Catalytic hydrogen production

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Hydrogen production strategies

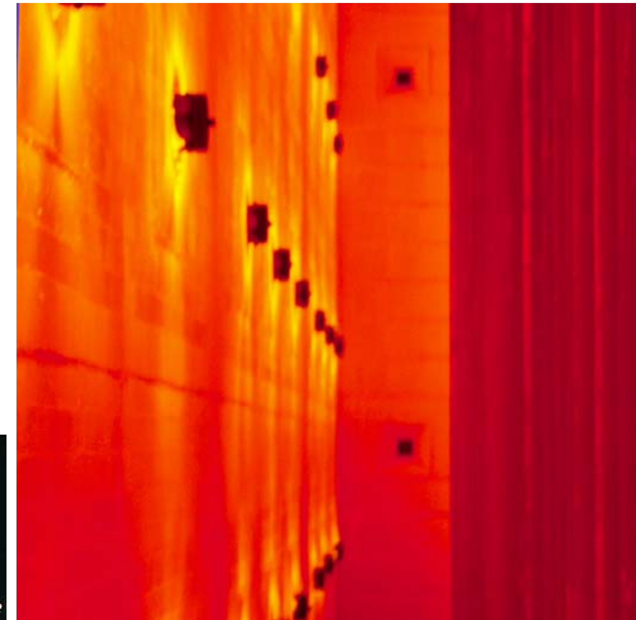
- Reforming of hydrocarbons
- Reforming of biomass
- Electrolysis
- Photolytic conversion
- Biological conversion
- …..

Steam reforming

$CH_4 + H_2O \rightarrow 3H_2 + CO$

$\Delta H = +206$ kJ/mol

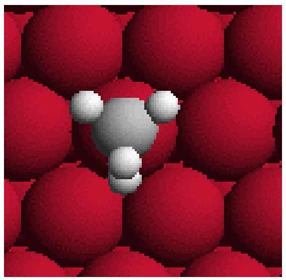
Ni catalyst



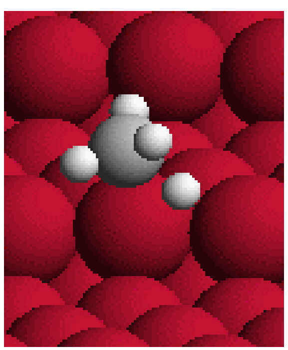
Rostrup-Nielsen, Sehested, Nørskov
Adv. Catal. 47, 65 (2002)

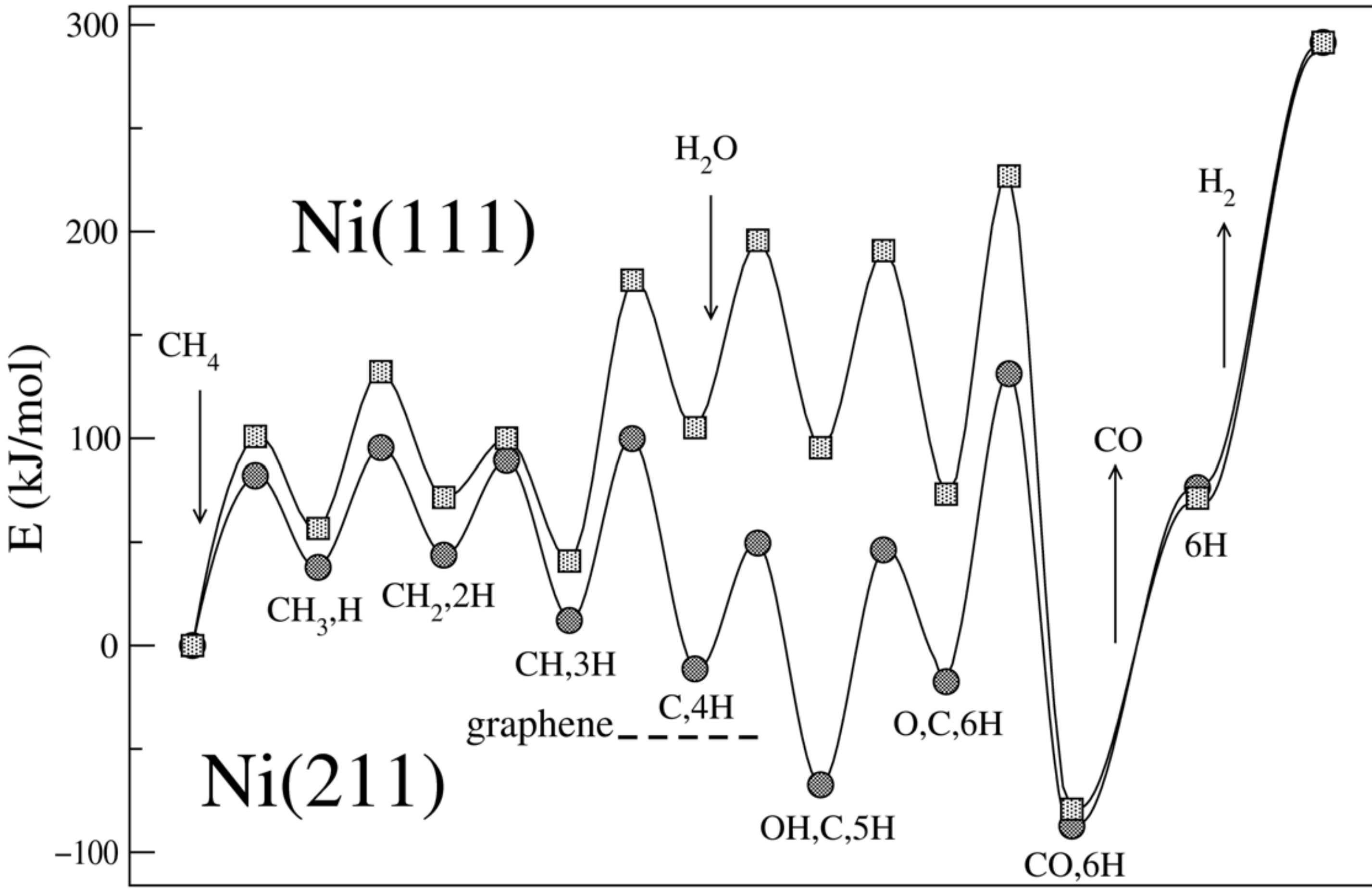
The atomic-scale picture

Ni(111)



Ni(211)

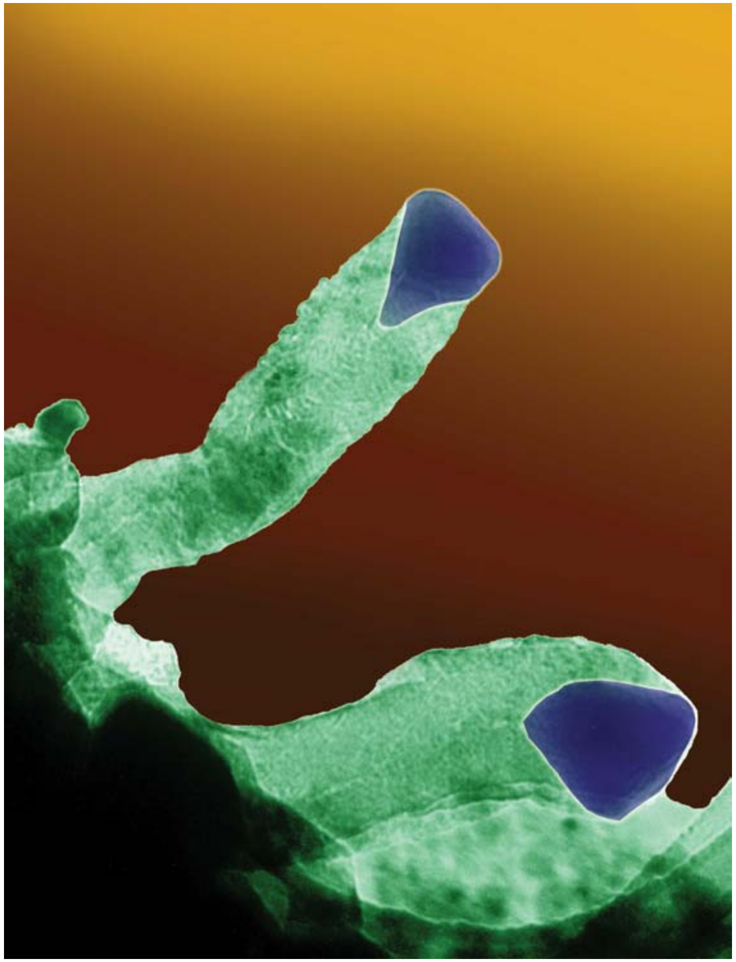




Bengaard, Nørskov, Sehested, Clausen, Nielsen, Molenbroek, Rostrup-Nielsen: J. Catal. **209**, 365 (2002)

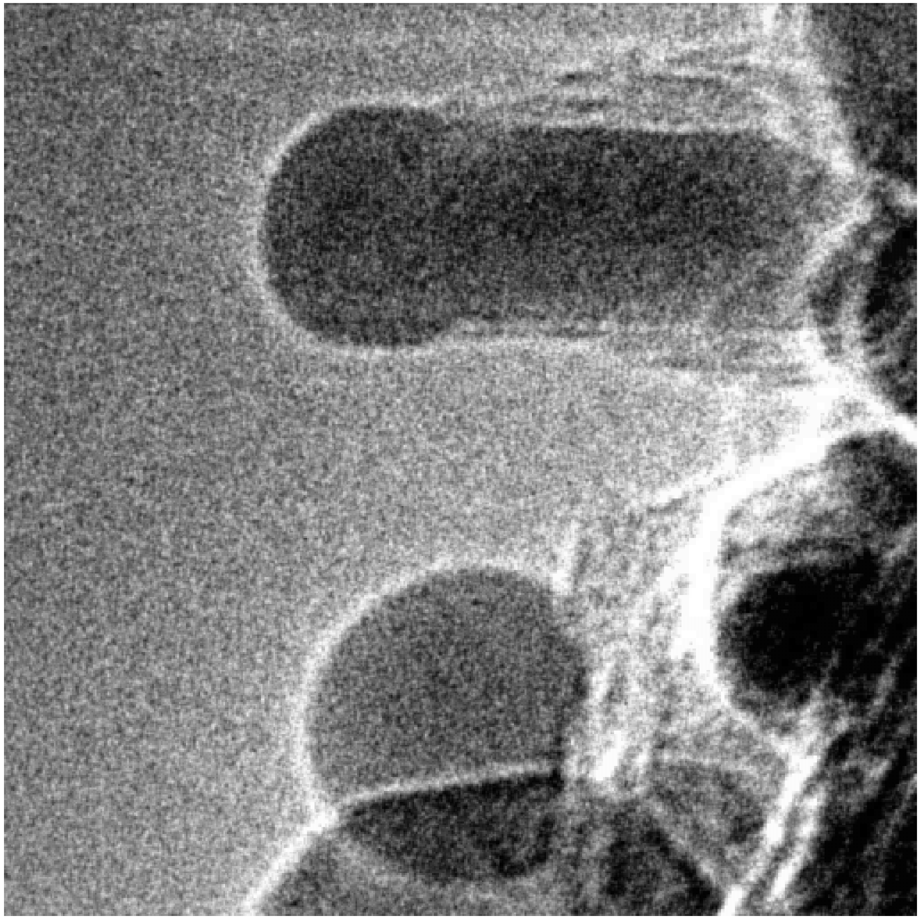
Problems

1. Carbon formation
2. Metal dusting
3. Too much CO



Formation of Carbon Nano-fibers

In situ (high temperature and pressure) Transmission Electron Microscopy (TEM)

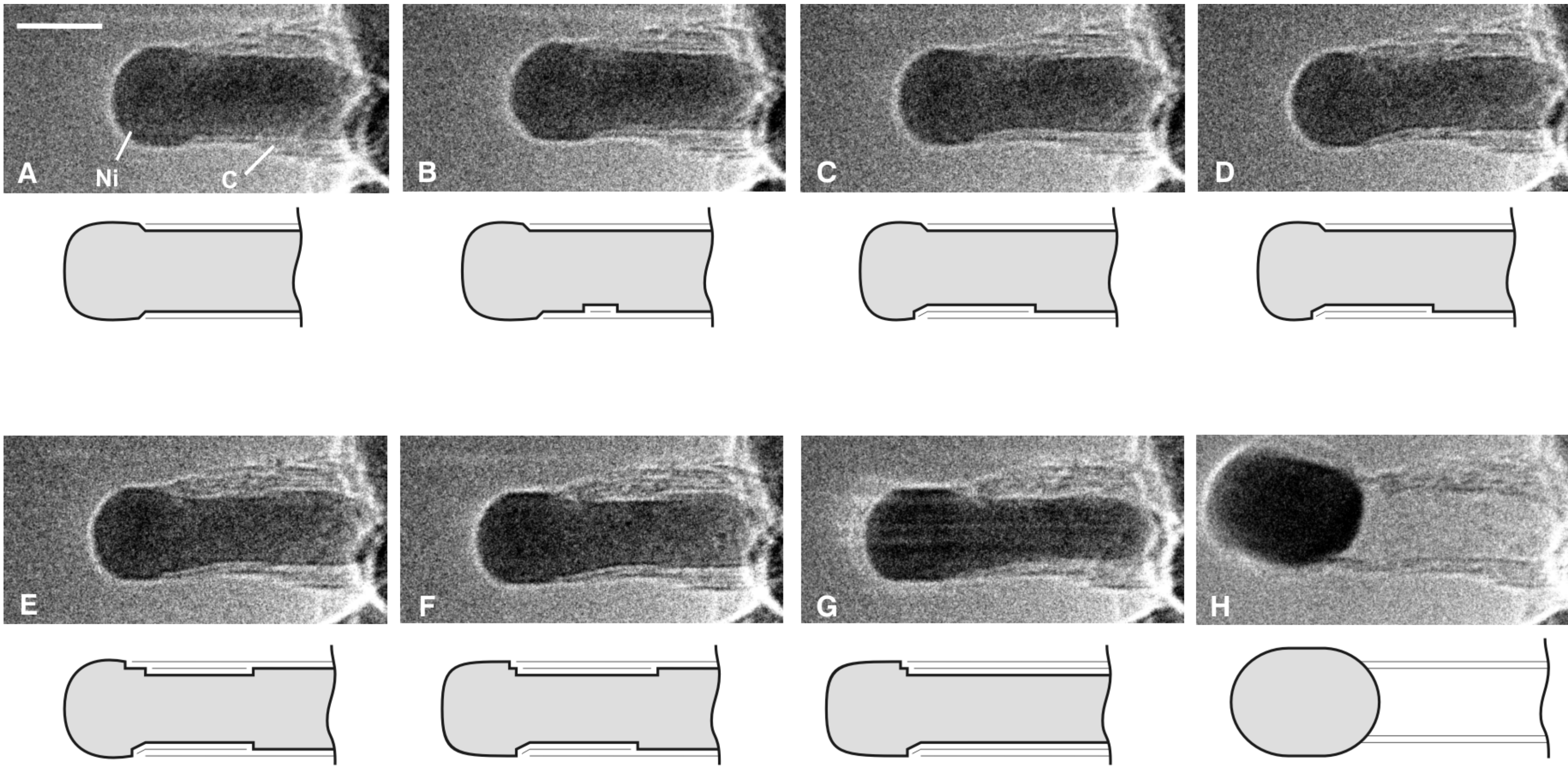


The movies:

http://www.haldortopsoe.com/site.nsf/all/EOTT-5VTMPT?OpenDocument

Helveg, Cartes, Sehested, Hansen, Clausen, Rostrup-Nielsen, Abild-Pedersen, Nørskov
Nature **327**, 426 (2004)

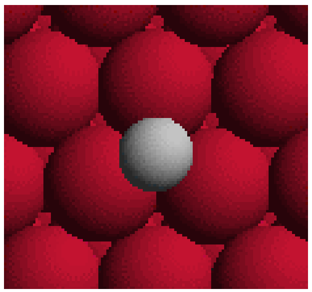
The role of steps



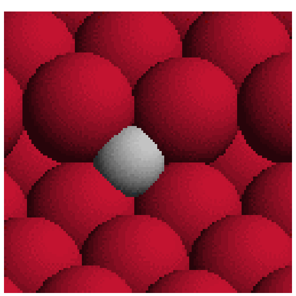
Helveg, Cartes, Sehested, Hansen, Clausen, Rostrup-Nielsen, Abild-Pedersen, Nørskov
Nature **327**, 426 (2004)

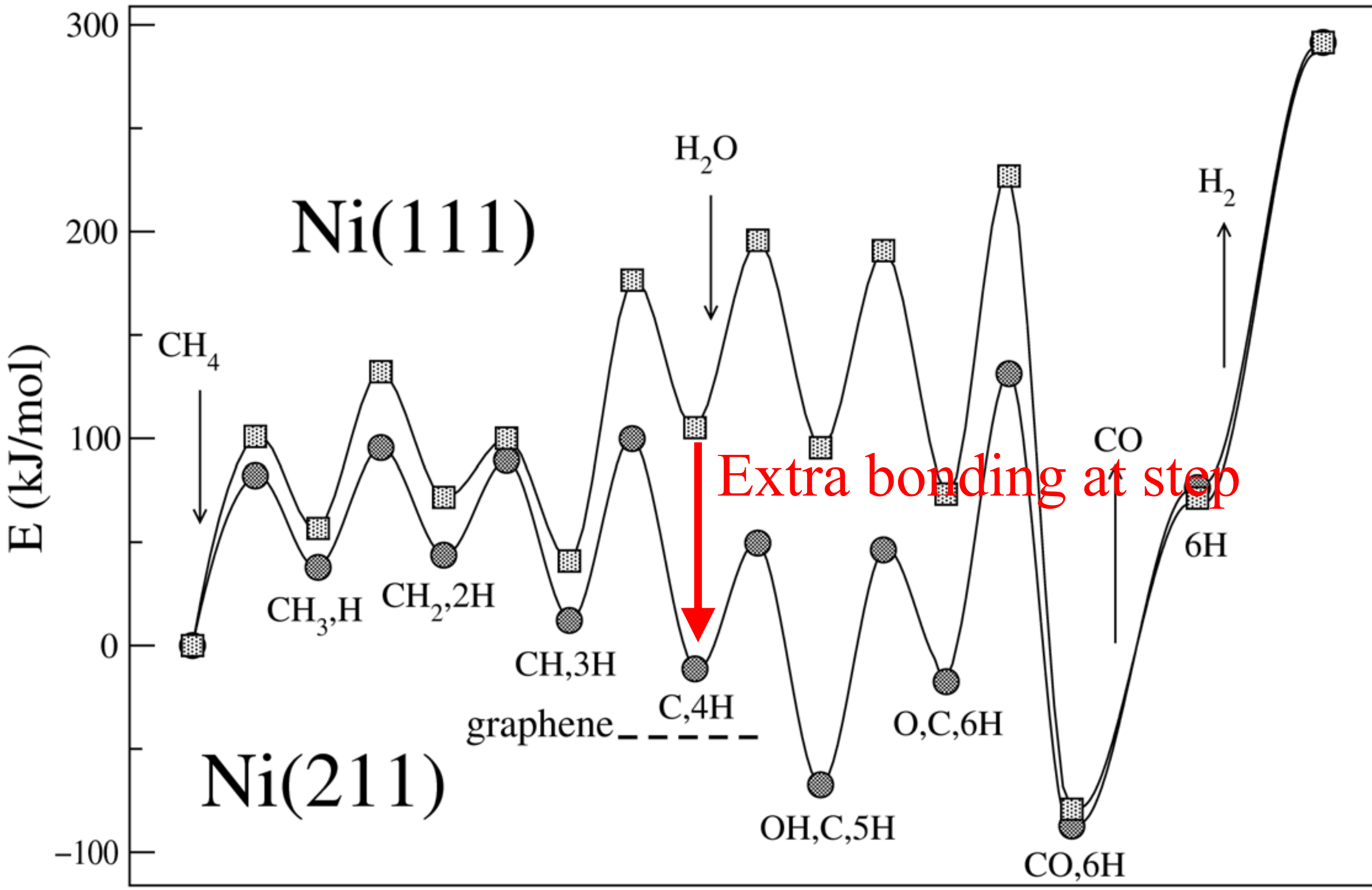
Carbon nucleation at steps

Ni(111)



Ni(211)

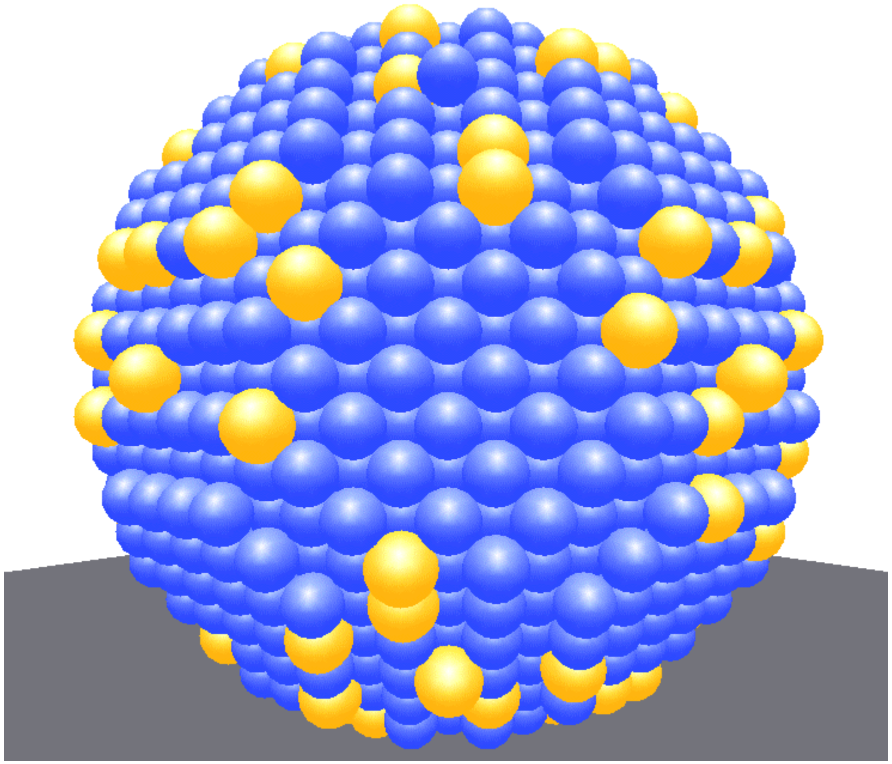




Bengaard, Nørskov, Sehested, Clausen, Nielsen, Molenbroek, Rostrup-Nielsen: J. Catal. **209**, 365 (2002)

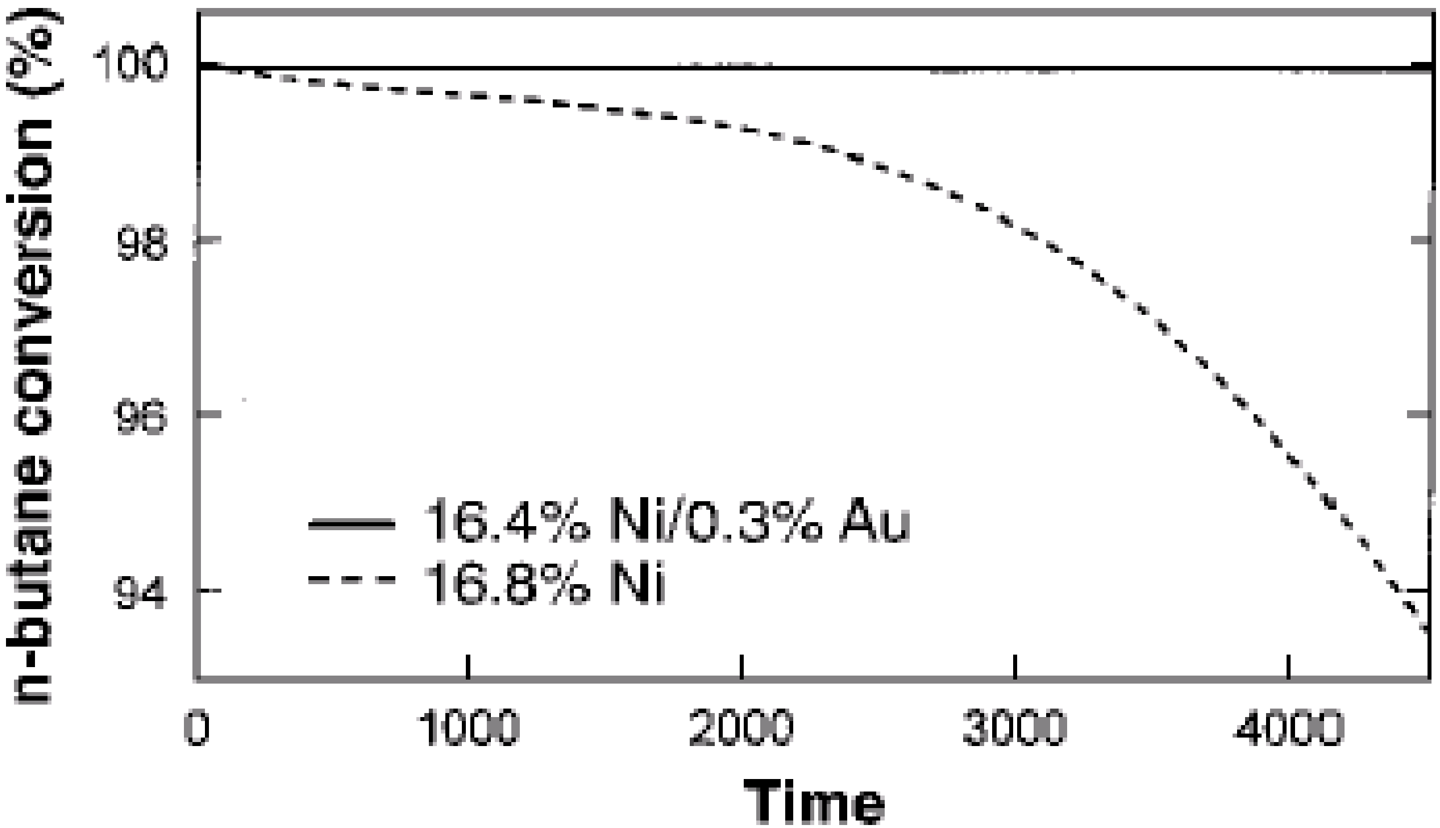
Step blocking

MD simulation – Au/Ni



Molenbroek, Nørskov, Clausen
J. Phys. Chem. B **105**, 5450 (2001)

Catalyst design at the nano-scale



Besenbacher, Chorkendorff, Clausen, Hammer, Molenbroek, Nørskov, Stensgaard, Science **279**, 1913 (1998)

Too much CO

CO is a product:

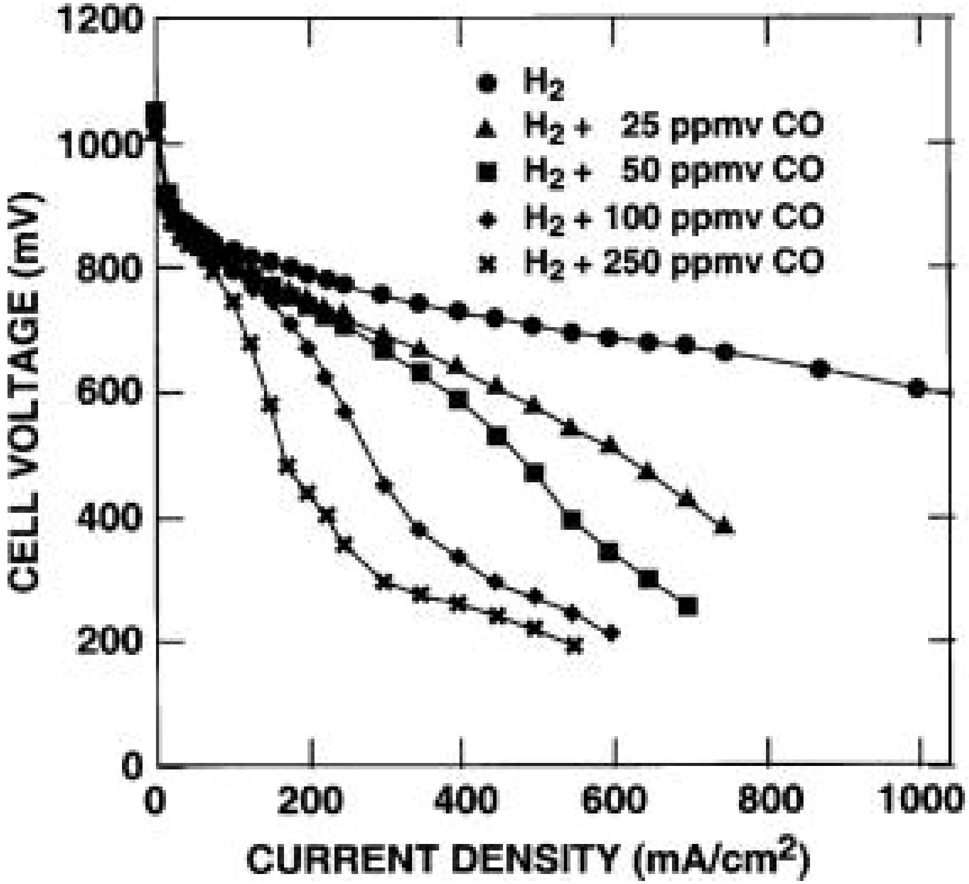
$CH_4+H_2O \rightarrow 3H_2+CO$

Possible solutions:

- Make fuel cell less CO poisoned

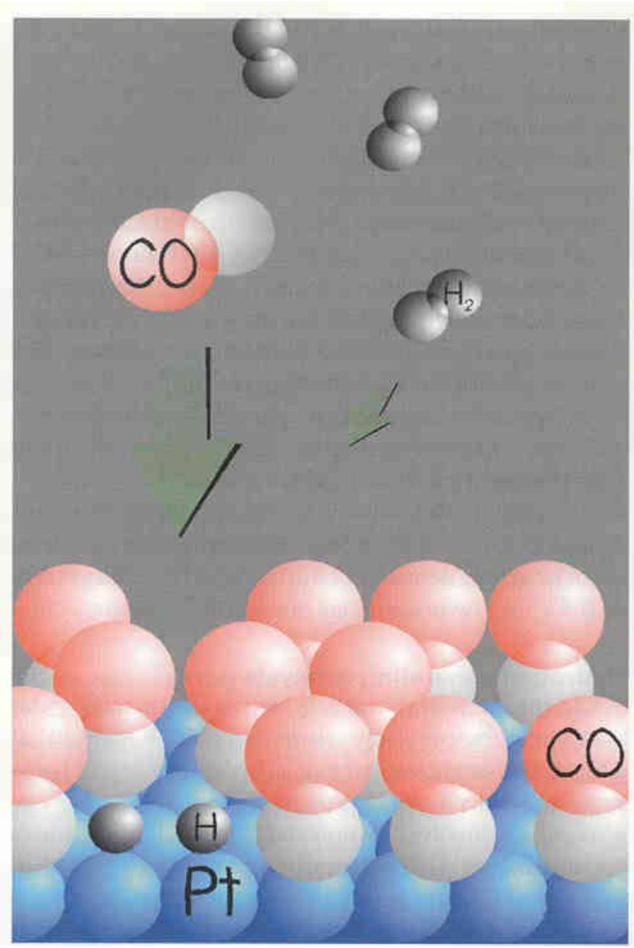
- Remove CO

CO poisons PEM fuel cell:

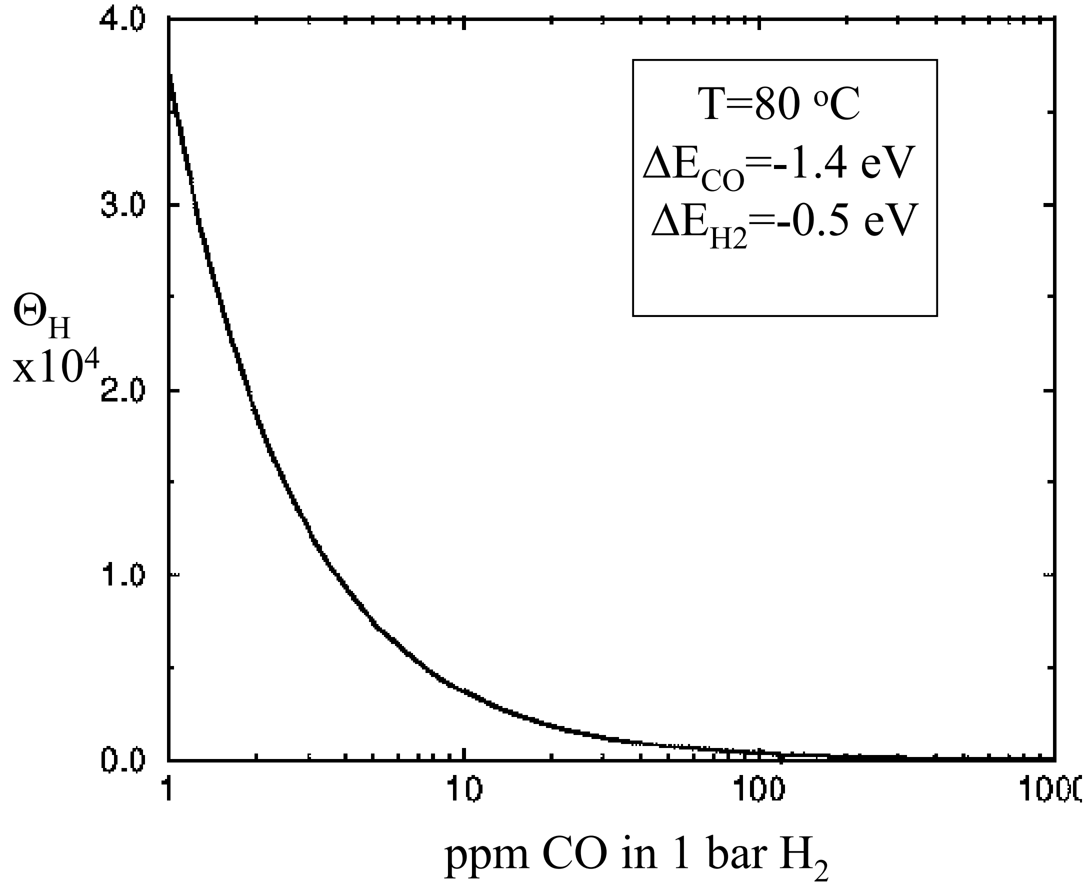


S. Gottesfeld et al., J. Electrochem. Soc. **148** (2001) A11.

CO blocks for hydrogen adsorption at the anode



H coverage in the presence of CO:

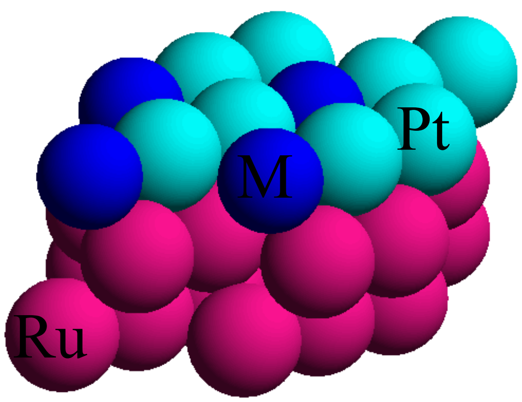


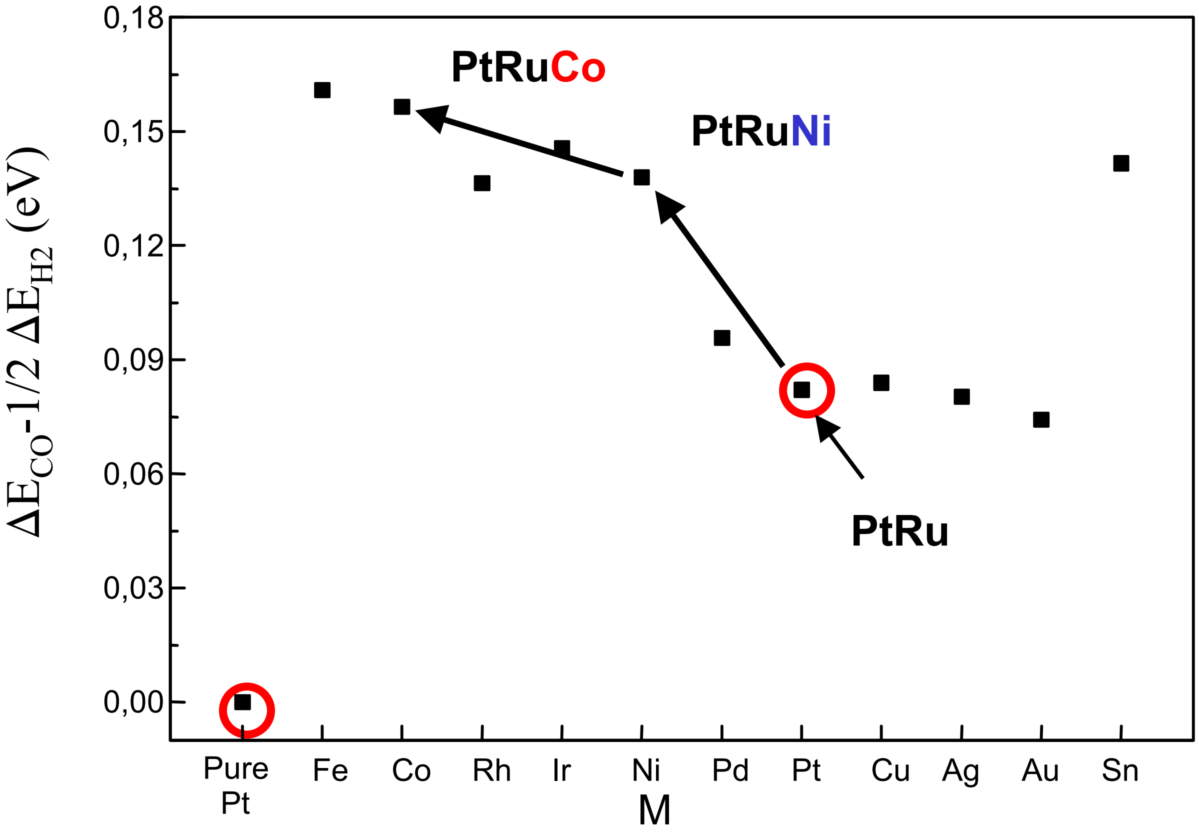
Christoffersen, Liu, Ruban, Skriver, Nørskov: J.Catal. **199**, 123 (2001)

New 3-component alloys from DFT

Measure of competition
Between CO and H:

ΔE_{CO}-1/2 ΔE_{H2}





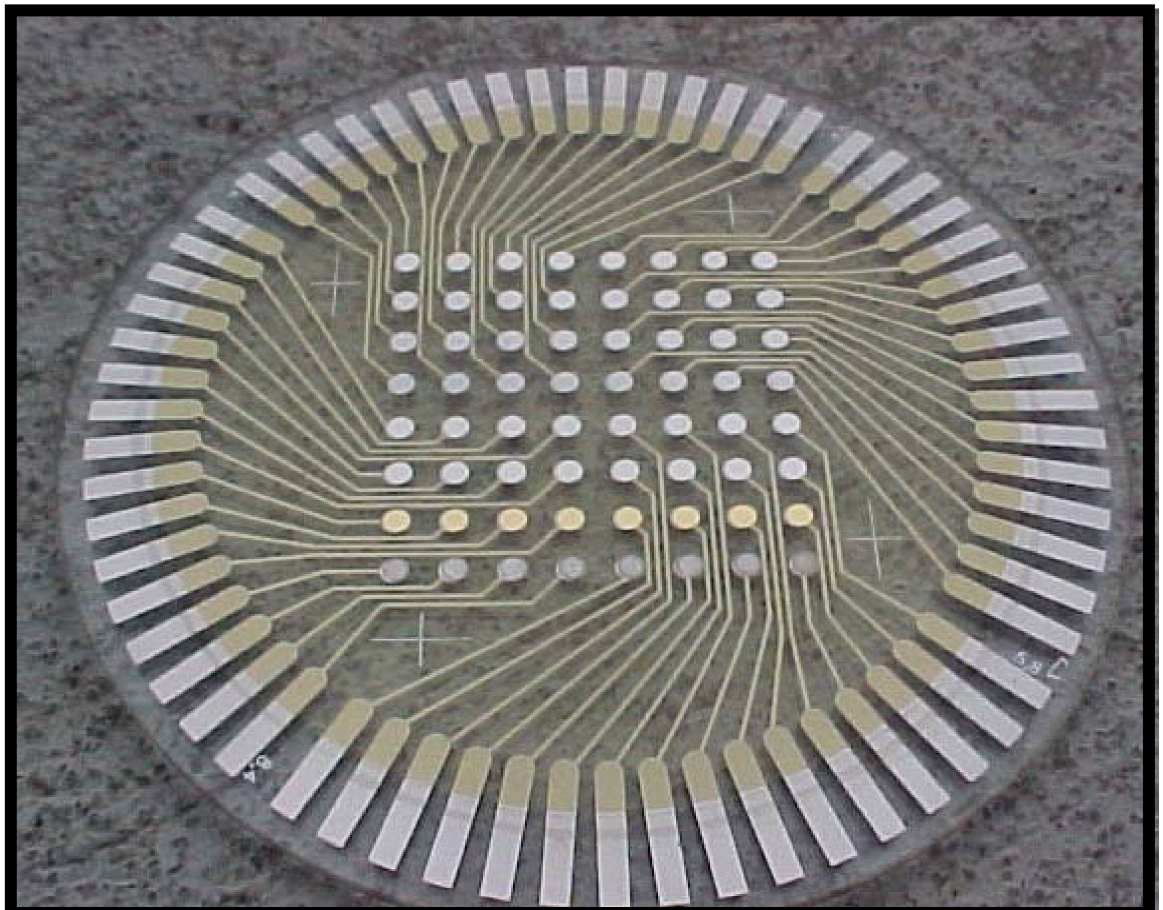
Strasser, Fan, Devenney, Weinberg, Liu , Nørskov, J. Phys. Chem.B, **107**, 11013 (2003)

Combinatorial Electrochemistry

Electrochemical Multi-electrode array

64 addressable electrodes

Photolitographic Fabrication

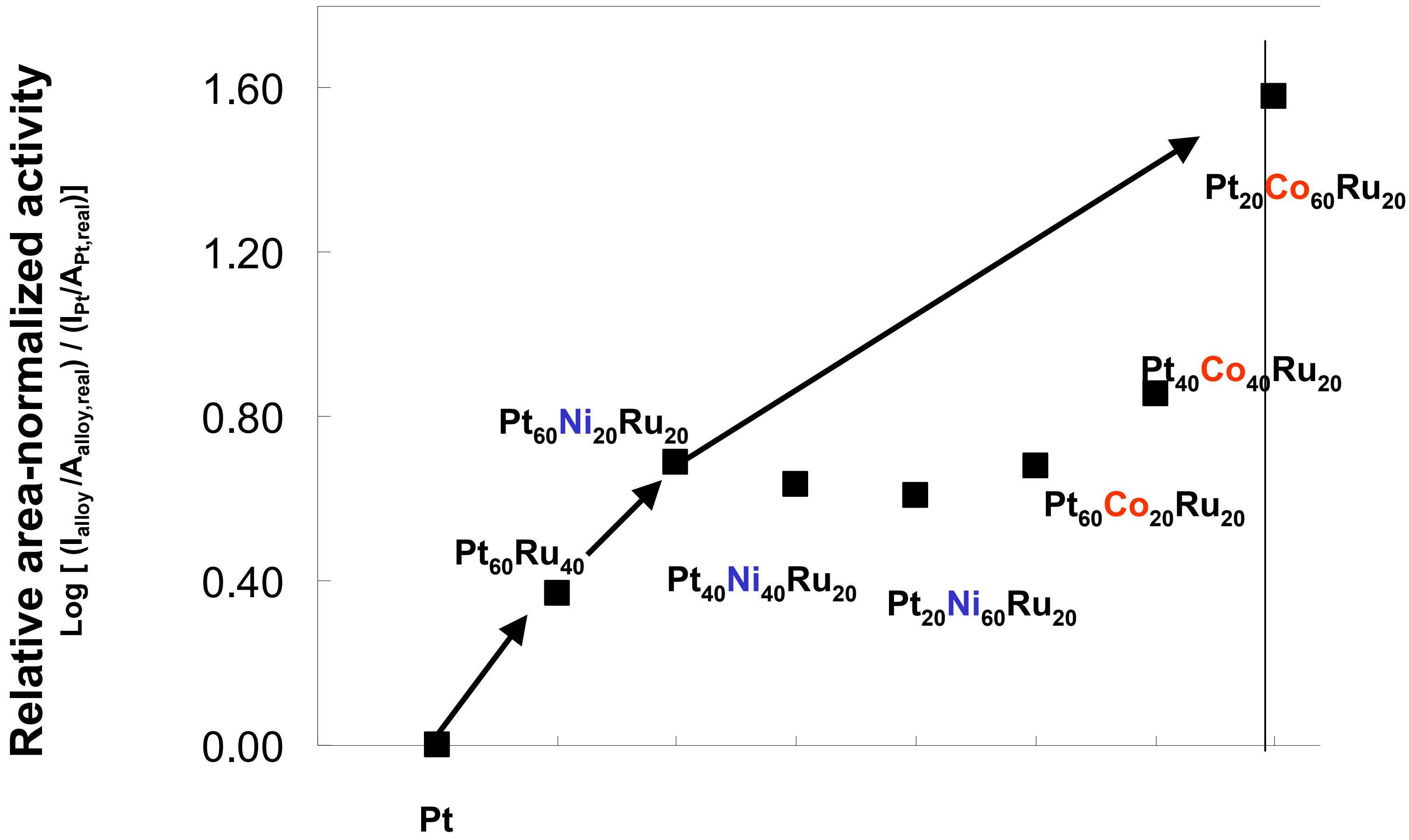


Symyx Technologies proprietary

US Patent No 6,187,164; 5,985,356; 6,004,617.
Additional US and foreign patents pending

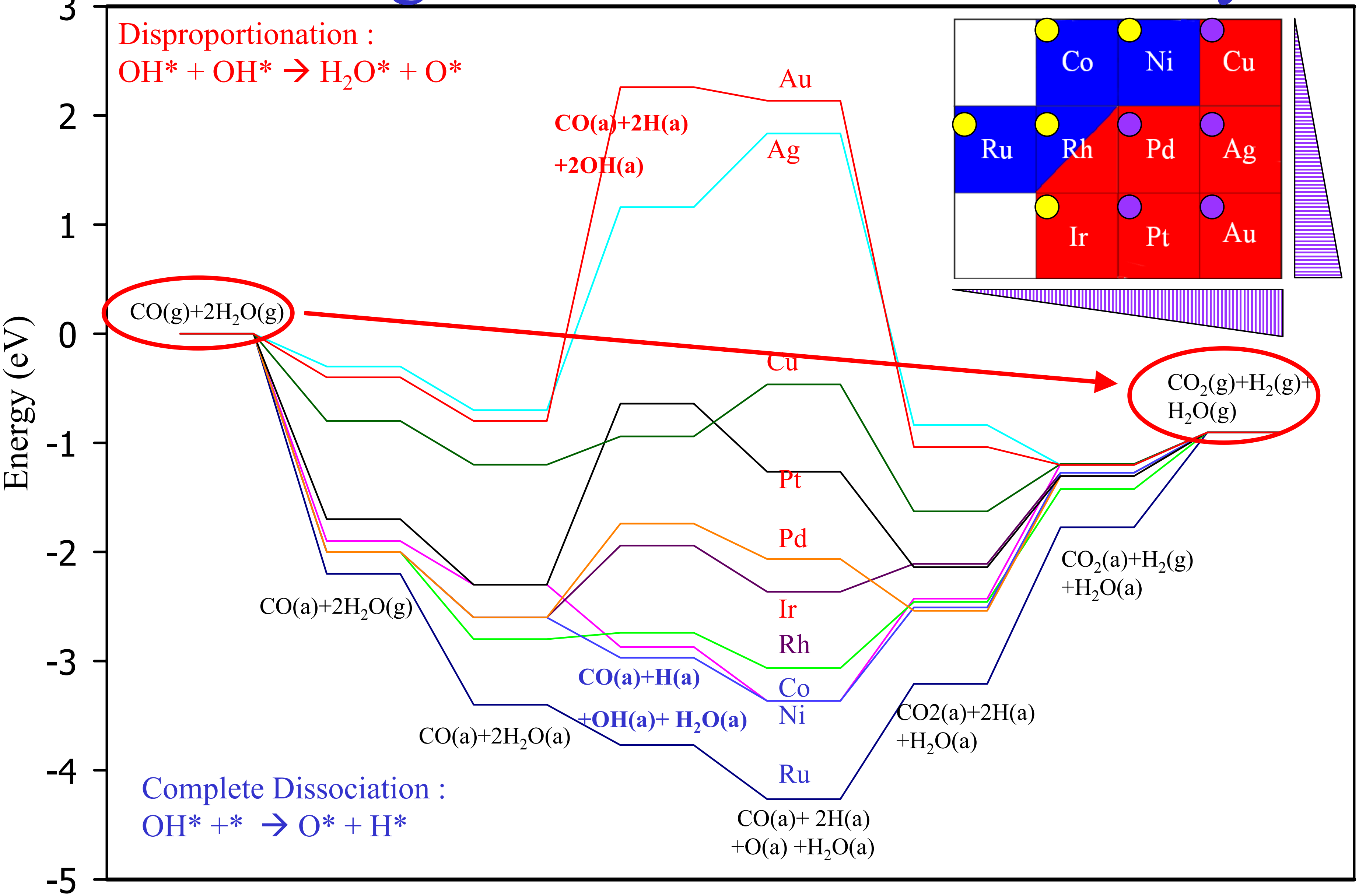
Results from parallel screening experiments

Strasser, Fan, Devenney, Weinberg
Symyx Technologies



Strasser, Fan, Devenney, Weinberg, Liu, Nørskov *J. Phys. Chem.B* **107**, 11013 (2003)

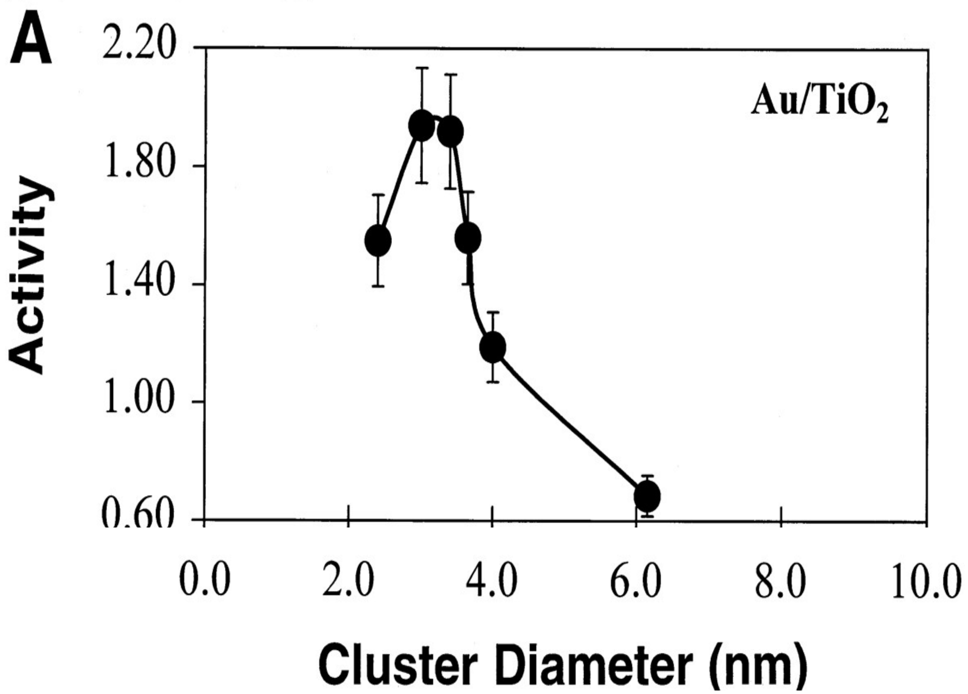
Water gas shift: Thermochemistry



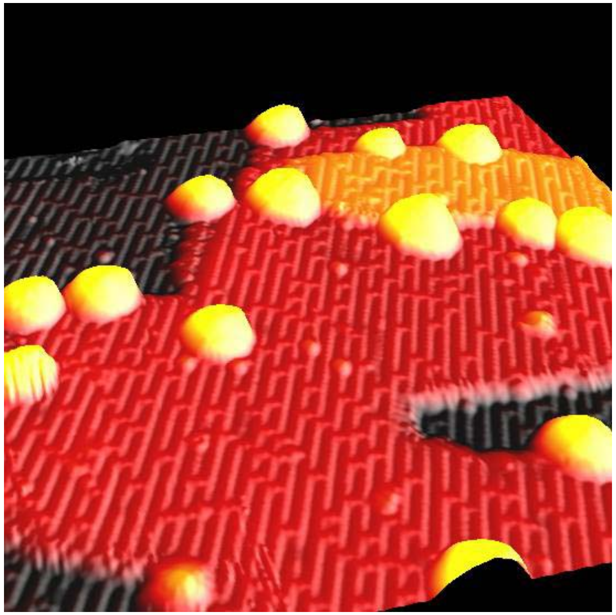
Courtesy of M. Mavrikakis – UW Madison

Nano effects in catalysis

CO oxidation on Au particles supported on TiO_2



Valden, Lai, Goodman,
Science **281**, 1647 (1998)

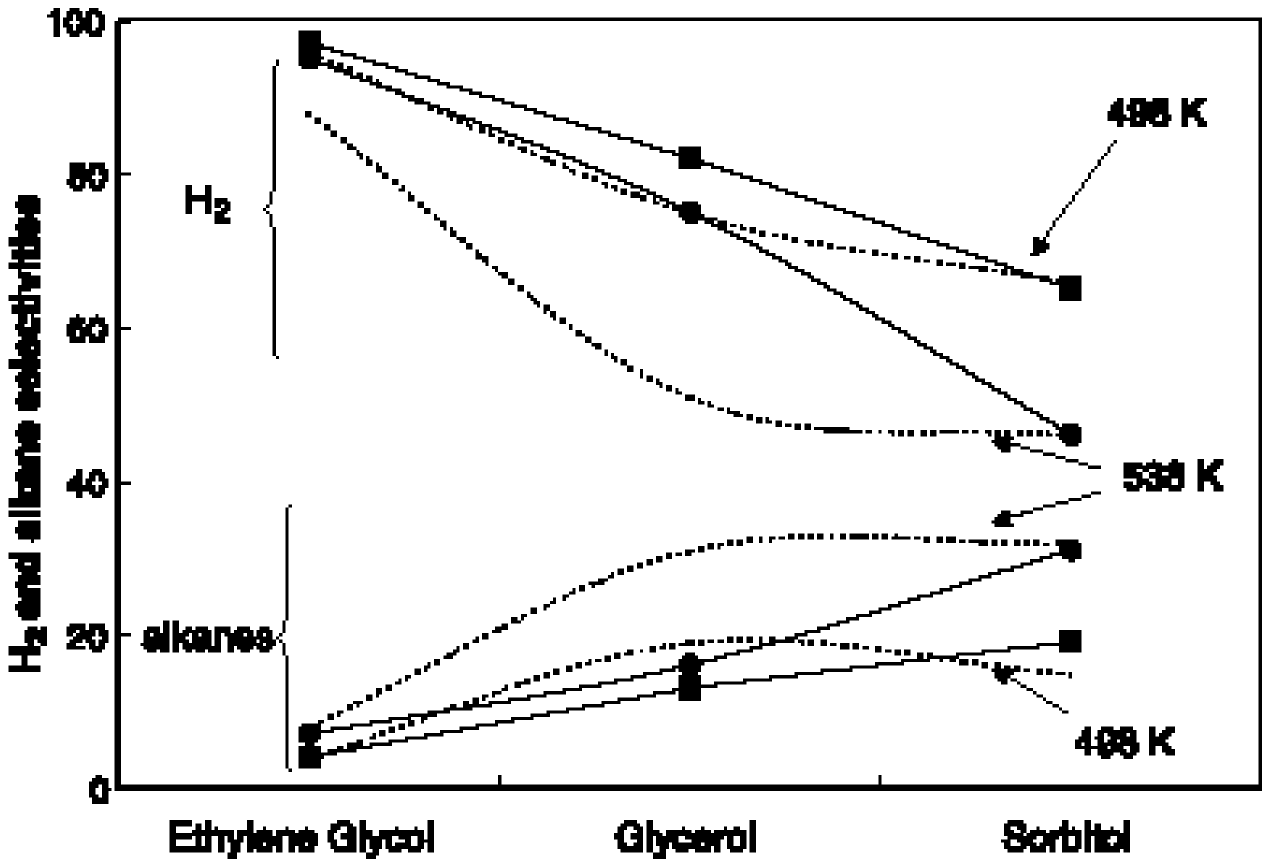


Wahlström, Lopez, Schaub, Thostrup,
Rønnau, Africh, Lægsgaard, Nørskov,
Besenbacher, PRL **90**, 026101 (2003)

No generally accepted explanation yet!

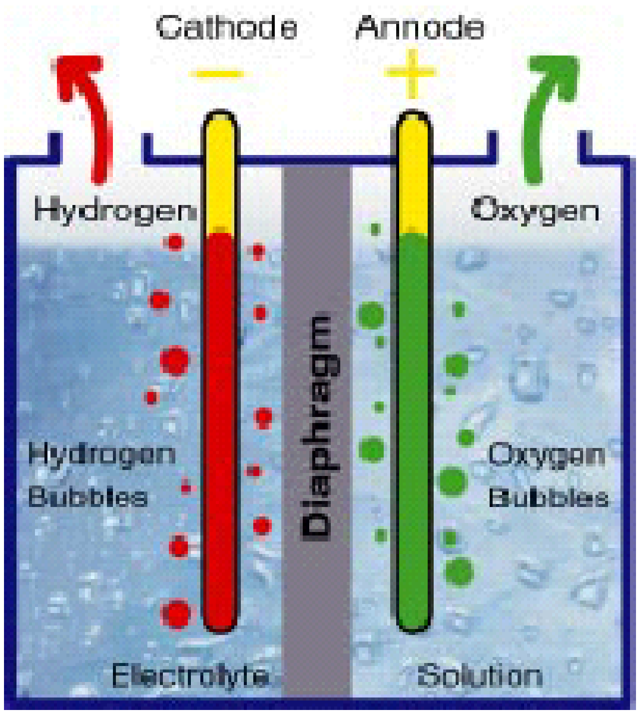
Reforming of biomass

Reforming of oxygenated hydrocarbons over Raney-NiSn.



Huber, Shabaker, Dumesic, *Science* **300**, 2075–2077 (2003).

Electrolysis



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

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

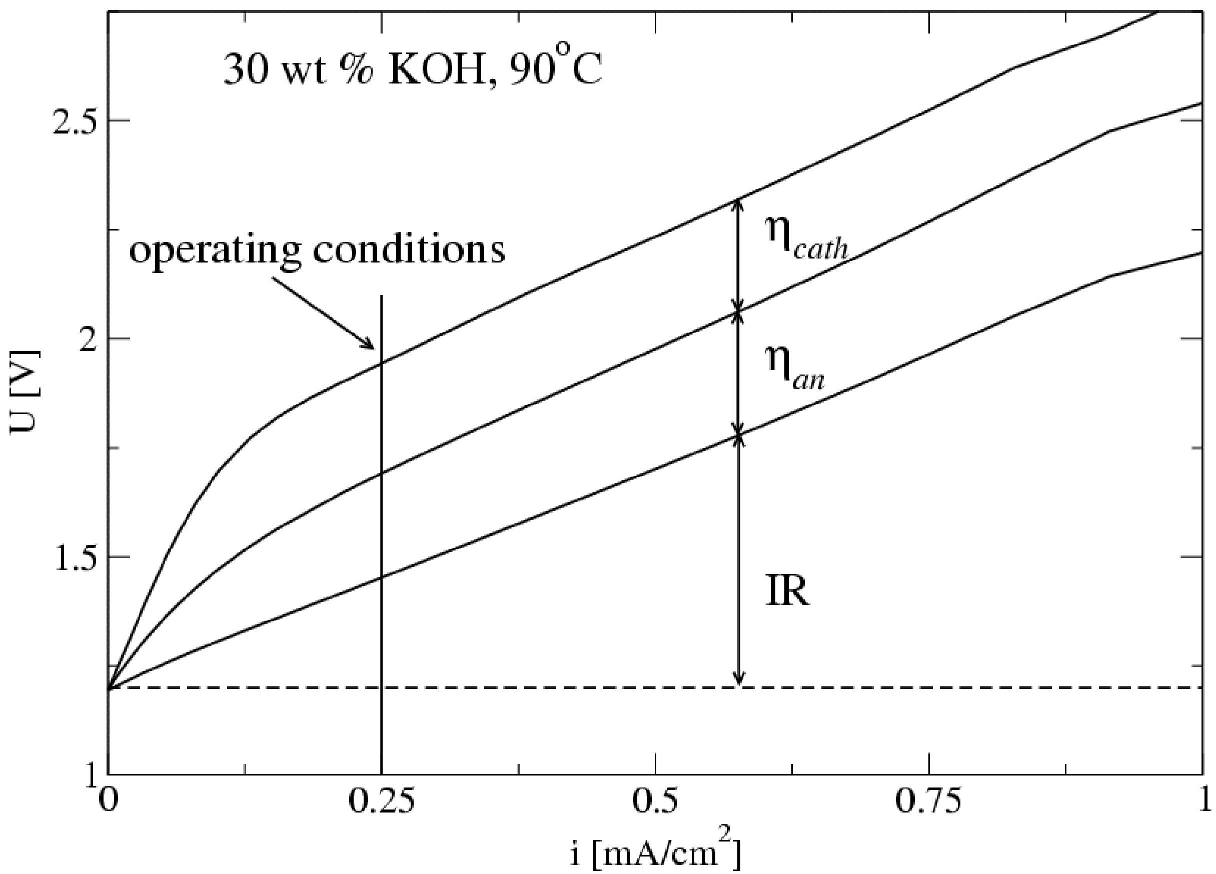
Total: $H_2O \rightarrow \frac{1}{2} O_2 + H_2$

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

The overpotential

Ni-based electrolyzer:

$$U = U_0 + \eta_{cathode} + \eta_{anode} + I\,R$$

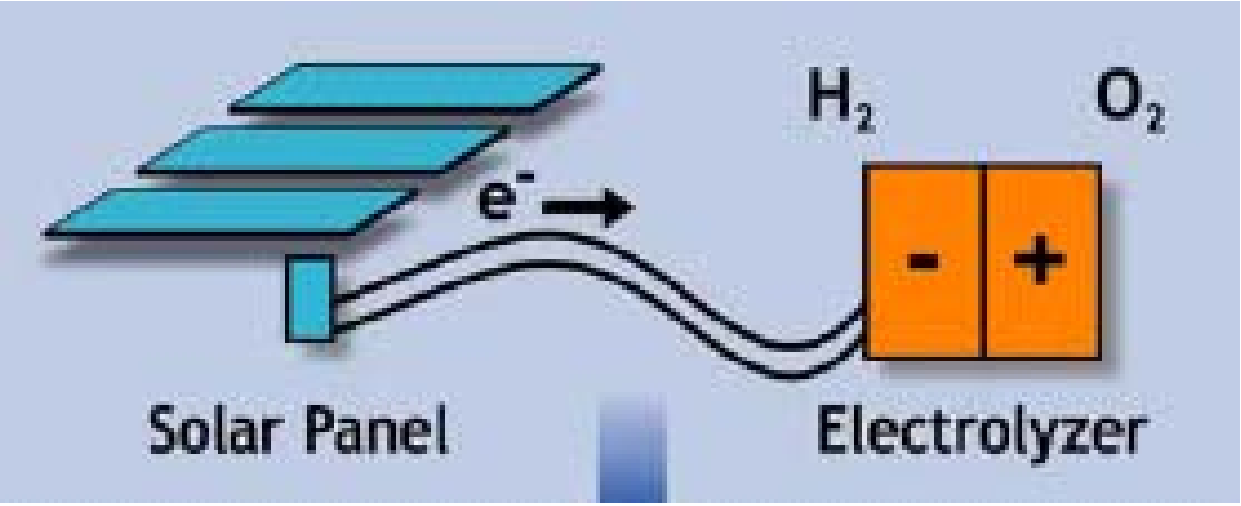


Efficiency:

$$\frac{U_0}{U(i)} \sim \frac{1.23\,V}{1.9\,V} \sim 65\%$$

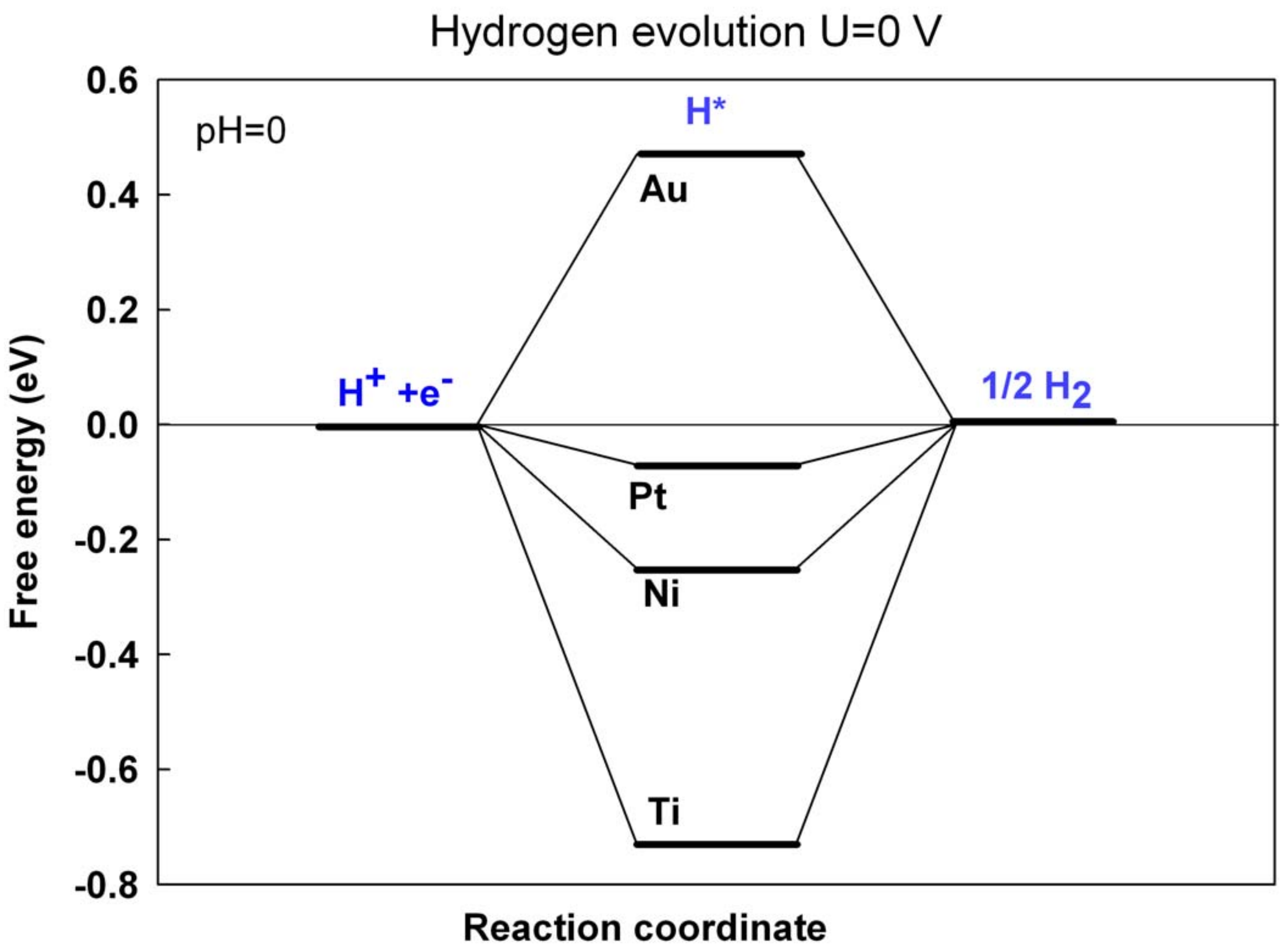
Wendt, Imarisio, J. Appl. Electrochem. **17**, 1 (1988)

Photovoltaics+electrolyzer



12% x 65% = 7.8%

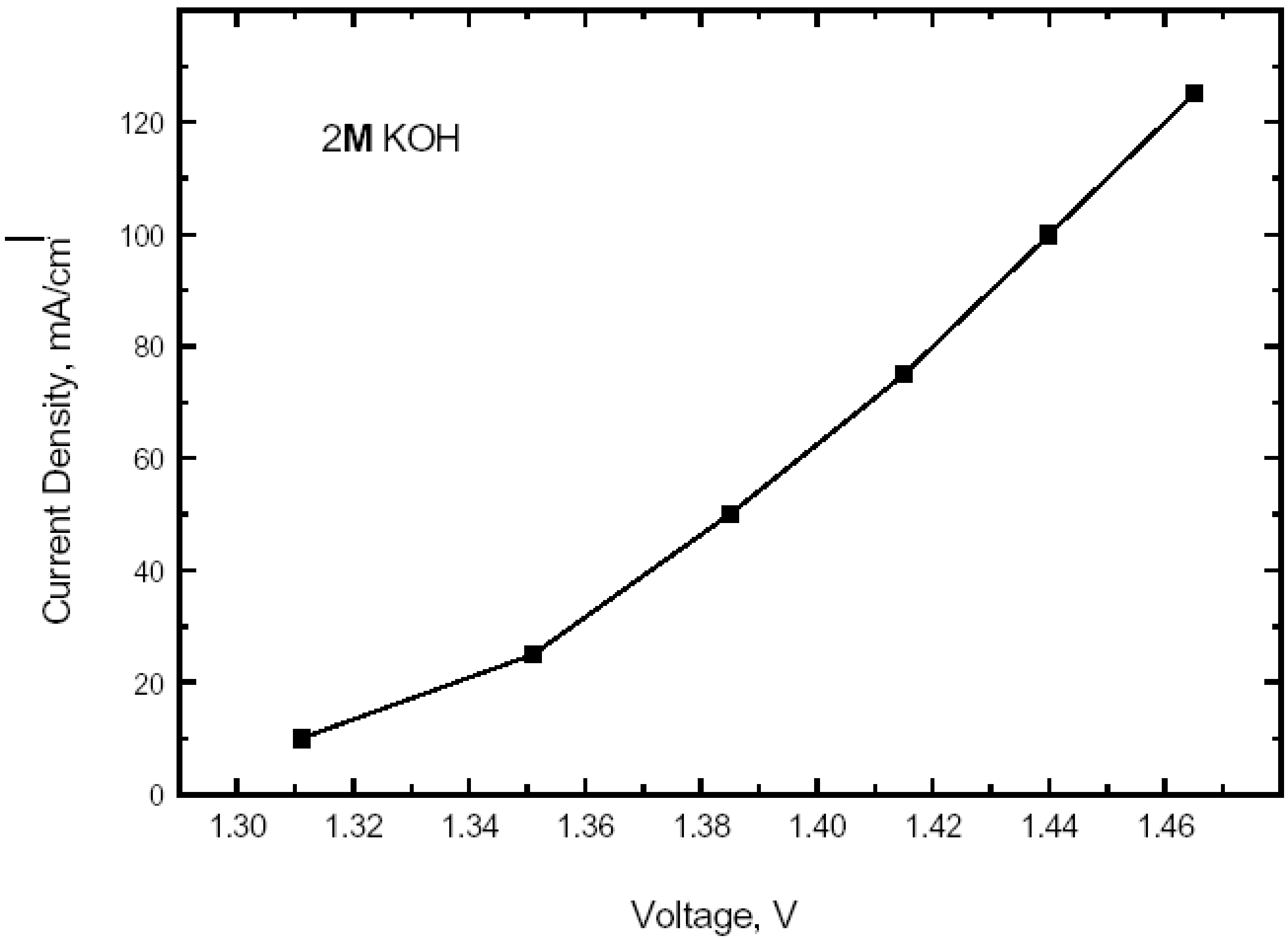
The origin of the overpotential



Even larger barriers at the anode!

Kitchin, Bligaard, Stimming, Nørskov

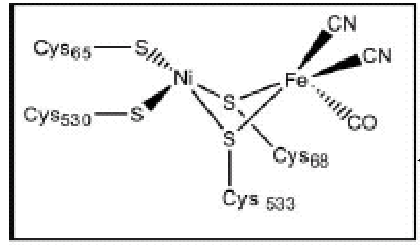
A Pt/Pt cell



Khaselev, Bansal, Turner, Int. J. Hydrogen Energy **26**, 127 (2001)

Biomimetic hydrogen production

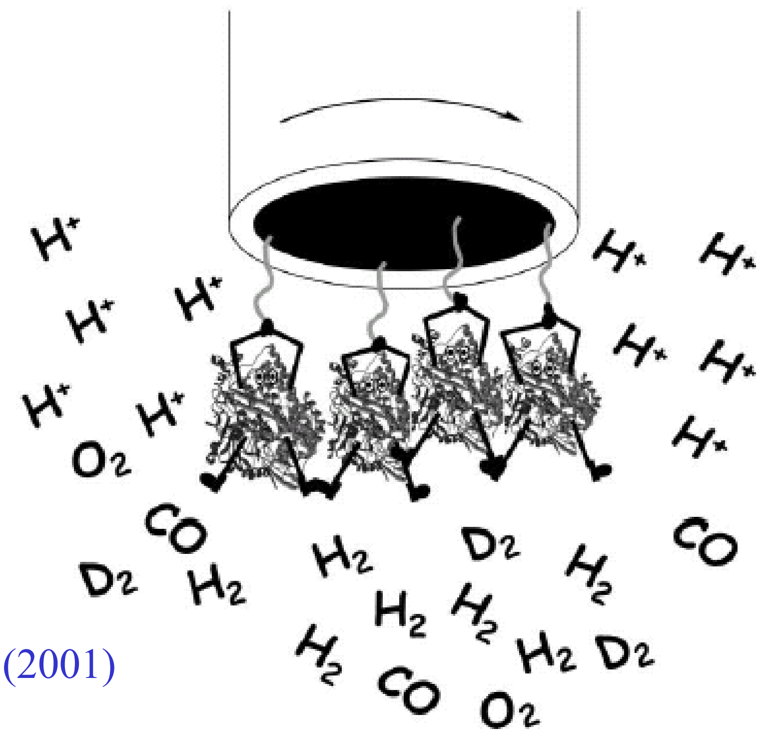
Hydrogenase catalyses



The active site

$H^{+} + e^{-} \rightarrow \frac{1}{2}H_2$

Add active site to electrode?



Or make structure with

similar properties?

Gloaguen, Lawrence, Rauchfuss, JACS 123, 9476 (2001)

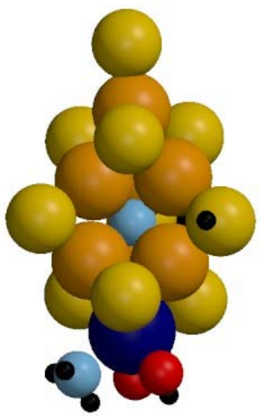
Siegbahn, Blomberg, Wirstam, Crabtree
J. Biological Inorganic Chemistry. 6, 460 (2001)

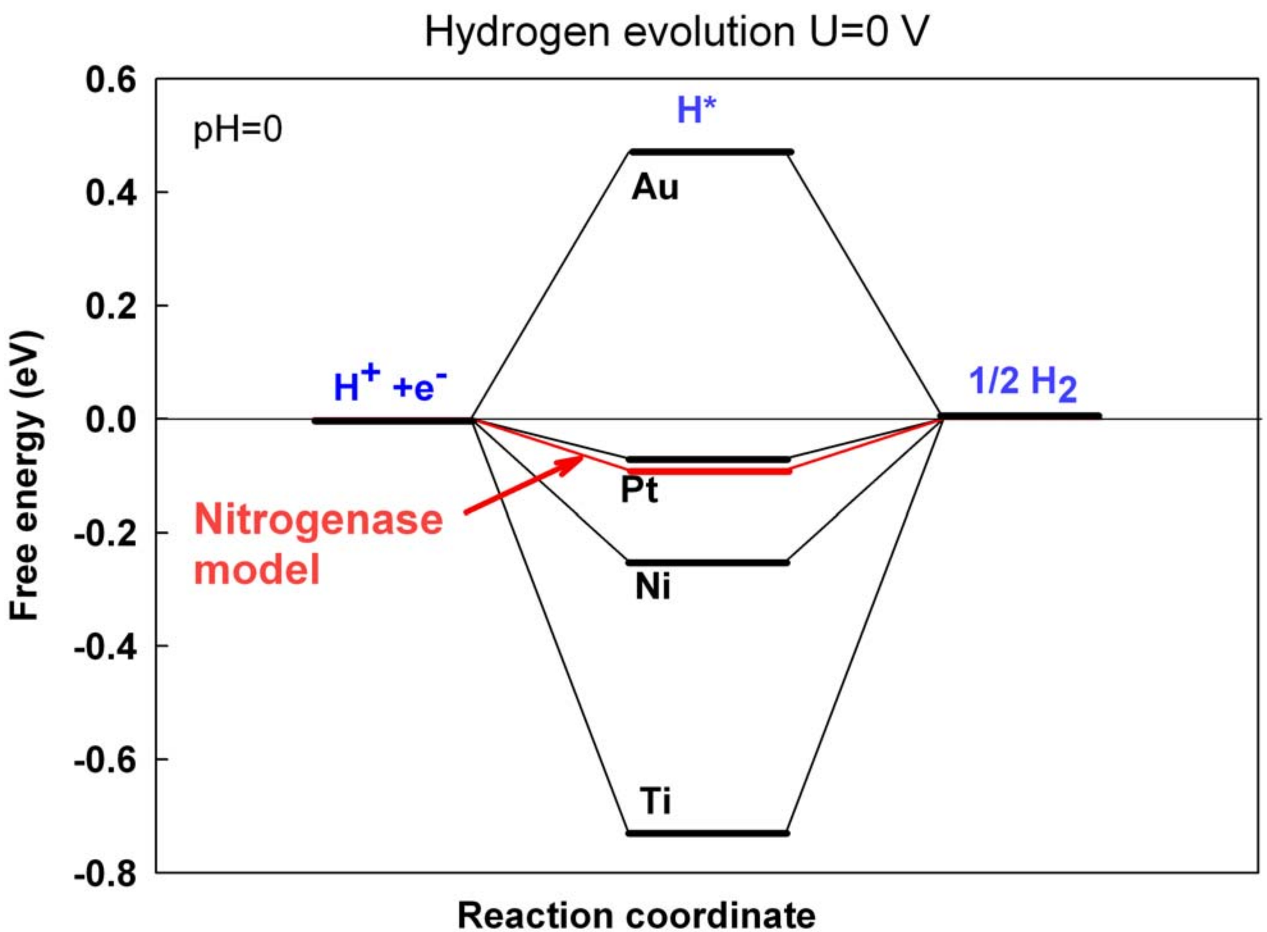
Lamle, Vincent, Halliwell, Albracht,

Armstrong, Dalton Trans. 2003 4152

Biomimetic hydrogen production II

Nitrogenase:





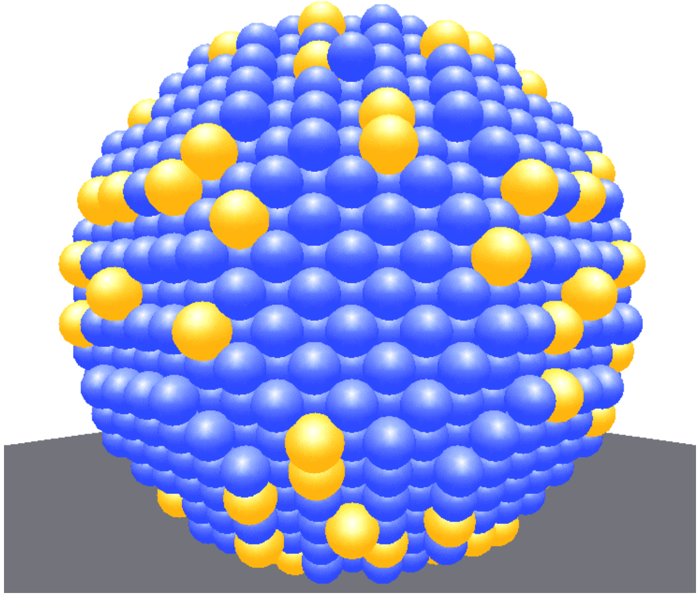
Hinnemann, Nørskov, JACS **126**, 3920 (2004)

The grand challenge

Understand relationship between
surface structure and catalytic properties

Use insight for rational
(atomic-scale)
design of new catalysts

- Theory
- Model experiments
- Synthesis of new nano particle catalysts
- Testing and characterization



Thanks to

B. Hinnemann, K. Honkala, T. Bligaard, H. Beengaard, F. Abild-Pedersen, P. Liu, A. Logadottir, I. Chorkendorff
Center for Atomic scale Materials Physics, Technical University of Denmark

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S. Helveg, B. S. Clausen, J. Rostrup-Nielsen, J. Sehested, A. Molenbroek
Haldor Topsøe

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