Hydrogen production by electrolysis

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International Conference on Electrolysis
Copenhagen 2017

When did you last participate in an international electrolyzer conference?

Electrolyzer events are rare and real conference series perhaps non-existing. Electrolyzers are equivalent to fuel cells. but while conferences devoted to fuel cells are plentiful, electrolyzer conferences are certainly not. …

The aim of this initiative is to start a conference series devoted to electrolysis for energy conversion. Let us make a forum in which electrolysis is the main theme and not a sub-topic among many others.

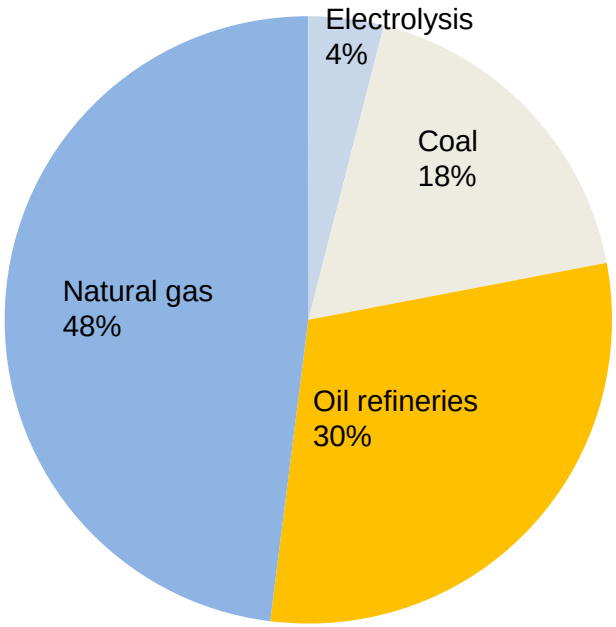
Be part of it. If you find this idea appealing then I hope you will come and take part in ICE2017 and make it a success. We will prepare the setting in a nice venue, but only the participants can ensure the success.

Welcome at ICE2017 in Copenhagen
From Tue 12th to Thu 15th of June, 2017

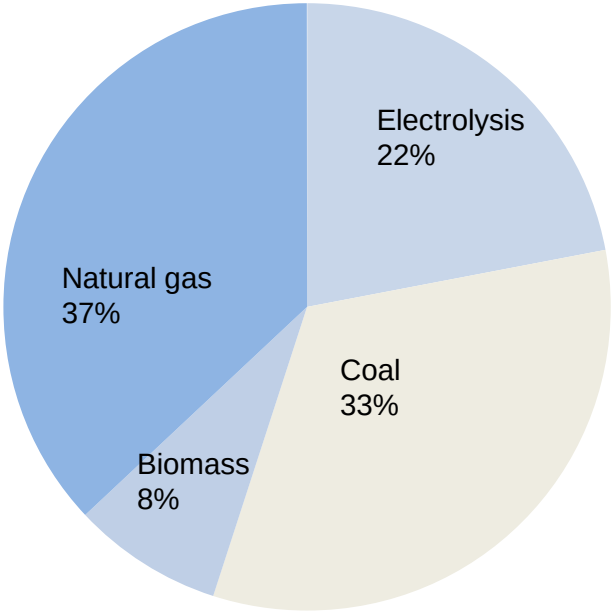
Jens Oluf Jensen
Chair of ICE2017

Sources for hydrogen

International Energy Agency. Technology Roadmap – Hydrogen and Fuel Cells, 2015



Today



Prediction year 2050

Electrolysis for H_2-production

Only large scale alternative for fossil-free production

Expensive method

Pure gases produced

Water electrolysis:

	Acidic conditions	Alkaline conditions
Anode	$H_2O \rightarrow ½\ O_2 + 2H^+ + 2e^-$	$2OH^- \rightarrow ½\ O_2 + 2H_2O + 2e^-$
Cathode	$2H^+ + 2e^- \rightarrow H_2$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

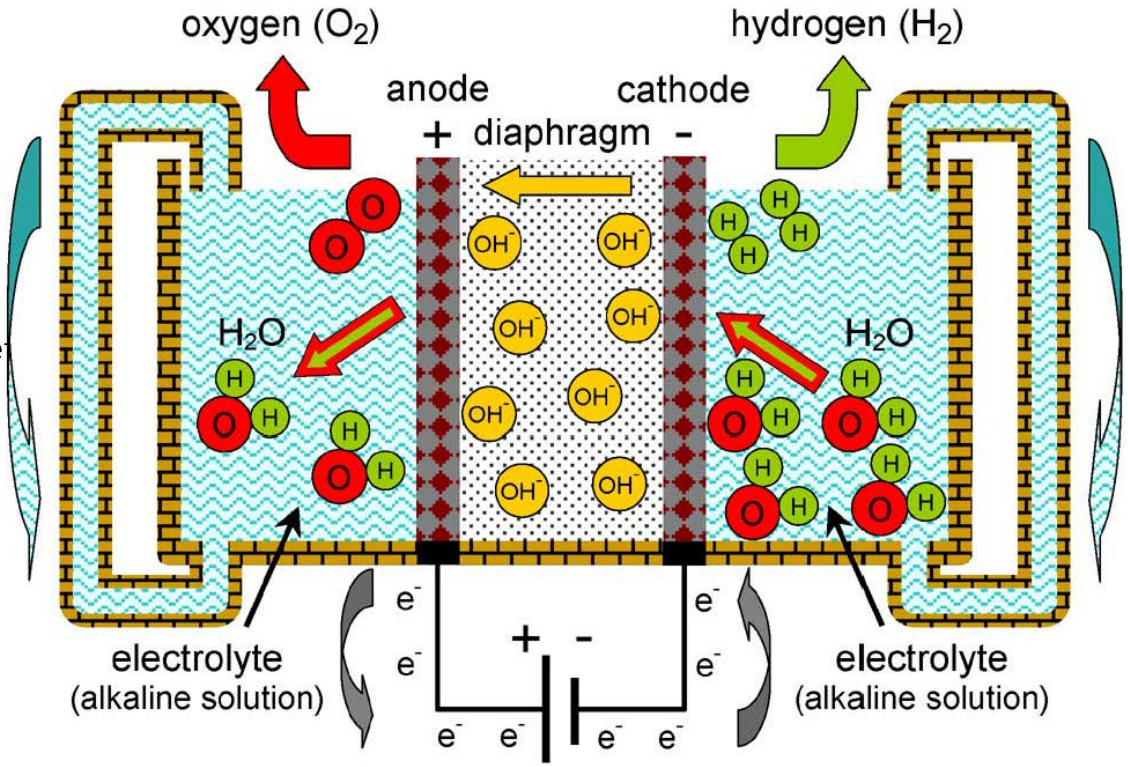
Total reaction: $H_2O \rightarrow H_2 + ½\ O_2$

Commercial techniques water electrolysis

Technology	Alkaline water electrolysis	SPE (Solid polymer electrolyte) electrolysis
Process	Aqueous electrolysis	”Reversed PEFC”
Feed	80% KOH, 80^{o}C	Pure H_2O, 80^{o}C
Charge carriers	OH^-	H^+
Industrial use	Well developed Large scale	High current densities Differential pressure Expensive catalysts

Alkaline water electrolysis

$2OH^- \rightarrow \frac{1}{2} O_2 + 2H_2O + 2e^-$



$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Alkaline water electrolyser

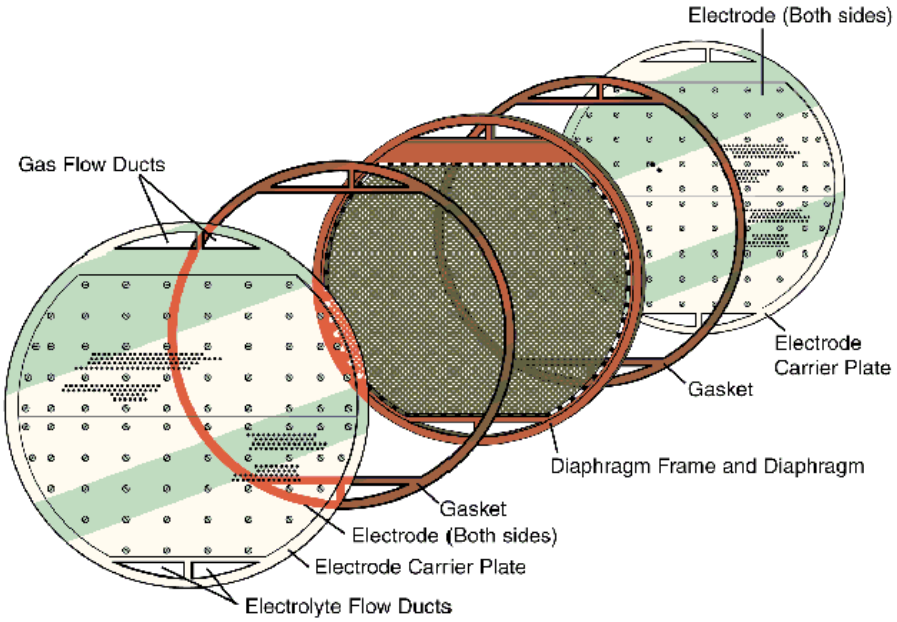
By courtesy of StatoilHydro

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

Cathode: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

Electrolyte: 25% KOH 80^oC

Inside a water electrolyser

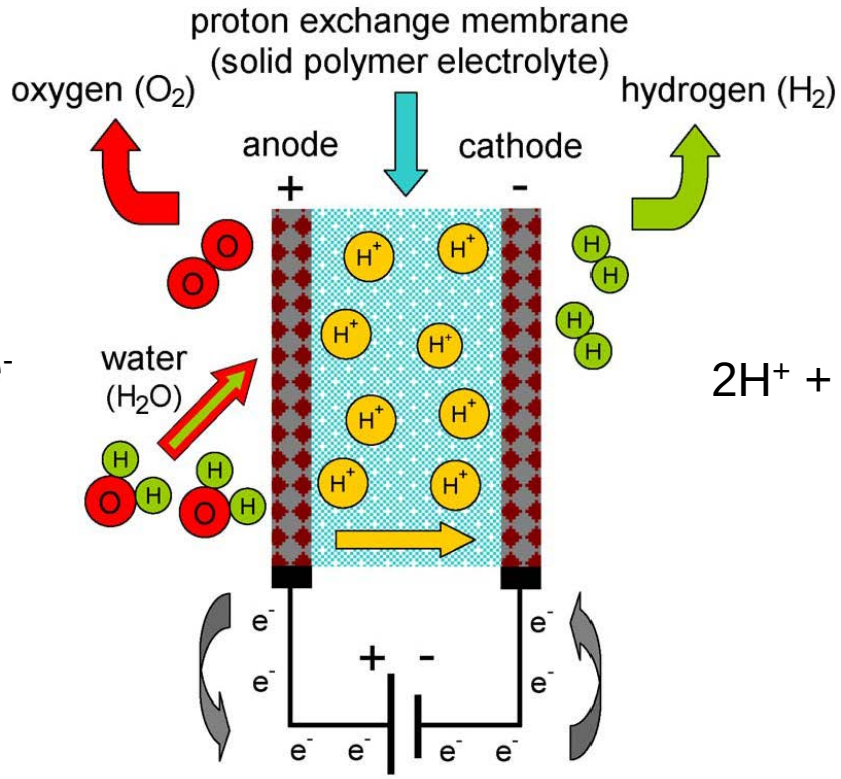


Bipolar technology
Electrodes of coated mild steel

By courtesy of StatoilHydro

Solid polymer electrolyte electrolysis

$H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^-$



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

Alkaline membrane cells

Less noble catalysts can be used than under acidic conditions (e.g. nickel)

Development of alkaline membranes

Still not commercially available

Steam electrolysis at 1000ºC:

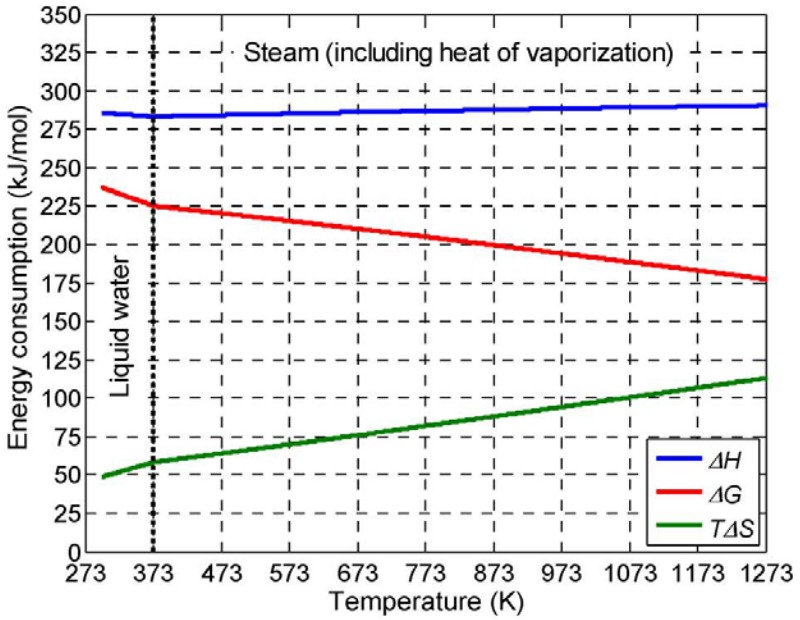
- low equilibrium cell voltage (0.91 V, compare 1.23 V)
- low overpotentials and IR drops

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

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = - zFE$$

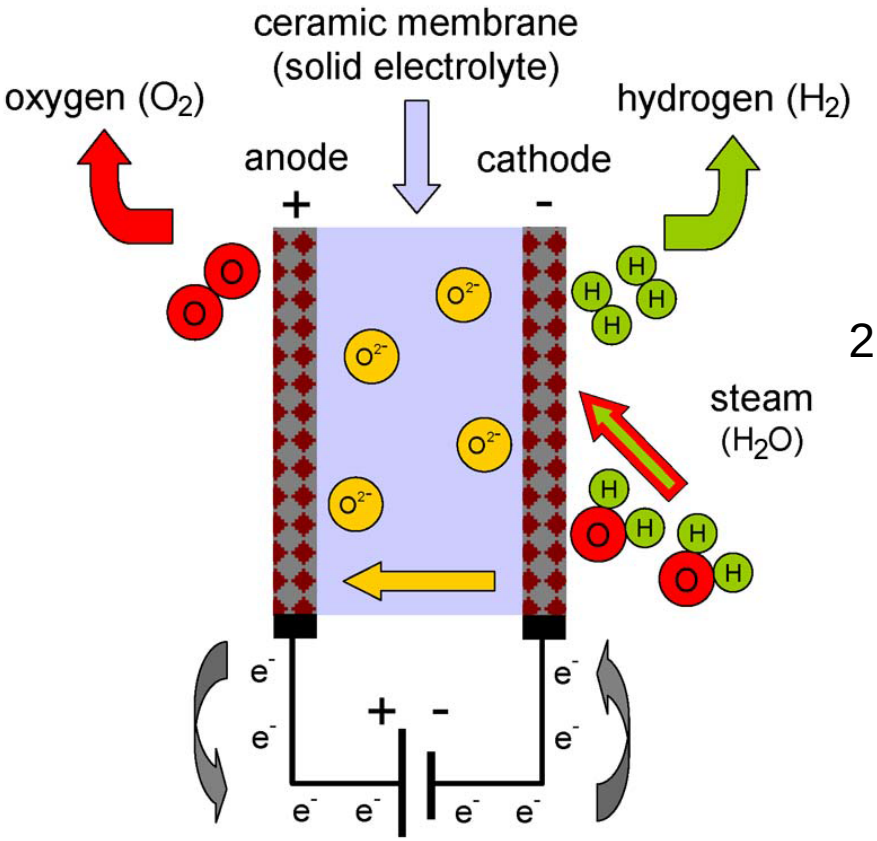
G, Gibbs free energy J/mole
H, enthalpy J/mole
T, absolute temperature K
S, entropy J/mole,K
z, moles electrons/moles substance
F, Faradays constant 96500 As/mole
E, equilibrium cell voltage



Technologies for water electrolysis

Technology	Alkaline water electrolysis	SPE (Solid polymer electrolyte) electrolysis	SOEC (Solid oxide electrolysis cell)
Process	Aqueous electrolysis	”Reversed PEFC”	”Reversed SOFC”
Feed	80% KOH, 80^{o}C	Pure H_2O, 100^{o}C	Steam, 800-900^{o}C
Charge carriers	OH^-, K^+	H^+	O^{2-}
Industrial use	Well developed Large scale	High current densities Differential pressure Expensive catalysts	Not yet commercial Pilot scale

High temperature steam electrolysis (SOEC)



$2O^{2-} \rightarrow O_2 + 4e^-$

Mix of H_2 and steam

$2H_2O + 4e^- \rightarrow H_2 + 2O^{2-}$

Electrolytic hydrogen production from other processes than water electrolysis…

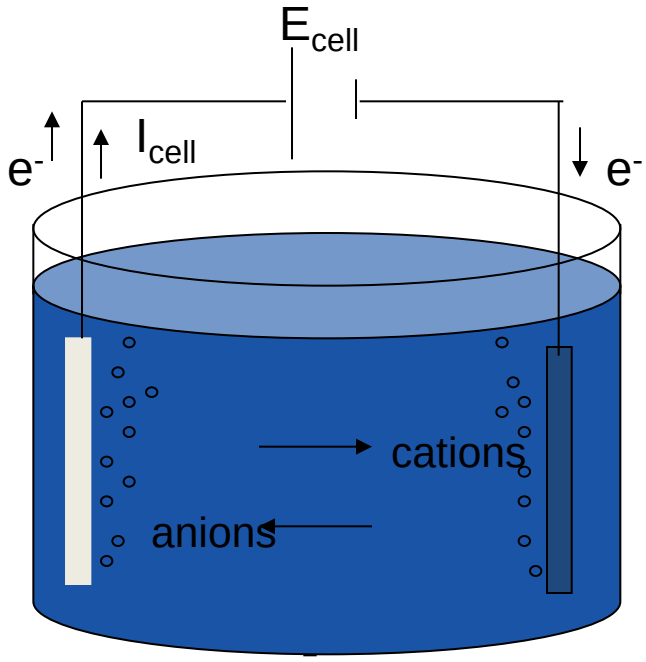
Why oxygen evolution as anode reaction?

- Oxygen often not used
- High E_{eq}
- Slow kinetics

Other anode reaction?

Anode reaction

$Red \rightarrow Ox + ne^-$



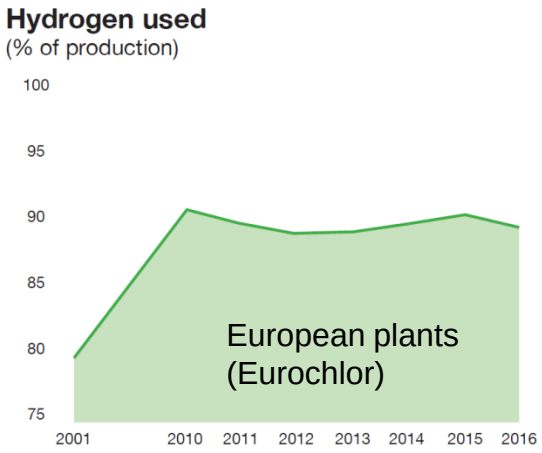
Anode reaction $2Cl^- \rightarrow Cl_2 + 2e^-$

Chlor-alkali

$2Cl^- + 2H_2O \rightarrow Cl_2 + H_2 + 2OH^-$

~60 million tonnes/year Cl_2 produced world wide

Many uses for the products



Chlorate

$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$

About 4 million tonnes/year $NaClO_3$ produced world wide

Main use in the bleaching of chemical pulp

In some plants the hydrogen formed is not used at all

These processes produce close to 2 Mtonnes H_2/year

Hydrogen from chlorate production

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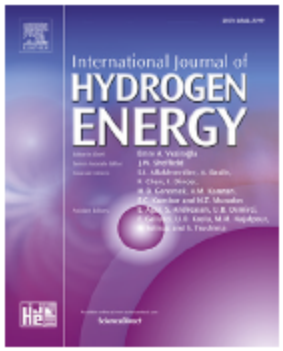

Operational experiences of PEMFC pilot plant using low grade hydrogen from sodium chlorate production process

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Anode reaction oxidation of alcohols, sugars etc organic compounds

Equilibrium cell voltage

Oxygen evolution (water electrolysis) E_{eq} = 1.23 V at 25^{o}C

Alcohol oxidation corresponding E_{eq} ~ 0.1- 0.2 V

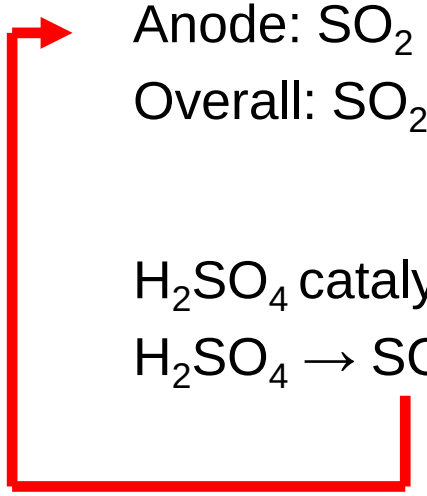
Electricity need directly proportional to the cell voltage (E_{cell}*I*t)

Hydrogen can be produced at significantly lower electricity consumption compared to in water electrolysis!

Thermo electrochemical cycles

Part thermal energy, part electricity

Example sulfur-hydrogen cycle



Anode: $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$

Overall: $SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$ E_{eq}= 0.17 V (compare 1.23 V)

H_2SO_4 catalytically decomposed back to SO_2

$H_2SO_4 \rightarrow SO_2 + H_2O + ½O_2$

Summary

- Hydrogen an important energy carrier in a future fossile free society
- Only large scale production alternative today produced without emission of greenhouse gases is electrolysis
- Oxygen produced often not used – other useful anodic products in aqueous based electrolytic processes, for example chlor-alkali
- Possibility to considerably reduce the electrical energy need if chosing certain anode reactions
- Future development: steam electrolysis, alkaline membrane electrolysis, alternative anode reactions, hybrid thermal/electrochemical cycles, improvement of existing techniques. (Also much reseach on photo chemical electrolysis.)