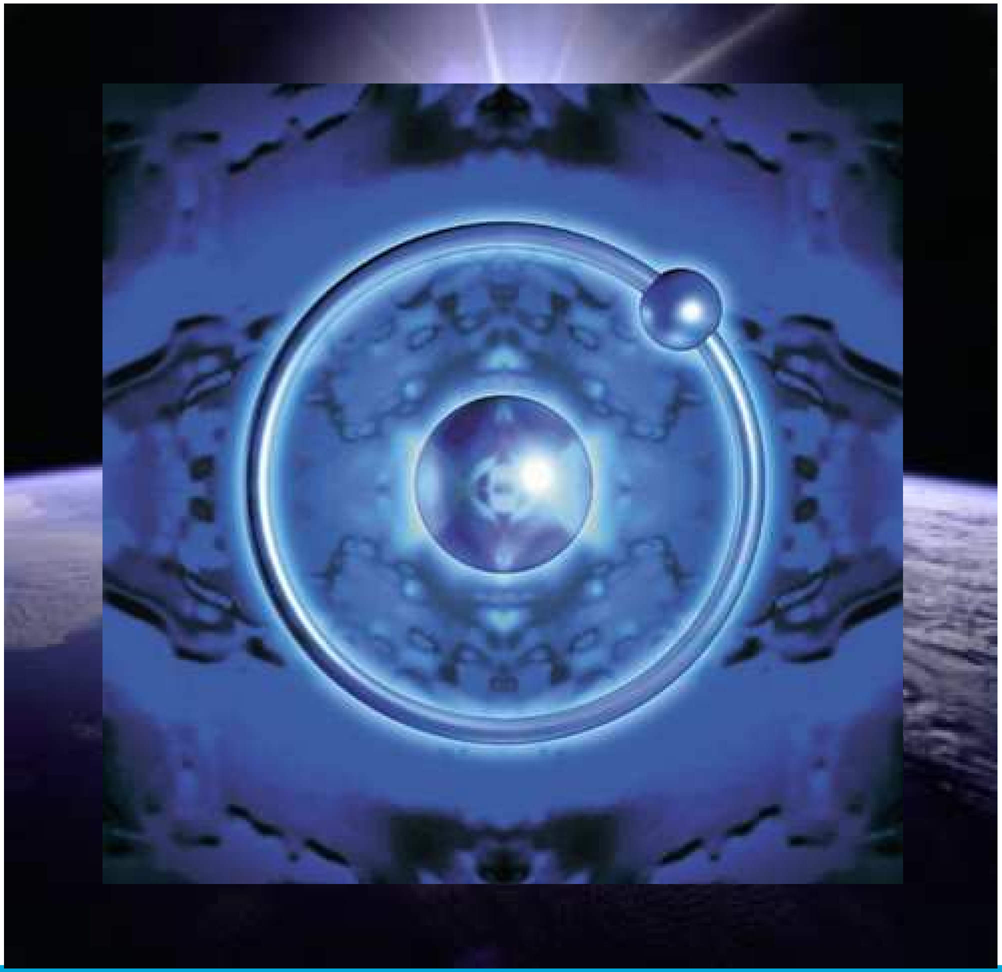
Sustainable Hydrogen and Electrical Energy Storage
06-05-2013



F.M. Mulder & M. Wagemaker

Production of hydrogen

- fossil fuels
- biomass
- electrolysis of water
- thermonuclear
- photocatalysis
- …

Production of hydrogen via electrolysis Gupta 5.2

Implementation of electrolysis:

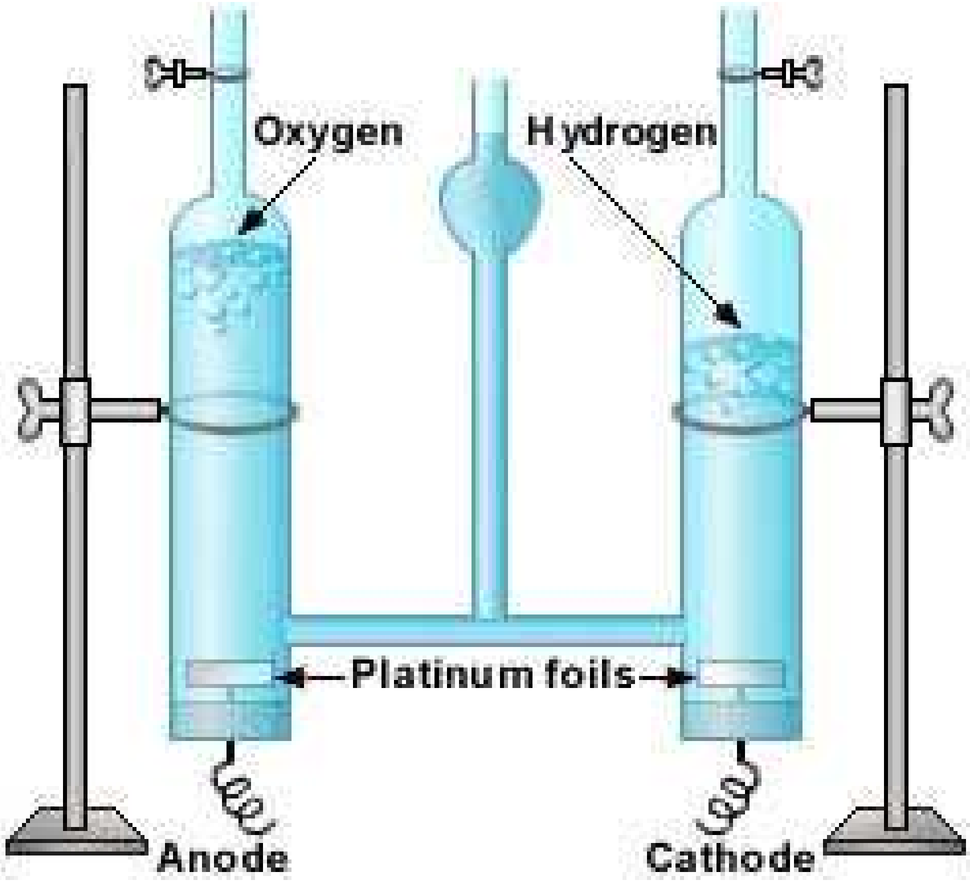
- collect solar, wind, hydropower in order to produce electricity

- transport electricity to central electrolysis facilities

- use water: either fresh water, or seawater.

- seawater electrolysis may be the first option near desert areas where solar power is collected.

History: Hoffman electrolysis apparatus



Anode :
$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$
Cathode :
$2\ H^+ + 2\ e^- \rightarrow H_2$

Overall:
$2\ H_2O \rightarrow O_2 + 2H_2$

H^+ (H_3O^+) is traveling
from anode to cathode

Currently: an alkaline KOH electrolyte is used with Ni electrodes:

- KOH solution as electrolyte: has high conductivity
- Ni electrodes: cost effective and stable in KOH solution
- Separating membrane for keeping dissolved H_2 and O_2 apart

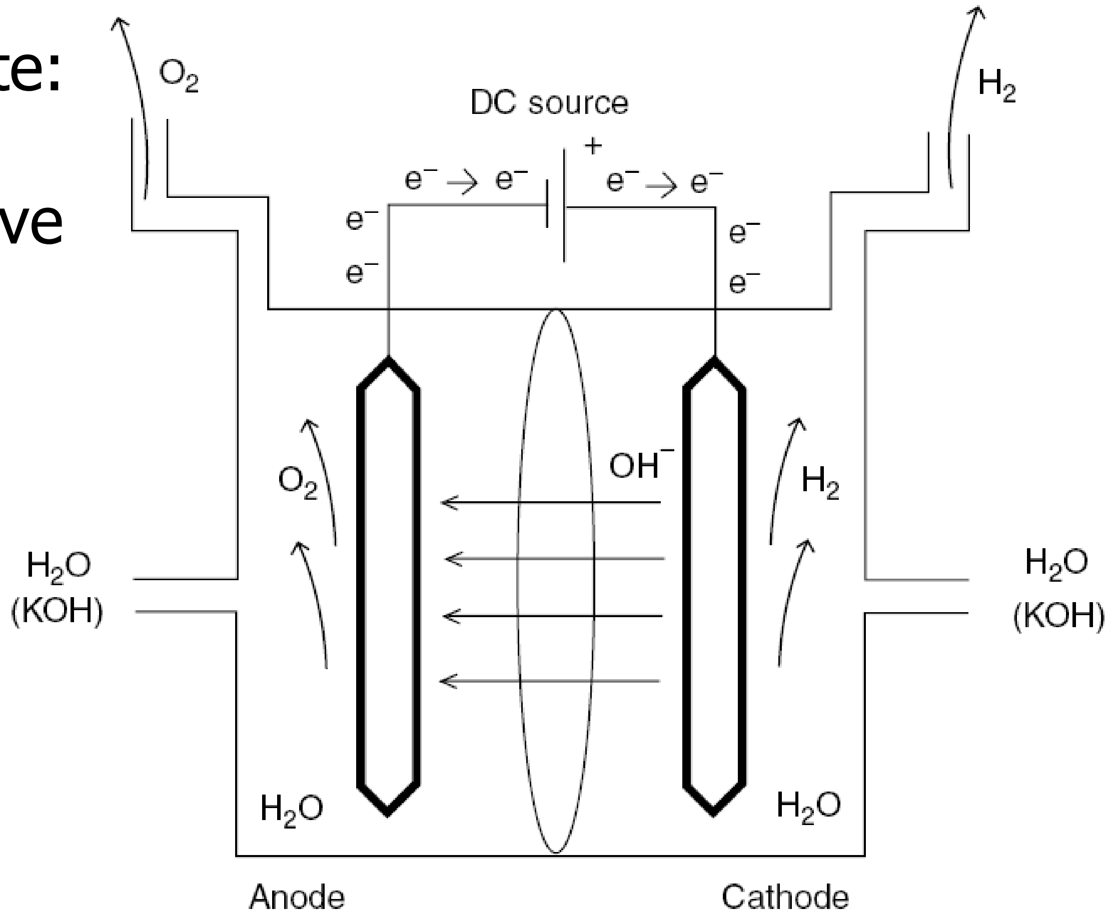


FIGURE 5.1
Schematic view of an alkaline electrolytic cell.

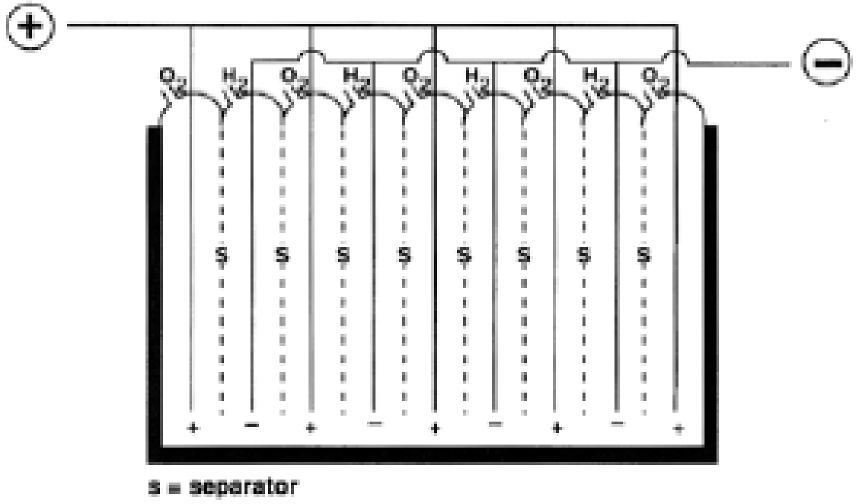
Charge travels through electrolyte as OH^-
What is concentration of OH^- in 'normal' water?

10^{-7} mol/l (Ph ~ -log $[H_3O^+]$ = 7
and $[H_3O^+] \times [OH^-] = 10^{-14}$ mol^2/l^2)

How to increase the ionic conductivity?

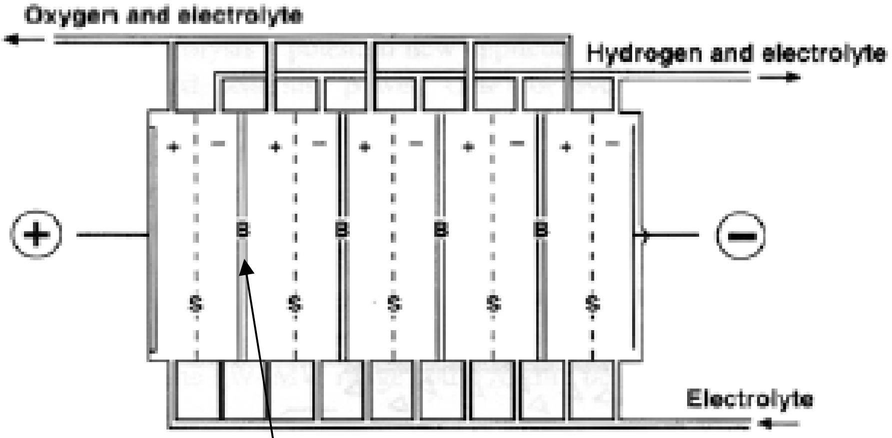
→ Put base or acid in the water to increase density of charge carrying ions

(a) **Monopolar electrolyzer**



Voltage ~ max 2.2V

(b) **Bipolar**



High voltages:
n x cell voltage

B = ‘bipolar plates’

Large electrolyzer Stacks. Power is fed through the stack in bipolar plate configuration.

Most commonly used gas production units under reference conditions are:
Normal cubic meter (Nm3) - Temperature: 0 °C, Pressure: 1.01325 bar

This amounts to 89.88 gram of H_2

Standard cubic meter (Sm3) - Temperature: 15 °C, Pressure: 1.01325 bar
Because of the higher T this is a little bit less grams of H_2

$$E_0 = -\frac{\Delta G_0}{nF}$$

ΔG_o is the change in the Gibbs free energy under standard conditions (1 bar, 25 ^oC), n is the number of electrons transferred.

$\Delta G_0 = \Delta H_0 - T_0 \Delta S_0$

For H_2O (l) -> $H_2 + 0.5O_2$ (1)

ΔH_o = 285.8 kJ/mol,
$\Delta S_o(H_2)$ =130.6, $\Delta S_o(O_2)$ = 205.1, $\Delta S_o(H_2O)$ (l) = 70 J/mol K,
ΔS_o total = 130.6 + ½ 205.1 - 70 = 163.14 J/mol K, and ΔG_o = 237.2 kJ/mol

$E_o = -\Delta G_o/nF$ = 1.23 V is the open circuit potential, and the theoretical minimum voltage to be applied to let the reaction (1) proceed to the right.

Note:

$\Delta G_0 = \Delta H_0 - T_0 \Delta S_0$

Since entropy increases in going from 1 liquid water molecule to 1.5 gas molecules heat is released; this heat is extracted from the environment and invested in the forming of the molecules H_2 and $0.5O_2$.

$\Delta H_o = 285.8$ kJ/mol > $\Delta G_o = 237.2$ kJ/mol

Consequence: under continuous electrolysis heat is extracted from environment which needs to be compensated (or system cools down, decreasing the kinetics).

'Thermo neutral potential' is defined as: $E_{0thermo-neutral} = -\frac{\Delta H_0}{nF}$

Extra potential leads to ohmic resistive heating, compensating the heat loss.

Theoretical efficiency is defined as the higher heating value of hydrogen divided by the equilibrium potential:

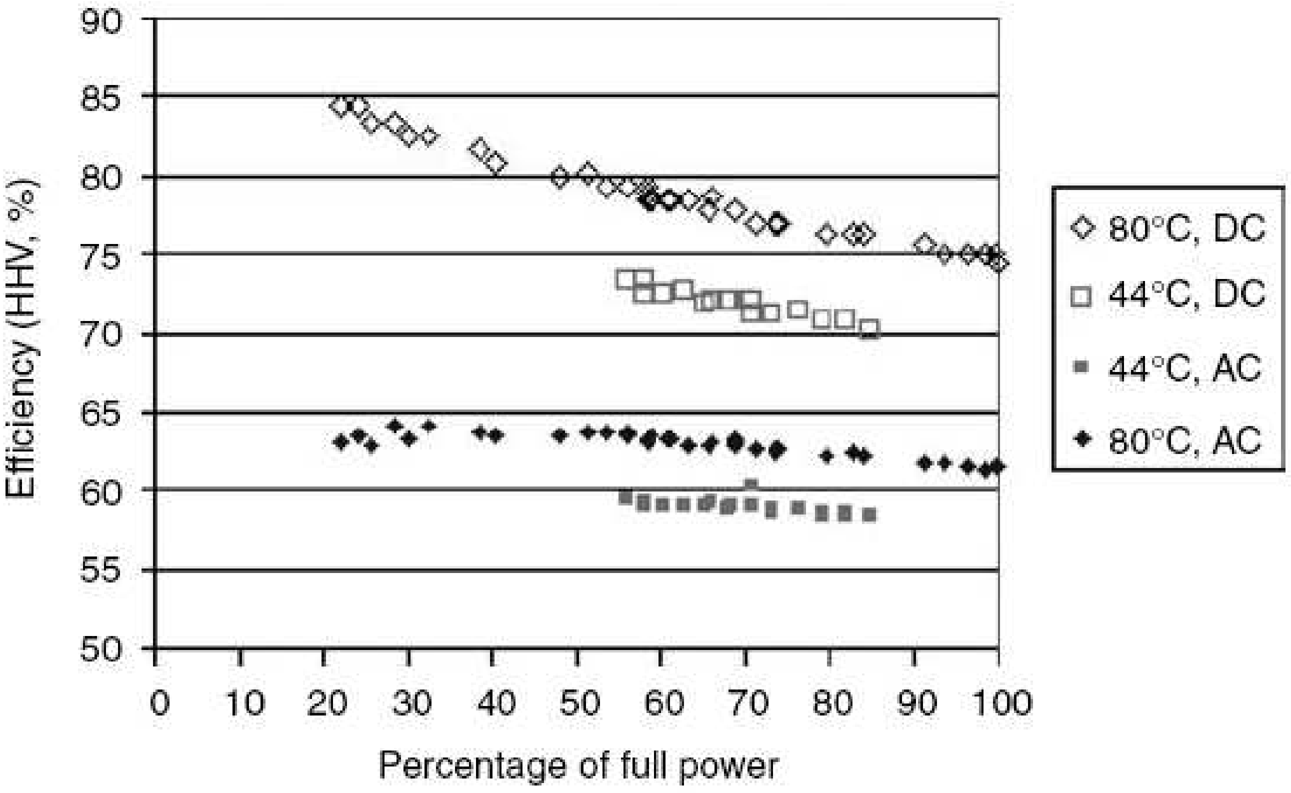
$$\varepsilon = \frac{\Delta H_0}{\Delta G_0} = -\frac{\Delta H_0}{nFE_{cell}}$$

Practical efficiency is defined as the higher heating value of hydrogen divided by the actual potential:

$$\varepsilon_{real} = -\frac{\Delta H_0}{nFE_{real}}$$

$E_{real} = (\Delta G_0/\mathrm{nF}) \quad + \mathrm{IR} + \eta$

Efficiency



<u>Electrical</u> efficiency goes up with T, but reduces for larger power (currents).

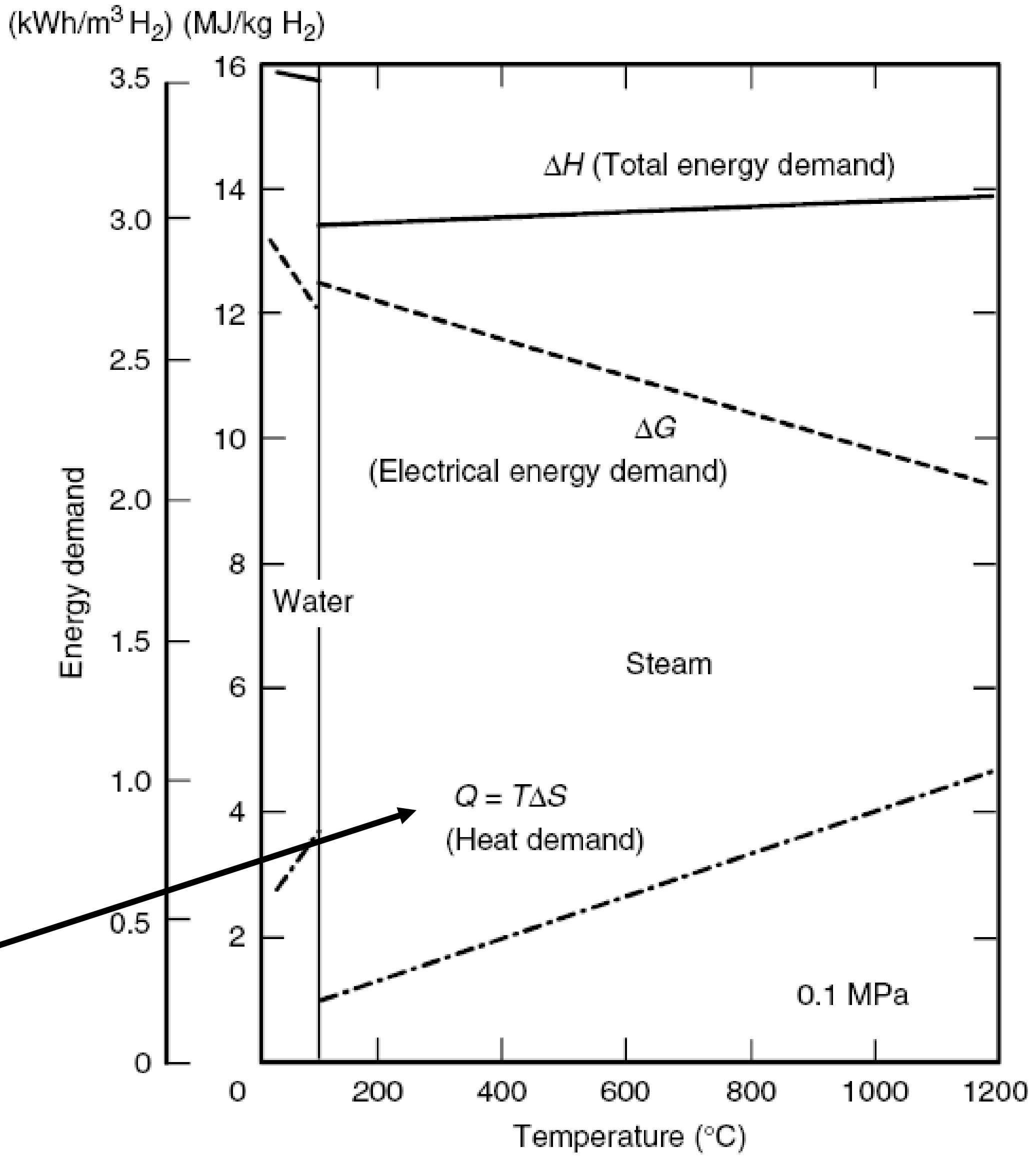
Gupta 4.2

For the reaction

$$H_2O(g) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

a Nernst equation holds:

$$E = E_o + \left(\frac{RT}{2F}\right)\ln\left(\frac{P_{H_2}P_{O_2}^{1/2}}{P_{H_2O}}\right) + \eta$$



Entropic term linear in T

http://en.wikipedia.org/wiki/Nernst_equation#Derivation

Essentially the entropic term increases with T, so more heat is extracted from environment upon H_2 + O_2 production at higher T.

Then the required electrical energy to split H_2O is lower

→ this means that the required amount of electricity will reduce, which may be interpreted as higher electrical efficiency. However, one requires larger heat input to heat the system.

Is it still advantageous to operate at higher T?

Yes since one converts heat to chemical energy in the H_2. And the losses for electricity production from thermal sources are omitted.

The total energy input increases with T. Why?

Volume expansion: 2 $H_2O \rightarrow 2H_2 + O_2$
2 molecules become 3, this exerts work against the environment and this becomes larger at larger T.

Efficiency: input voltage compared to standard electrode potentials: up to 2.2 V versus 1.23 V

This is a result of the required overpotentials η in each of the steps for O_2 and H_2 formation

oxidant (electron acceptor)		**reductant** (electron donor)	**E°, volts**
$2\,H^+ + 2e^-$	->	$H_2(g)$	**0.000**
$O_2(g) + 4H^+ + 4e^-$	->	$2\,H_2O(l)$	**+1.23**

$$2H_2O + 4H^+ + 4e^- \rightarrow O_2 + 4H^+ + 4e^- + 2H_2,$$

$$E_{cell} = E_{H2} - E_{H2O} = 0.000 - 1.23 = -1.23\text{V}$$

Efficiency and the Oxygen formation problem

Production of H_2 at the cathode, consuming electrons, appears to occur readilly. In order to close the current loop at the anode the reaction should take place that produces electrons:

To water, i.e. H_3O^+

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

To anode

This reaction, however, appears less simple:

it appears that the formation of oxygen requires a significant ‘overpotential’ η ~ 0.3 - 0.5V (in top of 1.23V potential difference).

How does overpotential influence efficiency?

$E_0 = 1.23$ V
$\eta = 0.4$ V

Efficiency: $1.23 / (1.23 + 0.4) = 0.75$

Efficiency & Oxygen formation, overpotential at Pt, Ir electrodes

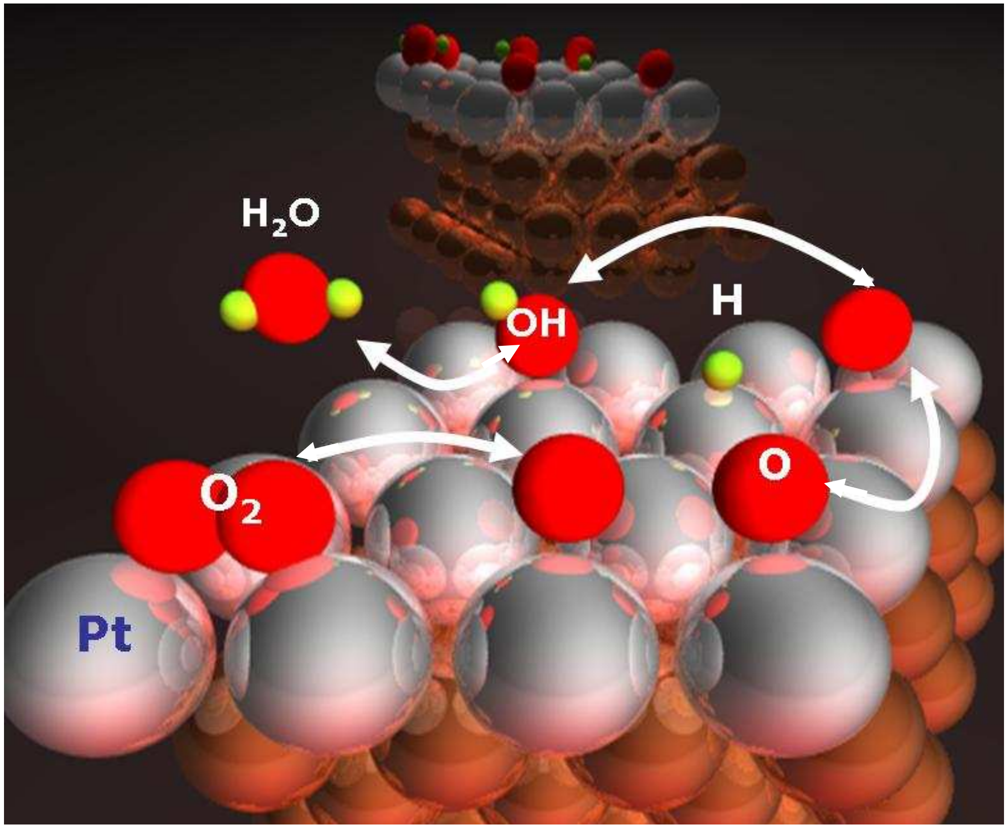
Reason:

-on electrode surfaces of e.g. Pt and Ir there is formed an oxide layer, and this oxygen is not readilly released as O_2. This makes that charge transfer is hindered. For Ir this effect is smaller than for Pt. The Ir oxide species formed still have reasonably metallic conduction.

- intermediate OH^- ions formed after $H_2O \rightarrow OH^- + H^+$ interact most with the oxidised electrode surface and can promote charge transfer $2OH^- \rightarrow O_2 + 2H^+ + 4e^-$, but this works better when there is more interaction between OH^- and electrode surface.

J. Chem. Soc.-Faraday Trans.72: 2431-2440 1976

Efficiency and Oxygen formation



The intermediates from

$2H_2O \rightarrow 2OH^- + 2H^+$
$\rightarrow O_2 + 4H^+ + 4e^-$

need to be formed, held at the surface and two O's need to find each other. In practice a significant **overpotential** is needed to realize the reaction. One may think: the overpotential makes that the OH^- remain longer at the positively charged surface, and can react.

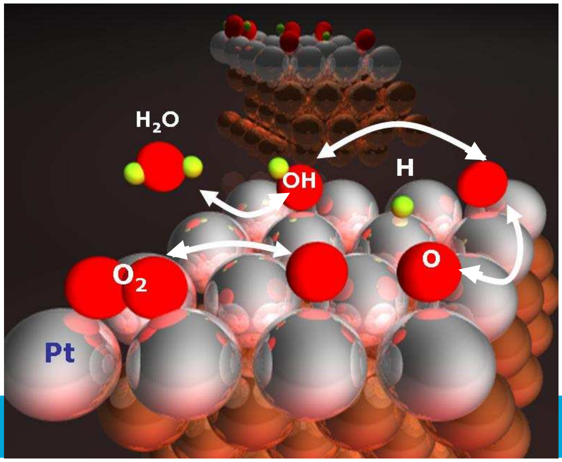
Note the role of the electrocatalytic surface:

- it makes that relevant intermediates are concentrated at a surface, and do not float away into the electrolyte

- it can hold several types of intermediates, OH^-, O

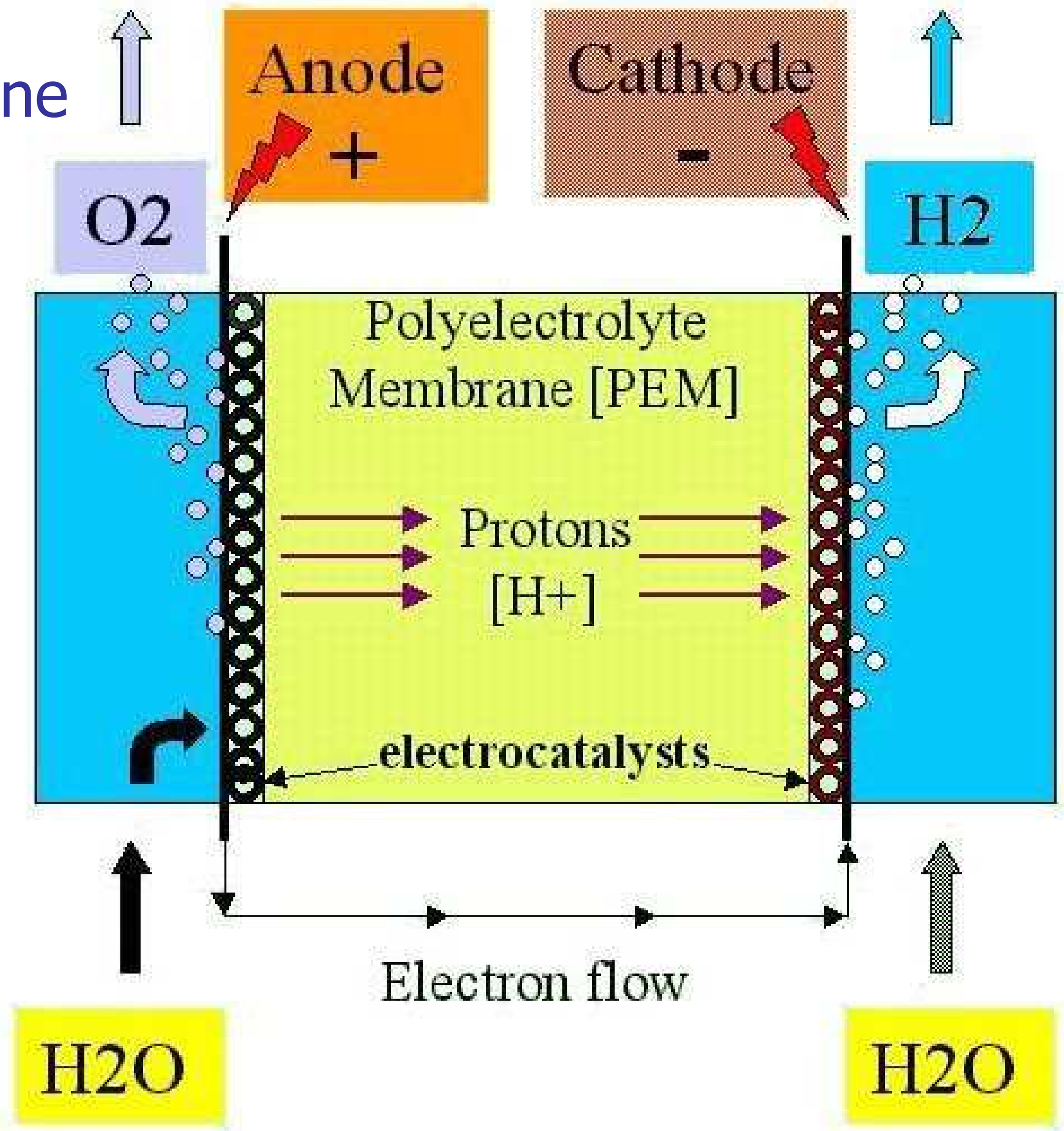
- it should not hold H^+ in order to prevent back reaction (then overpotential helps: more positive charge repels H^+)

- it can transfer electrons



More recent development: Polymer electrolyte membrane (PEM) electrolyzer: acid electrolyte

Use the same polymer electrolyte membranes as used in fuel cells: e.g. Nafion has a high density of bound HSO_3 groups that can release their H^+ ion to H_2O inside the PEM, resulting in very high conductivity of the membrane.



Advantages of PEM electrolyser

- the acid is contained in the PEM material, which leads to much lower corrosion concerns of the containment materials than in the case of acidic or caustic solutions.

- because the PEM is a solid it can be made very thin while still separating the H_2 and O_2 gas on the sides of the PEM. This leads to good separation of the gases, lower internal resistance, and higher efficiencies

- efficiencies of up to 50-70% are reported in commercial PEM electrolysers (electricity to hydrogen)

Efficiency: High pressure electrolysis to reduce compression costs

- if the hydrogen produced would be stored in high pressure gas cylinders one needs to compress the gas if ambient pressure electrolysers are used. Compression of gas to a certain pressure (e.g. 700Bar) costs significant amounts of energy.

- Pressurizing water in the electrolyser costs much less energy (a liquid has low compressibility)

- Could high pressure electrolysis in which high pressure H_2 is produced be more energy efficient?

- Answer: the required over potential does increase (slightly) because the gas needs to be produced against the pressure. In theory there might still be a 5% gain[1], in practice it may not be more efficient[2]

[1] J.Power Sources 132 (2004) 64

[2] Int.J. Hydrogen Energy 31 (2006) 1964

Compressibility:

$$\beta = -\frac{1}{V}\frac{\partial V}{\partial P}$$

Low compressibility of liquid: dV small for certain V and dP. This means that with equal force just a short translation of a pressure piston is covered, i.e. low amount of energy (translation x force) is involved when applying the same dP on a liquid instead of a gas.

Most abundant, cheapest source of water: seawater

Seawater composition

Component	**Concentration (mol . kg^{-1})**
H_2O	53.6
Cl^-	0.546
Na^+	0.469
Mg^{2+}	0.0528
SO_4^{2-}	0.0283
Ca^{2+}	0.0103
K^+	0.0102
C in CO_2,HCO_3^-	0.00206
Br^-	0.000844
B	0.000416
Sr^{2+}	0.000091
F^-	0.000068

Is the presence of other elements problematic?

Yes! Especially Cl^- for Cl_2 formation

Electrochemical cells, driving force

oxidant (electron acceptor)	**reductant** (electron donor)	**E°, volts**
$2\ H^+ + 2e^-$ ->	**$H_2(g)$**	**0.000**
$O_2(g) + 4H^+ + 4e^-$ ->	$2\ H_2O(l)$	+1.23
$Cl_2(g) + 2e^-$ ->	$2\ Cl^-(g)$	+1.36

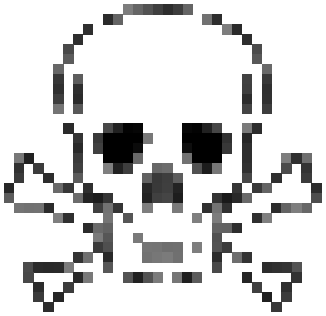
Slightly higher potential for $Cl^- \rightarrow Cl_2$, but because of the overpotential required to produce O_2 there appears to be produced much more Cl_2 than O_2 when using Pt electrodes directly in seawater!

In addition overpotential for O_2 production gets worse because of Cl_2 gas evolution (bubbles).

Because of the large production scale that is required to have a significant contribution to the future hydrogen production, any side product will need to be monitored/assessed.

What is the problem with chlorine?

Chlorine is unsafe: - it is poisonous, 1000 ppm in air is fatal



- heavier than air, accumulates
- strong oxidizer, can react violently with flammable materials

Chlorine (HCl) added appears to inhibit oxygen formation at noble metal electrode

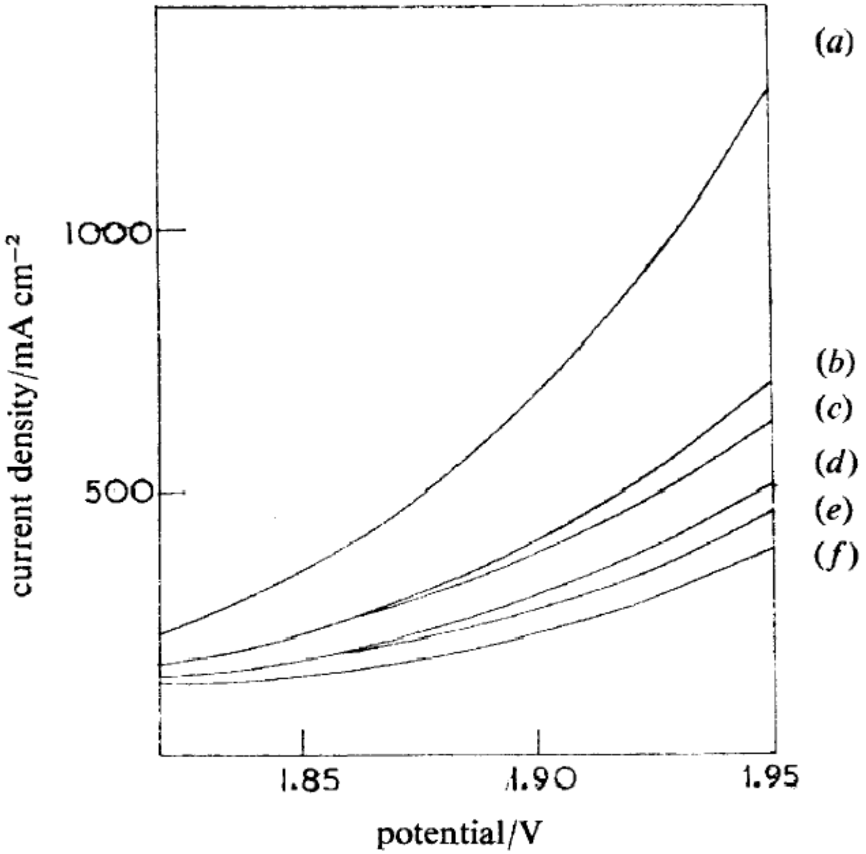


FIG. 7.—Effect of HCl concentration on the current/potential behaviour of an iridium electrode in 1.0 mol dm^{-3} H_2SO_4 at 25°C and a scan rate of 0.5 V min^{-1}. HCl conc. (mol dm^{-3}): (*a*) 0.00, (*b*) 5×10^{-4}, (*c*) 1.0×10^{-3} (*d*) 2.0×10^{-3}, (*e*) 3.0×10^{-3}, (*f*) 5.0×10^{-3}.

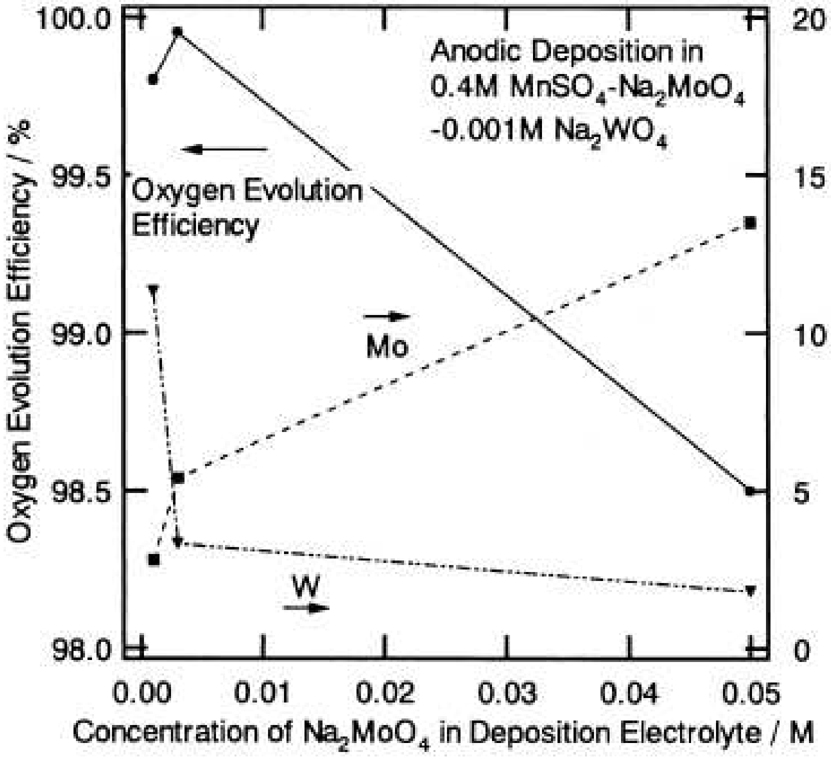
Reason: bulky, hydrated Cl^- and Cl_2 at the electrode hinders mass transport of OH^- to anode surface.
Also: for each Cl_2 only $2e^-$ are involved, for O_2 4 e^- (so less current if making Cl_2)

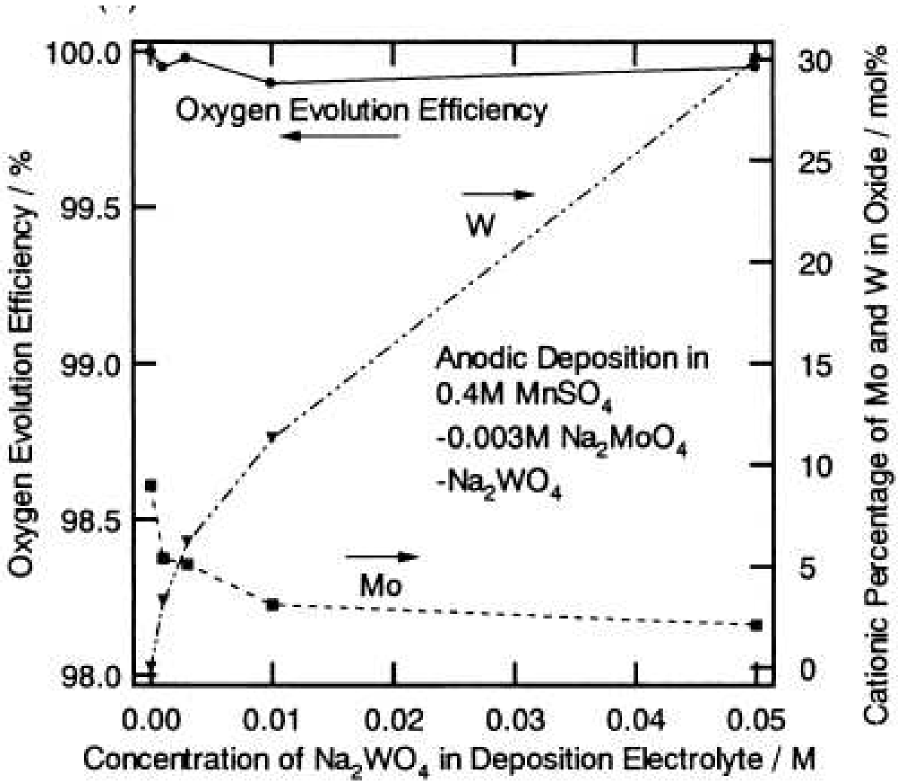
J. Chem. Soc.-Faraday Trans.72: 2431-2440 1976

Can chlorine evolution be suppressed?

yes

Electrolysis of seawater: selective electrode materials





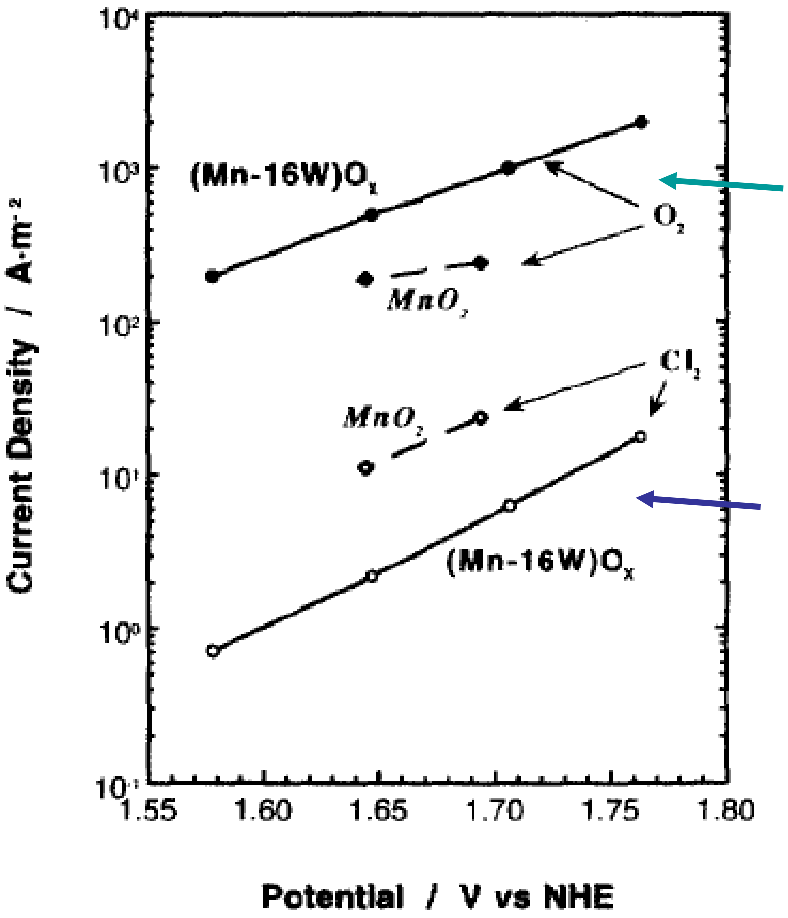
MnO_2 deposited in the presence of Na_2MoO_4 or W analogue show high Selectivity for O_2 production in 0.5M NaCl solutions: prevent Cl_2 production

Scripta Mater. 44 (2001) 1659

Efficiencies for O_2 evolution as high as 99.7% are reported for test periods up to 2000h for nanocrystalline deposited $(Mn_{0.89}Mo_{0.05}W_{0.06})O_{2.11}$

Test conditions: 1000 Am^{-2}, $30^{o}C$, 0.5 M NaCl

Tafel plot: currents versus applied potential



O_2 production

Cl_2 production

Fig. 8. Current density–potential curves of oxygen evolution and chlorine evolution for the anodically deposited MnO_2 and $(Mn–16W)O_X$ electrodes.

Other threads when using seawater?
→ Mineral deposition in seawater electrolysis

Deposition of minerals results from alkaline conditions created at the cathode by the reduction reaction:

$2H_2O + 2e^- = H_2 + 2OH^-$

which precipitates calcium and magnesium minerals from seawater:

$OH^- + HCO_3^- + Ca^{2+} = CaCO_3 + H_2O$

$2OH^- + Mg^{2+} = Mg(OH)_2$

These minerals are clearly unwanted since they may block the activity.

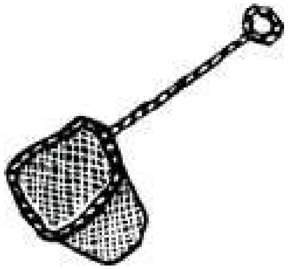
Water purification: option to desalinate seawater

Large scale purification can be done by reverse osmosis:

Apply a pressure larger than the spontaneous osmotic pressure to the seawater that is on one side of a semi-permeable membrane. Only water can pass the membrane and will emerge in purified form at the other side.

For sea water an osmotic pressure of 24 Bar has to be overcome (applied pressures: 40-70Bar).

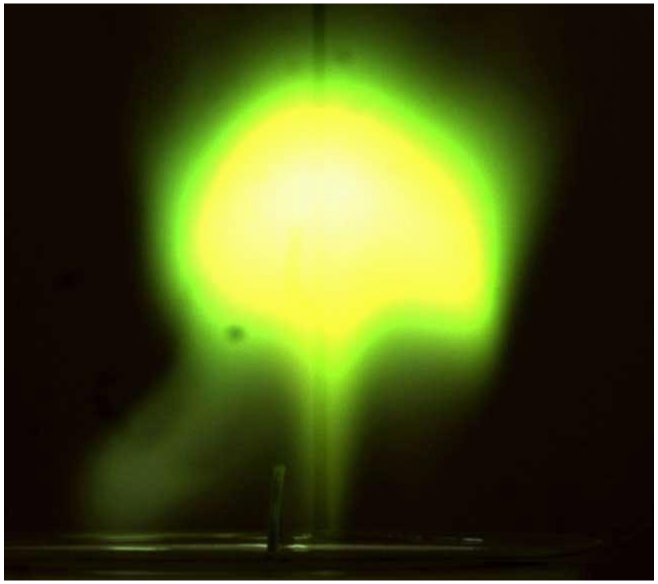
The system may also need:
- fishnet
- a sediment filter to trap larger particles
- an activated carbon filter to trap organic chemicals



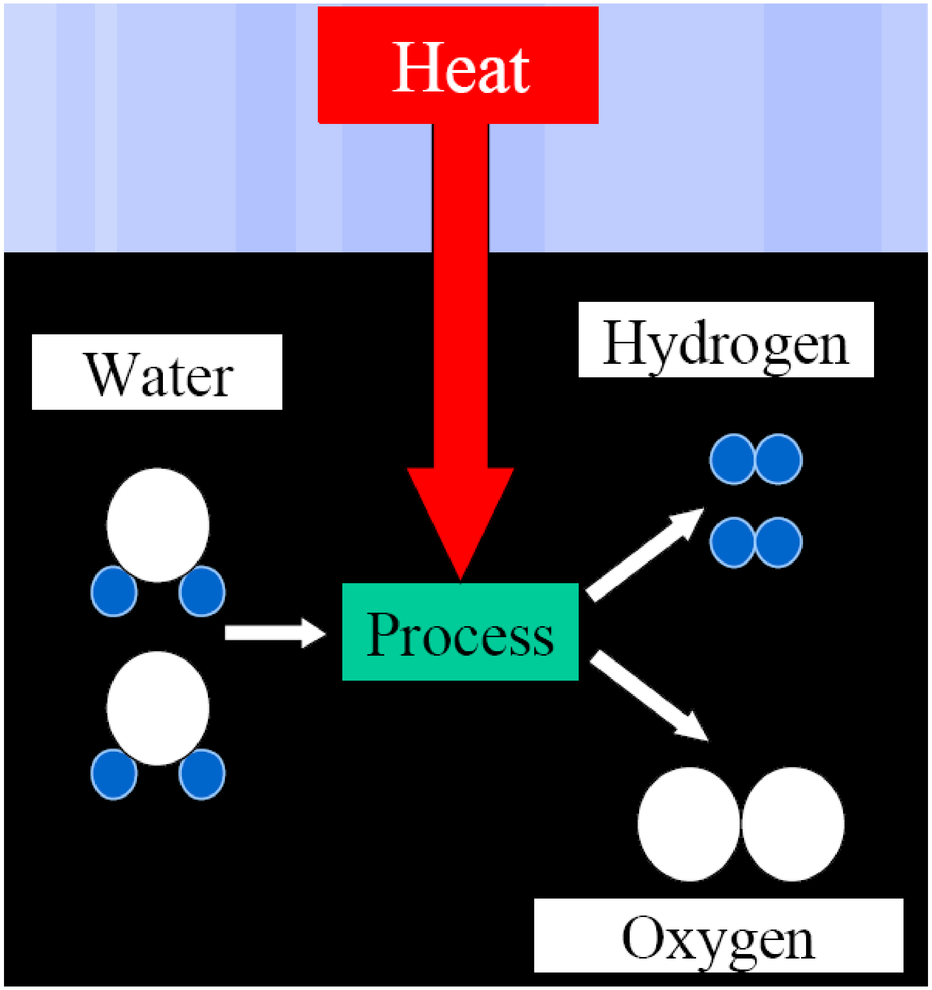
High temperature methods to produce hydrogen

Hydrogen production methods: direct thermolysis

Plasma: matter at high temperature falls apart in ions and electrons



Another plasma



Forget about electricity, just put on the heat!

Direct thermolysis

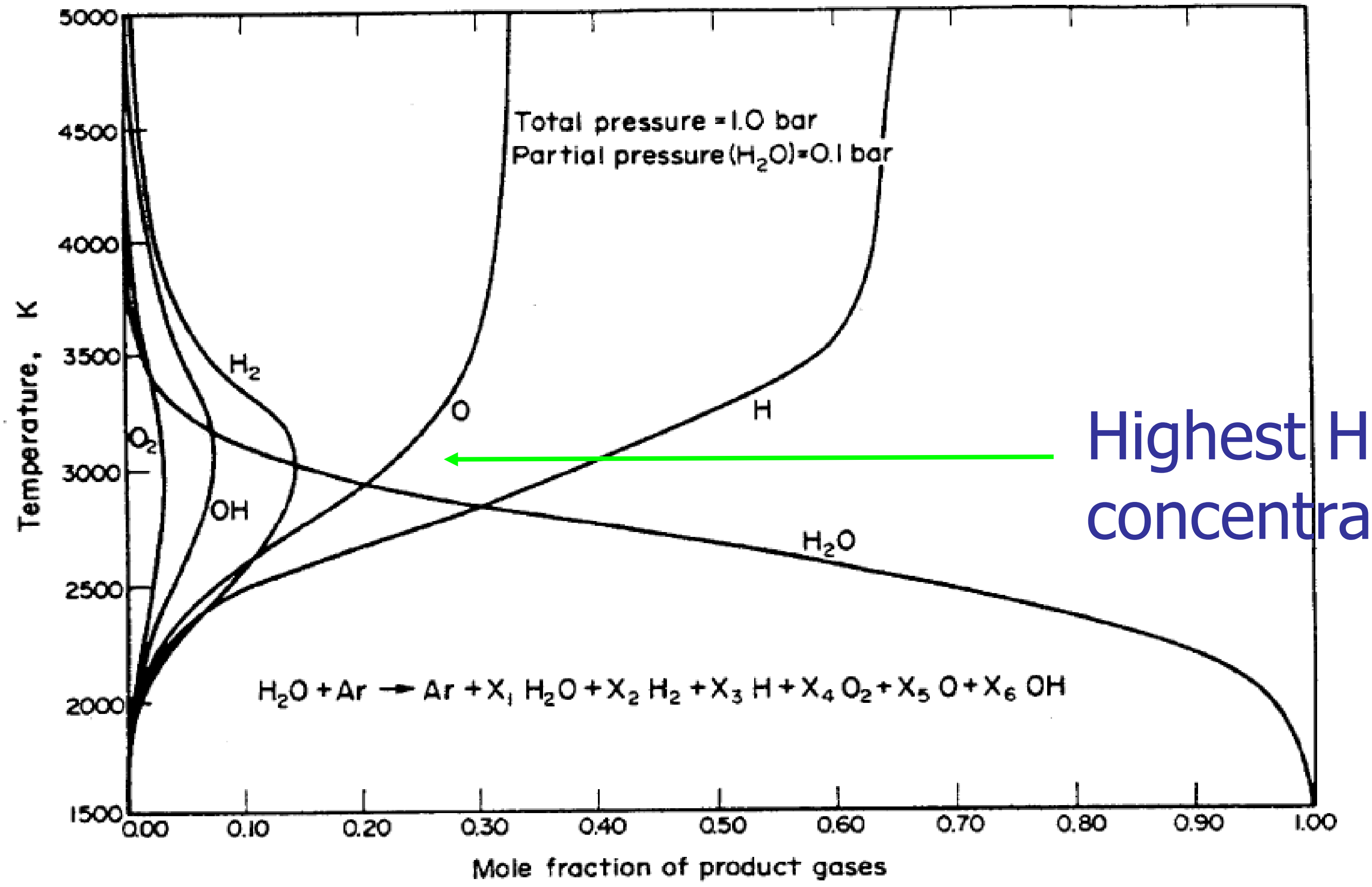
At temperatures above 3000 ^{o}C water is in equilibrium with its decomposition products:

$$H_2O \leftrightarrow x_1H_2O + x_2OH + x_3O + x_4H + x_5O_2 + x_6H_2$$

At even higher temperature mainly atomic O and H are formed.

This topic is in the research stage

Composition as a function of temperature



Highest H_2 concentration

How to produce heat: e.g. Solar concentrators (Cologne)

Mirrors that can be oriented

Parabolic focusing mirror

Solar power engine in Font Romeu France

H_2 and O_2 separation at high temperature > 1500K

In order to get the H_2 out one needs separation techniques

- porous membranes: works best at low pressures when the free path length between collisions of gas molecules is larger than the pore diameter

- oxygen conducting membranes made of e.g. ZrO_2, CeO_2, Y_2O_3

Separation of H_2 by metallic membranes like Pd works only at temperatures < T_{melt}. Then one needs to ‘quench’ the reaction mixture to ‘low’ temperatures (without burning H_2 again while being above spontaneous ignition temperature @ Pd)

Thermochemical Cycles for Water Splitting Gupta 4.3

For direct thermolysis one needs T > 3000°C: very demanding on materials. Instead, spread enthalpy load over cycle of a few reactions at less high T's

– each giving useful equilibrium product concentrations

– at lower temperatures

– allowing easier separation of Hydrogen & Oxygen

- more than100 possible reaction cycles identified

- Sulphur Iodine Process - most international interest

Efficiency of H_2 production using S-I cycle, compared to other methods

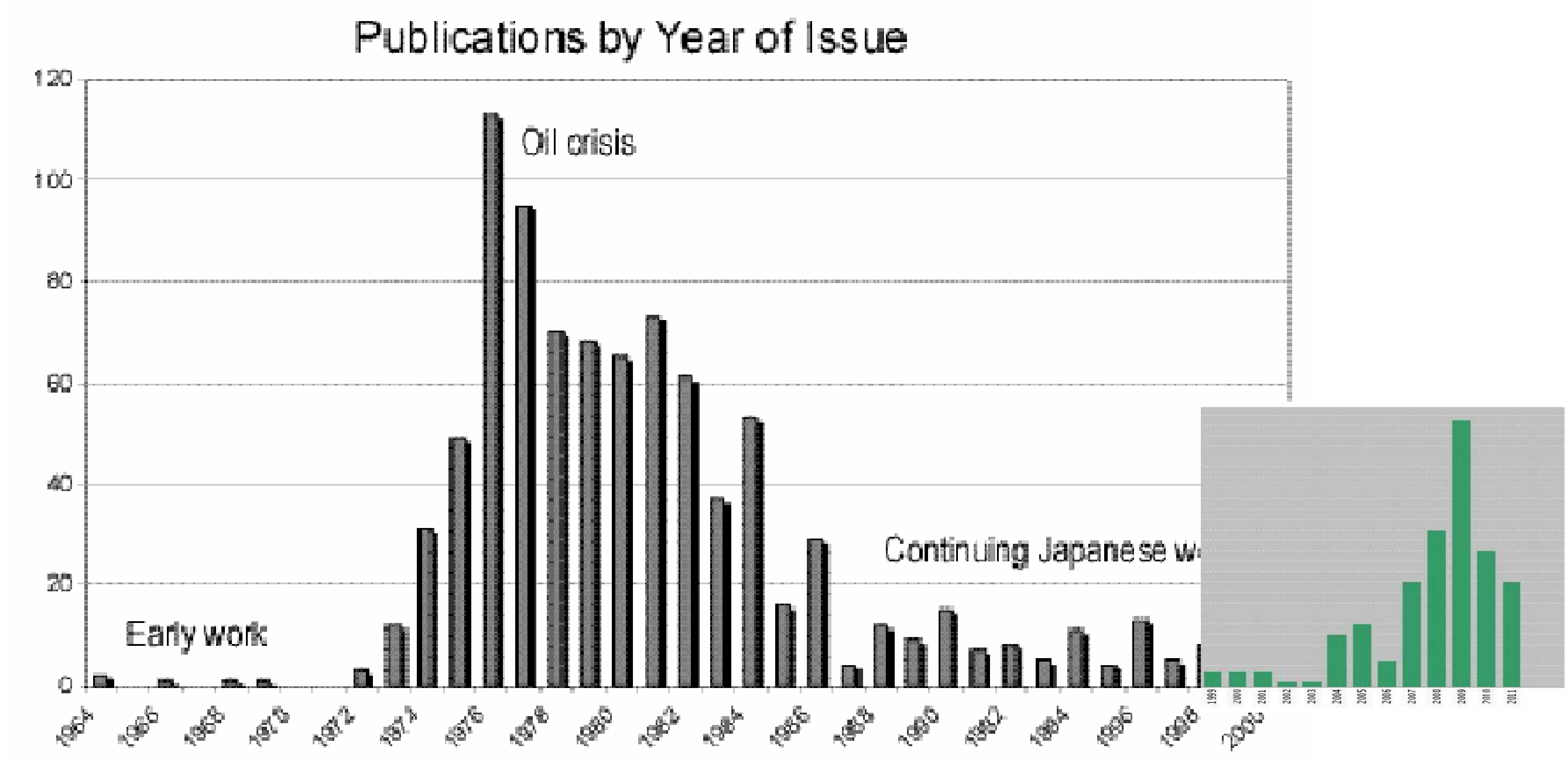
Method	Maximum process temperature (°C)	Overall efficiency (%)	Status
Sulfur-iodine thermo-chemical cycle	850	45−49	Calculation[a]
Calcium-bromine thermo-chemical cycle	760	36−40	Pilot plant[b]
Copper-chlorine thermo-chemical cycle	500	41	Bench[c]
Steam methane reforming (SMR)	900	77	Commercial[e]
SMR with CO2 sequestration	900	58	Calculation[g]

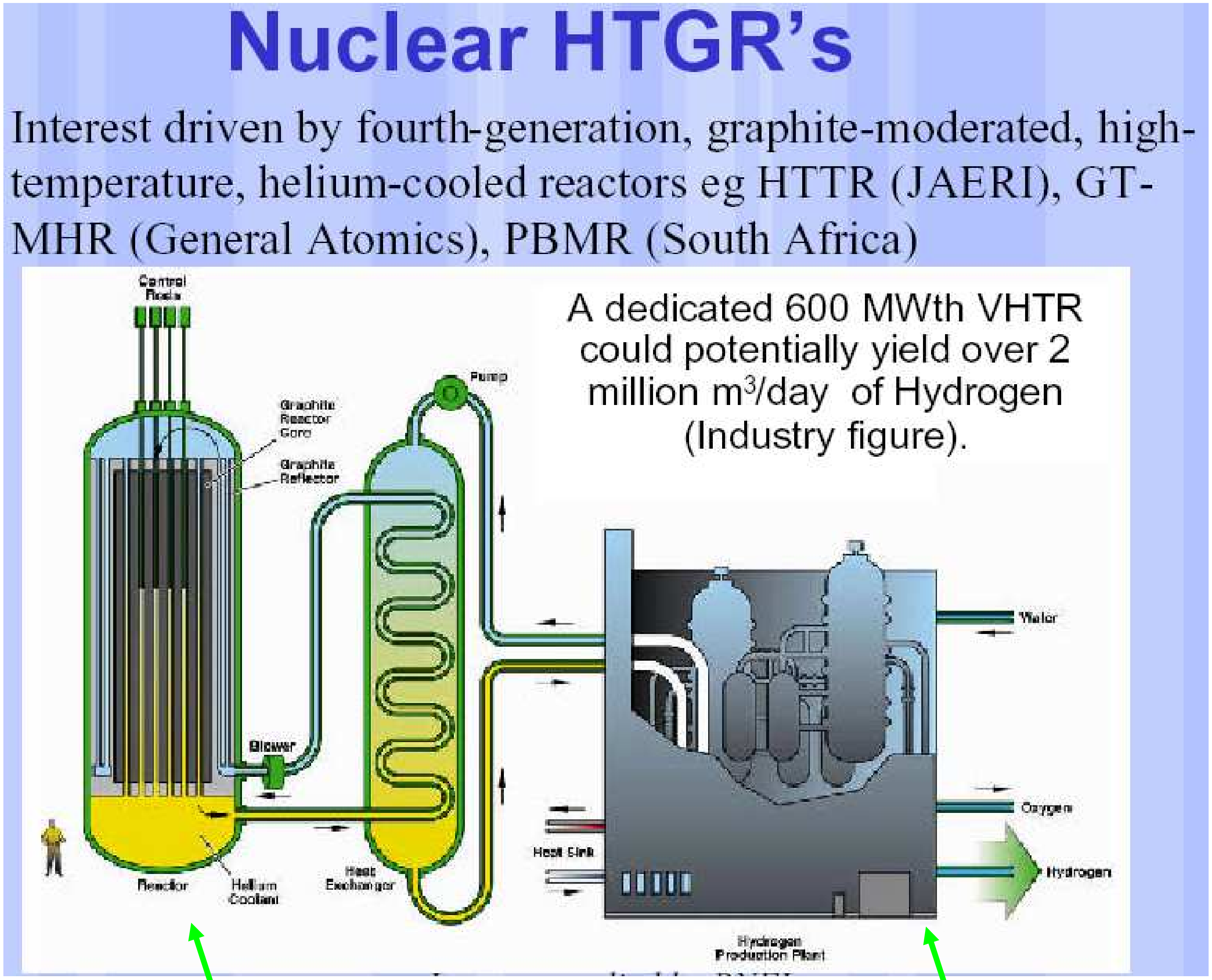
Source:

Argonne National Laboratory (ANL), *Meeting U.S. Transportation Needs in the Hydrogen Economy*, http://www.hydrogen.anl.gov/pdfs/meeting_transportation_needs.pdf, May 2003, and updates from ANL.

Note: The efficiency is the ratio of the energy value of the hydrogen produced to that of the heat used

Sulfur iodine cycle research publications, most of them performed by nuclear institutes: still not finished…


Publications by Year of Issue



Nuclear HTGR's

Interest driven by fourth-generation, graphite-moderated, high-temperature, helium-cooled reactors eg HTTR (JAERI), GT-MHR (General Atomics), PBMR (South Africa)

A dedicated 600 MWth VHTR could potentially yield over 2 million m^3/day of Hydrogen (Industry figure).

Heat producing reactor and Sulphur Iodine Cycle

The Sulphur Iodine Cycle:

The Bunsen Reaction: (Exothermic)

$$SO_2 + I_2 + 2\,H_2O \rightarrow H_2SO_4 + 2HI$$

(120°C, $\Delta G = -41$, $\Delta H = -216$ kJ/mole)

Hydrogen Iodide Dissociation: (Endothermic)

$$2\,HI \rightarrow H_2 + I_2$$

(450°C, $\Delta G = 124$, $\Delta H = 12$ kJ/mole)

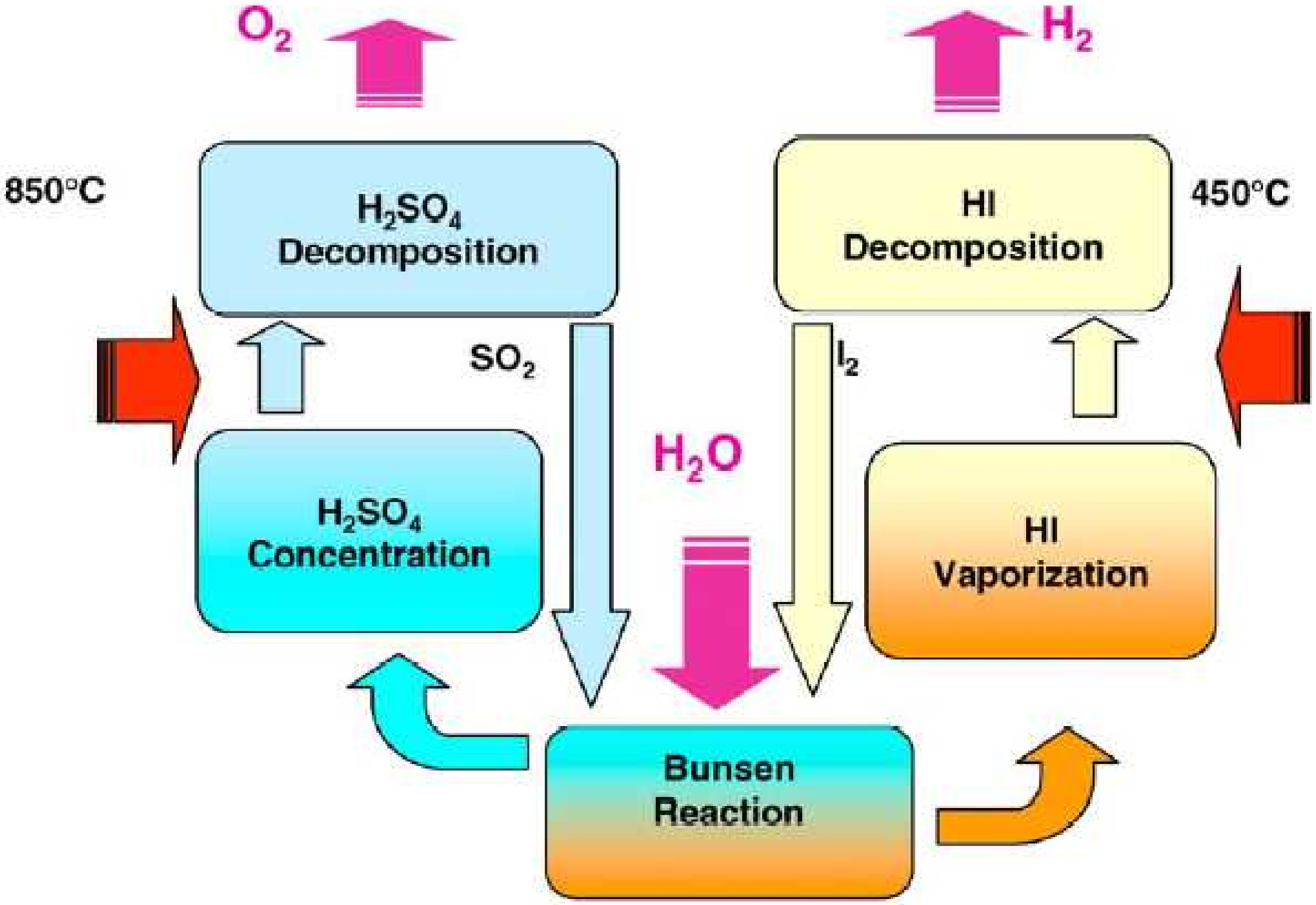
Sulphuric Acid Decomposition: (Endothermic)

$$H_2SO_4 \rightarrow H_2O + SO_2 + \tfrac{1}{2}\,O_2$$

(850°C, $\Delta G = -137$, $\Delta H = 371$ kJ/mole)

These sum to:

$$H_2O \rightarrow H_2 + ½\, O_2$$


O_2
H_2
850°C
H_2SO_4 Decomposition
HI Decomposition
450°C
SO_2
I_2
H_2O
H_2SO_4 Concentration
HI Vaporization
Bunsen Reaction

In more detail:

$$(9\mathrm{I}_2)_\mathrm{l} + (\mathrm{SO}_2)_\mathrm{g} + (16\mathrm{H}_2\mathrm{O})_\mathrm{l} \Rightarrow (2\mathrm{HI} + 10\mathrm{H}_2\mathrm{O} + 8\mathrm{I}_2)_\mathrm{l} + (\mathrm{H}_2\mathrm{SO}_4 + 4\mathrm{H}_2\mathrm{O})_\mathrm{l} \quad [120\ {}^\circ\mathrm{C}] \tag{1}$$

$$\underline{\mathrm{L}_2 = (2\mathrm{HI} + 10\mathrm{H}_2\mathrm{O} + 8\mathrm{I}_2)_\mathrm{l}} \Rightarrow (2\mathrm{HI})_\mathrm{g} + (10\mathrm{H}_2\mathrm{O} + 8\mathrm{I}_2)_\mathrm{l} \quad [230\ {}^\circ\mathrm{C}] \tag{2}$$

$$(2\mathrm{HI})_\mathrm{g} \Rightarrow \mathrm{H}_2 + (\mathrm{I}_2)_\mathrm{l} \quad [330\ {}^\circ\mathrm{C}] \tag{3}$$

$$\underline{\mathrm{L}_1 = (\mathrm{H}_2\mathrm{SO}_4 + 4\mathrm{H}_2\mathrm{O})} \Rightarrow (\mathrm{H}_2\mathrm{SO}_4)_\mathrm{l} + (4\mathrm{H}_2\mathrm{O})_\mathrm{l} \quad [300\ {}^\circ\mathrm{C}] \tag{4}$$

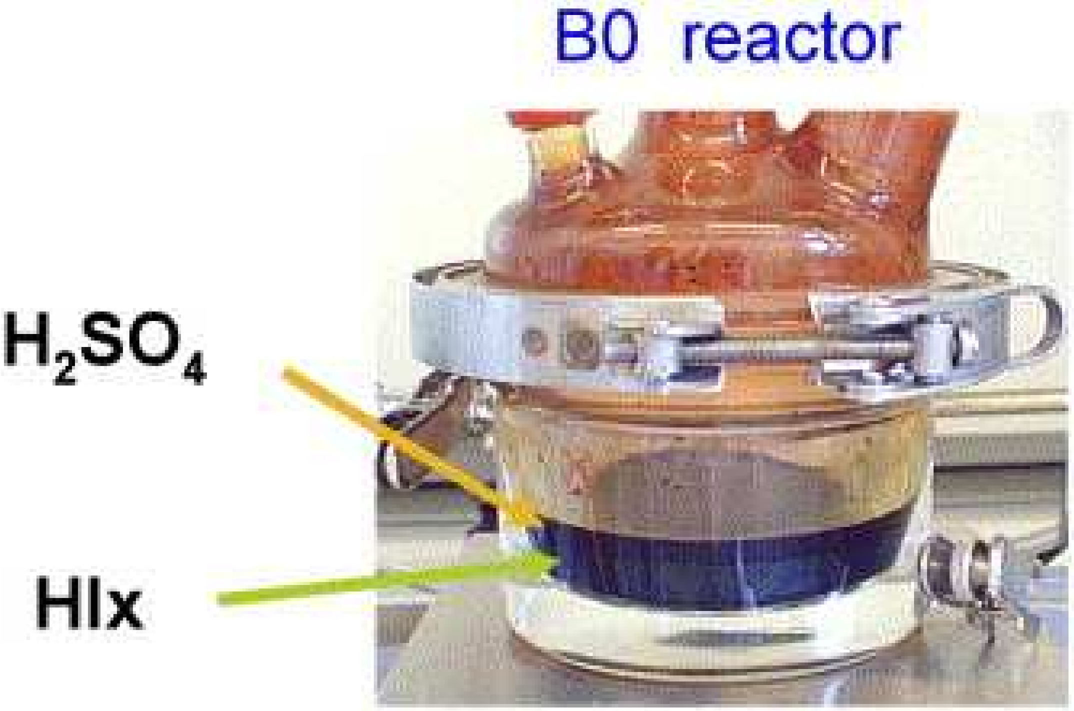
$$(\mathrm{H}_2\mathrm{SO}_4)_\mathrm{l} \Rightarrow (\mathrm{H}_2\mathrm{SO}_4)_\mathrm{g} \quad [360\ {}^\circ\mathrm{C}] \tag{5}$$

$$(\mathrm{H}_2\mathrm{SO}_4)_\mathrm{g} \Rightarrow (\mathrm{SO}_3)_\mathrm{g} + (\mathrm{H}_2\mathrm{O})_\mathrm{g} \quad [400\ {}^\circ\mathrm{C}] \tag{6}$$

$$(\mathrm{SO}_3)_\mathrm{g} \Rightarrow (\mathrm{SO}_2)_\mathrm{g} + \frac{1}{2}\mathrm{O}_2 \quad [870\ {}^\circ\mathrm{C}] \tag{7}$$

Energy Conv. Management 47 (2006) 2740

Phase separation between L_1 and L_2 occurs, the heavy HI containing liquid can thus be separated from the lighter rest



The HI should be separated from the HI containing liquid.

Barriers to overcome:

- the extraction of HI from the HI_x mixture is difficult because of the presence of an ‘azeotrope’ in the mixture, which prevents simple distillation (liquid and vapour have similar HI concentration)

- the extraction of HI from the HI_x mixture requires very large heat exchanges, due to the large heat capacity induced by the high water content of the mixture

- the decomposition reaction 3 is incomplete and slow

Iodine questions

- availability: a 600 MW coupled hydrogen production plant, requires~ 3000 t. A single reactor seems ‘realistic’ when compared to the world yearly production of 20 000 t and the estimated world reserves of 15 × 10^6 t.
Large number of reactors? Less realistic (I price will rise).

- iodine losses. Average cost of \$15 per kg of iodine, the production of 1 kg of H_2 requires the handling of \$20 000 of iodine. This implies that iodine molar losses must be well below 10^{-4} to reach the hydrogen production cost goal (~ order of \$2 per kg of H_2).

Heat source for sulfur iodine cycle:

- High temperature nuclear reactor.
- Solar concentrators? They can reach the temperatures required but don’t work continuously, which can lower overall efficiencies. Heat storage materials may deliver heat at those times (night, clouded sky)?
- ‘Waste heat’ from various sources.
- Geothermal power

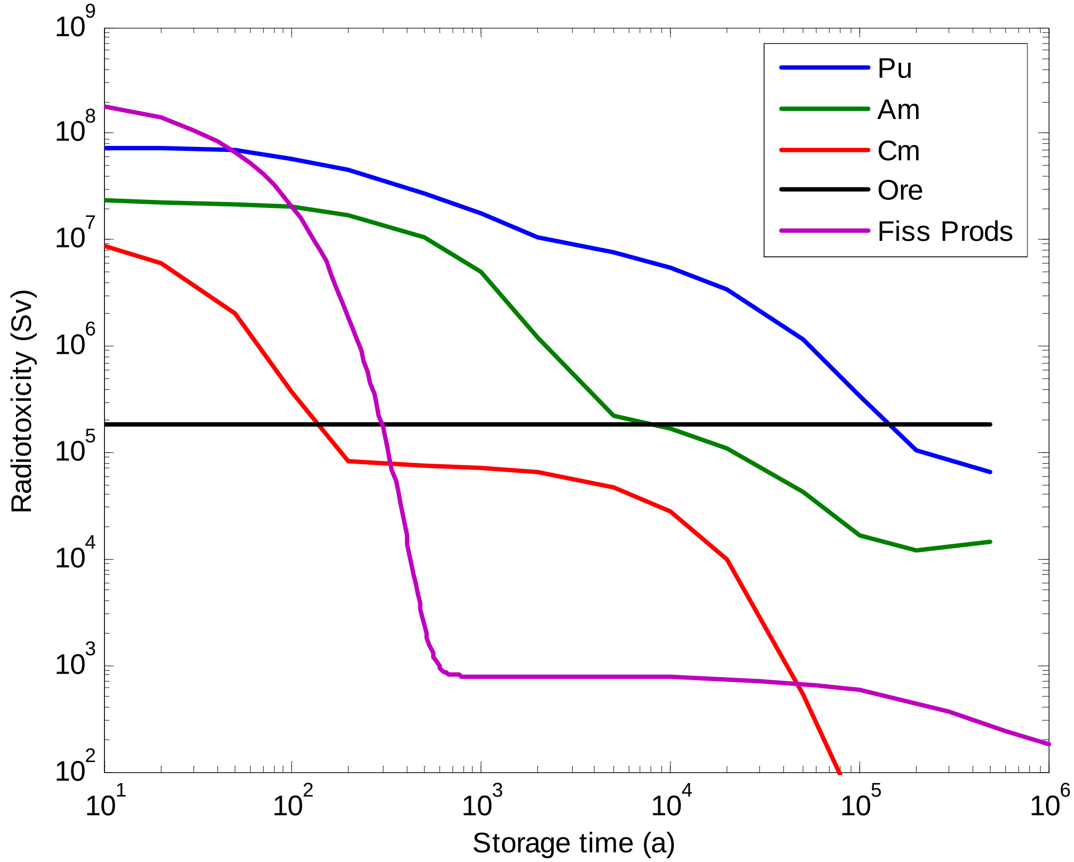
Nuclear option: sustainability issues of fission energy

- low CO_2 emission
- it provides a significant contribution to electricity supplies today
- there are methods to reduce long lived nuclear waste, especially when using high temperature reactors

but…

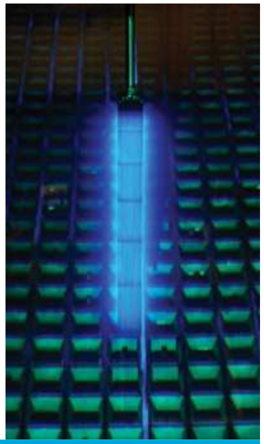
- production of nuclear waste, short lived
- currently still production of nuclear waste, long lived
- safety of handling high level waste during storage, preparation for transmutation, etc.
- mining of U ores has environmental impact (as all mining)
- proliferation of knowledge and fission materials (Pu)
- decommissioning of old reactors
- risks of earthquakes, terrorists, …

Spent fuel



Long lived: several
x 10000 years

Volume: few m^3 of insoluble, glassy material per year for one reactor.



Spent fuel
in cooling
basin

‘Short lived’ means ~ few 100 years

Sustainable Hydrogen and Electrical Energy Storage