Catalysis for sustainable energy: The challenge of harvesting and converting energy
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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
- Electro catalysis
- Photocatalysis

Steam reforming and methanation

Strongly Endothermic

\[
\text{CH}_4 + \text{H}_2\text{O} \quad \overset{\text{Ni, 1000 } ^\circ\text{C}}{\longrightarrow} \quad \text{CO} + 3\text{H}_2
\]

Exothermic

\[
\text{CO} + \text{H}_2\text{O} \quad \overset{\text{Cu, 200 } ^\circ\text{C}}{\longrightarrow} \quad \text{CO}_2 + \text{H}_2
\]
Deposition at 500K on Ni(14 13 13) only B5 sites

240L CO at 500K

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

The Steam Reforming

CH$_4$ + H$_2$O $\leftrightarrow$ CO + 3H$_2$

Methanation

Steam reforming

Ru slightly better than Ni

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

Methane becomes RLS for 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


Catalysis for sustainable Energy (CASE)

14 W/m²  4 W/m²  0.7 W/m²
Electrifying seems to be the future

Solar, Wind, and Hydro, Energy

Electrify

Biomass

Power plant

Electrolysis/Fuel Cells H2 and O2

H2 Storage

Fuel Storage

Opgrading Biomass

CO2 Hydrogenation

H2

CH4, CH3OH...

Fuels for long distance transport

Chemicals

Consumer

Possible Solar Fuels

4H2 + CO2 = CH4 + 2H2O

3H2 + CO2 = CH3OH + H2O

8H+ + CO2 + 8e− = C2H4+ 2H2O

Averaging renewal energy sources

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

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

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

\[\Delta G^0 = 2.46 \text{ eV} \ (1.23 \text{ eV/electron})\]

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

Horns rev 80 x 2MW

DK West January 2008

Demand and Wind power January 2008 + 3,000 MW
**Working Principles PEM fuel cell**

PT or Pt/Ru clusters

\[ 2H_2 + 4e^- \rightarrow 4H^* \]

\[ 4H^* + 4e + 4H^+ \rightarrow 4H^* + 2O^* \]

\[ 4H^* + 2O^* \rightarrow 2H_2O \]

**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


R. Parson 1957
Composition of Earth's Crust

Element No

H  Ne  O  Si  Ca  Fe  Ar  Mo  Ba  W  H  Ne  O  Si  Ca  Fe  Ar  Ru  Rh  Pd  Re  Os  Th  U  He  Ca  Na  Mg  Ti  Si  Fe  Al  Fe  Ca  Na  K  Mg  Ti  Sum 47.4%

Composition of Earth's Crust

The hydrogen evolution process

$\Delta G \approx 0$
The most efficient materials

Heat

Overpotentials
A \((\sqrt{3} \times \sqrt{3})_{R30^\circ}\) H-coverage on 3-layer slab with 16 different metals:

Fe, Co, Ni, Cu, As, Ru, Rh, Pd, Ag, Cd, Sb, Re, Ir, Pt, Au, and Bi

<table>
<thead>
<tr>
<th>Pure Metal</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Metal Overlayer</td>
<td>240</td>
</tr>
<tr>
<td>1/3 Surface Alloy</td>
<td>240</td>
</tr>
<tr>
<td>2/3 Surface Alloy</td>
<td>240</td>
</tr>
</tbody>
</table>

Leading to a total of 736 surface alloys

- \(\Delta G \approx 0\) - 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

Stability Criteria

180 binary surface alloys have good predicted activity.
Check for surface-bulk segregation effects:
Reject all alloys where $\Delta \Omega_{seg} < 0$.
$\sim 105$ alloys remain.

Check for intrasurface rearrangements and islanding:
Reject all alloys where $\Delta \Omega_{surf}<0$.
$\sim 45$ alloys remain.

Check for electrochemical stripping effects: $\sim 25$ alloys remain.
$pH=0$
$M(s) \rightarrow M^{n+} + ne^-$

Check for adsorption of oxygen: $\sim 15$ alloys remain.

Pareto-optimal plot

The knees are always the point of interest i.e. PtBi taking uncertainty of DFT into consideration.

J. Greeley, T. Jaramillo, J. Bonde, I. Chorkendorff, and J. K. Nørskov,
Test of PtBi\textsubscript{surface alloy} HER


The surface alloy shows enhanced activity.

Standard bulk alloys of CuW
How does nature do it?

Nitrogenase:


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MoS$_2$ as a catalyst for hydrogen evolution

- The coverage cannot be changed continuously.
- Probably only coverage changes between 25% and 50% contribute.
1) Synthesis and STM of MoS$_2$ on Au(111) under UHV.

2) Measure electrochemical activity of the MoS$_2$ just characterized with STM.

Combining surface science and electrochemistry.


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MoS$_2$ on the volcano

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

Mo$_3$S$_4$ going small

The smallest entity of the active site of MoS$_2$?


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

Z range: 1.22 nm

Fuel cell
H$_2$O + 4h$^+$ $\rightarrow$ O$_2$ + 4H$^+$

The dream device

H$_2$O + 4h$^+$ $\rightarrow$ O$_2$ + 4H$^+$

The Helios concept (Nate Lewis)

4H$^+$ + 4e$^-$$\rightarrow$ 2H$_2$

Large band gap $>2.0$ eV

Small band gap $<1.1$ eV
Measurements on pillared structures

- UV-lithography and dry-etching of silicon
- 3 µm diameter circular with 6 µm spacing
- Hexagonal pattern and 60 µm long
- 32000 pillars/mm² increased area of ~15

The Major loss in ORR and OER

The anode reaction in a fuel cell: \( \text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O} \)

Adapted from Gasteiger et al.

Using \( \Delta E_0 \) 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

\[ \Delta E_0 - \Delta E_0^* \approx 0.2 \text{ eV} \]

Structural stability of ordered alloys

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.

\[ \Delta H (\text{eV}) \]

- 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$_3$X and Pd$_3$X alloys


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

Specific activity: $i_k$ [mA cm$^{-2}$] at 0.85V (RHE)


Proof of Pt skin?
Angle resolved XPS depth profile

All catalysts with ‘Pt-skin’ overlayers

50eV pass energy

150eV pass energy, background subtracted
The ORR volcano II

\[
\ln(\frac{j_{\text{O}_2}}{j_{\text{H}_2}}) = \Delta E_O - \Delta E_{O^\text{Pt}} [\text{eV}]
\]


Alloys invested so far

\[
\begin{array}{c}
\text{Pt}_3\text{Y} & \text{Pt}_3\text{Y} & \text{Pt}_3\text{La} & \text{Pt}_3\text{Sc} & \text{Pt}_3\text{Hf} & \text{Pt} & \text{Pt}_3\text{Zr} & \text{Pt}_2\text{Y} & \text{PtY} \\
\end{array}
\]

Specific and mass activity versus Size


Enhancement of activity

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

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, IrO₂, RuO₂)
- Fuel Cells (Pt, Ru)
- Synthesis of Solar Fuels (Ru, Pt,…)?

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