8th International Symposium Hydrogen & Energy,
16.-21. February 2014, Zhaoquing, China

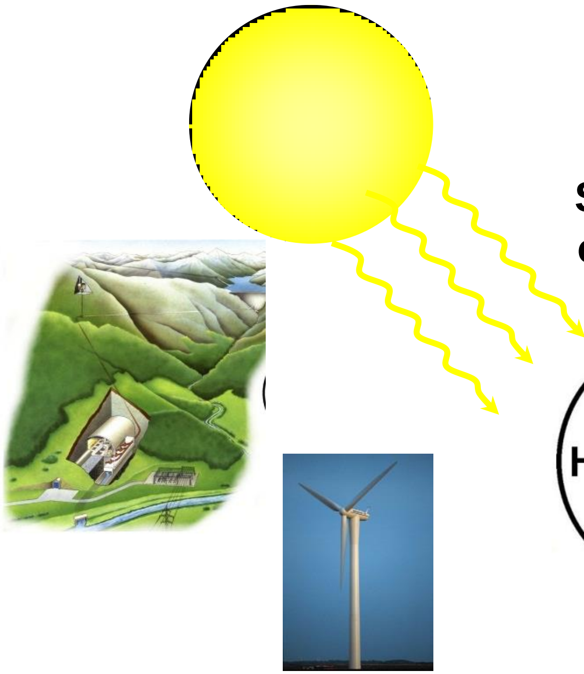
Novel Developments in Alkaline Water Electrolysis

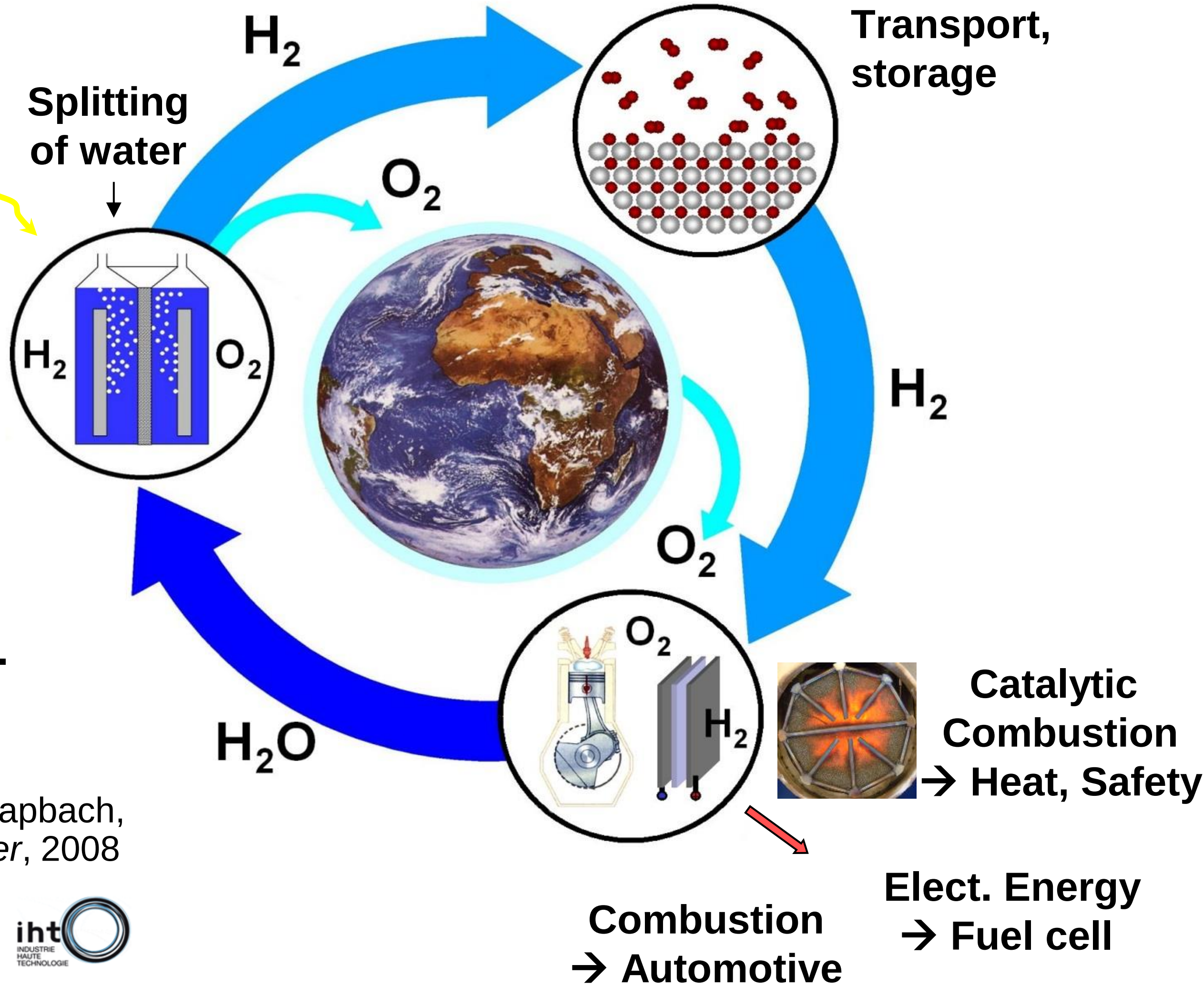
U.F. Vogt, M. Schlupp, D. Burnat, A. Züttel

Empa, Laboratory of Hydrogen & Energy, Abt. 505
Überlandstrasse 129
CH-8600 Dübendorf / Switzerland

Grant nº 278824

Hydrogen cycle





Renewable energy sources: solar, hydro, wind power etc.

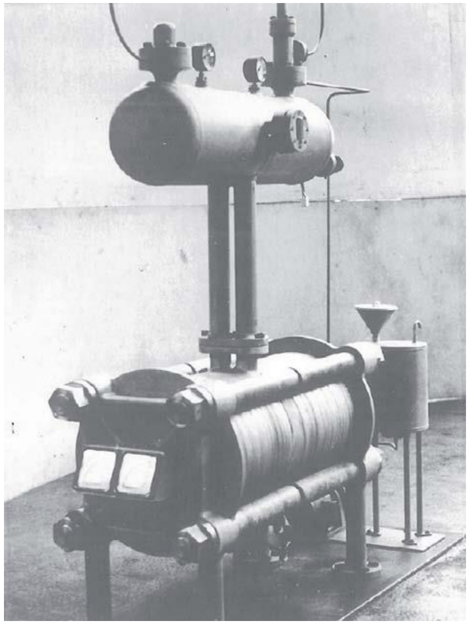
A. Züttel, A. Borgschulte, L. Schlapbach, *Hydrogen as a future energy carrier*, 2008

ELYGRID New Energy World JU Grant nº 278824 EMPA Materials Science & Technology iht INDUSTRIE HAUTE TECHNOLOGIE

History of Water Electrolysis: known for over 200 years

EMPA
Materials Science & Technology

- ~1800 : Electrolytic Water splitting (Ritter, Nicholson, Carlisle)
- 1834 : First use of the term «electrolysis» by Faraday
- 1900 : Oerlikon introduces first bipolar electrolyzer (2.5V, Zürich)
- 1939 : First 10'000Nm^3/h (900kg/h) electrolyzer
- 1948 : Zdansky develops pressure electrolyzer for Lonza
- 1951 : First commercial 30bar electrolyzer (Lurgi)
- 1967 : Zero-Gap Design



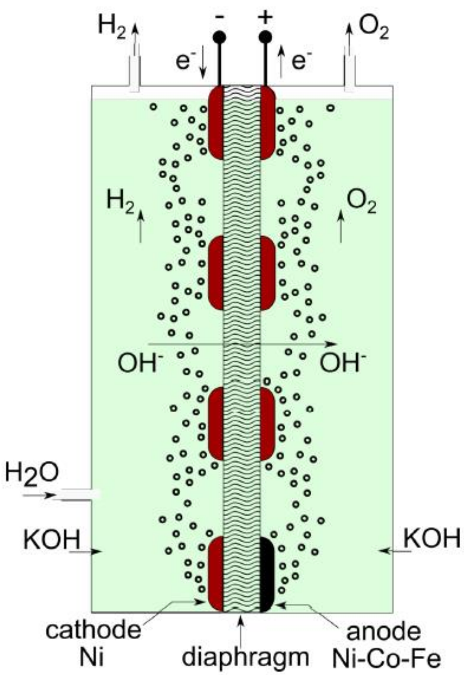
Lurgi-Zdansky prototype
alkaline electrolyser, 1949
Hydrogen Report Switzerland 2010/2011

- Water electrolysis accounts for > 5% of hydrogen production
- Most of hydrogen is used on side for the production of
  - Ammonia (Haber Bosch Process)
  - conversion of heavy petroleum sources by hydrocracking
  - cooling of generators
  - steel & glaas manufacturing
  - ………

Svein Sunde, NTNU, Trondheim, Halder Topse Catalysis Forum, 2006

Alkaline Water Electrolysis:

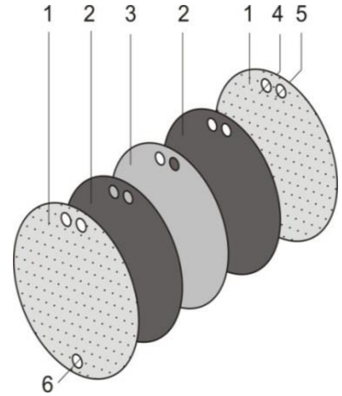
$H_2O \rightarrow H_2 + ½\ O_2$



Zero-gap geometry

Membrane to separate H_2 and O_2,
conduction of OH- via KOH
in open pore network

Source: Svein Sunde, NTNU, Trondheim,
Halder Topse Catalysis Forum, 2006



1) bipolar plates
2) electrode meshes
3) separator membrane
4), 5) H_2 and O_2 ducts
6) electrolyte ducts

Electrolyser at IHT, Giovanola SA, Monthey, CH

Working conditions: **32 bar, 85°C**, 25wt% KOH
Production rate: 760 m³/h H_2, equ. to 3.3 MW_{el}
Energy Consumption: 4,3 - 4,6 kWh/m³ H_2

H_2 purity: 99.8 - 99.9 vol%, O_2 purity: 99.3 - 99.6 vol%

556 cells, cell ϕ 1.6 m, length: 12 m, weight: 90 t

➢ 100 installed units

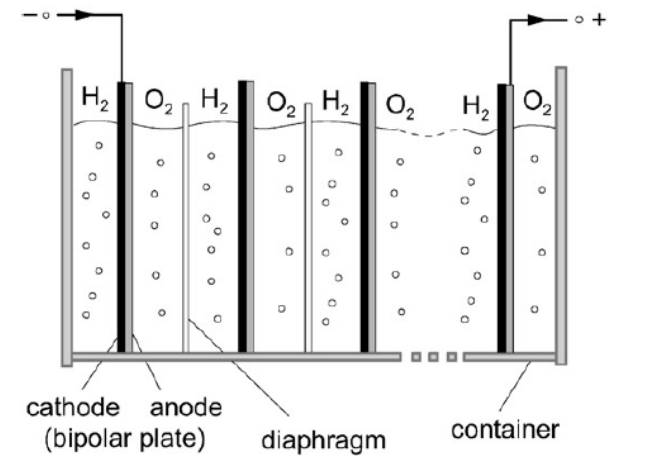
Souorce: IHT

Alkaline water electrolysis Historical aspects

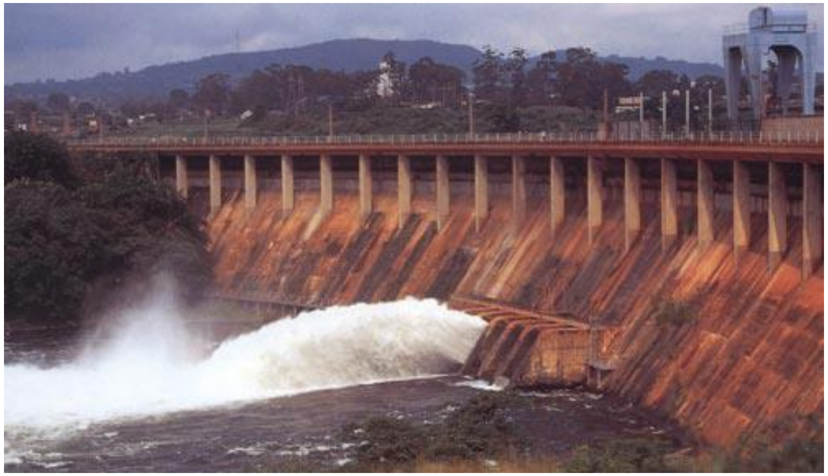
- Long established and well mature technology
- Reliable and safe
- Significantly efficient (~ 80%)
- The most extended technology at a commercial level

By 1902 over 400 industrial alkaline electrolysers world wide

- primarily for ammonia production (fertilizer industry)
- plants based on low cost hydroelectricity



Principle of a bipolar electrolyzer design



Aswan Dam - Egypt

Source: http://sitemaker.umich.edu/sec004_gp5/the_aswan_high_dam_benefits

Aswan Electrolyser (KIMA)

165MW - 37000 m³H_2/h

Source: ELT

State of the Art – IHT technology

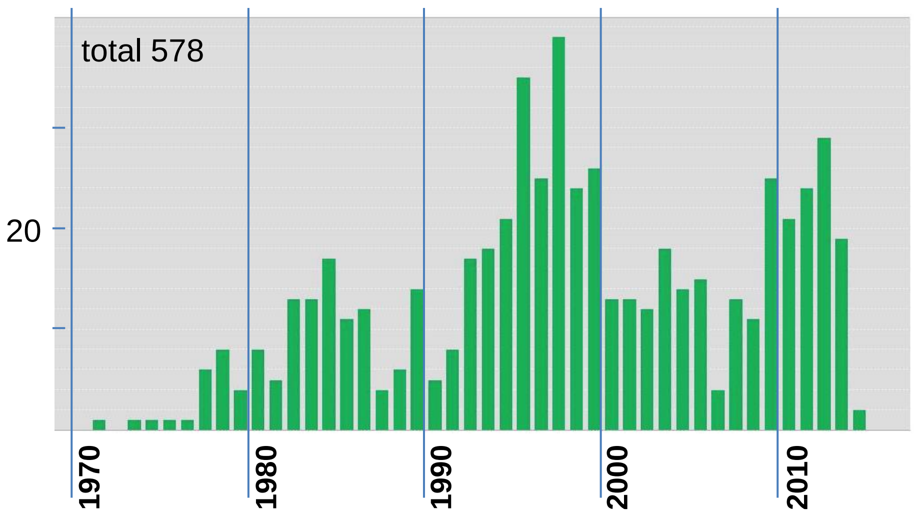
Zimbabwe (1975) 21,000 Nm3/h H_2
28 x 3.5 MW – 100MW

Peru (1965) 5,200 Nm3/h H_2
7 x 3.5 MW – 25MW

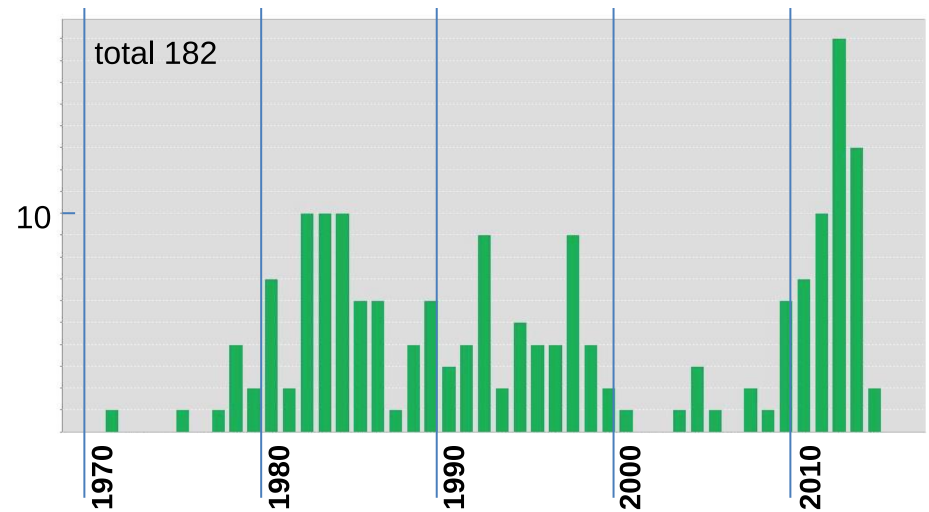
Electrolysis of Water: $H_2O \rightarrow H_2 + \frac{1}{2} O_2$

Water electrolysis is an electrochemical process
in which electricity is used to split water into Hydrogen and Oxygen

Published items with «alkaline water electrolys» in the title (web of knowledge):



Published items with «alkaline water electrolys*» in the title, excluding patents:



(For comparison: ~20'000 items for «solid oxide fuel cell».)

1973 Oil crisis, OPEC oil embargo

2010 EU National Renewable Energy Action Plan

1931 Patent on alkaline water electrolyser

Patented Jan. 13, 1931 1,788,904

UNITED STATES PATENT OFFICE

ARNO EWALD ZDANSKI, OF BERLIN, GERMANY, ASSIGNOR TO BAMAG-MEGUIN AKTIEN-GESELLSCHAFT, OF BERLIN, GERMANY

ELECTROLYTIC CELL FOR DECOMPOSING WATER

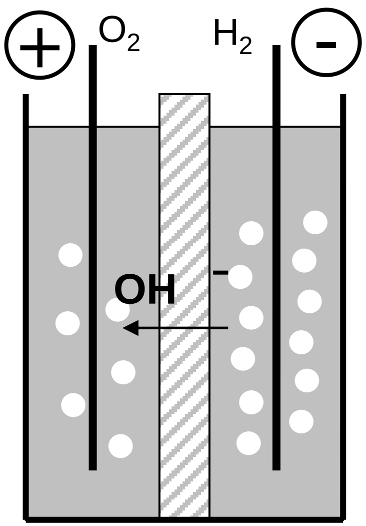
Reason for actual interest:

- Era of cheap petroleum will end
- Alternative fuels are needed

Three main technologies of water electrolysis

EMPA Materials Science & Technology

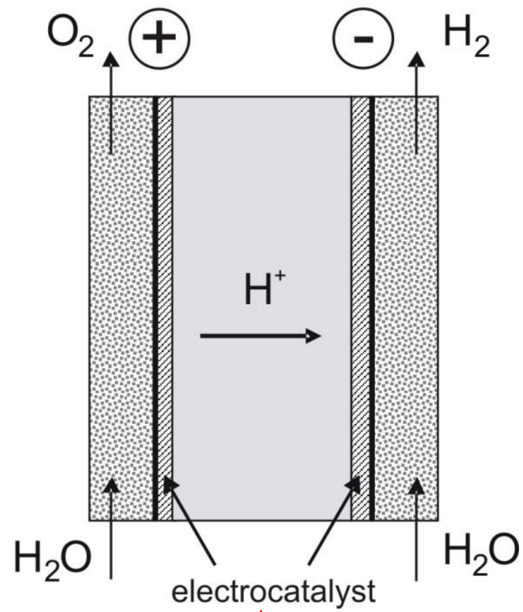
Alkaline Electrolysis



Separator: Asbestos (past)
Zirfon® (current)
Liquid electrolyte of KOH
50-120°C
1 – 60 bar

Commercial, MW scale

PEM Electrolysis
(Proton **E**xchange **M**embrane)

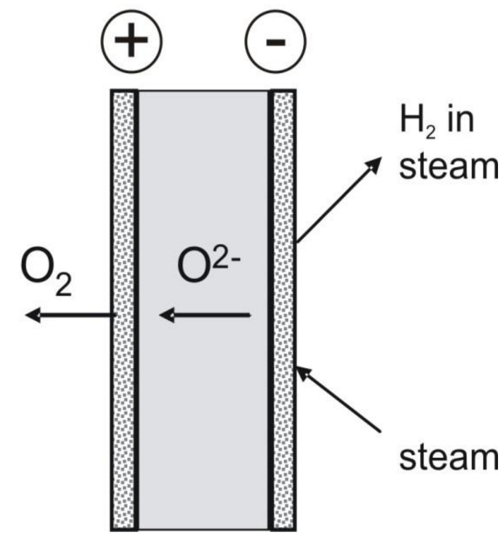


solid polymer electrolyte membrane (Nafion®)

60-100°C

Commercial, smaler scale

Solid Oxide Electrolysis (SOE)



gas tight solid oxide electrolyte, most common: $(Zr,Y)O_{2-\delta}$
700-1000°C

Research/Demonstrationt

Alkaline Water Electrolysis

EMPA Materials Science & Technology

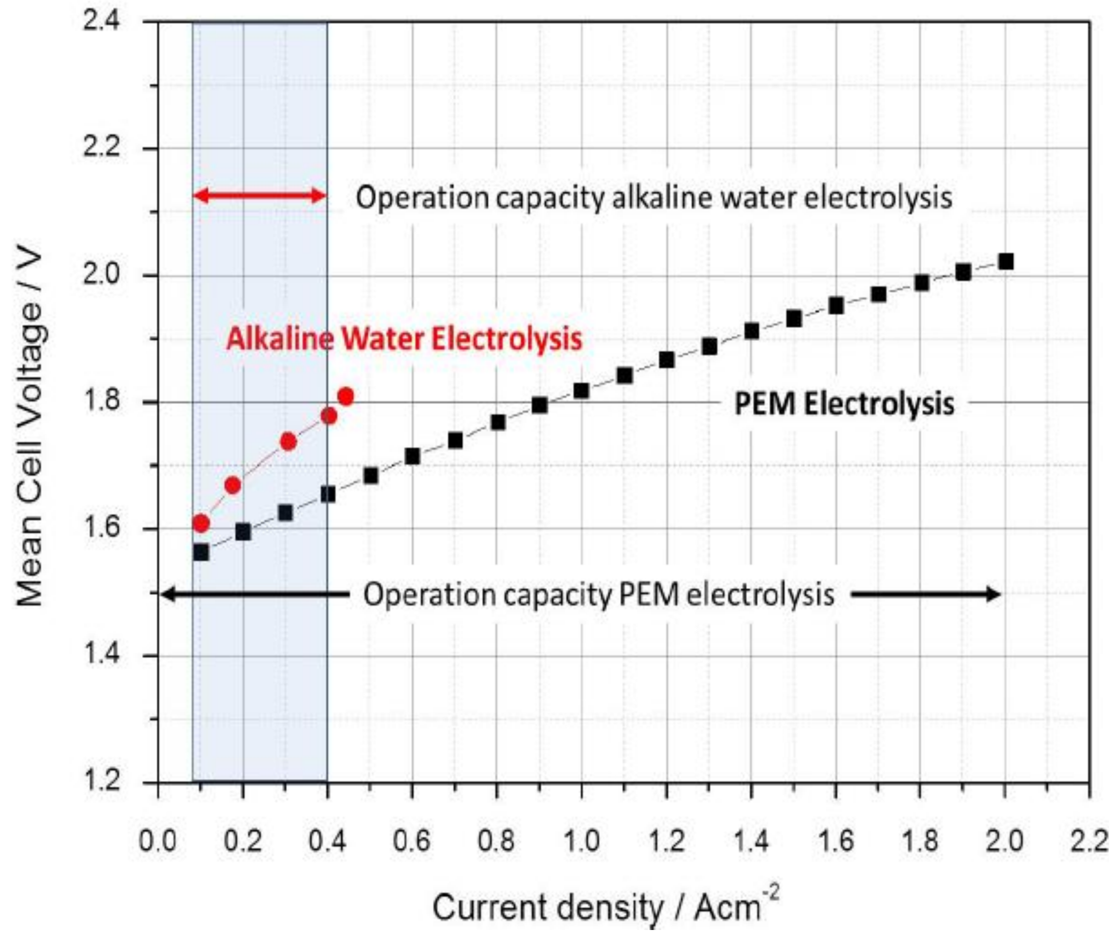
Advantages:

- Well developed technology
- Use of non-noble catalysts
- Long-term stability
- Units up to 750 Nm³/h (3,4 MW)

Challenges:

- Increase the current density
- Extend partial load capability
- Dynamics of the overall system
- Long term stable diaphragm

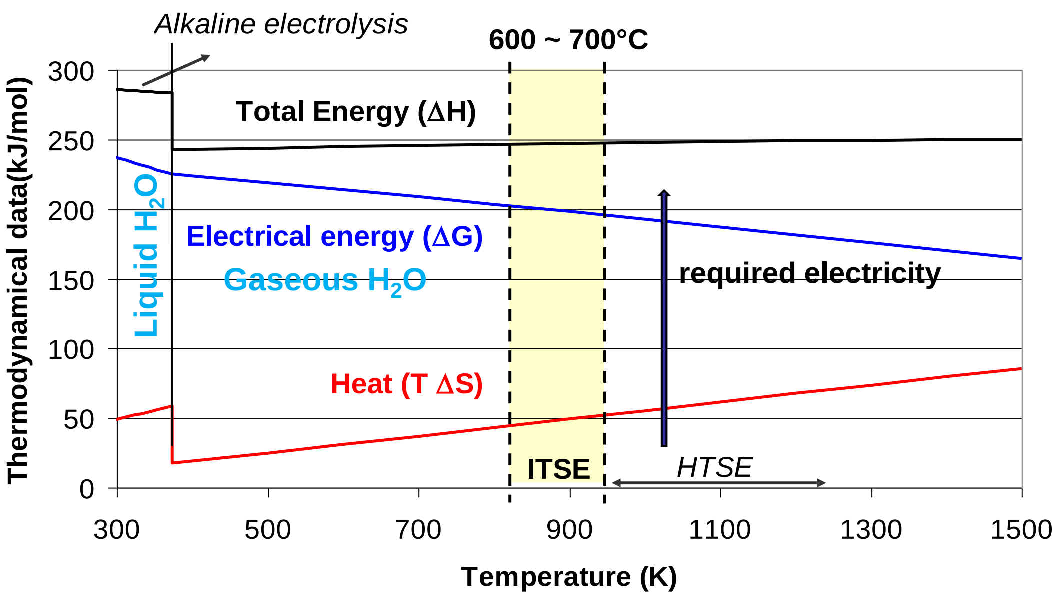
E/I performance of PEM and Alkaline Electrolysis



Source: Mergel, J; Carmo M, Fritz, D (2013). "Status on Technologies for Hydrogen Production by Water Electrolysis". In Stolten, D. Transition to Renewable Energy Systems. Weinheim: Wiley-VCH.

Thermodynamic properties as a function of temperature for the decomposition of liquid and gaseous water

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



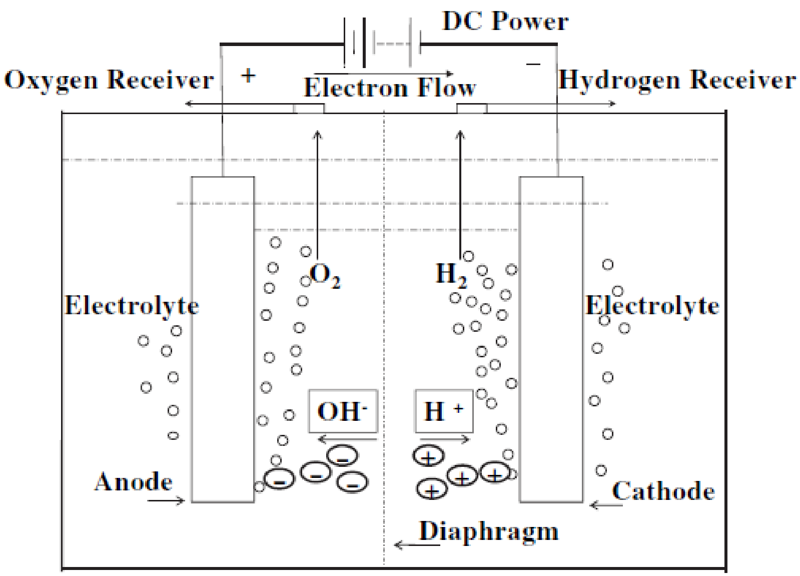
- the total energy demand ΔH for water splitting is lower in the vapour phase than in the liquid phase
  → the energy for vaporization can be provided thermally instead electrically
- the minimum demand for electrical energy ΔG decreases with increasing temperature
  → thus the total efficiency can be improved by providing part of the splitting energy thermally instead electrically
- the thermal energy T Δs for the endothermic reaction increases with increasing temperature
  → replacement of electrical by thermal energy
- the improved reaction kinetics at elevated temperatures are lowering overvoltage

$$\Delta H_{298K} = 286kJ/mol$$
$$\Delta S_{298K} = 163J/mol \cdot K$$
$$\Delta G_{298K} = 237kJ/mol$$

Δ H: stand.Enthalpy
ΔG: stand. Gibbs free Energy
T: Temperature K
ΔS: Entropy

E. Erdle, J. Gross, V. Meyringer, Proceedings of the 3th International Workshop, Vol. 2, High temperature Technology and its Applications, 1986, Konstanz, Germany, Becker M (eds) (DFVLR) p. 727-736

Chemistry of Alkaline Water Electrolysis



A schematic illustration of a basic water electrolysis system.

- Electrons are consumed by hydrogen ions (protons) to form hydrogen on the Cathode
- Hydroxy ions (anions) transfer through electrolyte solution to Anode
- OH^- ions give away electrons → electron flow

Electrolyte: potassium hydroxide
not as corrosive as acids

Electrodes: nickel (high activity, low cost)

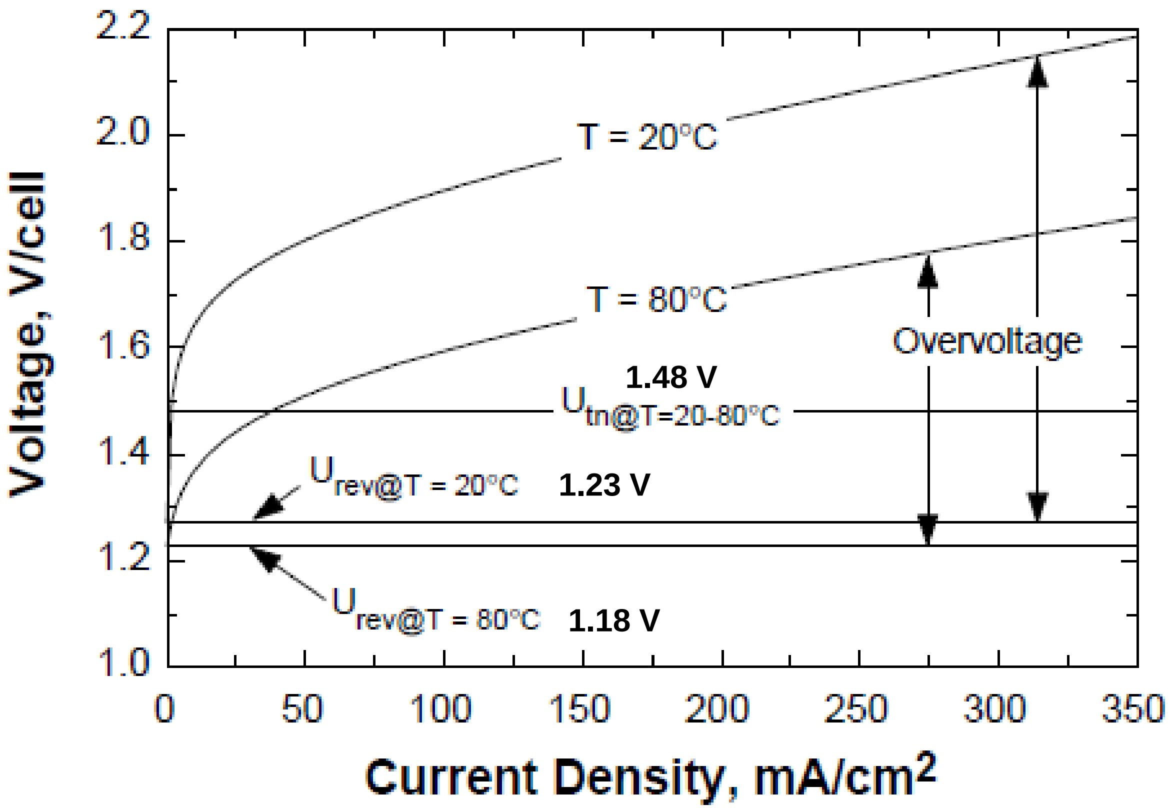
Diaphragm: asbestos (past), zirfon (new)
prevents intermixing of H_2 and O_2
permeable to OH^- ions

	Cathode (HER)	carrier ion	Anode (OER)
alkaline	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	OH^- →	$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$
		diaphragm	

K. Zeng, D. Zhang / Progress in Energy and Combustion Science 36 (2010) 307–326

cell voltage versus current density at a high and low operation temperature

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



Typical I–U curves for an electrolyzer cell at high and low temperatures

the difference between the two I–U curves is mainly due to the temperature dependence of the overvoltages

theoretical limits

$U_{thermoneutral} = 1.48V$

$U_{reversible} = 1.23V$

$$U_{\mathrm{tn}} = \frac{\Delta H}{zF}$$

$$U_{\mathrm{rev}} = \frac{\Delta G}{zF}$$

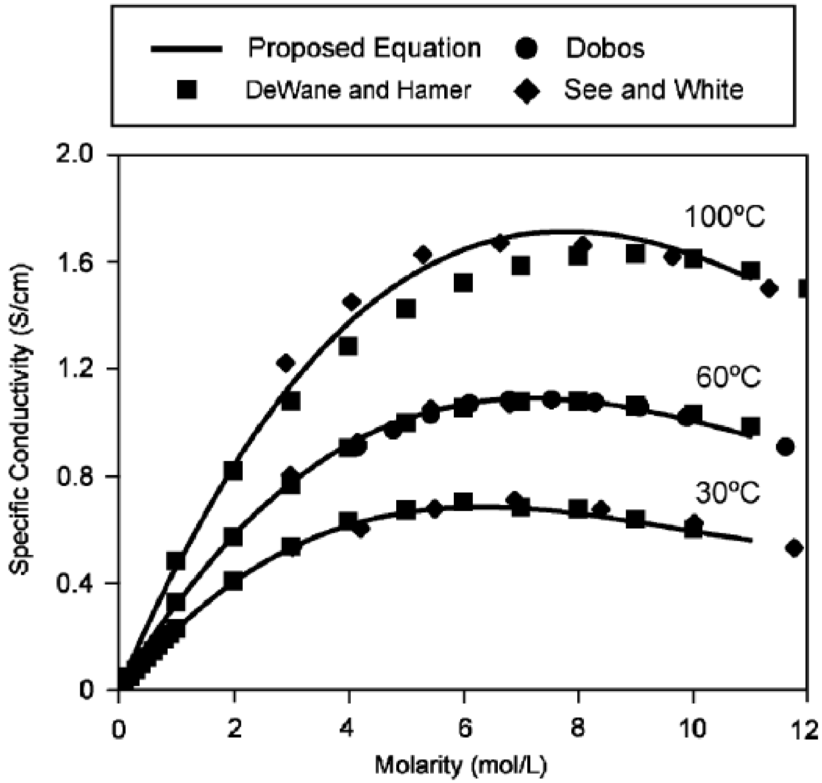
Energy efficiency $\eta_{\mathrm{e}} = \frac{U_{\mathrm{tn}}}{U}$

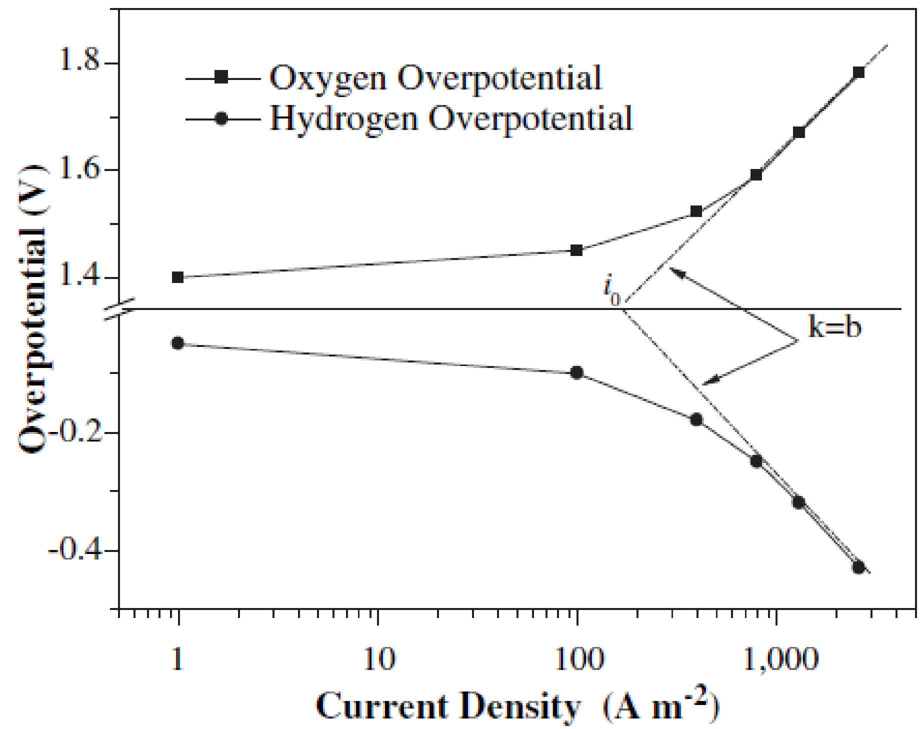
Δ H: stand.Enthalpy H_2O splitting
ΔG: stand. Gibbs free Energy
T: Temperature K
ΔS: Entropy

O. Ulleberg / International Journal of Hydrogen Energy 28 (2003) 21 – 33

Specific conductivity vs. molarity of KOH at 30, 60 and 100°C comparing reported data to proposed equation.

Typical Tafel plots for both hydrogen and oxygen evolution





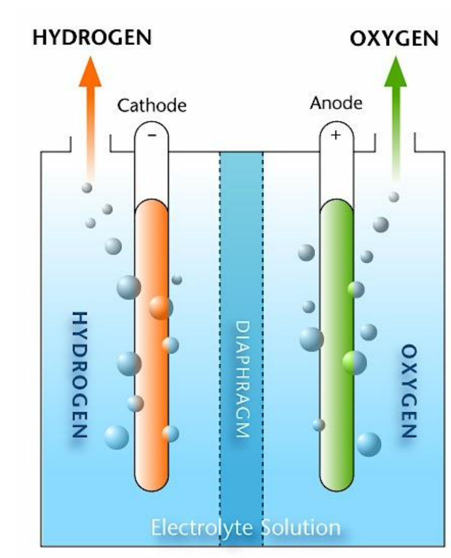
Giliam, R., et al International Journal of Hydrogen Energy 32 (2007) 359 – 364

K. Zeng, D. Zhang / Progress in Energy and Combustion Science 36 (2010) 307–326

Generation of heat mainly due to electrical inefficiencies

Electrical barriers include electrical resistance of:

- the circuit (R_1, R_2)
- activation energies of the electrochemical reactions on the surfaces of the electrodes
- availability of electrode surfaces due to partial coverage by gas bubbles formed
- Membrane resistance
- resistances to the ionic transfer within the electrolyte solution



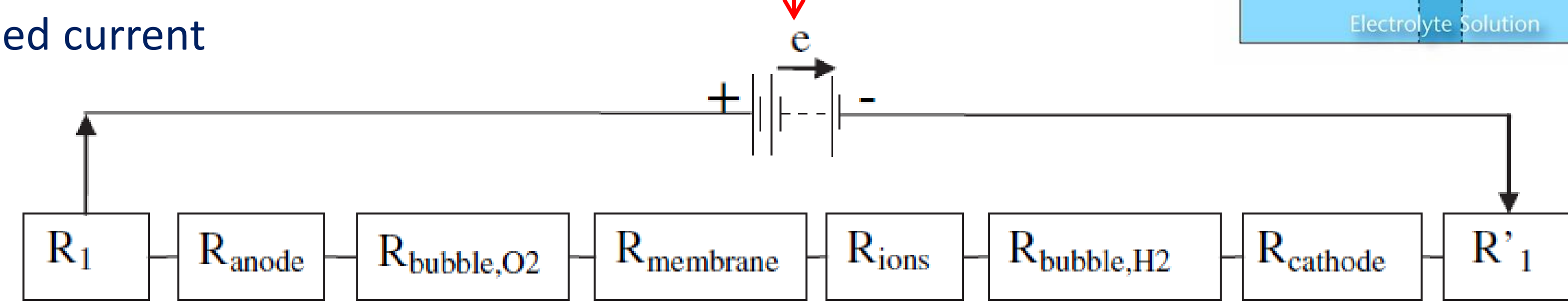
Electrolyzer cell potential:

$$E_{cell} = \boxed{E_0 + \eta_a + |\eta_c| + I} * \boxed{\boldsymbol{R}}$$

E_0: equilibrium cell potential

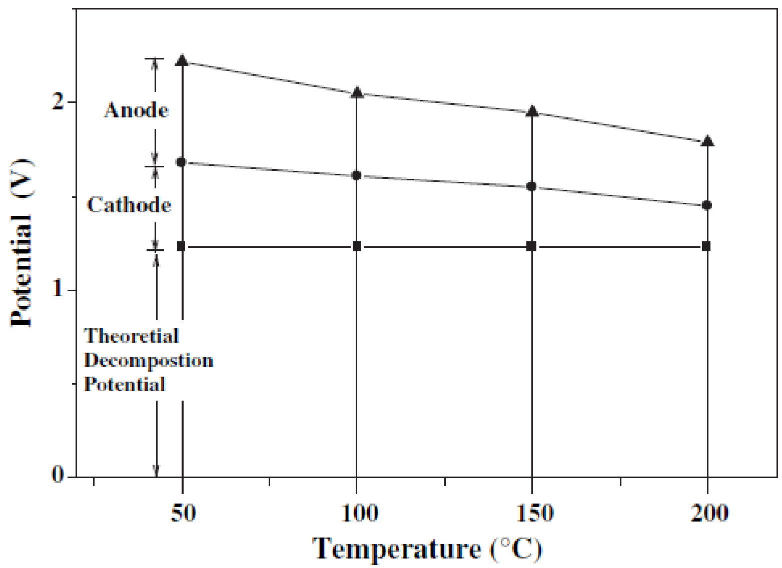
$\eta_{a,c}$: anodic, cathodic over potential

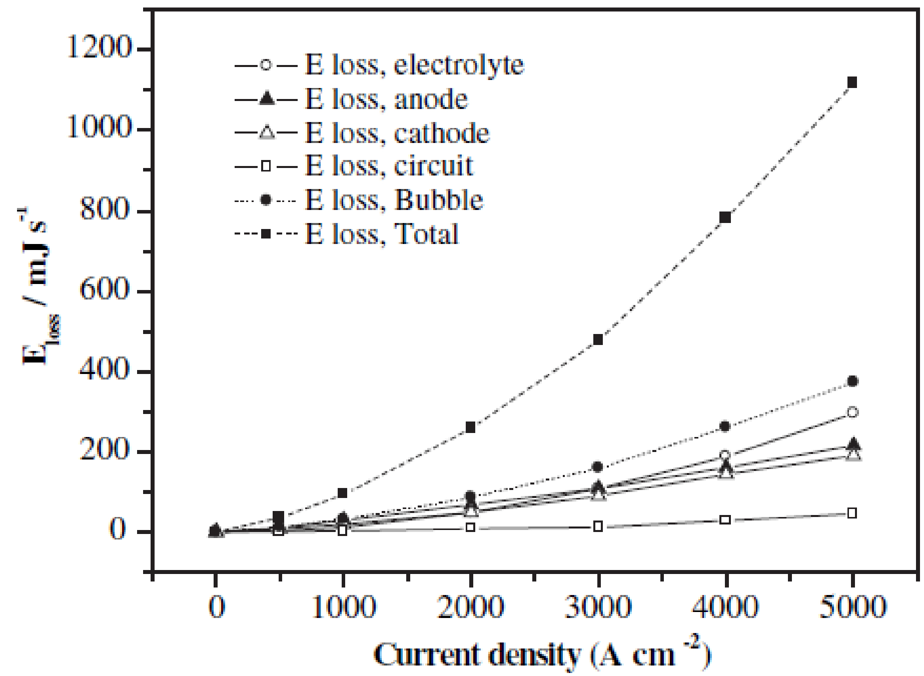
I: Applied current



Zeng *et al.*, *Progress in Energy and Combustion Science* **2010**, *36*, 307-326

Electrical resistance and bubble phenomena in alkaline water electrolysis



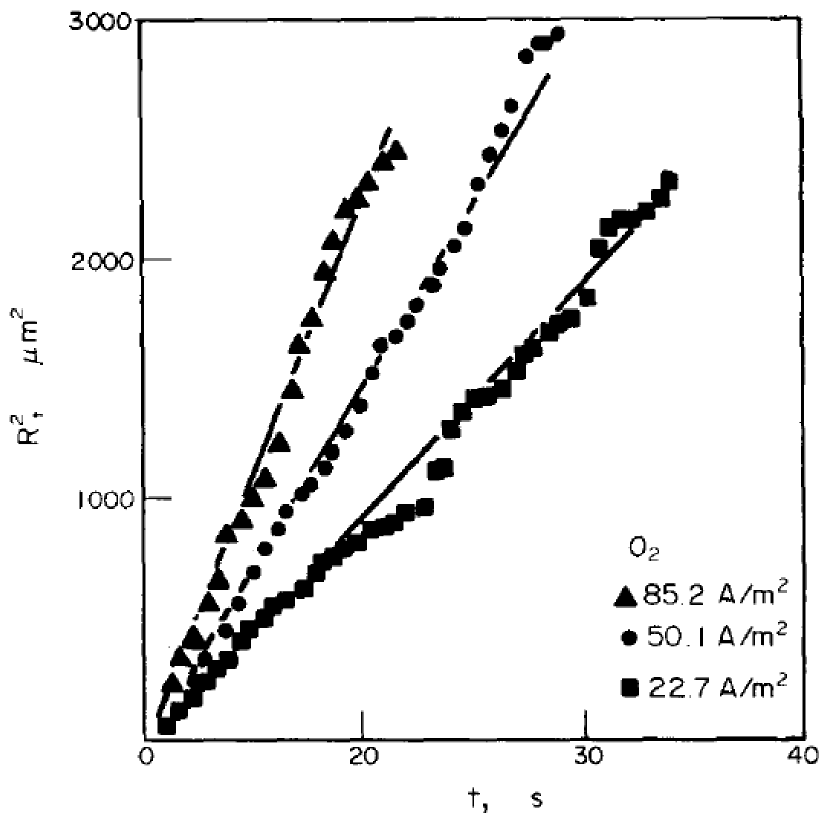


Ilustration of the contributions of anode and cathode polarisation to the cell voltage of an alkaline water electrolysis cell.

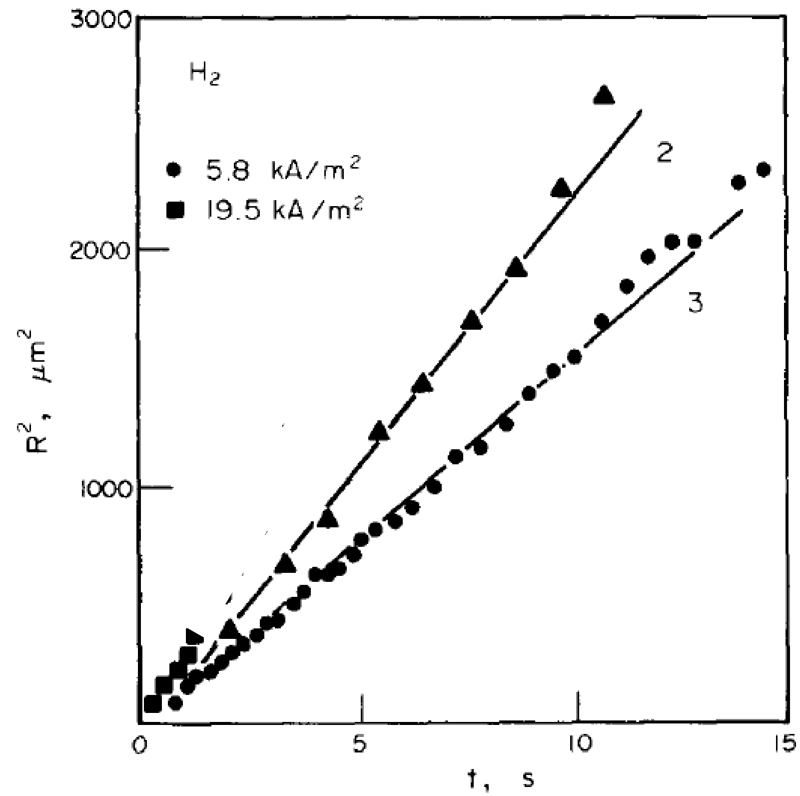
A qualitative comparison of the energy losses caused by reaction resistances:
ohmic resistance, ionic resistance and bubble resistance

K. Zeng, D. Zhang / Progress in Energy and Combustion Science 36 (2010) 307–326

Square of radius [R], vs time [t], for Oxygen and Hydrogen bubbles, growing on a nickel expanded metal gauze at natural convection at room temperature and atmospheric pressure during electrolysis in a 30 wt% KOH solution.

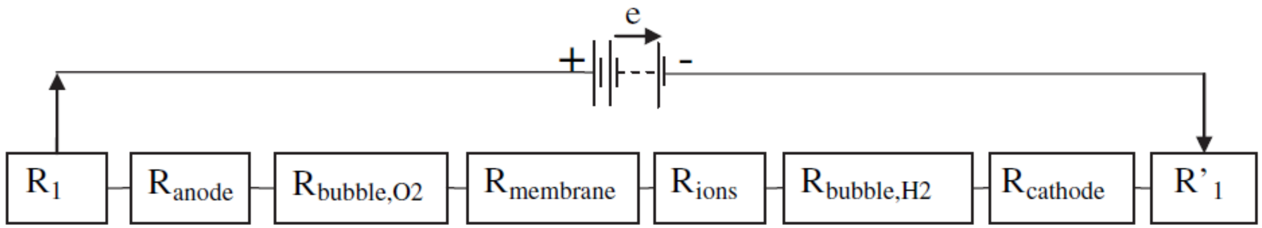


Effect of current density on O_2 bubble growth.

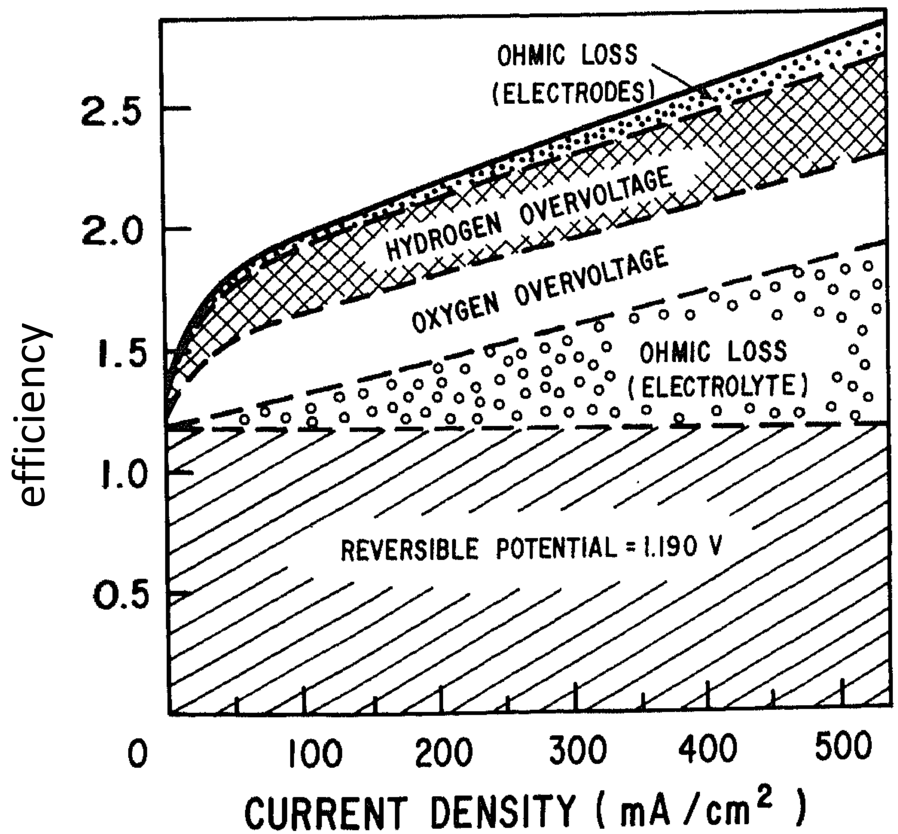


Effect of current density on H_2 bubble growth.

C. W. M. P. SILLEN, E. BARENDRECHT, L. J. J. JANSSEN AND S. J. D. VAN STRALEN, Int. J. Hydrogen nEnergy, Vol. 7 No. 7 1982



unactivated electrodes



Design / gas bubble covering of electrodes

Catalysts

design / chemistry / temperature / gas bubbles

laws of nature, temperature

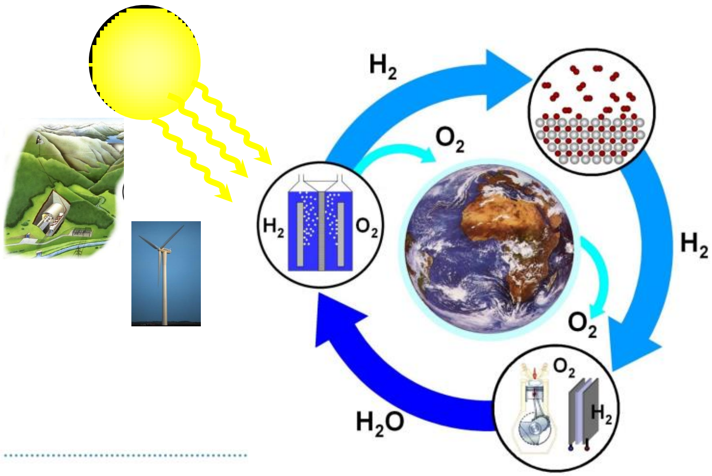
Electrical resistance leads to
heat generation
wastage of electrical energy as heat

Source: R.L. LeRoy, Int. J. Hydrogen Energy, 8(6) 1983 p.401-417

ELYGRID

Improvements to Integrate High Pressure Alkaline Electrolyzers for H_2 production from Renewable Energies to Balance the GRID

ELYGRID Project aims at contributing to the **reduction of the total cost** of hydrogen produced via electrolysis coupled to renewable energy sources (mainly wind turbines), and focusing on **mega watt size electrolyzers** (from 0,5 MW and up).



Main coals:

- **Big size alkaline electrolyzers**
- **Reduction of Total Cost of Ownership (TCO)**
- **Prototyping and testing with intermittent feeding**
- **Industrialization and market oriented approach**

PROJECT: ELYGRID

FUNDED BY: New Energy World JU — Grant nº 278824

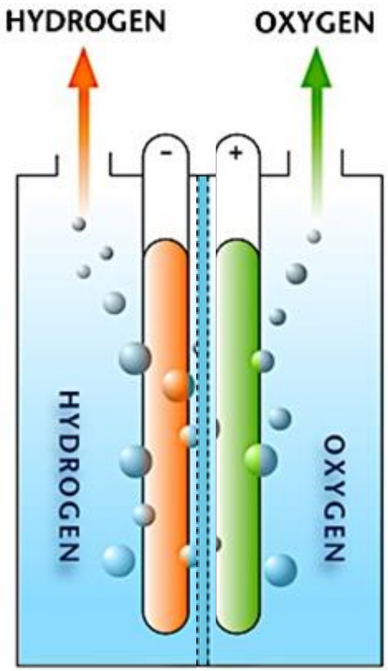
PARYNERS: iht, EMPA, HELION, JÜLICH, vito, lapesa, Inycom, Ingeteam, cea

COORDINATOR: Fundación para el Desarrollo de las Nuevas Tecnologías del Hidrógeno en Aragón

WP2: Development of separator membranes

EMPA Materials Science & Technology

Alkaline Electrolysis



- Membran to separate H_2 and O_2
- Conduction of OH- via KOH in open pores
- Zero-gap geometry

✓ High OH^- conductivity via KOH in open pore network during gas production

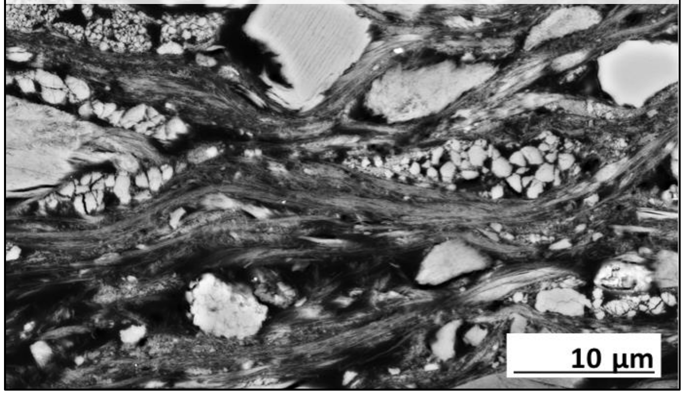
✓ Chemical and mechanical stability

- separator thickness ↓
- operating temperature ↑, pressure ↑, c(KOH) ↑

⇨ Efficiency ↑

Only one separator commercially available: Zirfon®Perl (Agfa), 0.5 mm thickness

56% porosity of Asbestos membrane $Mg_3Si_2O_5(OH)_4$



Alternative filler material

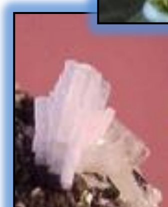
Mineral base fillers

$Mg_3Si_2O_5(OH)_4$ Chrysotile Asbestos

$CaSiO_3$ Wollastonite

$(Mg,Fe)_2SiO_4$ Olivine

$BaSO_4$ barite 99% purity



Synthetic based fillers

$BaTiO_3$ 98% purity, perovskite str., electroceramics

ZrO_2 3YSZ (TOSOH), technical ceramics, SOFC

Chemical corrosion experiment

T = 85°C - 120°C

KOH (25wt% - 35wt%)

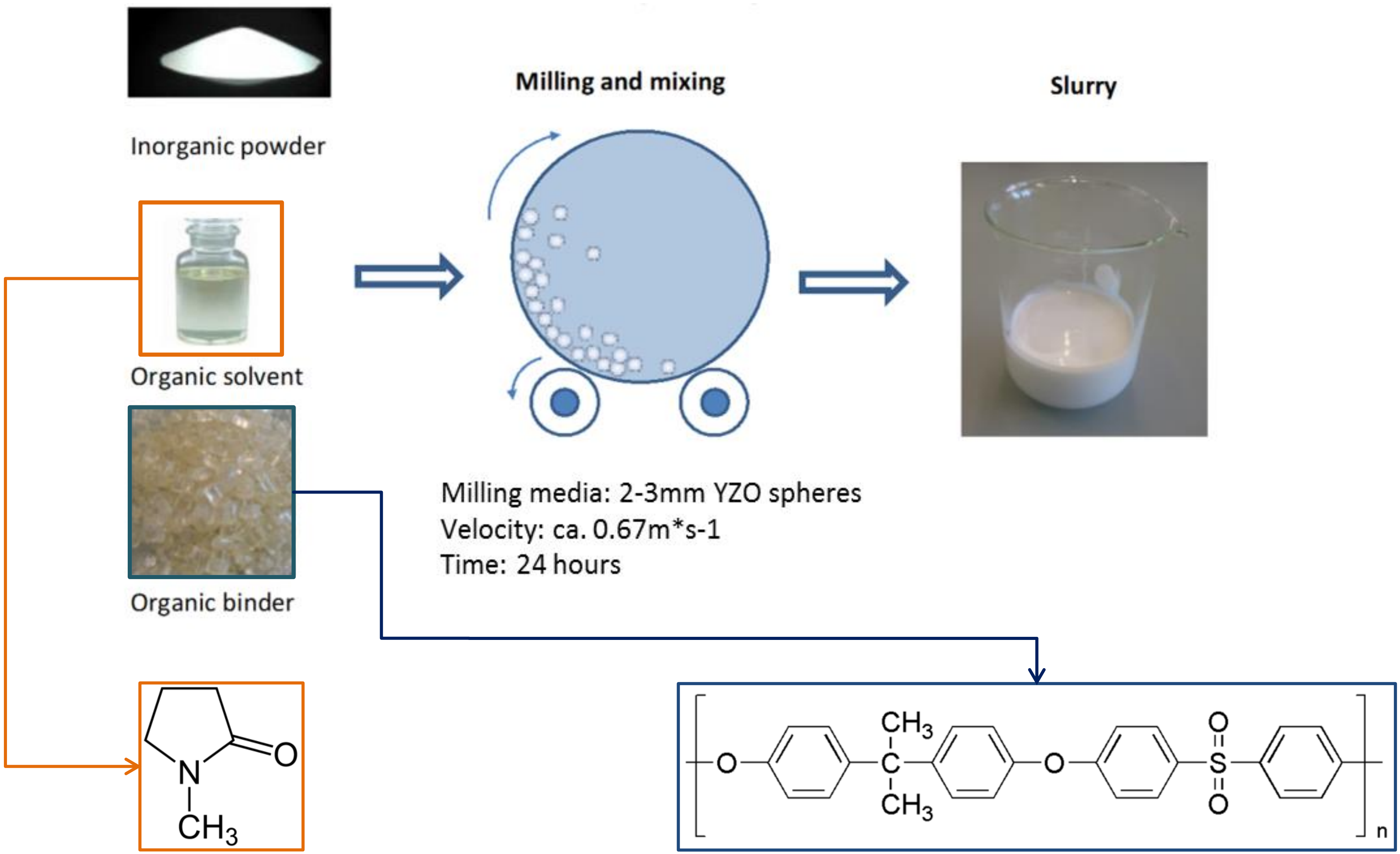
filler : KOH = 20 mM : 200 mM

t(h) = 50, 150, 255, 500; 1000; 2000; 4000; 8000

Method:
ICP-MS (Inductively coupled plasma mass spectroscopy)

www.webmineral.com

NOVAL MEMBRANE DEVELOPMENT

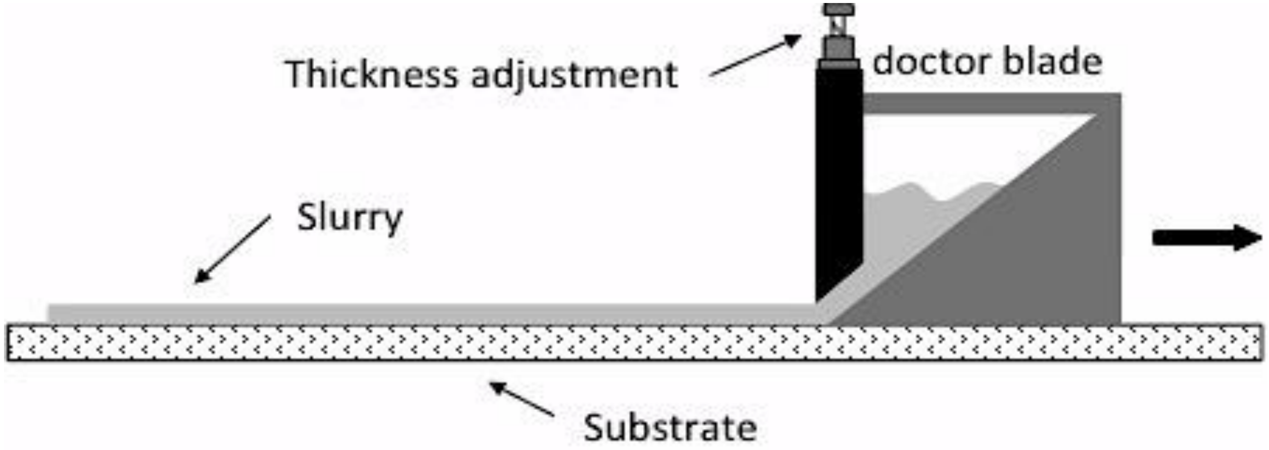


NMP

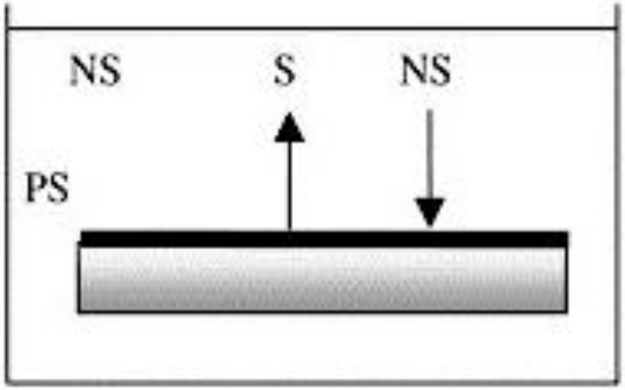
PSF

tape casting and phase phase inversion process

Reinforcement: PPS net (Polyphenylensulfid)

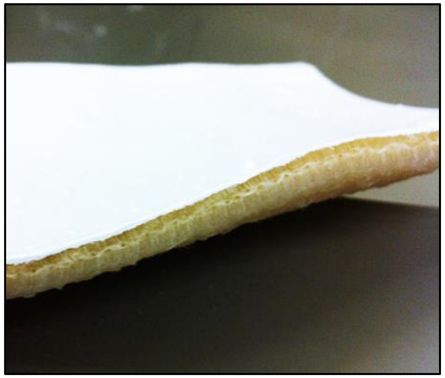


Nonsolvent coagulation bath



Schematic depiction of the immersion step.

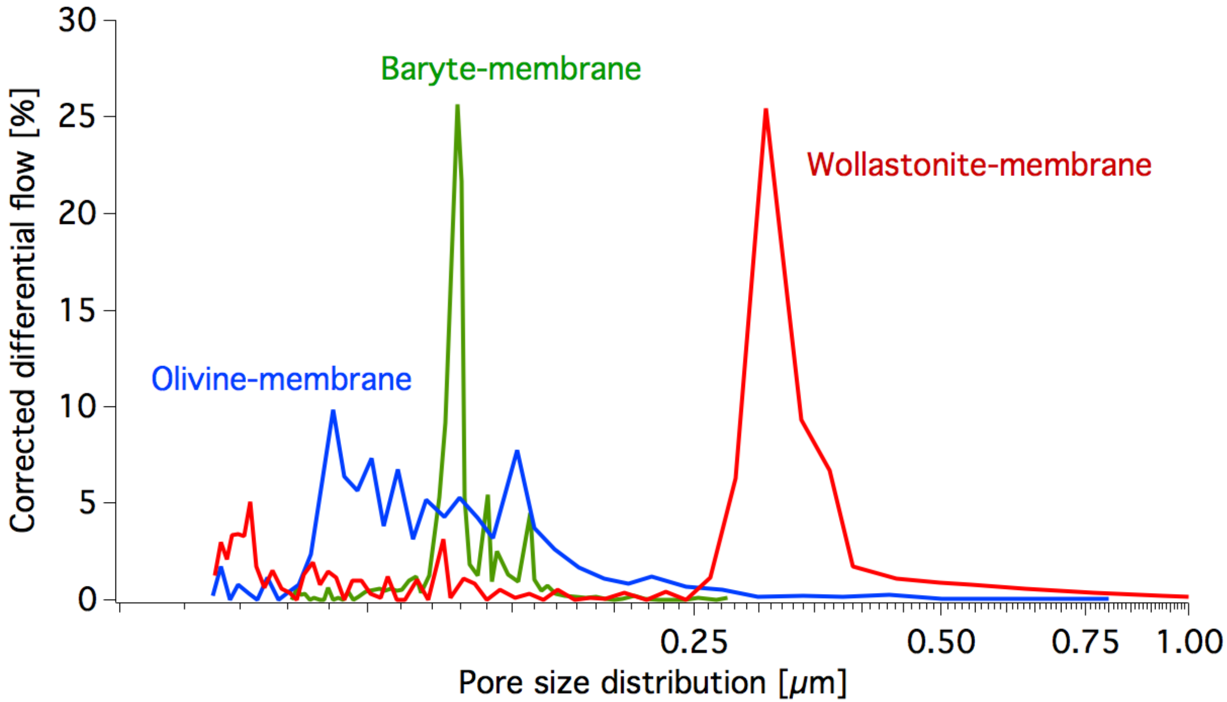
PS: polymer+solvent, S: solvent, NS: nonsolvent

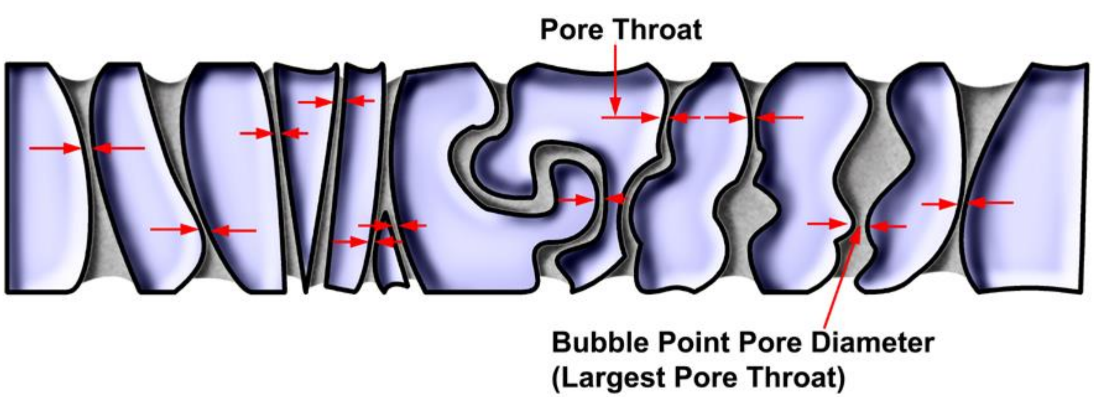


coated PPS substrate
thickness of coating:
0.2 – 1.5 mm

Kyoung-Yong Chun et al. Journal of Membrane Science, Volume 169, Issue 2, 2000

Pore size distribution determined by Bubble Point Measurementt (BPM)



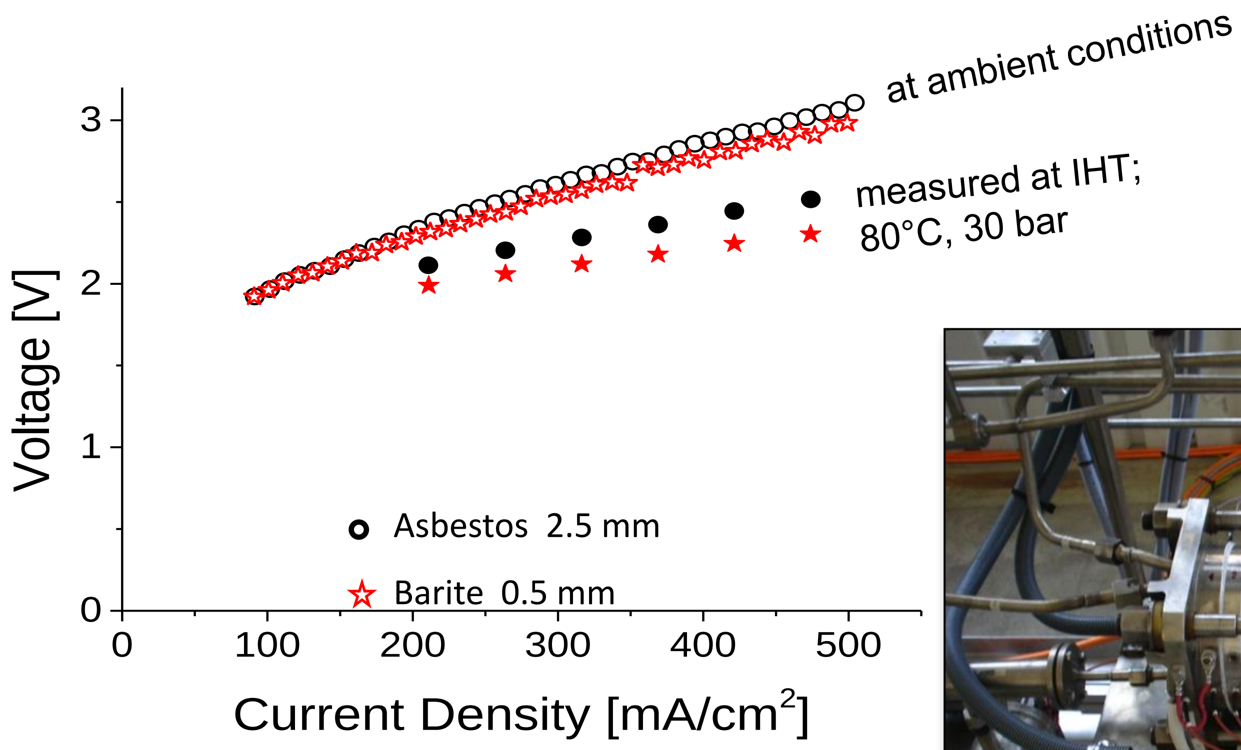


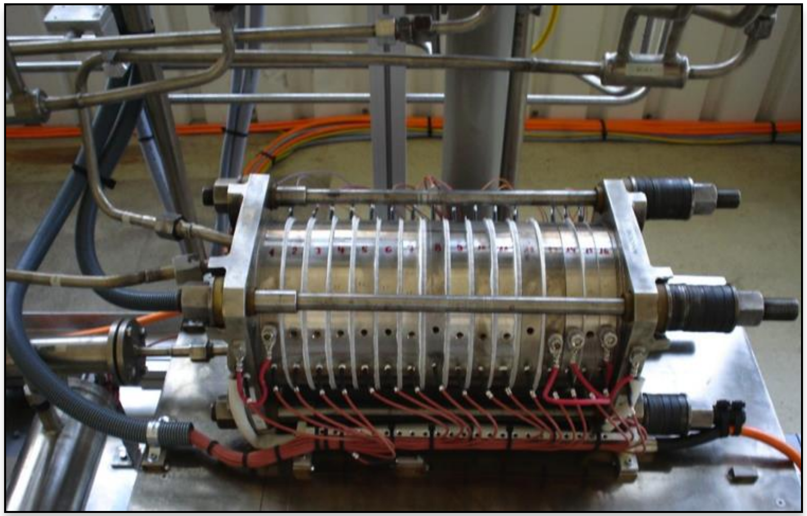
	POROLUX™ 1000
Measuring principle	Pressure Step
Max pressure	35 bar
Min pore (1)	18 nm
Max pore (2)	500 µm
Max flow	200 l/min
Sample holders	13-25-47 mm
Pressure sensors	2-50 bar
Flow sensors	10-200 l/min
FBP regulator	5-30 ml/min

Laboratory Electrolyser, ambient conditions vs Pilot Electrolyser (IHT) 80°C, 30 bar, 12 cells

EMPA
Materials Science & Technology

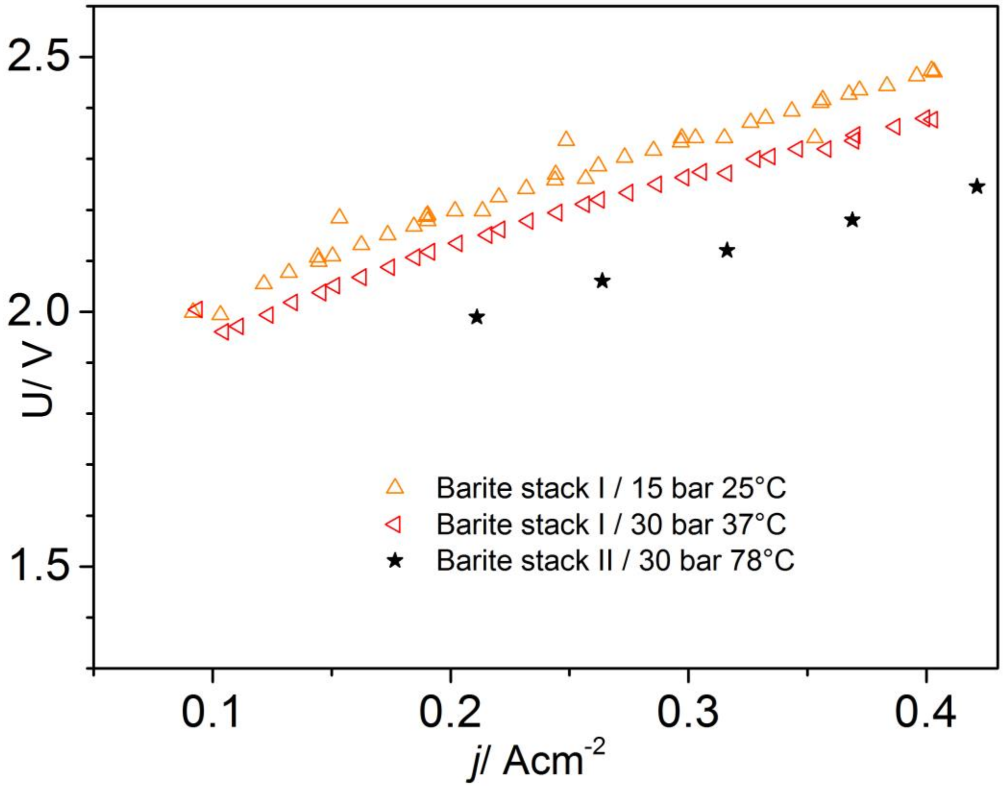
- Analysis of current—voltage curves at increased **temperature and pressure**

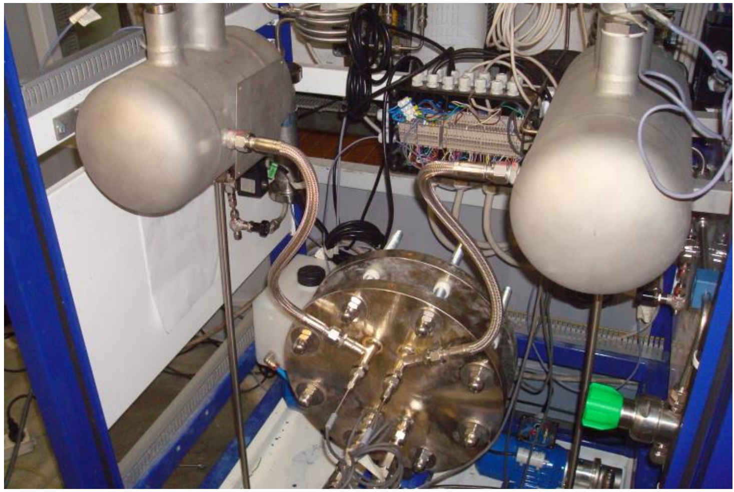




Nitidor Pilot Electrolyser, 0.2 Nm_3/h, 5 cells

Materials Science & Technology





significant influence of temperature to cell voltage

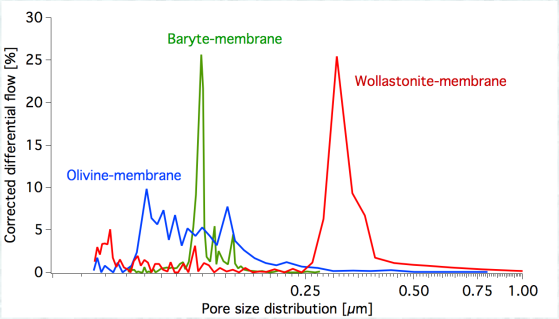
Alkaline Electrolysis: Summary and Outlook

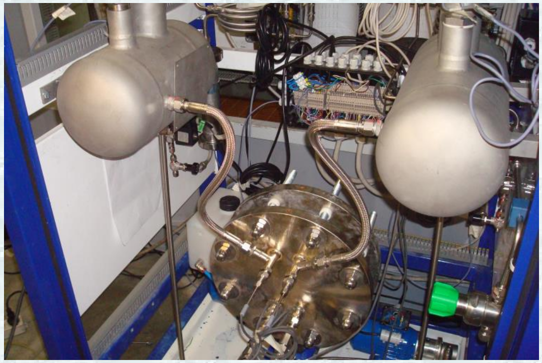
- Alkaline Electrolysis is still a promising and robust process for large scale hydrogen production

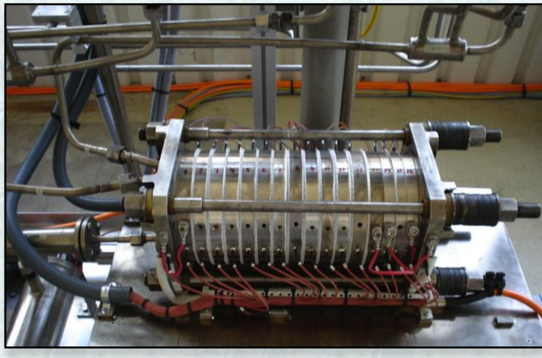
→ **Challenges:**

- Increase of power density
- Reduction of anode and cathode overpotential
- Improving the electrocatalytic properties of the electrodes
- New gas separator diaphragms for better system efficiency

Correlate **microstructure/ porosity**
(total porosity, pore size distribution, tortuosity, …)
with
material properties (wettability, physisorption, chemisorption …) and
cell performace at working conditions (> 85°C, > 30 bar)







Thank you for your attention

Hydrogen & Energy
Swiss Federal Laboratories for Research and Testing
Dübendorf, Switzerland

Acknowledgement

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fel Cell and Hydrogen Joint Technology Initiative under grant agreement n° 278824