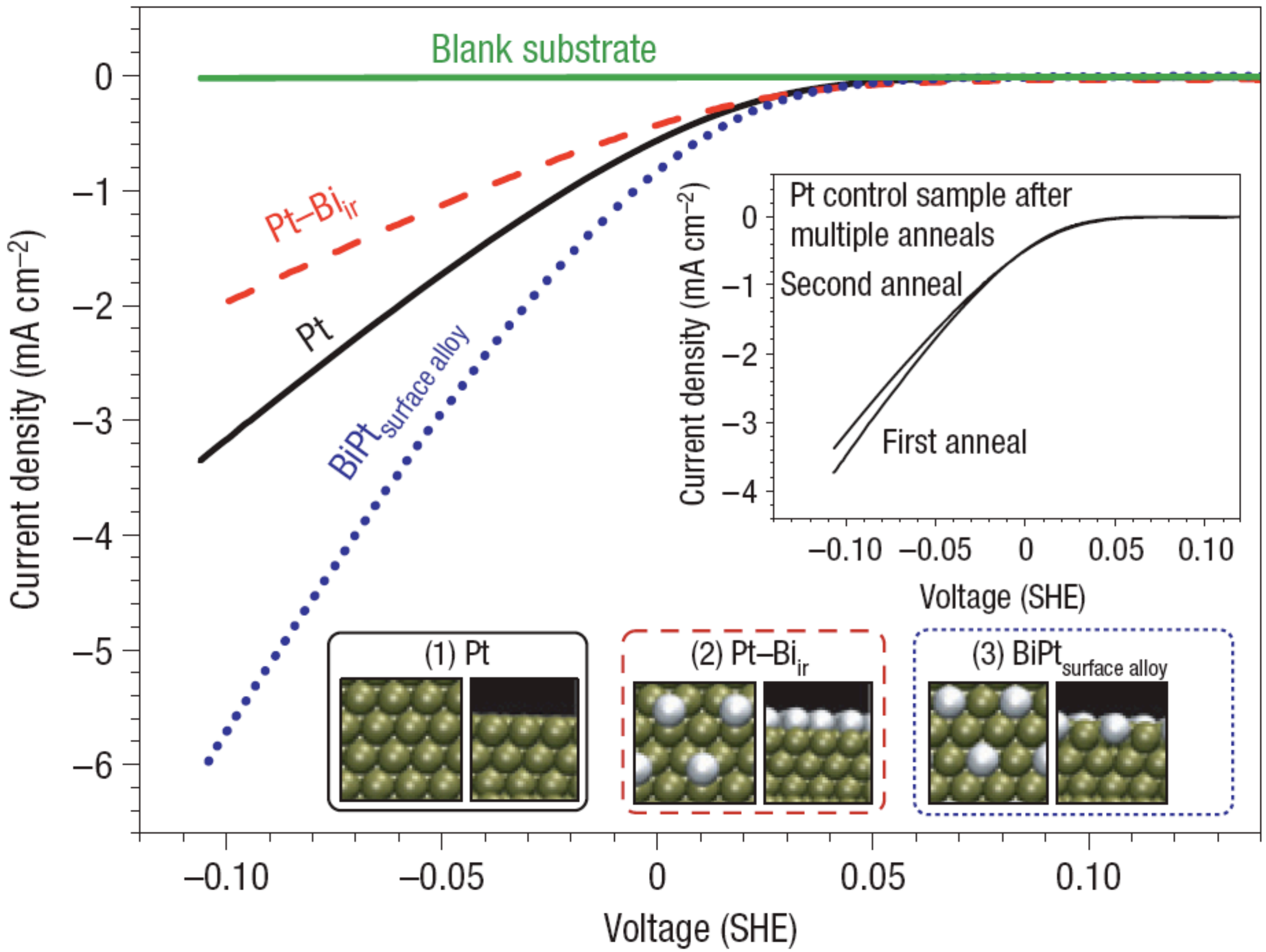
Greeley, Jaramillo, Bonde, Chorkendorff,
Nørskov, *Nature Materials* (2006)

Computational High-throughput Screening



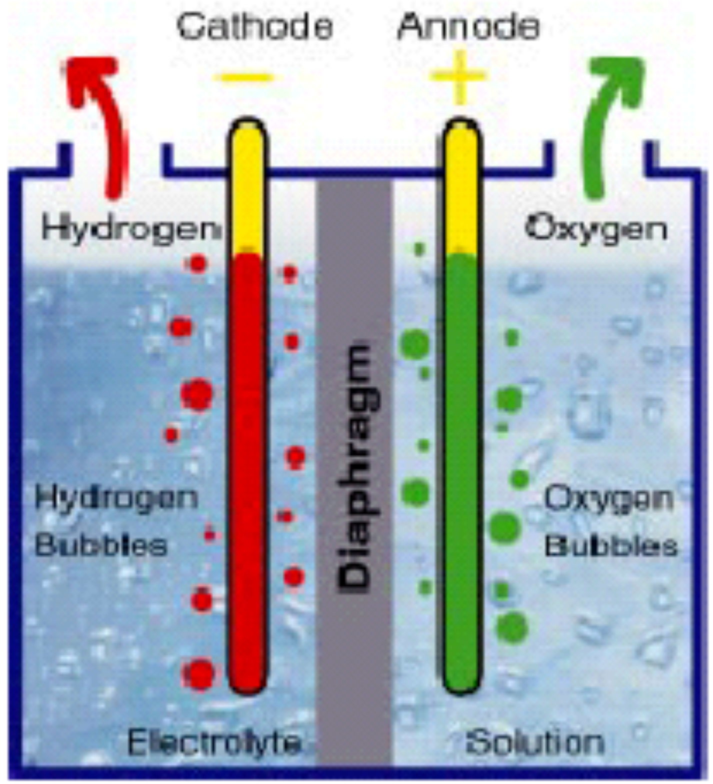
Greeley, Jaramillo, Bonde, Chorkendorff, Nørskov, *Nature Materials* (2006)

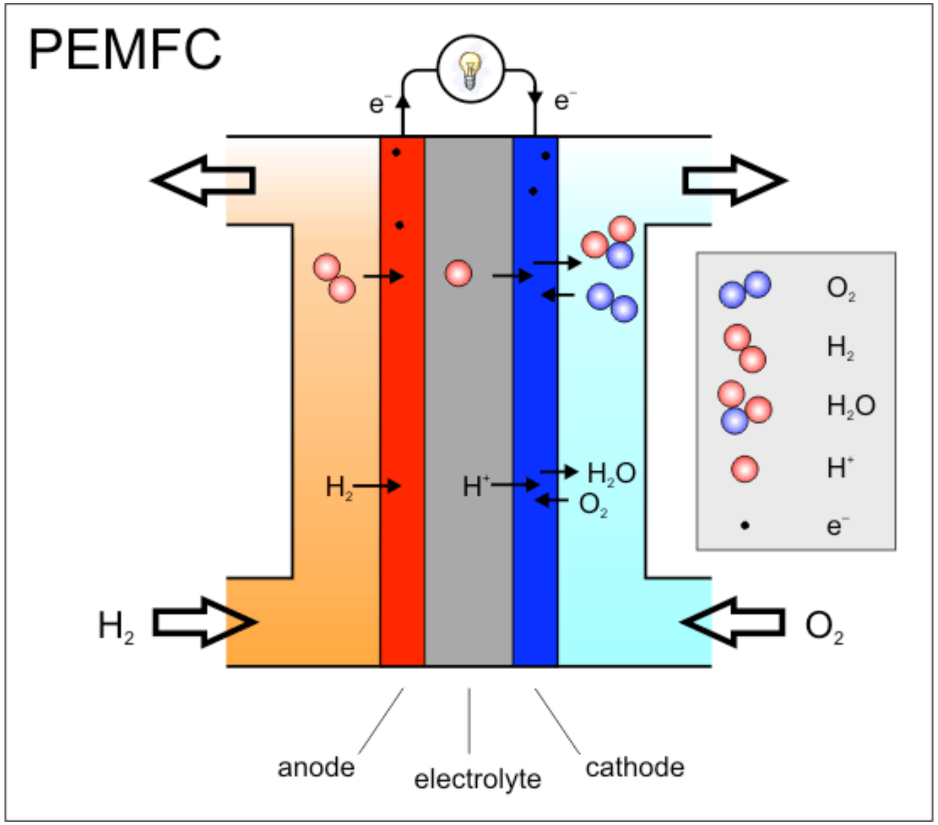
Computational High-throughput Screening



Greeley, Jaramillo, Bonde, Chorkendorff,
Nørskov, *Nature Materials* (2006)

Electrolysis vs PEM Fuel cell





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

Anode:
$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$

Anode:
$H_2 \rightarrow 2H^+ + 2e^-$

Cathode:
$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

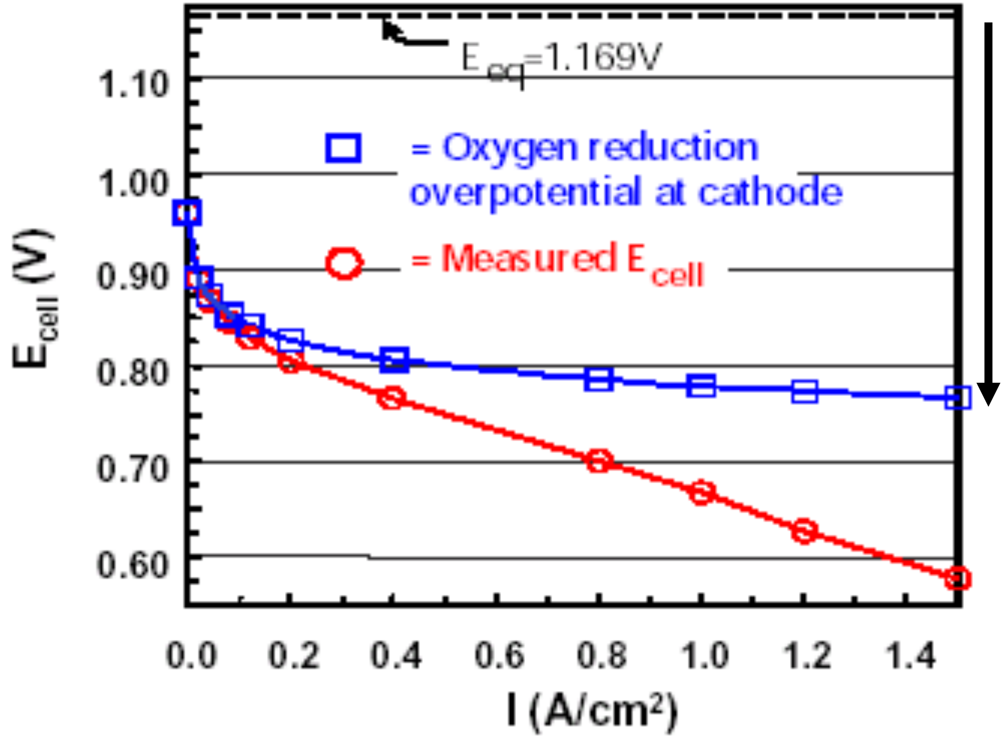
Total: $H_2O \rightarrow 1/2O_2 + H_2$

Total: $1/2O_2 + H_2 \rightarrow H_2O$ + electricity

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

The Cathode Problem

PEM fuel cell H_2/O_2 gas, Pt electrodes at 80°C



~0.4 V overpotential

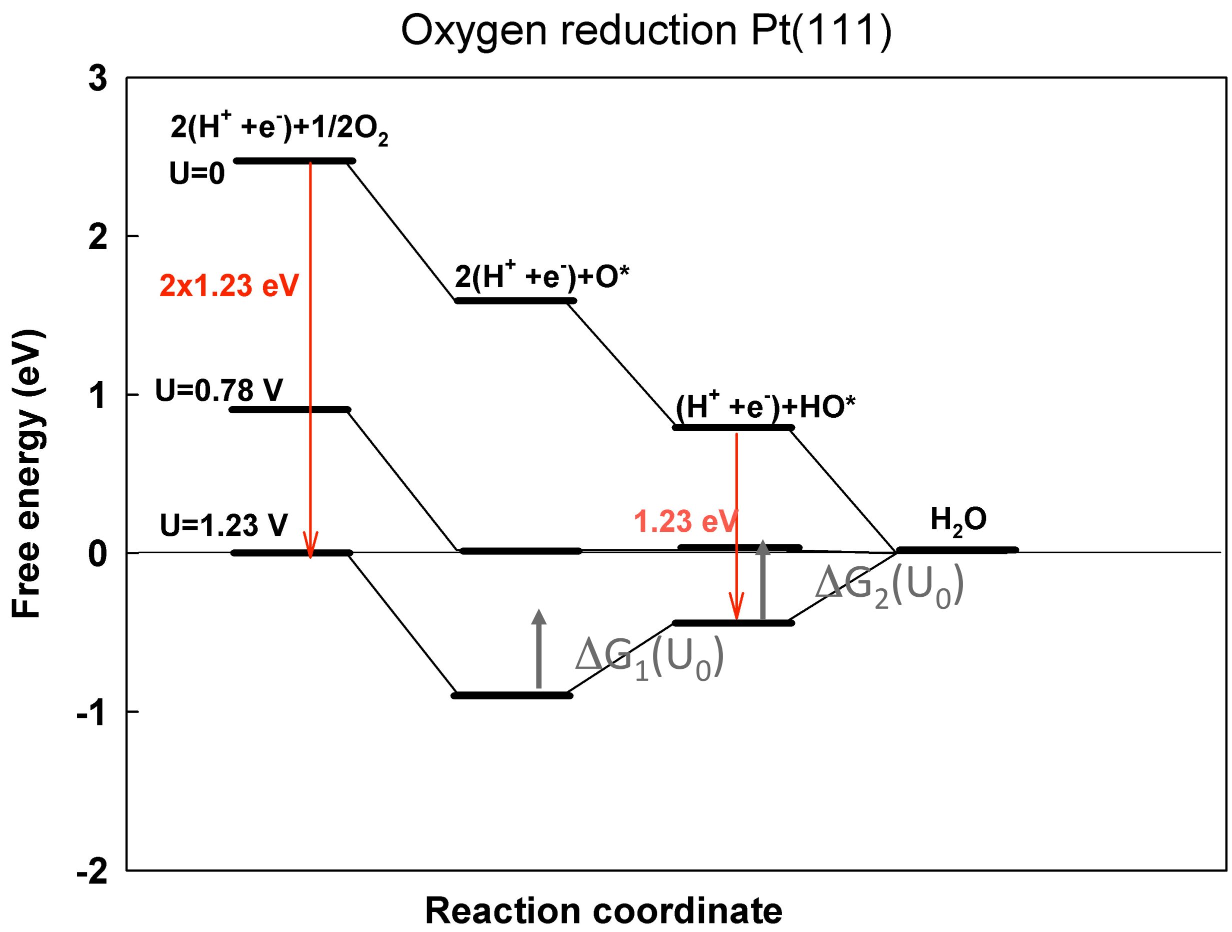
Gasteiger and Mathias (2002)

Why is Pt a good cathode material?

Why is there also a substantial overpotential for Pt?

Can we do better than Pt?

The origin of the overpotential



@ 1.23V ΔG=0.45V

@ 0.78V ΔG=0V

Overpotential:

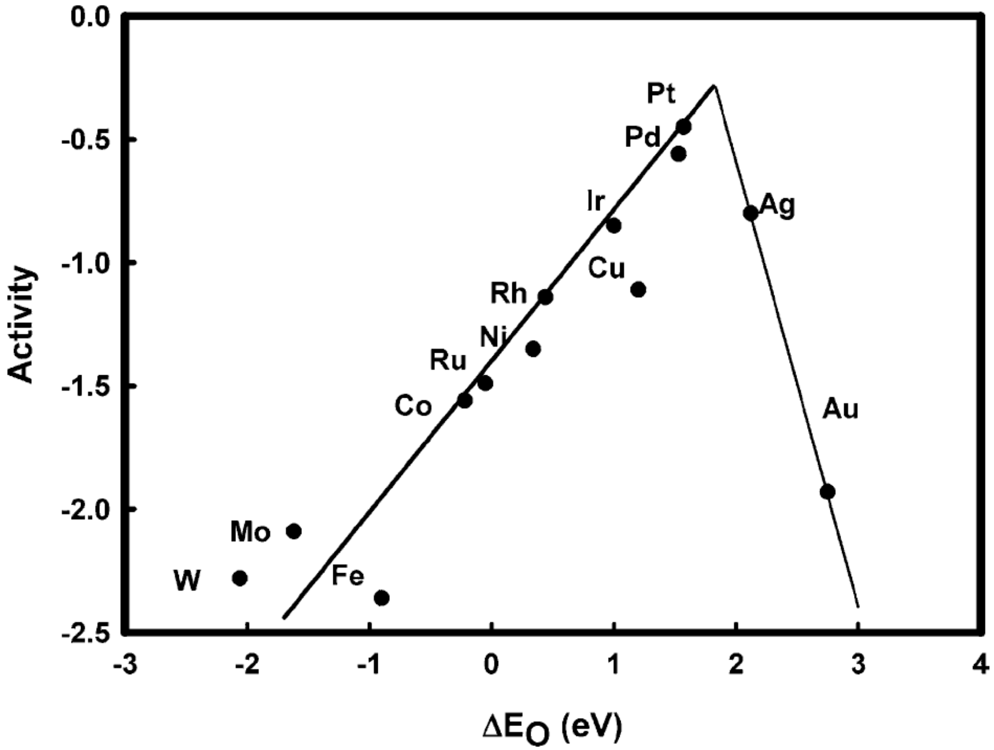
1.23V-0.78V=0.45V

The overpotential originates from strongly bound O/OH

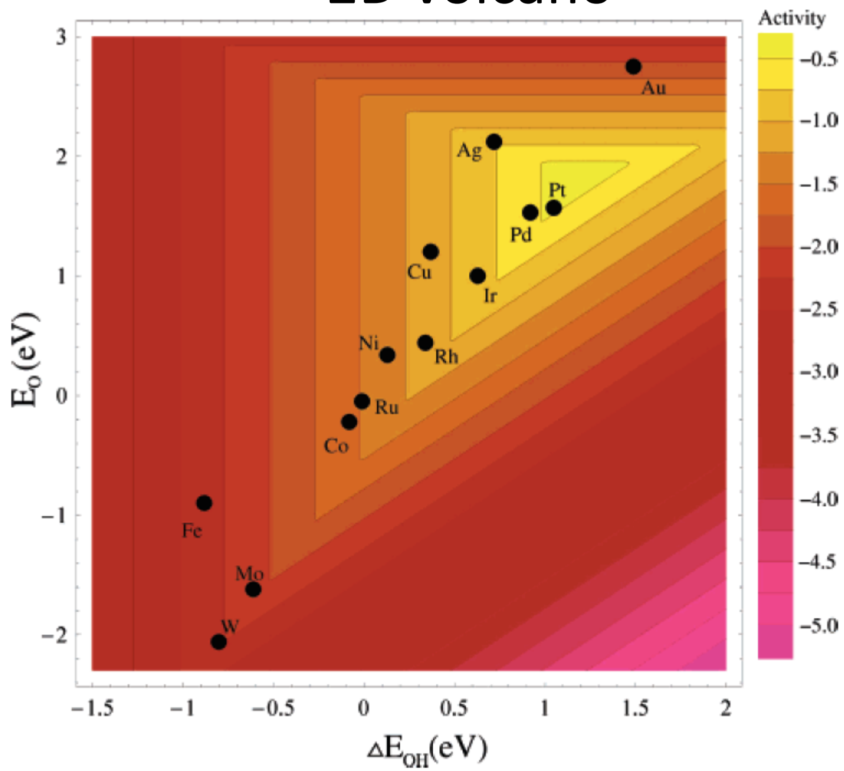
Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard, Jónsson, *J. Phys. Chem. B* (2004)

Trends in catalytic activity for ORR

1D volcano

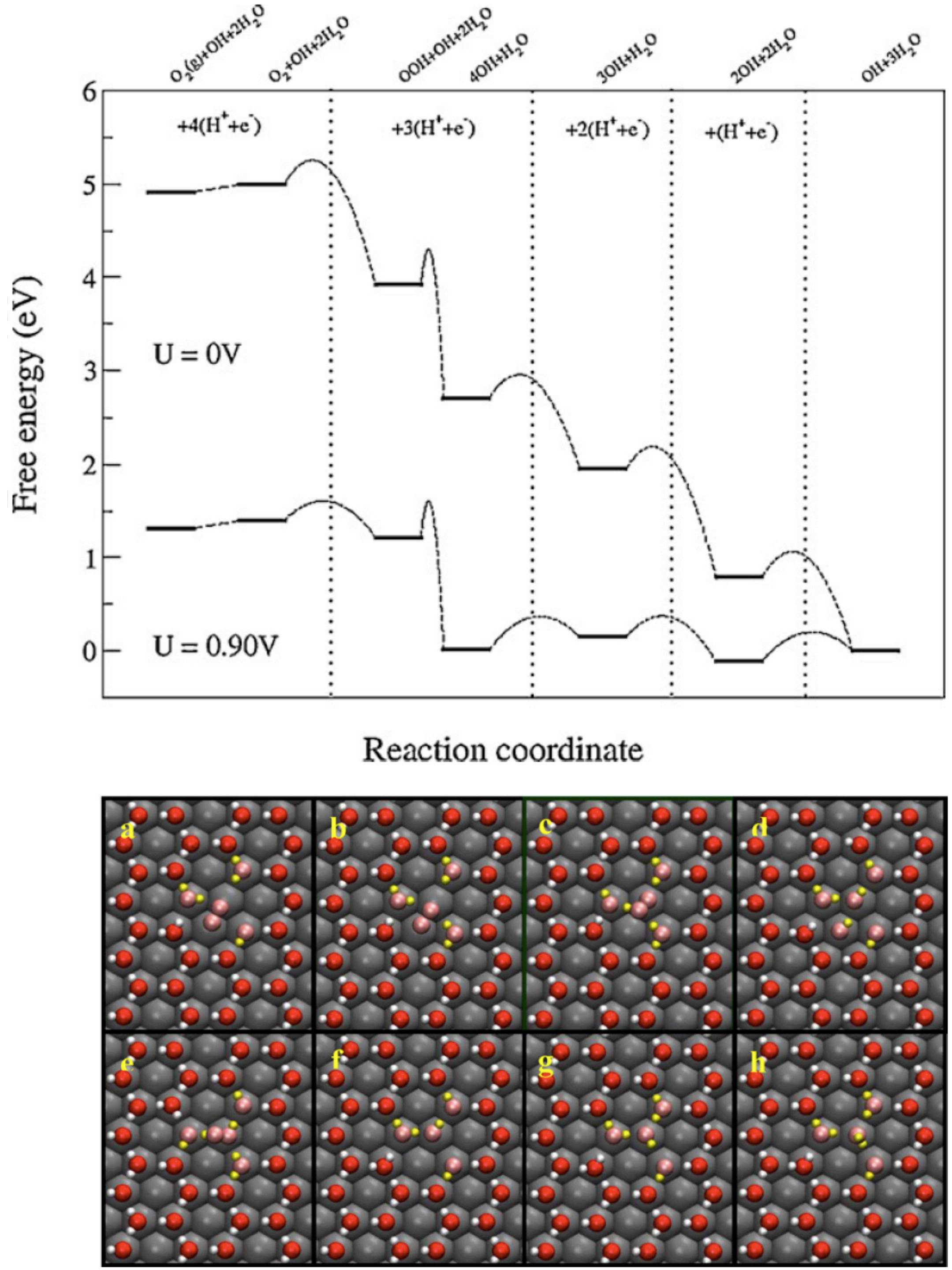


2D volcano



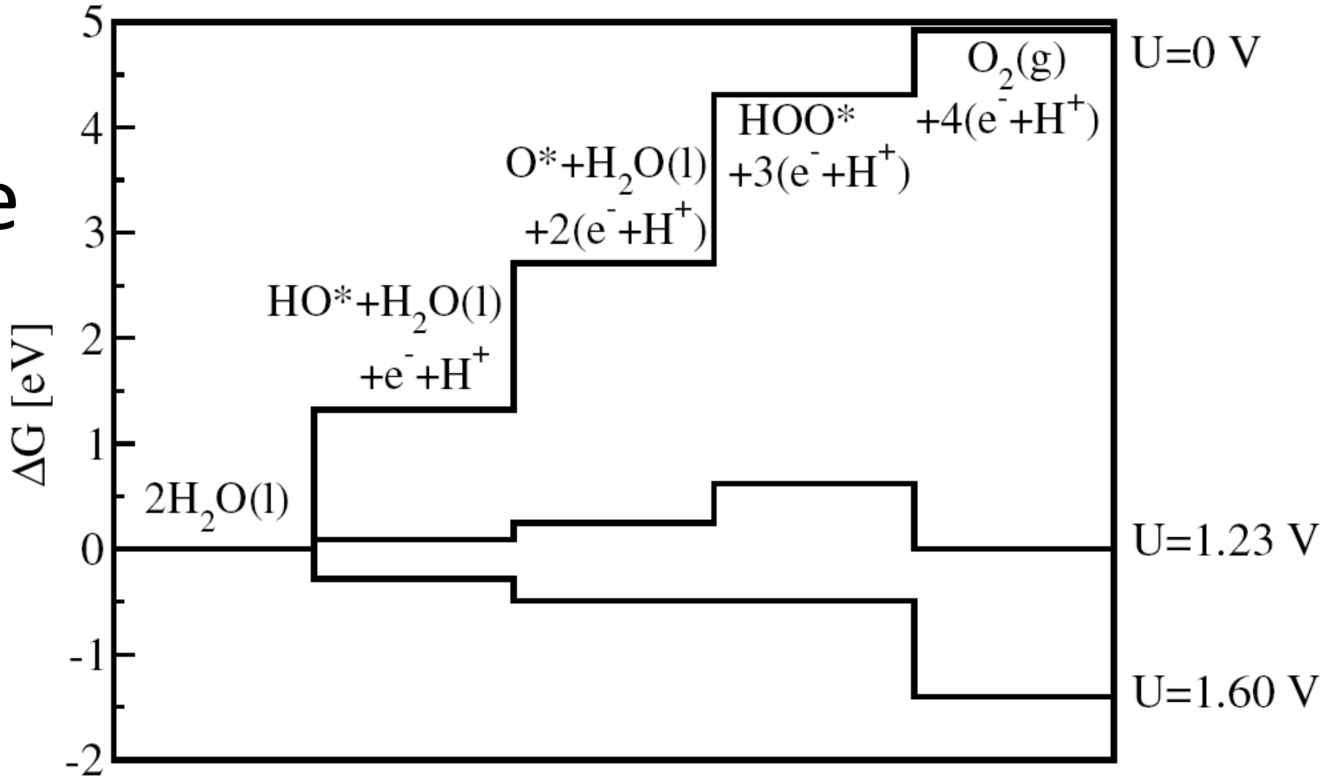
Nørskov, Rossmeisl, Logadottir, Lindqvist, Kitchin, Bligaard, Jónsson, *J. Phys. Chem. B* (2004)

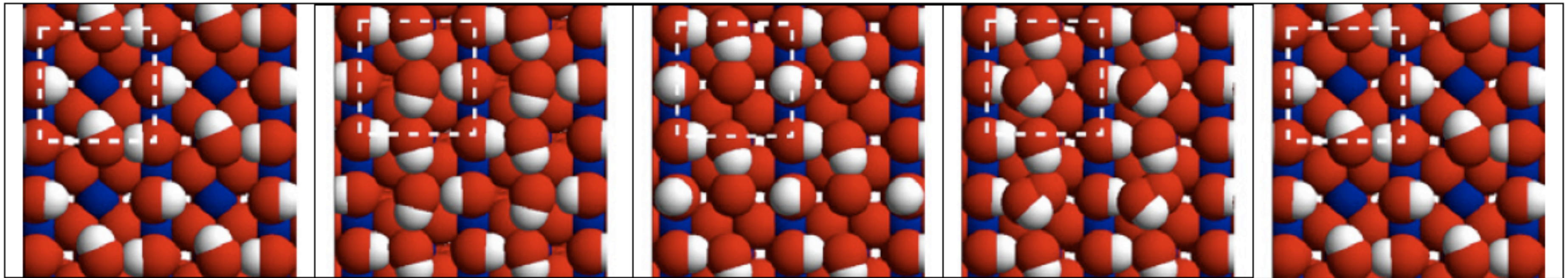
Activation barriers included in ORR



Tripkovic, Skulason, Siahrosami, Norskov, Rossmeisl, *Electrochimica Acta*, (2010)

Electrolysis of water on oxide surfaces



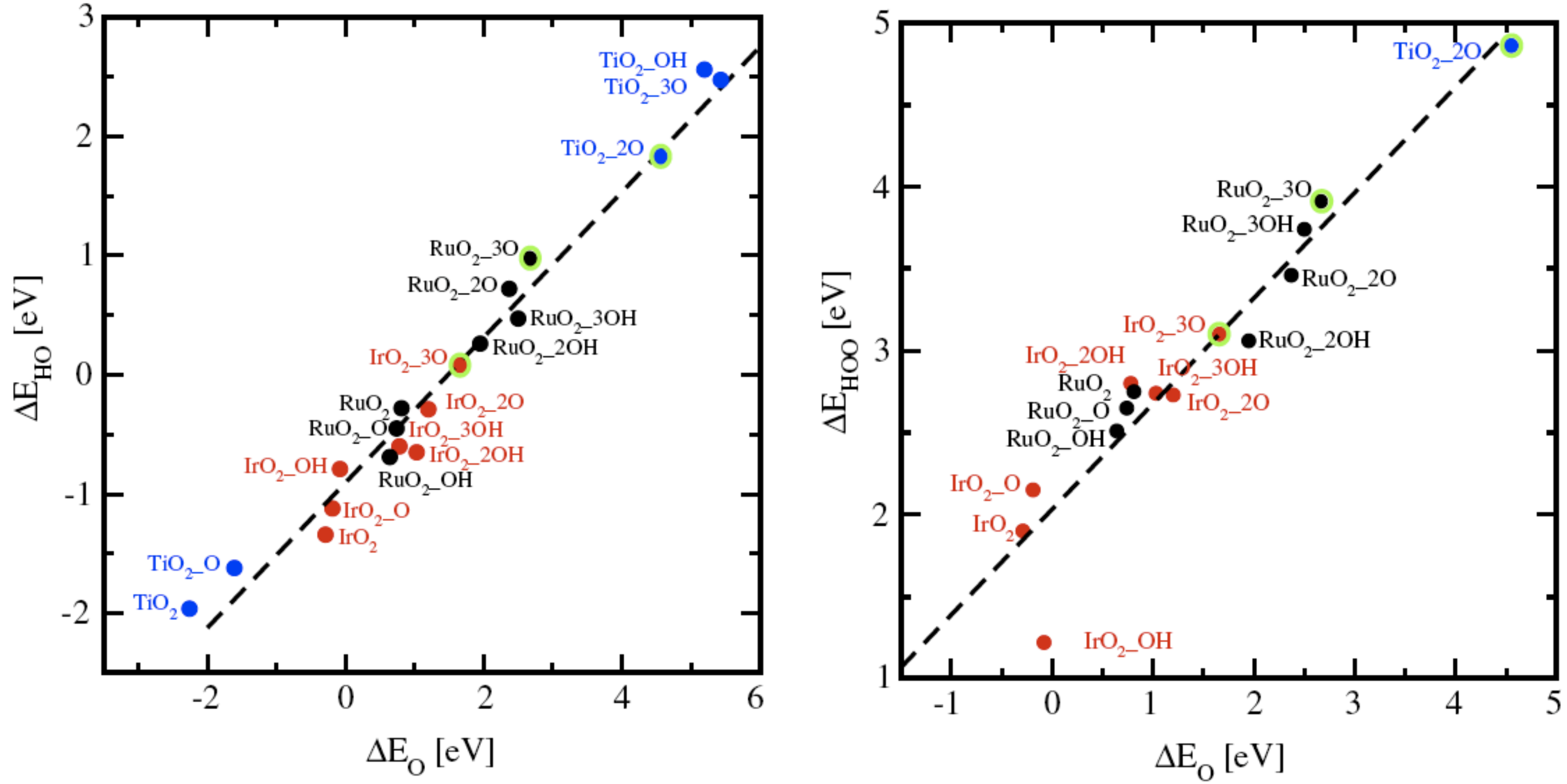


$+2H_2O(l)$	$+H_2O(l)+½H_2(g)$	$+H_2O(l)+H_2(g)$	$+3/2H_2(g)$	$+O_2(g)+ 2H_2(g)$
	ΔE_{HO}=0.47 eV	ΔE_{O}=2.50 eV	ΔE_{HOO}=3.74 eV	
ΔG_{water}=0.0 eV	ΔG_{HO}=0.82 eV	ΔG_{O}=2.55 eV	ΔG_{HOO}=4.14 eV	ΔG_{O2}=4.96 eV

J. Rossmeisl, Z.-W. Qu, H. Zhu, G.-J. Kroes, J.K. Nørskov, *J. Electroanalytical Chem.* (2007)

Electrolysis of water on oxide surfaces

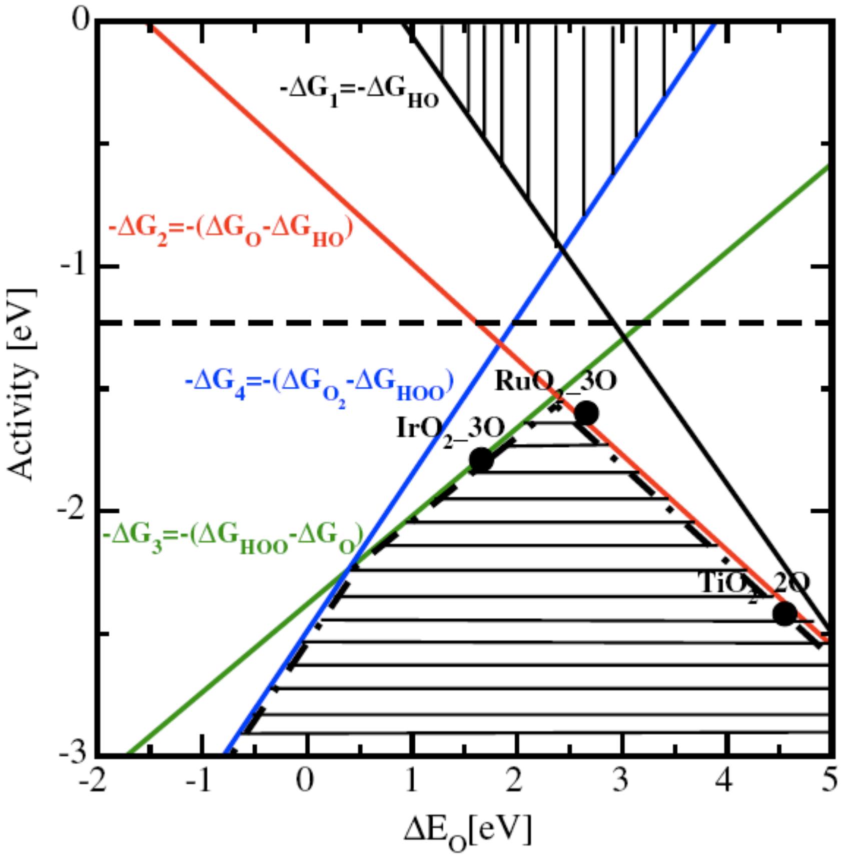
Binding energy of intermediate species are linearly correlated !



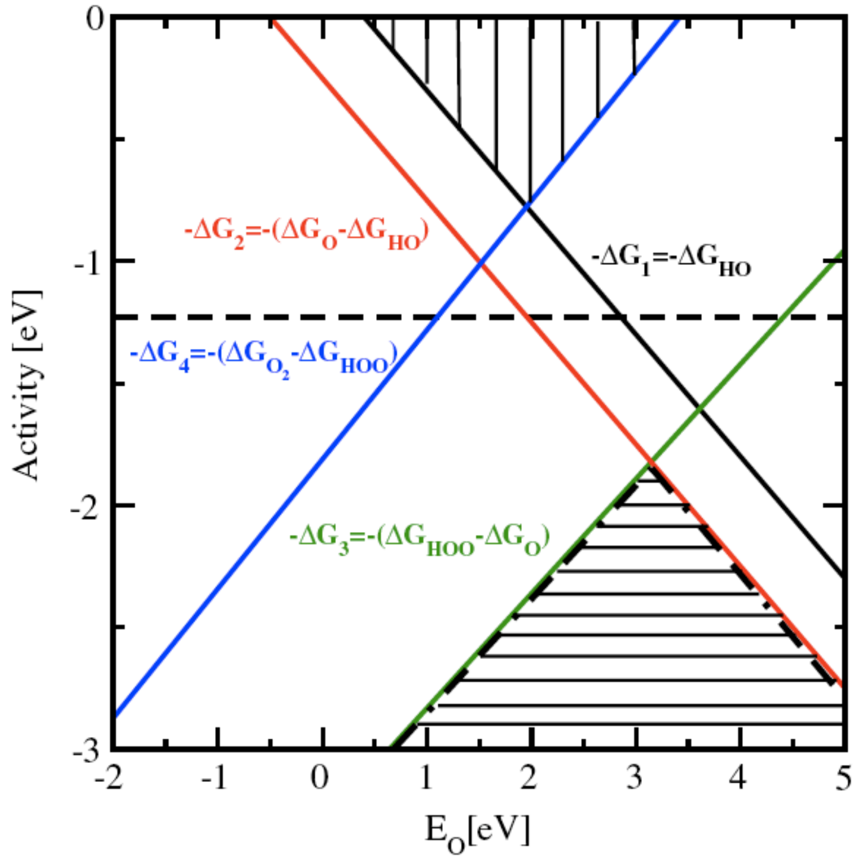
J. Rossmeisl, Z.-W. Qu, H. Zhu, G.-J. Kroes, J.K. Nørskov, *J. Electroanalytical Chem.* (2007)

Electrolysis of water on oxide surfaces

Oxides



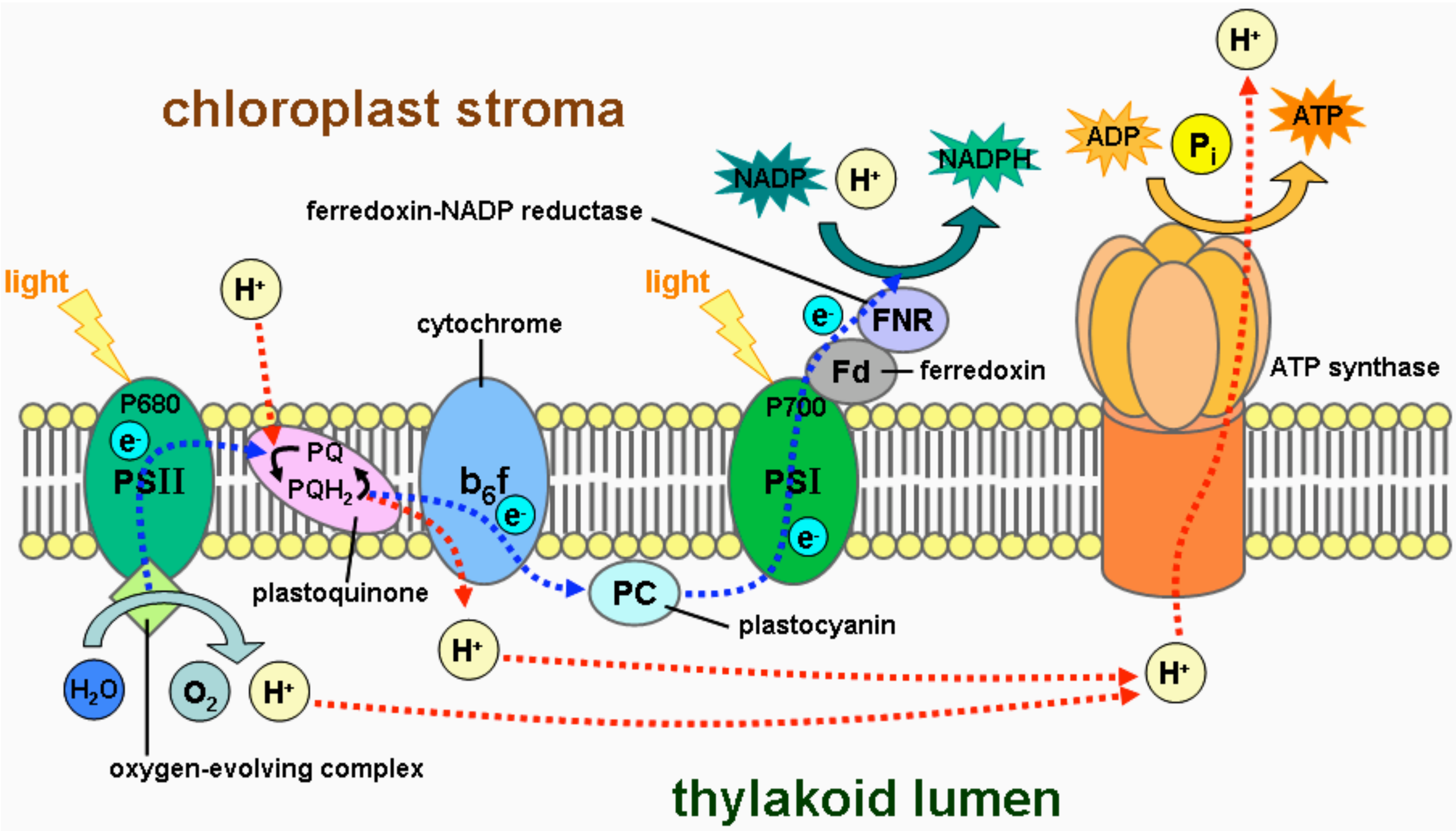
Pure metals



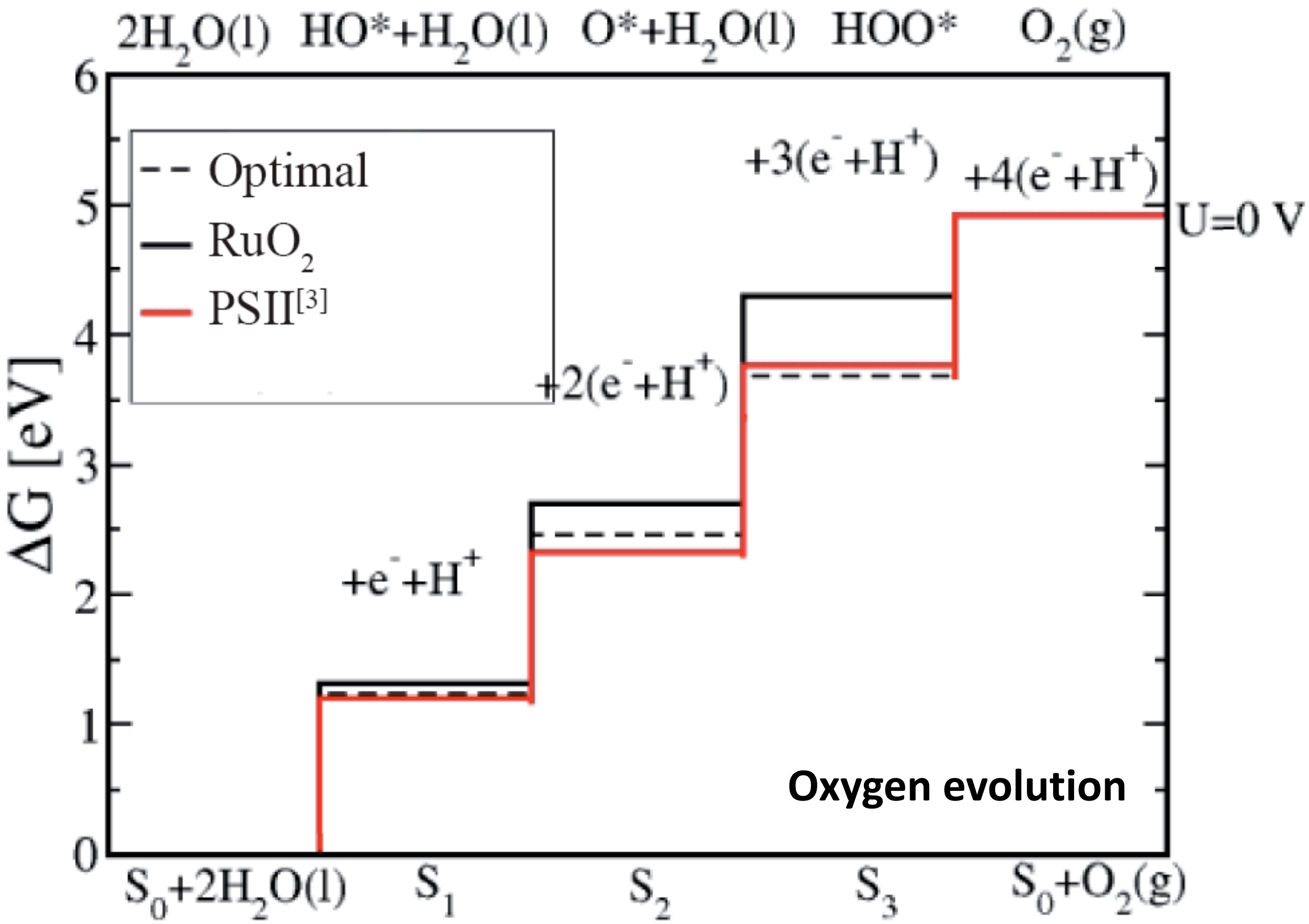
The oxide surfaces are much more active than the pure metals towards evolving oxygen

J. Rossmeisl, Z.-W. Qu, H. Zhu, G.-J. Kroes, J.K. Nørskov, *J. Electroanalytical Chem.* (2007)

Oxygen evolution in plants



Nothing beats Nature !



J. Rossmeisl, K. Dimitrievsky, P. Siegbahn, J. K. Nørskov; *J. Phys. Chem. C* (2007)