Karlsruhe Institute of Technology

Catalysis for Sustainable Chemicals and Energies
Chapter 9
On-line: 23.06.2020
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Photo- and Electrochemical Water Splitting and Fuel Cells

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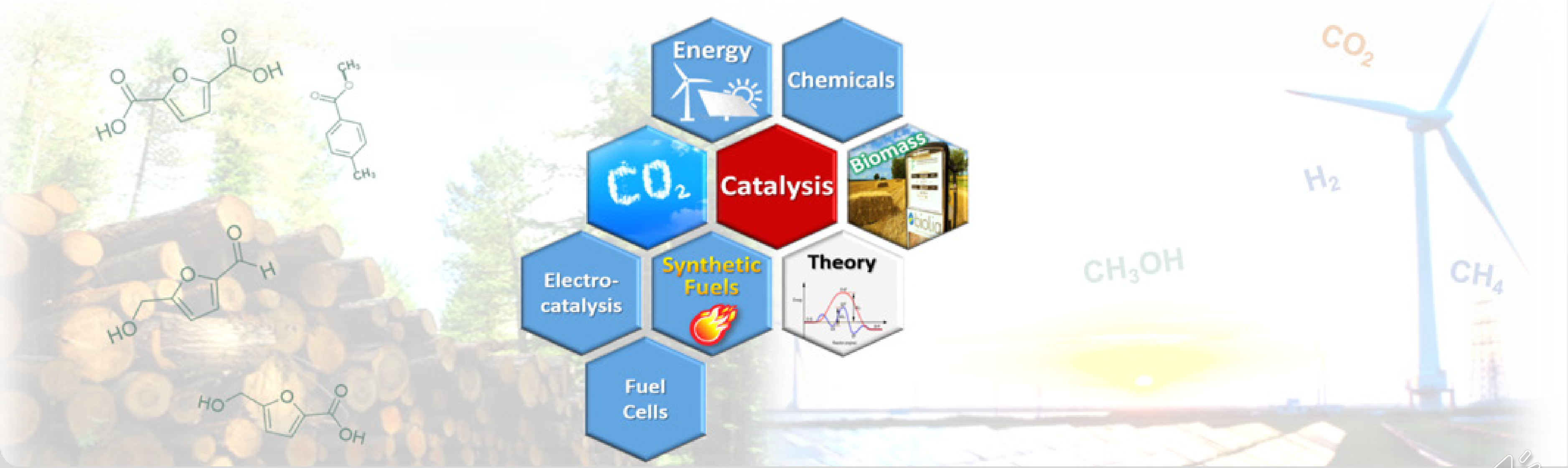
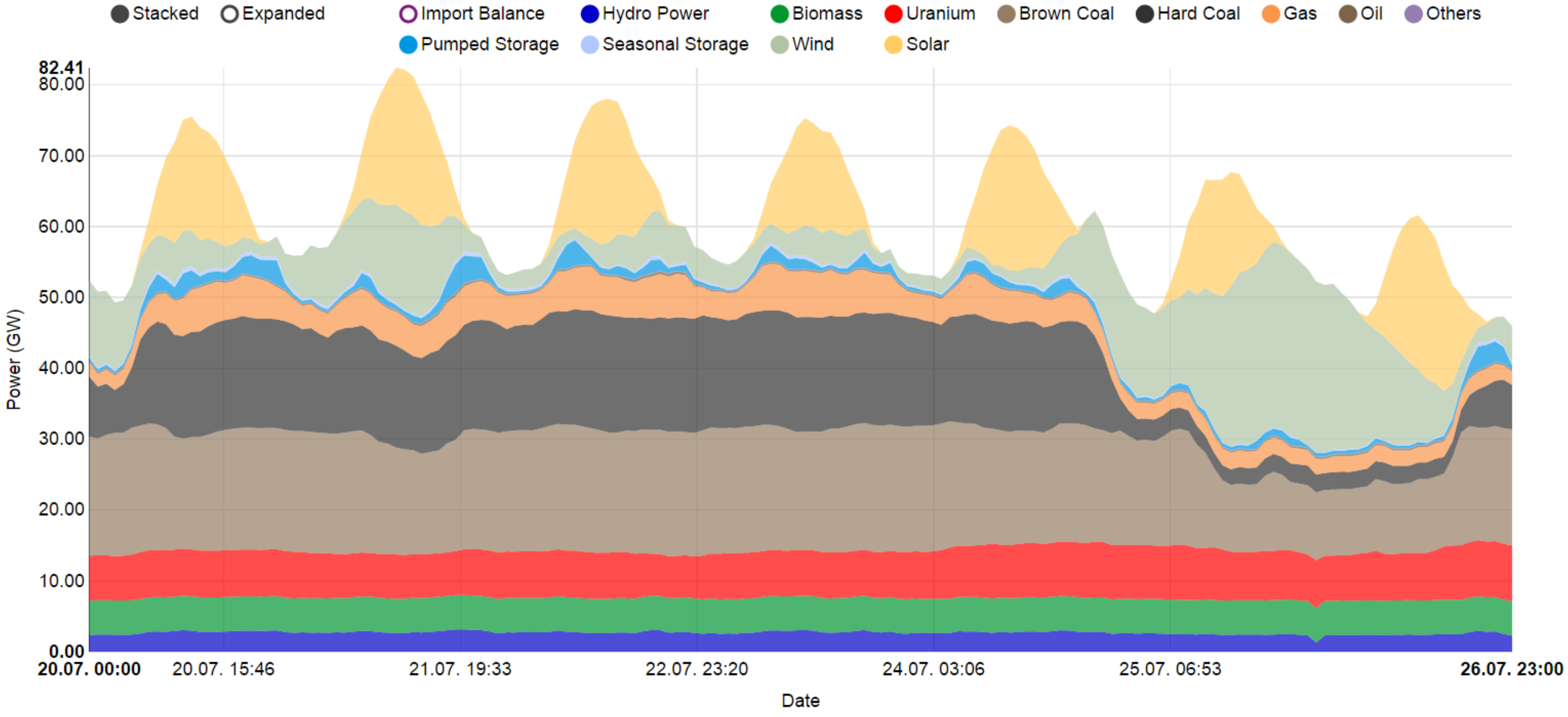


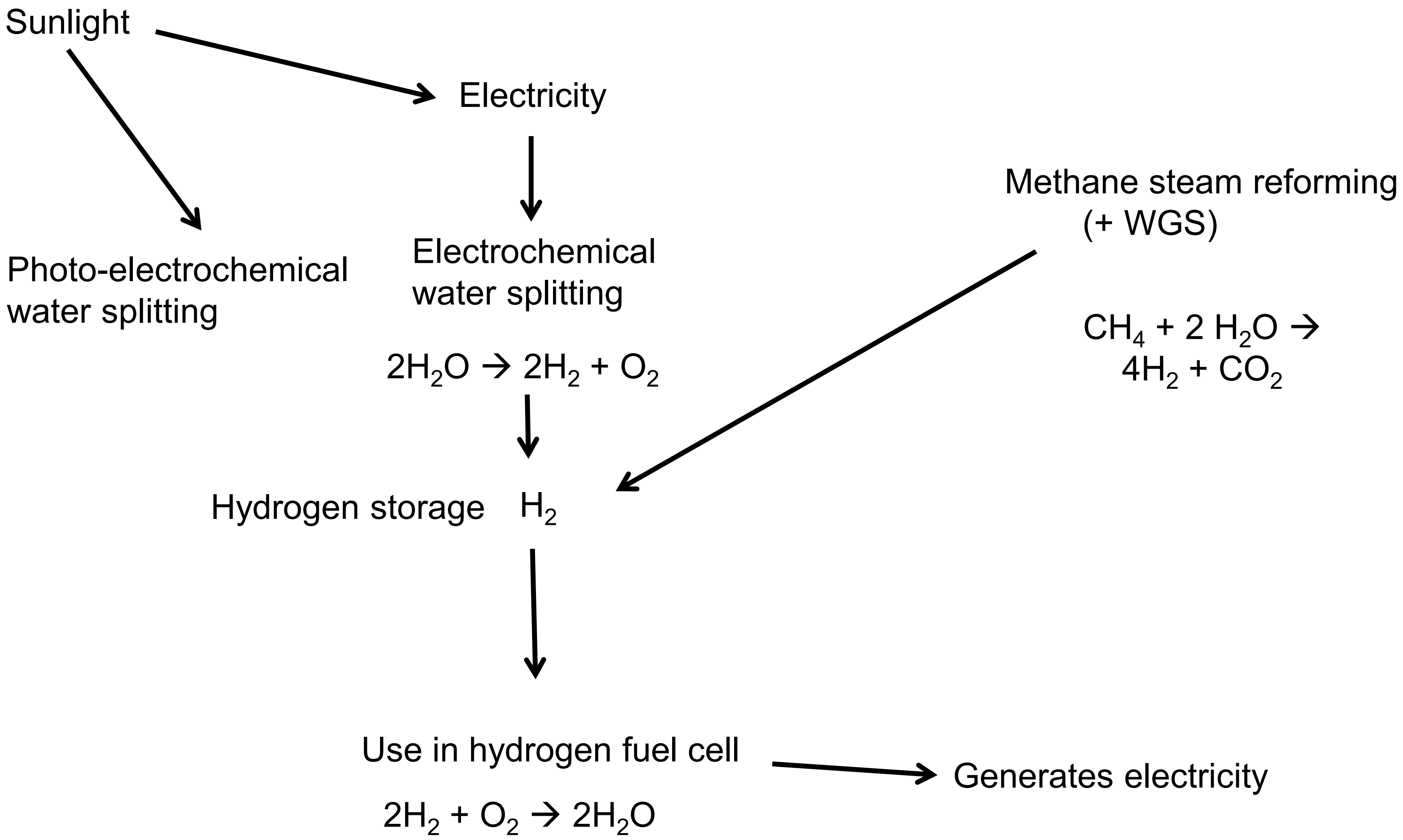
Uneven energy production by renewables

Electricity production in Germany in week 30 2015



https://energytransition.org/powerproduction_week30_2015/

The hydrogen society



Sunlight

Electricity

Photo-electrochemical water splitting

Electrochemical water splitting

$2H_2O \rightarrow 2H_2 + O_2$

Methane steam reforming (+ WGS)

$CH_4 + 2\,H_2O \rightarrow 4H_2 + CO_2$

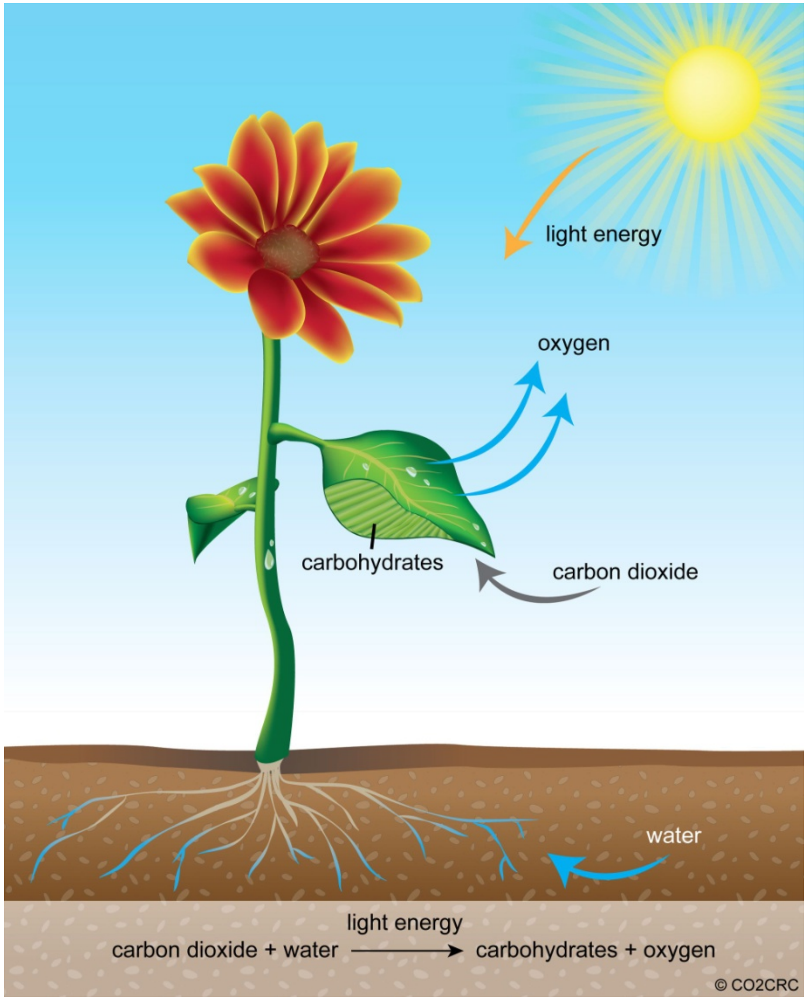
Hydrogen storage H_2

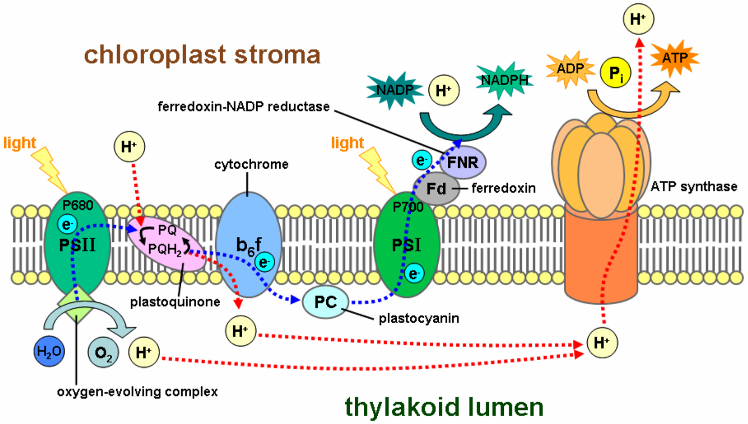
Use in hydrogen fuel cell

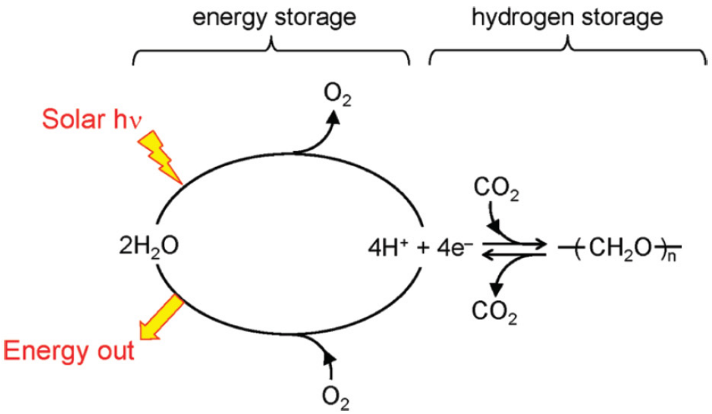
$2H_2 + O_2 \rightarrow 2H_2O$

Generates electricity

Photosynthesis





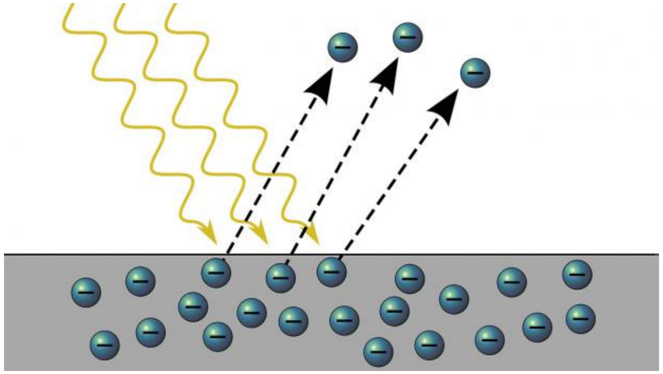


$H_2O \rightarrow H_2 + ½ O_2$ E° = 1.23 V

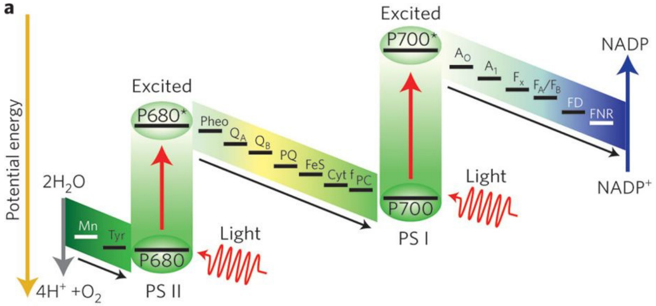
$CO_2 + H_2O \rightarrow 1/6\ C_6H_{12}O_6 + O_2$ E° = 1.24 V

The photovoltaic effect

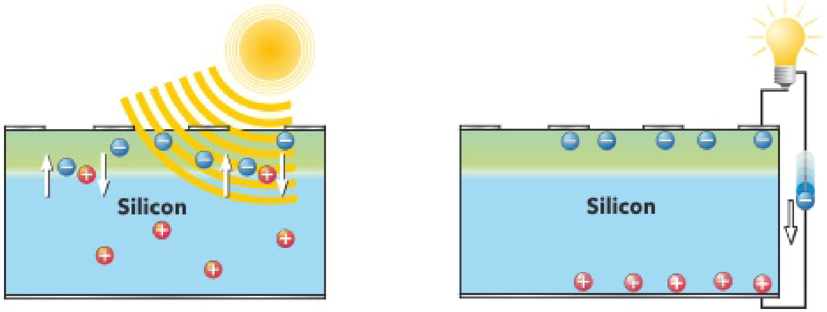
- Excitation of electrons by interaction with light
- Comparable to photoelectric effect



- Z-scheme in photosynthesis



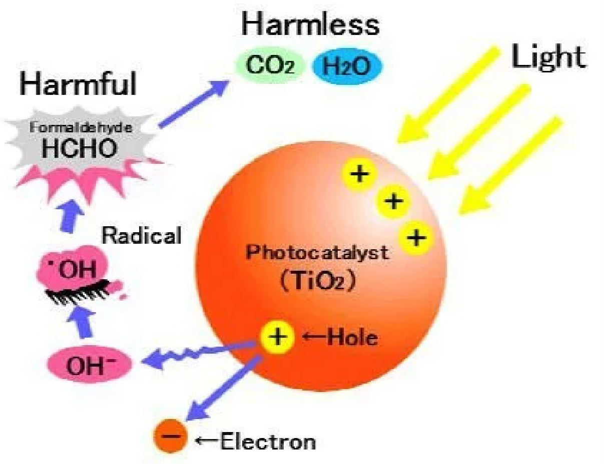
- Working principle in PVs
  - Excitation of electrons by light
  - Generation of an exciton
  - Charge seperation and harnesting of energy

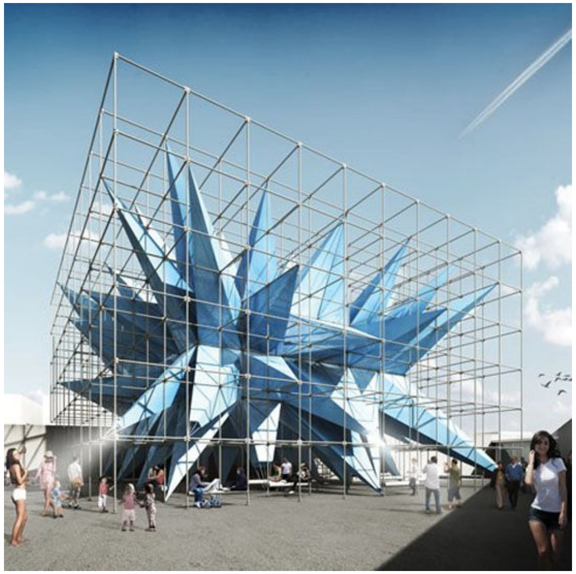


Nature Photonics **volume 6**, pages 511–518 (2012)

Photochemical air cleaning

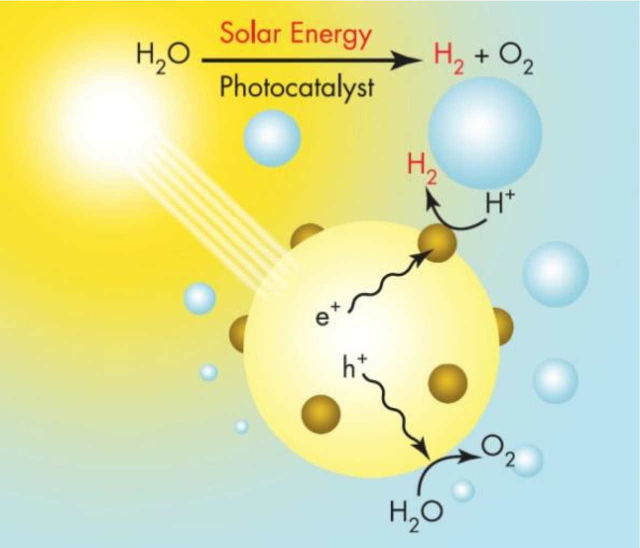
- Air cleaning with TiO_2
  - Degradation of harmfull chemicals by sunlight
- Applied in New York (MoMA)
- Planed for Pheonix towers in Wuhan/China



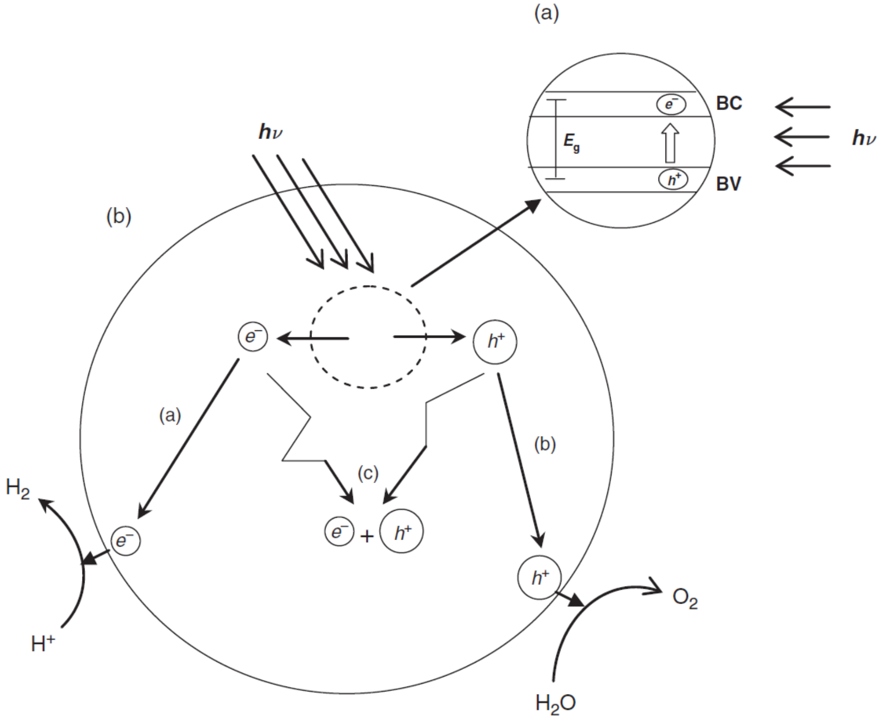


https://www.treehugger.com/green-architecture/wendy-sculpture-moma-ps1-cleans-air-hwkn-architects.html

Photochemical water splitting



- Oxygen Evolution Reaction - OER: $H_2O \rightarrow O_2 + H^+ + 2 e^-$
- Hydrogen Evolution Reaction - HER: $2 H^+ + 2 e^- \rightarrow H_2$

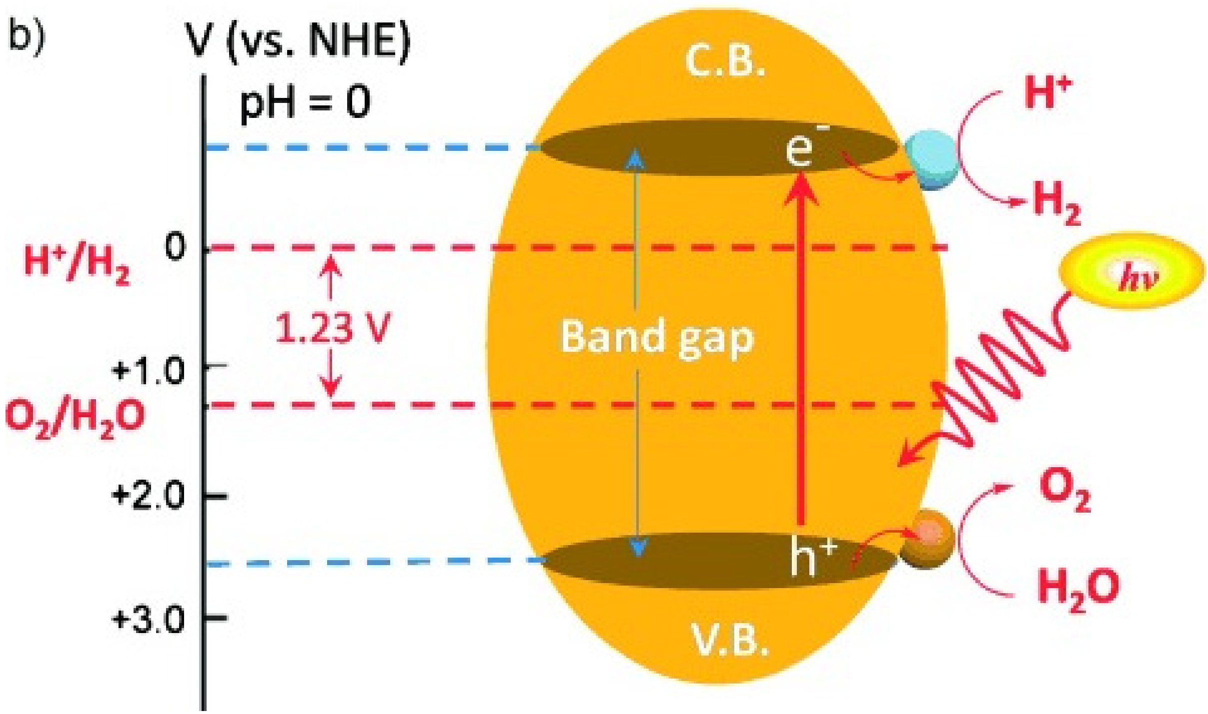


A.A. Ismail, D.W. Bahnemann / Solar Energy Materials & Solar Cells 128 (2014) 85–101

- Positive „hole“ oxidizes water to oxygen and protons
- Excited electron reduces protons
- Efficiency loss by recombination

Photochemical water splitting

Basic principle of water splitting on a heterogeneous photocatalyst

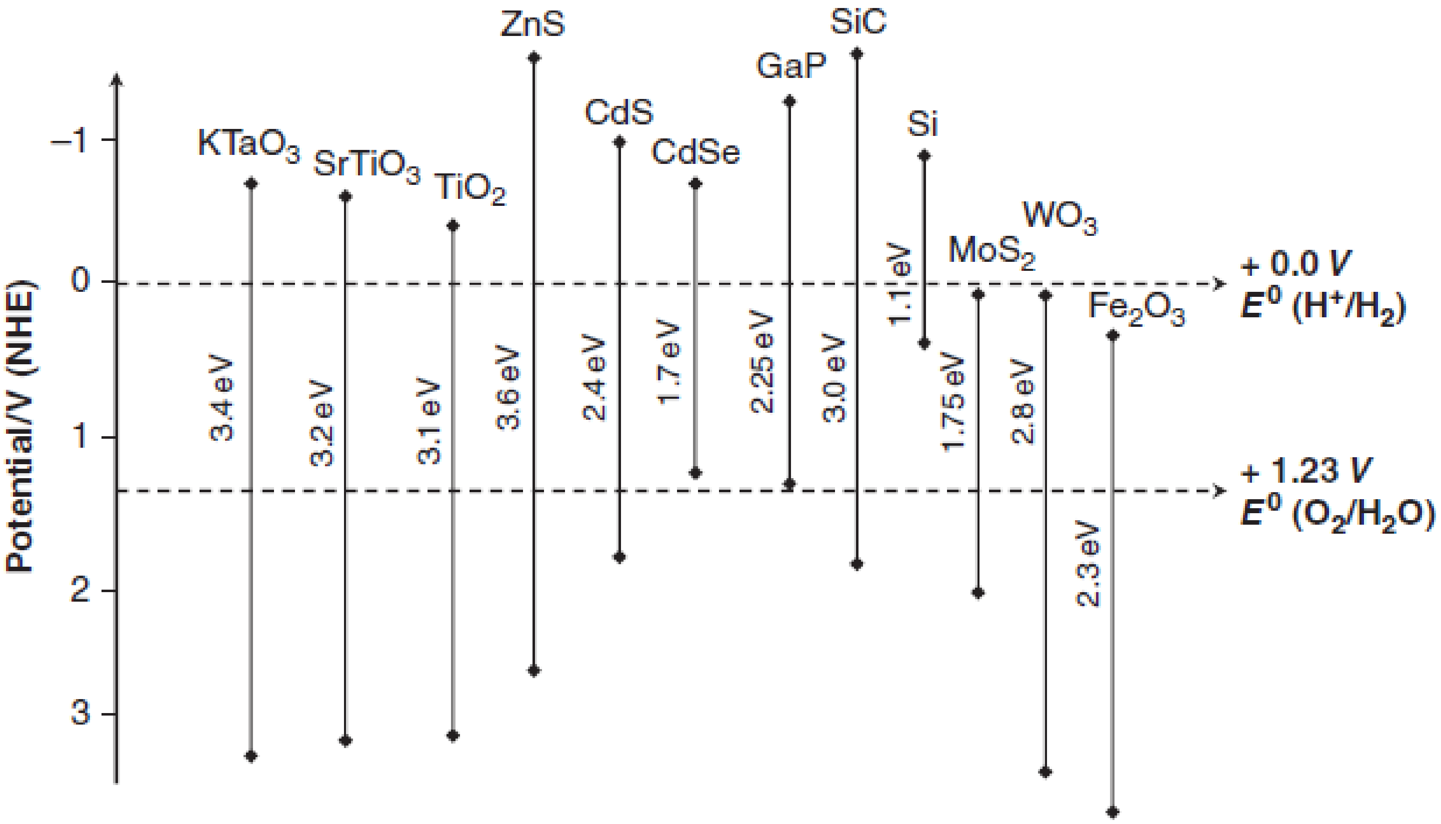


Potential difference > 1.8 V
→ Drives HER and OER

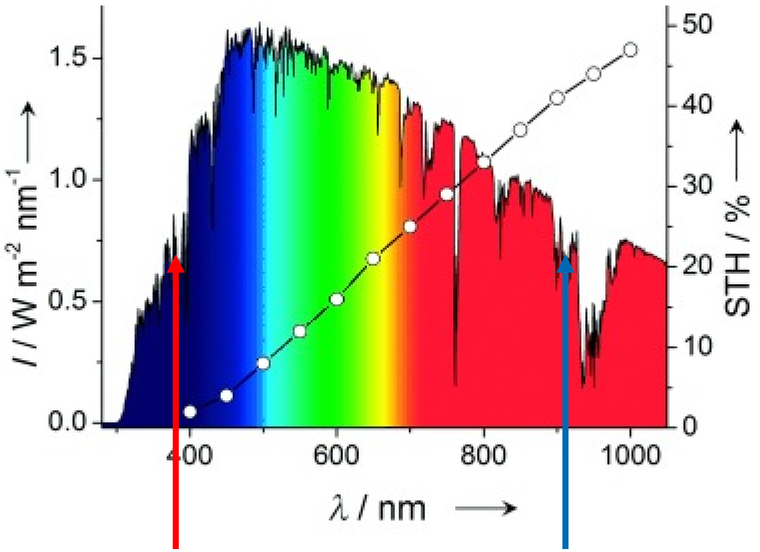
Only 1.23 V (+ overpotential) needed → 1.8 to 2 V needed (600 – 700 nm)

band gap of material needs to be aligned

Band gab considerations

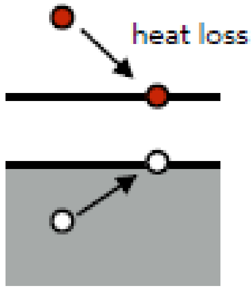


Photochemical water splitting



Too high
→ most of sunlight
not utilized

Too low → most of
sunlight utilized but
energy of photons wasted

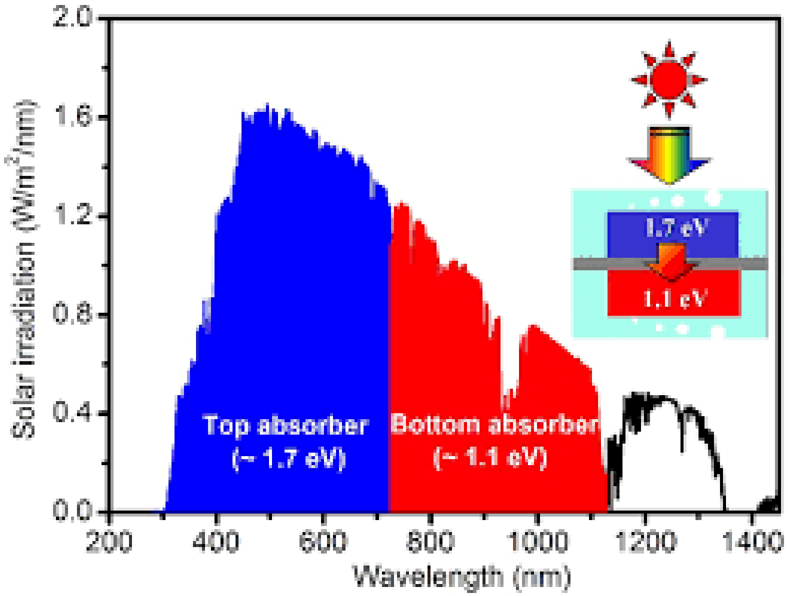


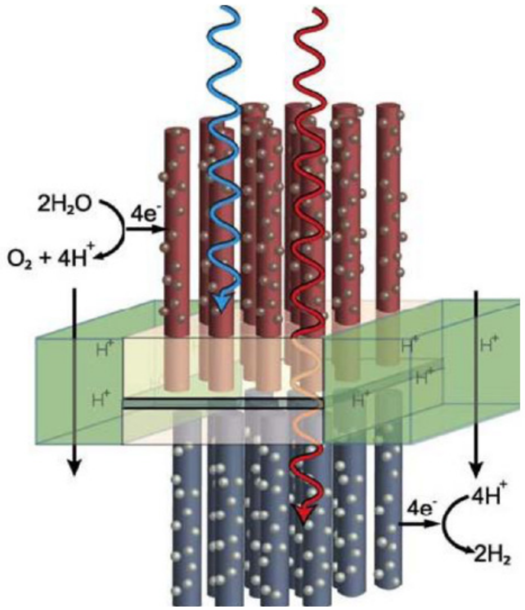
Excess energy is lost

Angew. Chem. Int. Ed. 2015, 54, 7230.

Tandem photocatalysts

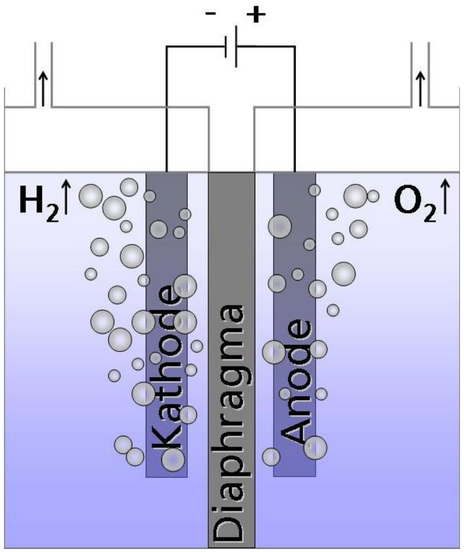
Increased efficiency by combination of materials with different band gaps





Adv. Energy Mat. 2016, 6,1600602.

Electrochemical water splitting



ifam-dd.fraunhofer.de

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

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

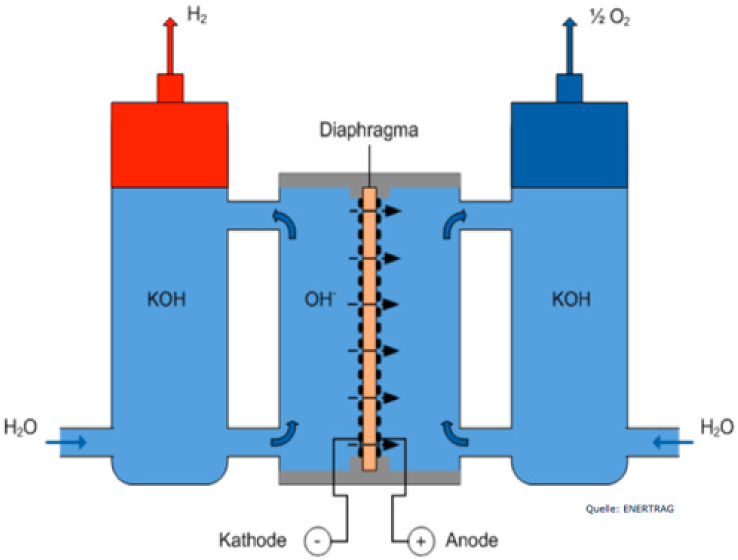
$2H_2O \rightarrow 2\,H_2 + O_2$ ΔGº = 474.2 kJ/mol = 4.92 eV

transfer of 4 protons and electrons
4.92 eV / 4 —> 1.23 eV
1.23 eV —> 1.23 V per electron

A minimum voltage of 1.23 V has to be applied to drive water splitting

Likewise: a maximum voltage of 1.23 V can be obtained through the reverse reaction

Water splitting at different pH



www.enertrag.com

Alkaline

- OER: $4\,OH^- \rightarrow O_2 + 2\,H_2O + 2\,e^-$
- HER: $2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$

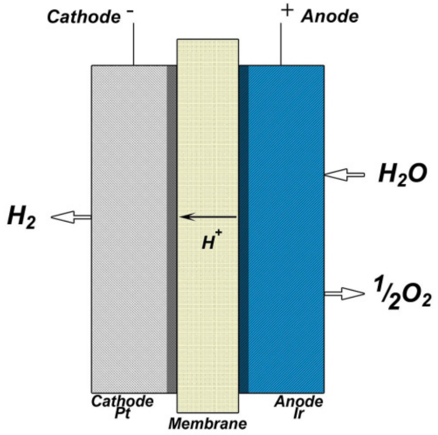
- Low conductivity of OH^-
- Cheap materials for the OER
  - Ni, Fe, Co, Cu

Acid

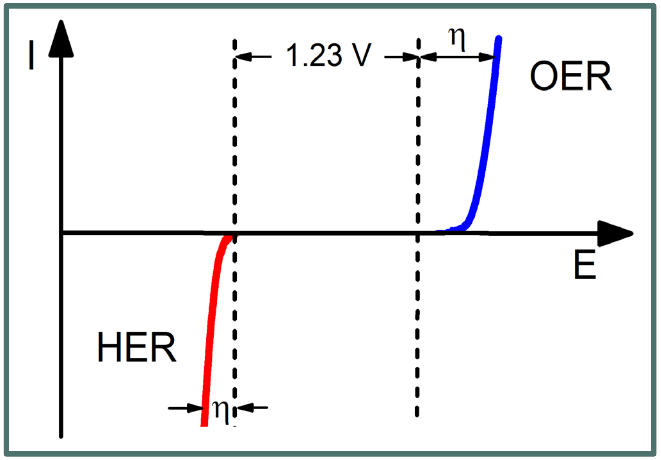
- OER: $H_2O \rightarrow O_2 + H^+ - 2\,e^-$
- HER: $2\,H^+ + 2\,e^- \rightarrow H_2$

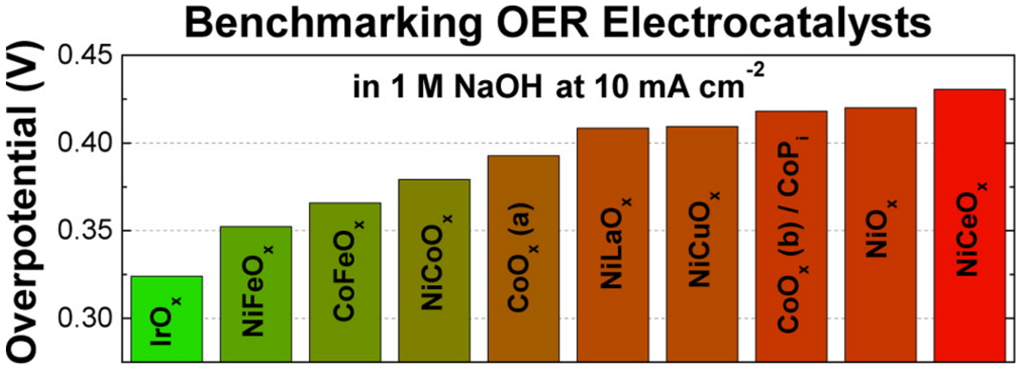
- Higher conductivity of H^+
- Sophisticated membranes (same as in PEMFC)

- Only very few elements suitable for the OER:
  - Pt, Au, Ir, Ru, Os



Benchmarking - OER





Potential which is higher than theoretical minimum is called overpotential

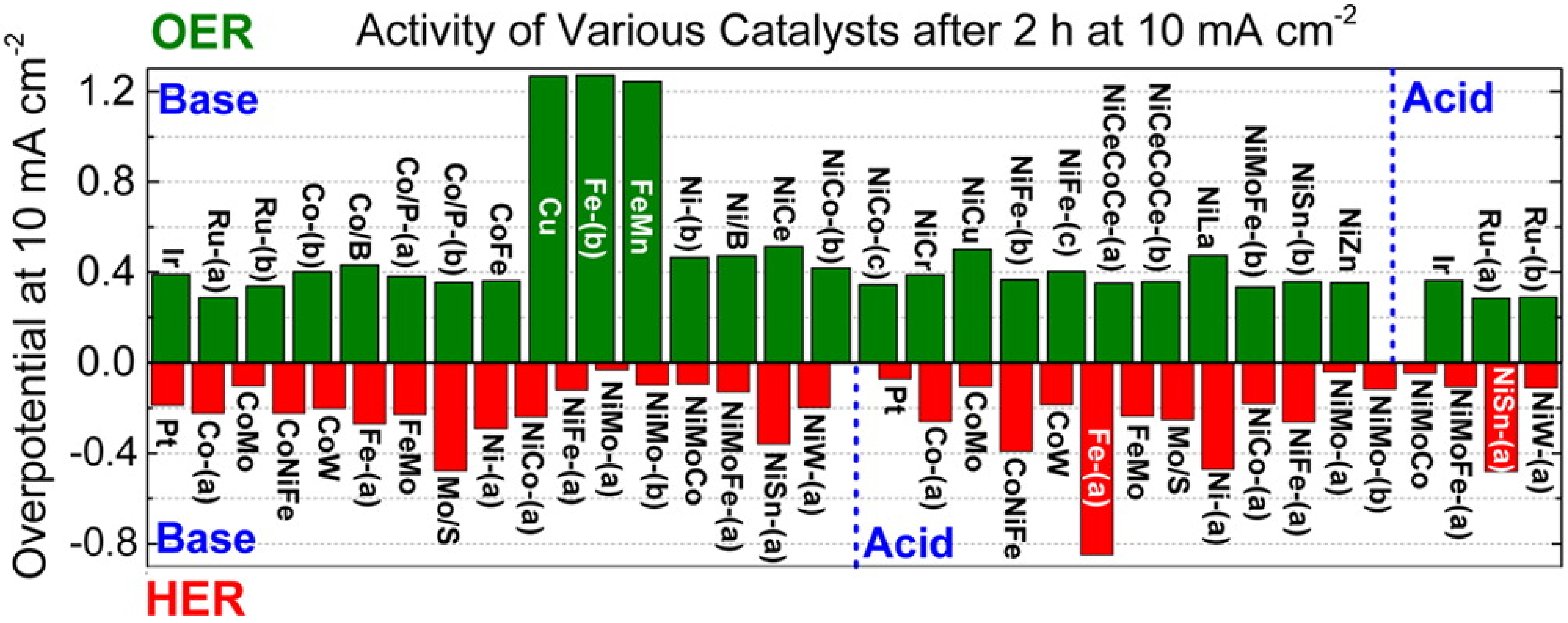
Current density of 10 mA/cm^2
(current density of app. 10 % efficient solar to fuels)

Alkaline systems (1M NaOH)

2h controlled-current electrolysis

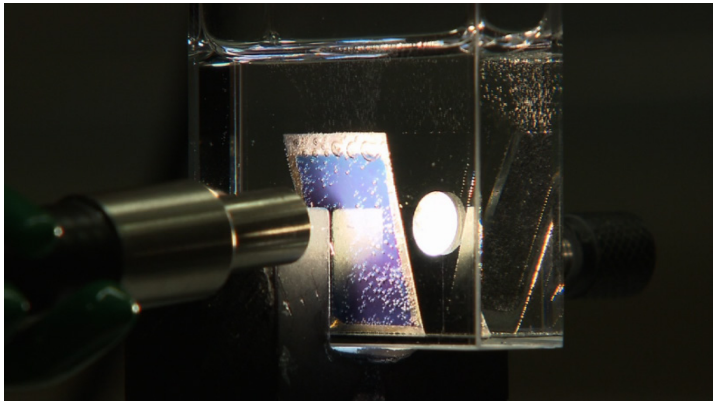
J. Am. Chem. Soc. 2013, 135, 16977.

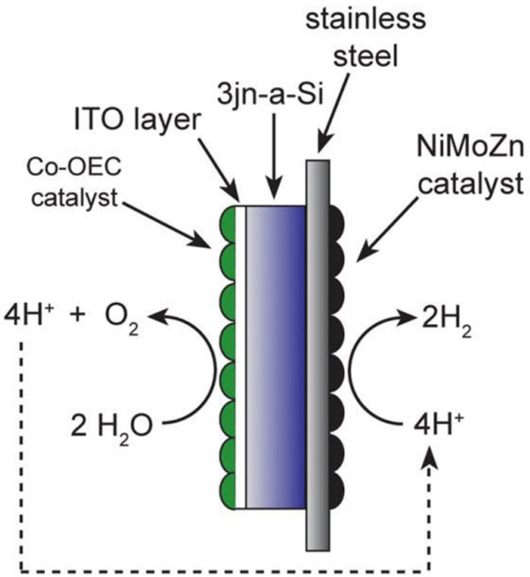
Benchmarking – OER and HER



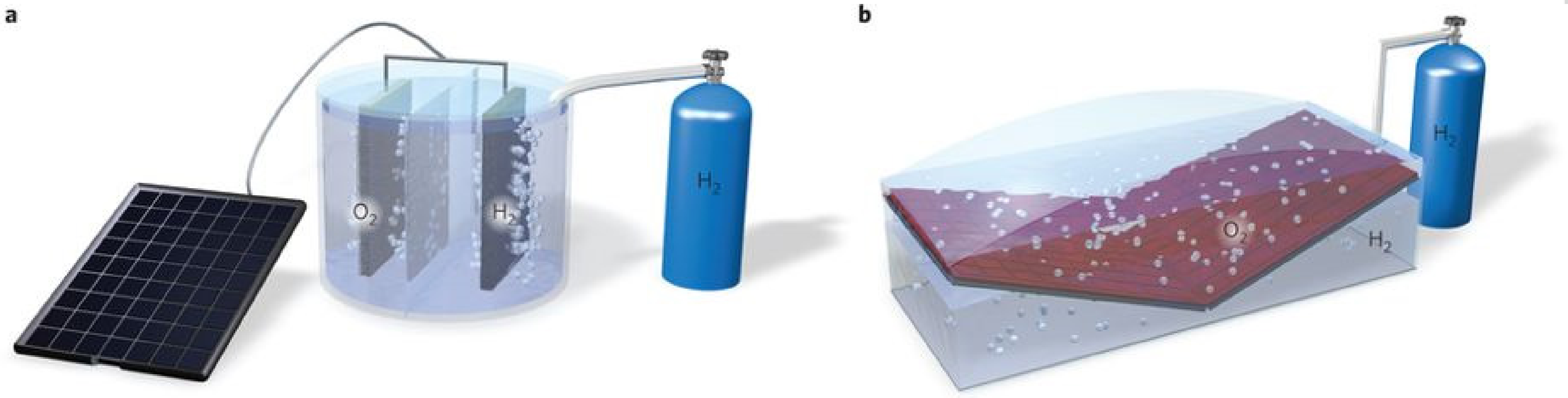
J. Am. Chem. Soc. 2013, 135, 16977.

The artificial leaf





Cost considerations



PV (or other) and electrolysis separately

PV/E —> STH efficiencies up to 30%

DOE estimates US\$4.00 - 10.40 kg^{-1} H_2

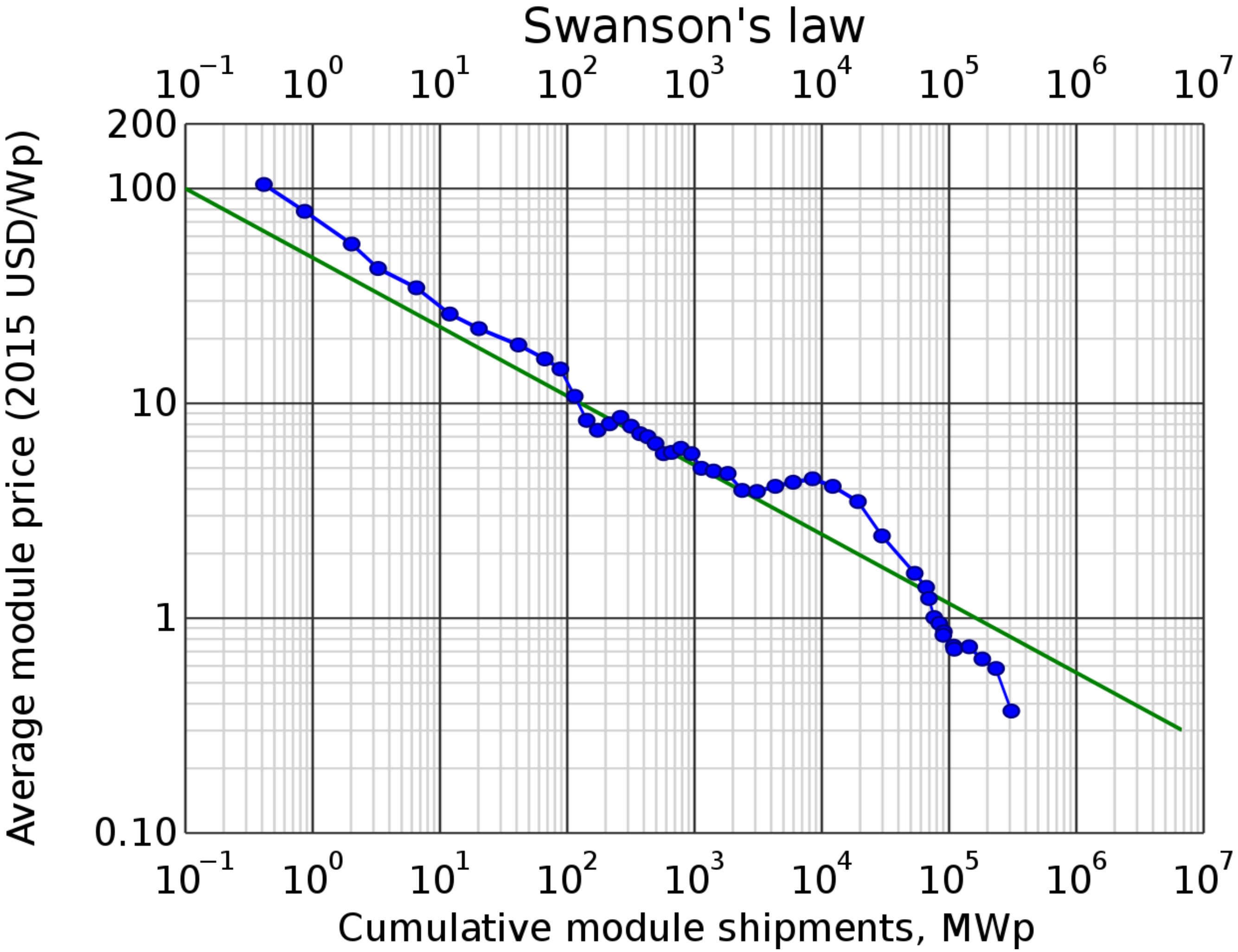
direct photo-electrochemical water splitting

PEC —> STH efficiencies usually less than 1%
but: some >10% have been reported

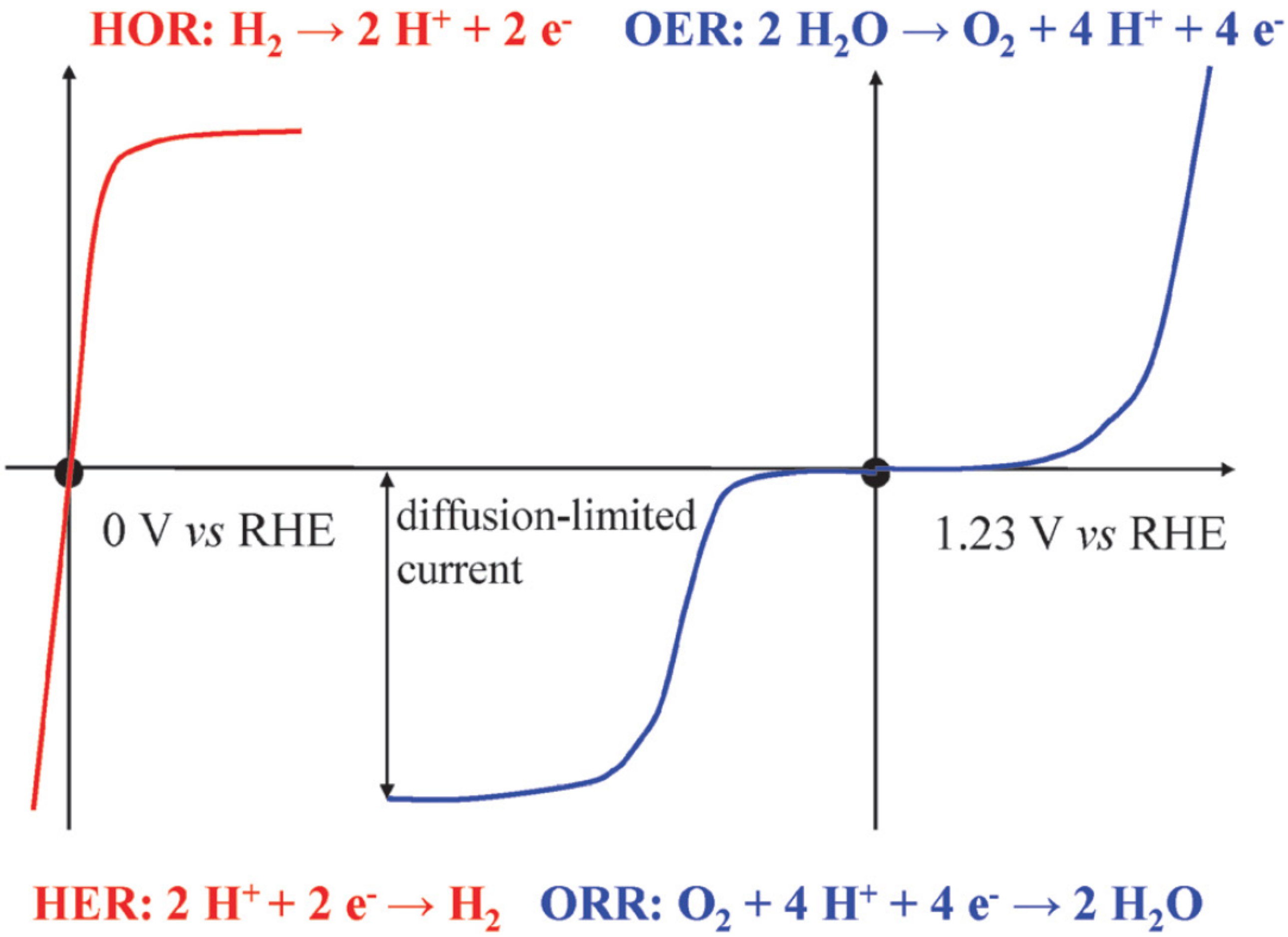
DOE estimates US\$1.60 - 3.20 kg^{-1} H_2
assuming 5-10% STH!!

Montoya et al, *Nature Mat.* 2017, *16*, 70.

Solar cell performances



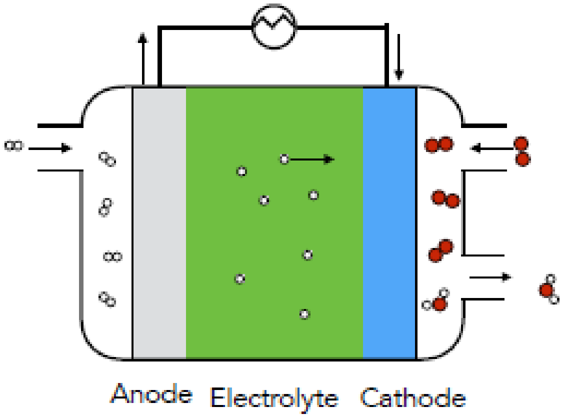
The ORR and HOR



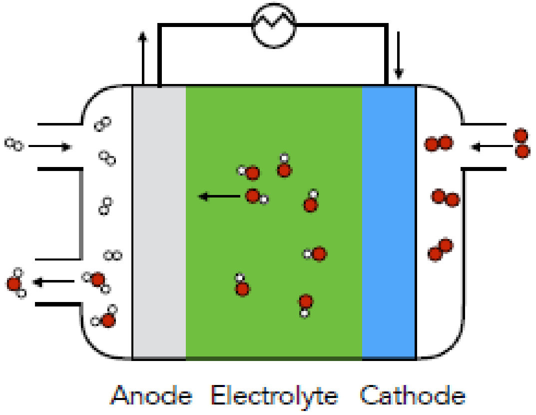
Chem. Soc. Rev., 2015, 44, 2060--2086

Hydrogen Fuel Cells

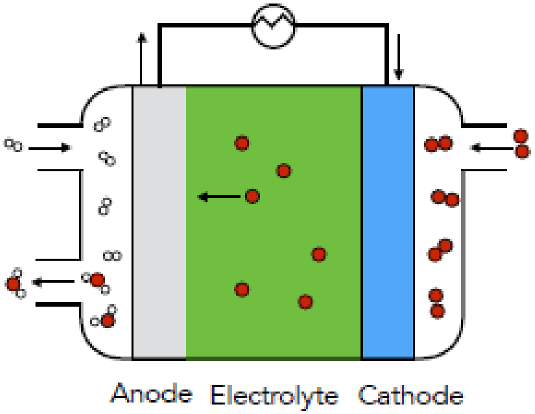
PEM / Phosphoric Acid Fuel Cell



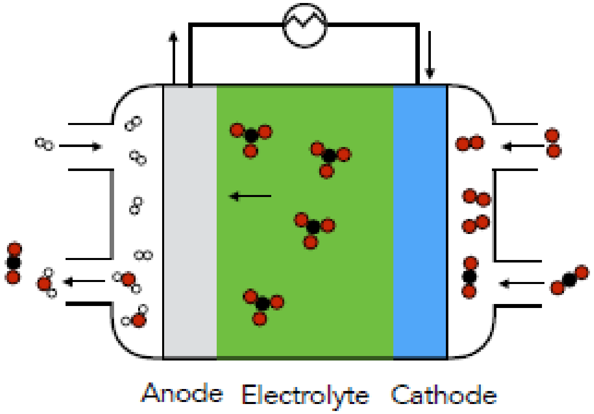
Alkali Fuel Cell



Solid Oxide Fuel Cell

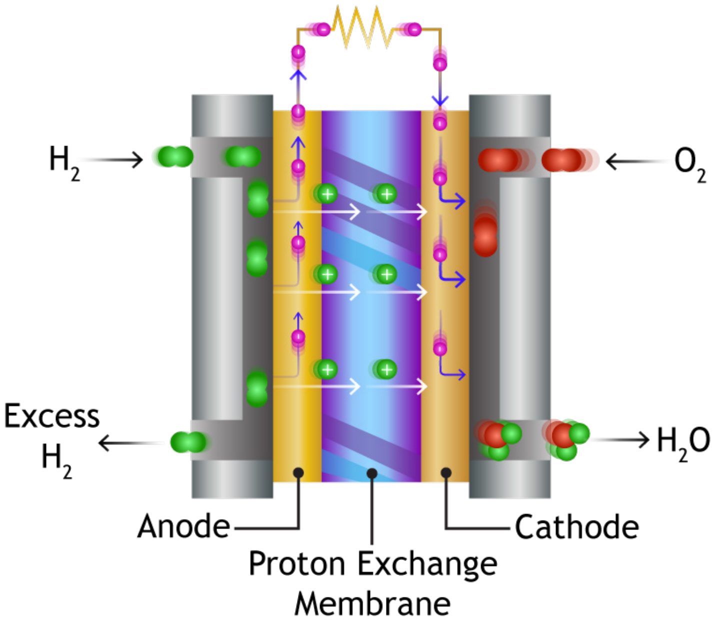


Molten Carbonate Fuel Cell

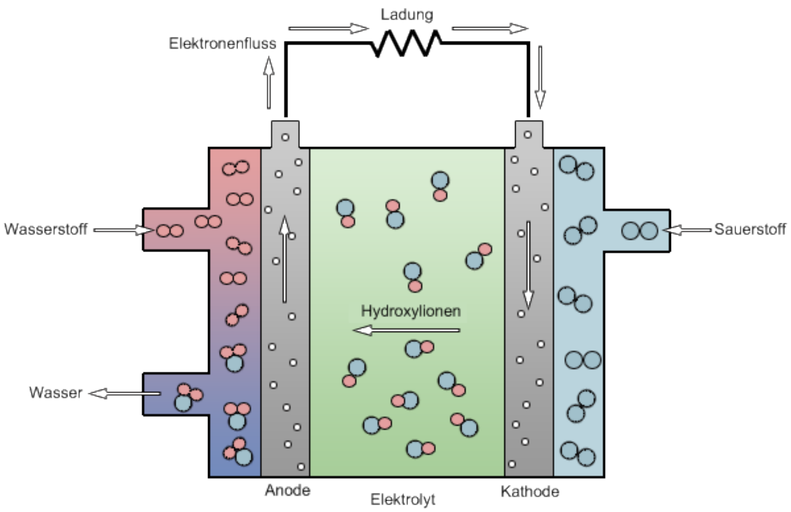


Hydrogen fuel cells

- Acid electrolyte fuel cells:
  - Transport of H^+ ions through electrolyte
  - No flow of electrons through electrolyte
  - Electrolyte:
    - Fluid acid
    - Polymers containing mobile protons („proton exchange membranes“, PEMs)



https://web.stanford.edu/group/frankgroup/research_topic_3.html



- Alkaline fuel cells
  - Same principle, mobile OH-

Comparison Acid-Base

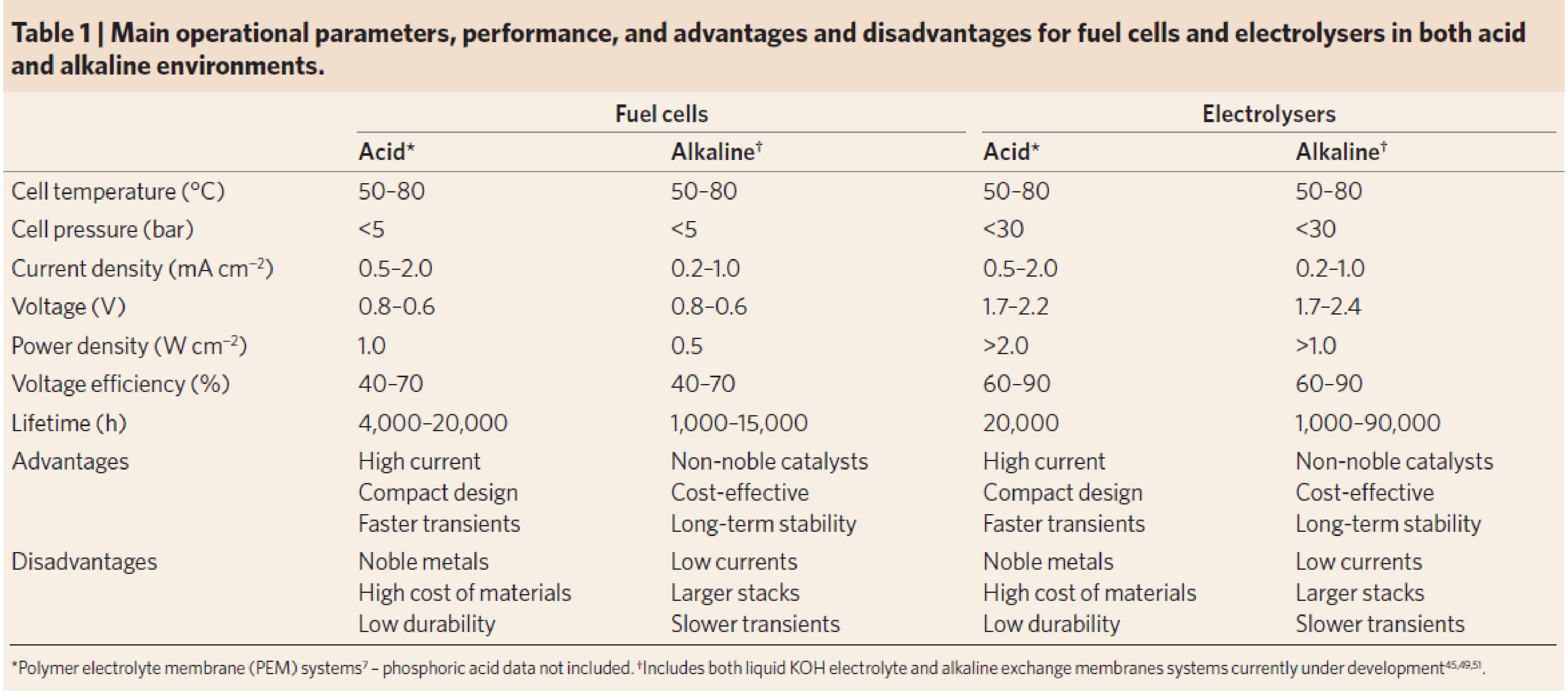


Table 1 | Main operational parameters, performance, and advantages and disadvantages for fuel cells and electrolysers in both acid and alkaline environments.

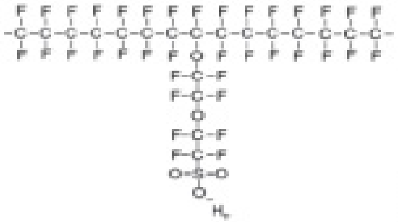
	Fuel cells		Electrolysers	
	Acid*	**Alkaline†**	**Acid***	**Alkaline†**
Cell temperature (°C)	50–80	50–80	50–80	50–80
Cell pressure (bar)	<5	<5	<30	<30
Current density (mA cm^{-2})	0.5–2.0	0.2–1.0	0.5–2.0	0.2–1.0
Voltage (V)	0.8–0.6	0.8–0.6	1.7–2.2	1.7–2.4
Power density (W cm^{-2})	1.0	0.5	>2.0	>1.0
Voltage efficiency (%)	40–70	40–70	60–90	60–90
Lifetime (h)	4,000–20,000	1,000–15,000	20,000	1,000–90,000
Advantages	High current Compact design Faster transients	Non-noble catalysts Cost-effective Long-term stability	High current Compact design Faster transients	Non-noble catalysts Cost-effective Long-term stability
Disadvantages	Noble metals High cost of materials Low durability	Low currents Larger stacks Slower transients	Noble metals High cost of materials Low durability	Low currents Larger stacks Slower transients

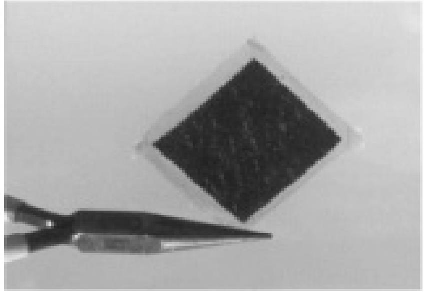
*Polymer electrolyte membrane (PEM) systems[7] – phosphoric acid data not included. †Includes both liquid KOH electrolyte and alkaline exchange membranes systems currently under development[45,49,51].

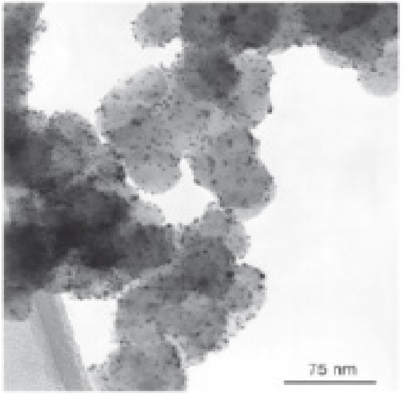
Stamenkovic et al., *Nat. Mater.*, 2016, 1, 57.

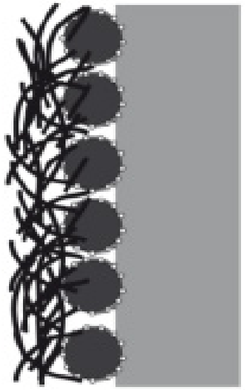
Proton Exchange Membrane Fuel Cell

- Developed in 1960´s by General Electric
- Ion conducting polymers,
- Standard membrane material: Nafion



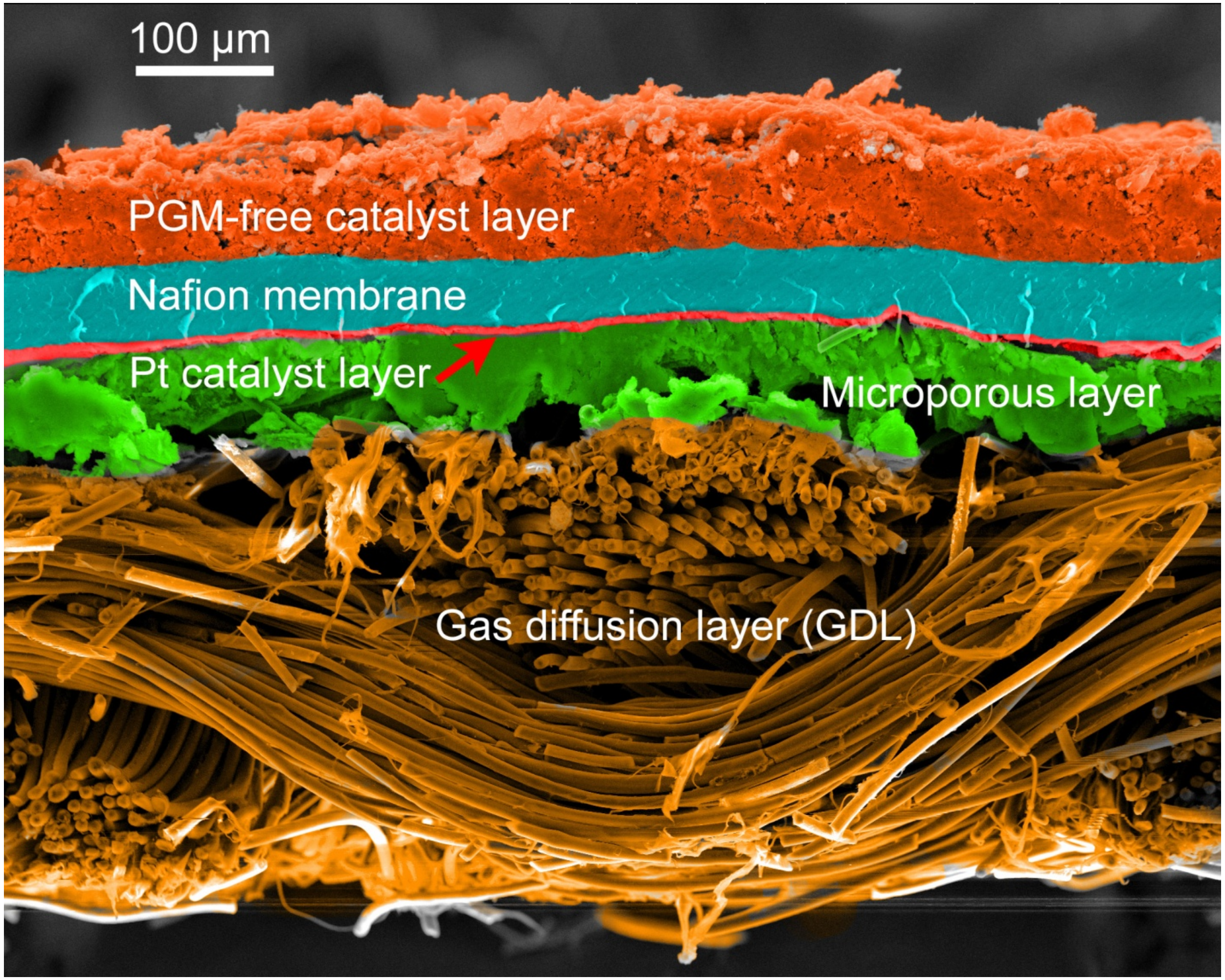






- Highly dispersed catalyst on support materials

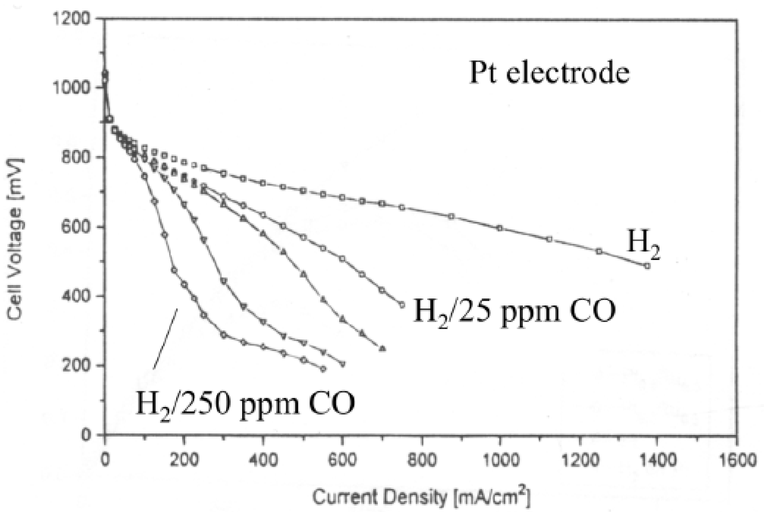
Proton exchange membrane



"Effects of MEA Fabrication and Ionomer Composition on Fuel Cell Performance of PGM-Free ORR Catalyst". ECS Transactions. ***77*** *(11): 1273–1281. doi:10.1149/07711.1273ecst.*

Phosphoric Acid Fuel Cells

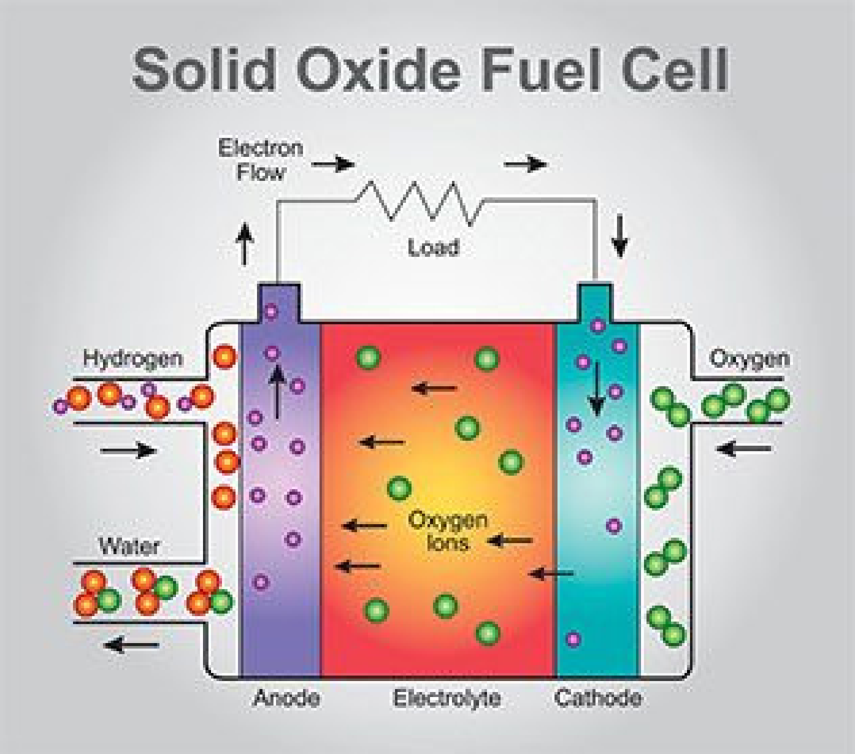
- Well-established in military, hospitals, factories, offices
- Well-understood technique
- Characteristics similar to PEM
- Electrolyte: H_3PO_4
- Operates at 200 °C
  - Noble metal catalyst necessary
  - Poisoning by CO in fuel gas



H.F. Oetjen et al. (1996)

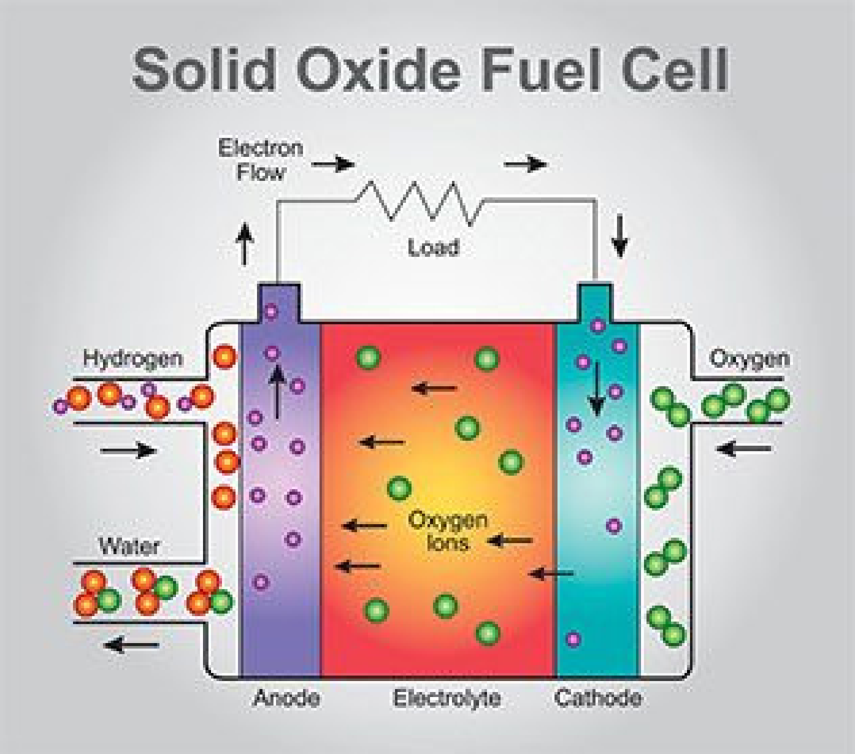
Absorption of CO on Pt and blockage

SOFC principle



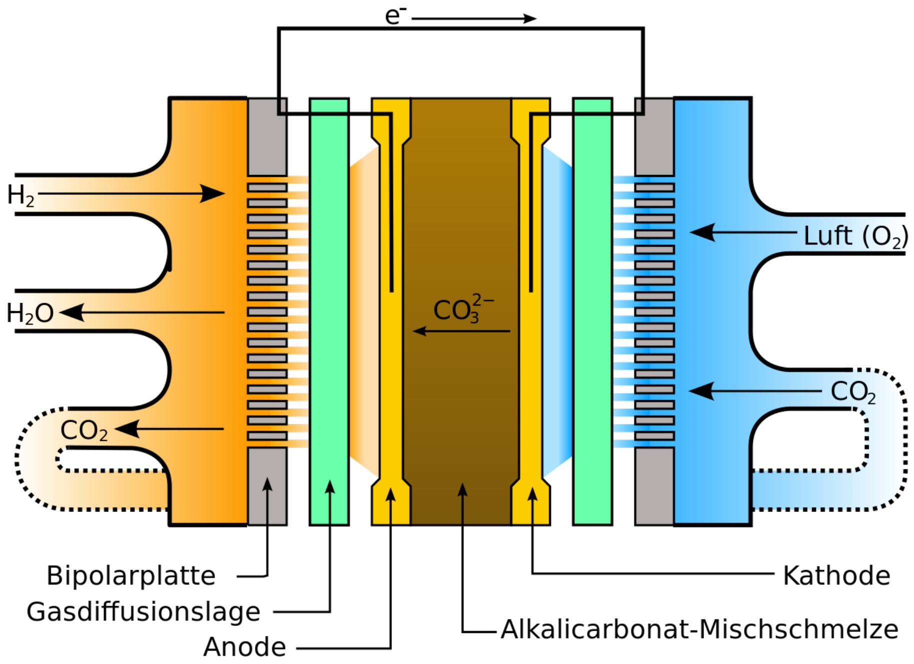
- Ion conducting ceramics as electrolyte
- Solid state devices
- Water formation at the anode
- Electrolyte : ZrO_2 doped with Y_2O_3
- Anode: zirconia cermet (composite of ZrO_2 and Ni)
- Cathode: conducting oxides or mixed electron and ion conducting ceramics

SOFC advantages



- Mechanically simple
- Solid-state device
- Production and size flexible
- Wide range of possible applications
- Can be made from various materials
- Operating temperatures 650 °C – 1000 °C
- No precious metal catalysts

Molten carbonate fuel cell

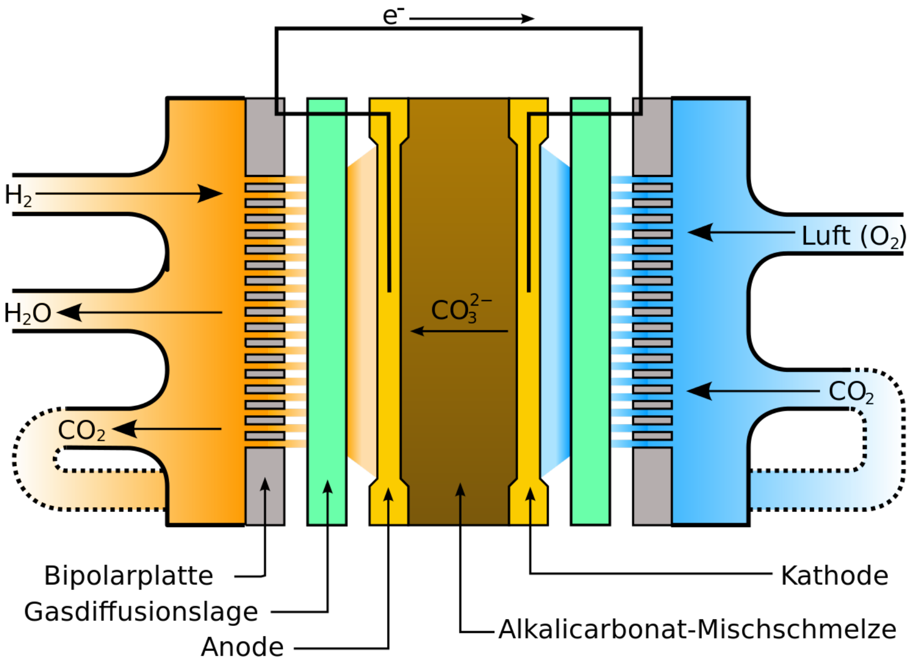


- Anode:

  $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$
- Cathode:
  - $1/2O_2 + CO_2 + 2\ e^- \rightarrow CO_3^{2-}$

- Overall reaction:
  - $2\ H_2 + O_2 + 2CO_2 \rightarrow 2\ H_2O + 2\ CO_2$

Molten carbonate fuel cell

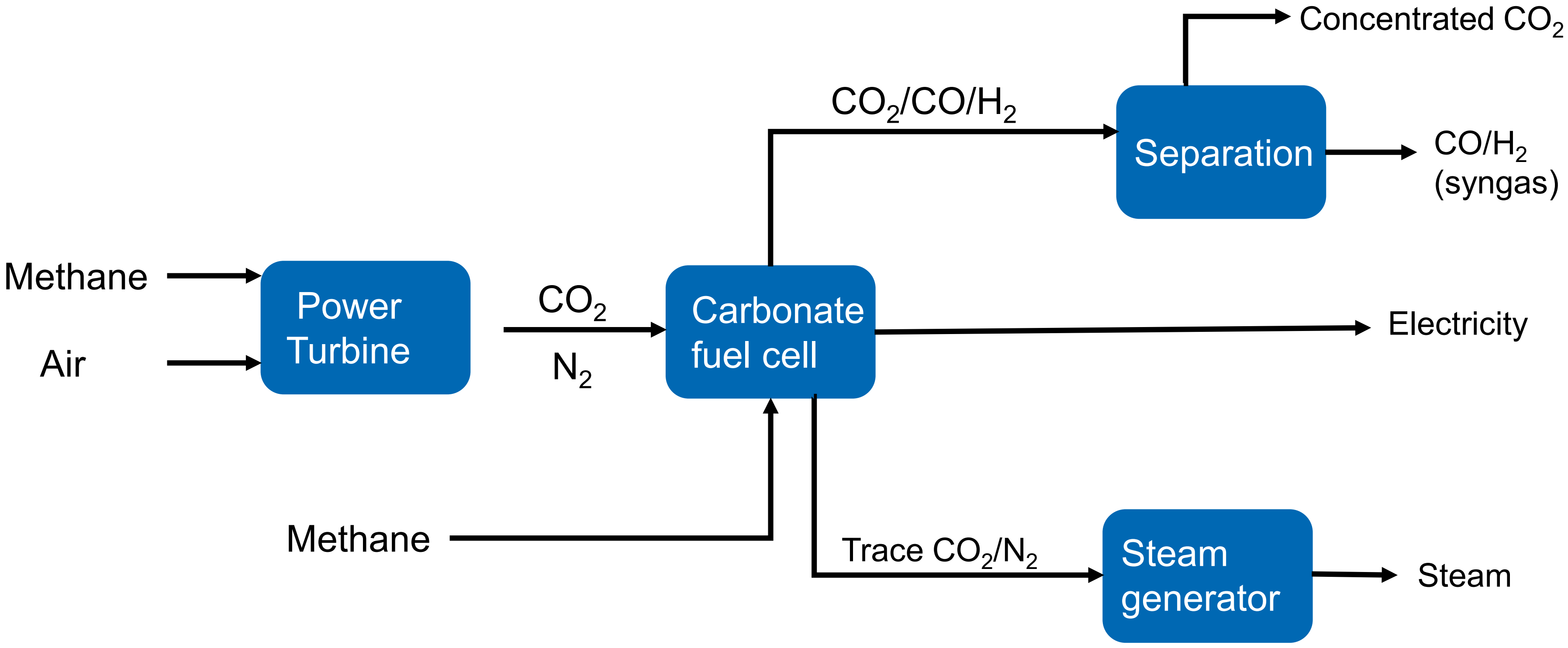


- Developed in 1920s
- Operating temperatures: 600 °C – 800 °C
- Electrolyte: molten mixture of alkali metal carbonates
- CO_2 supply at the cathode necesarry (net transfer of CO_2 from cathode to anode)
- Main problem: degradation of cell components over time

- No nobel metal catalysts required
  - Anode: Nickel
  - Cathode: nickel oxide

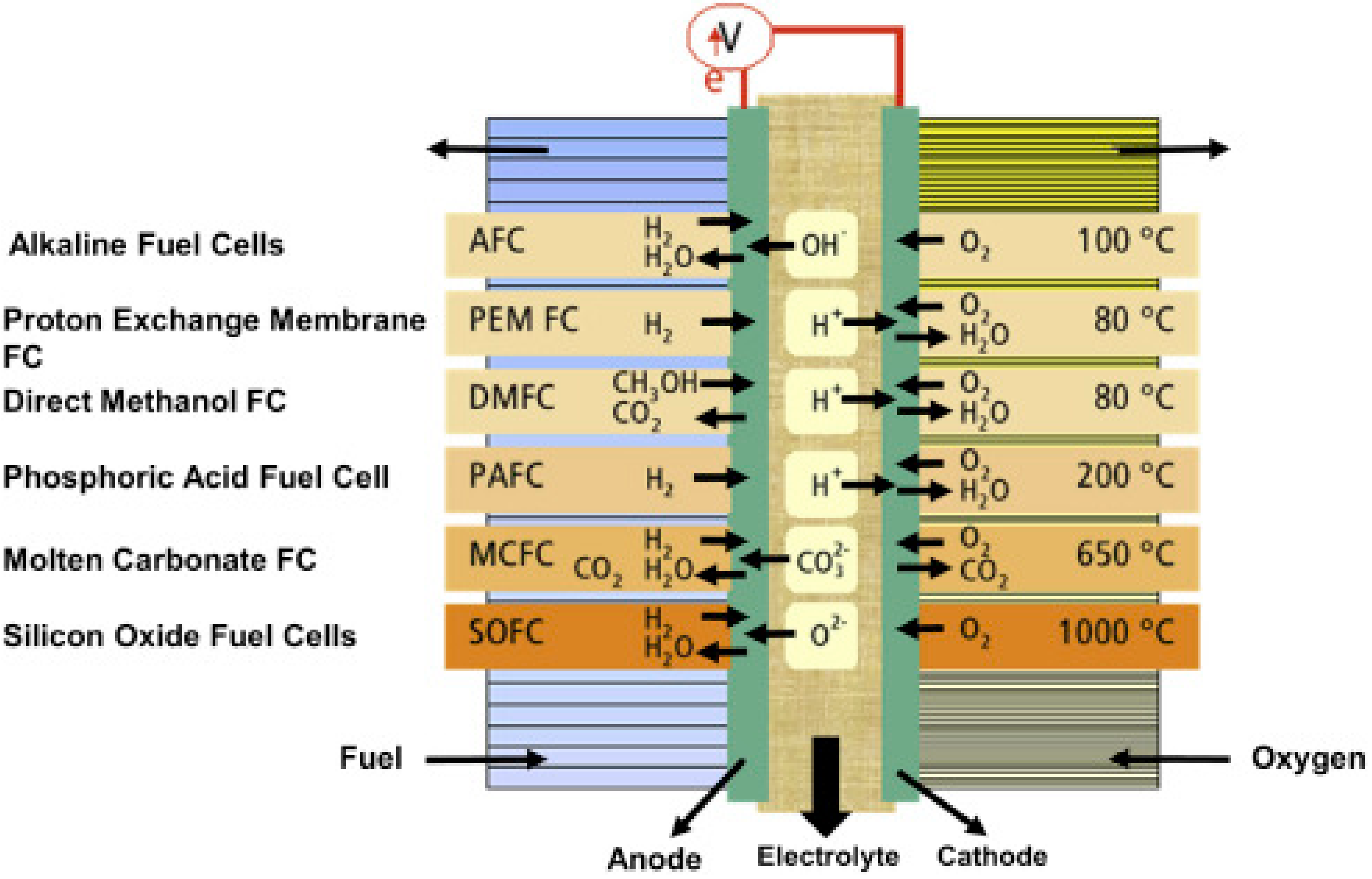
Planned application of carbonated FCs

- Fuell cell carbon capture enables typical 500 megawatt (MW) gas-fired power plant to generate additional 120 MW of power
- Potential to capture more than 90 percent of a natural gas-fired power plants CO_2 emissions
- Further potential to produce up to 150 million cf/day of hydrogen

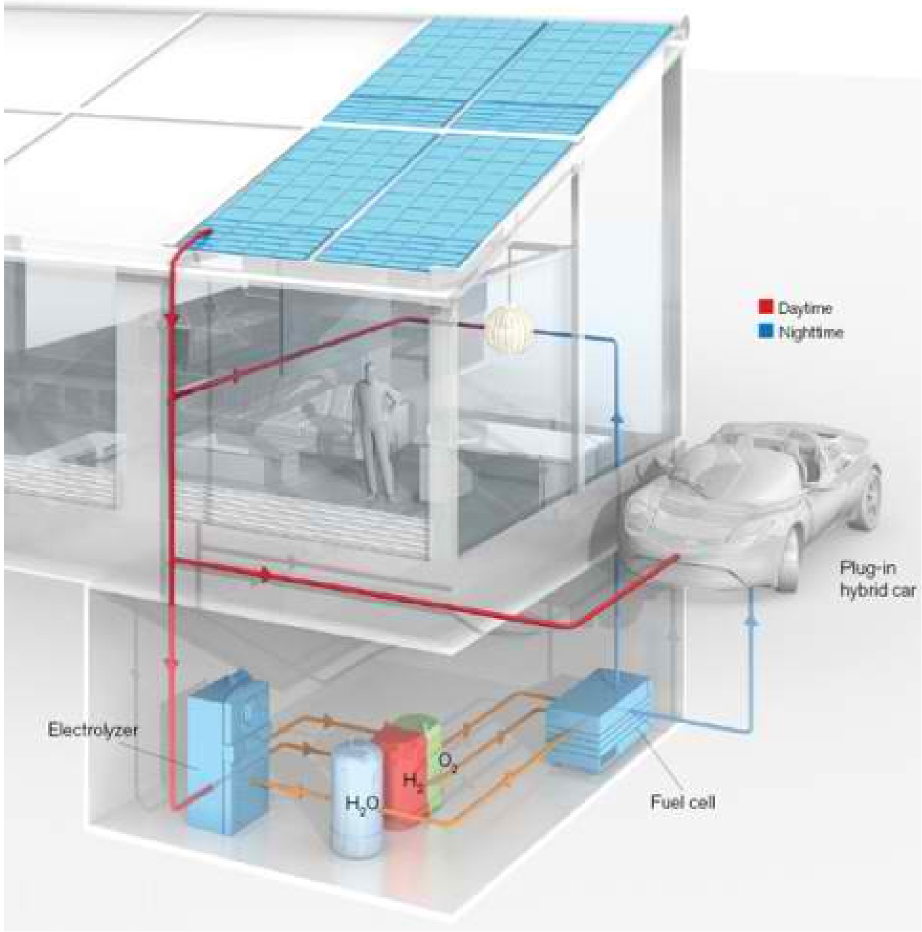


Project by ExxonMobil

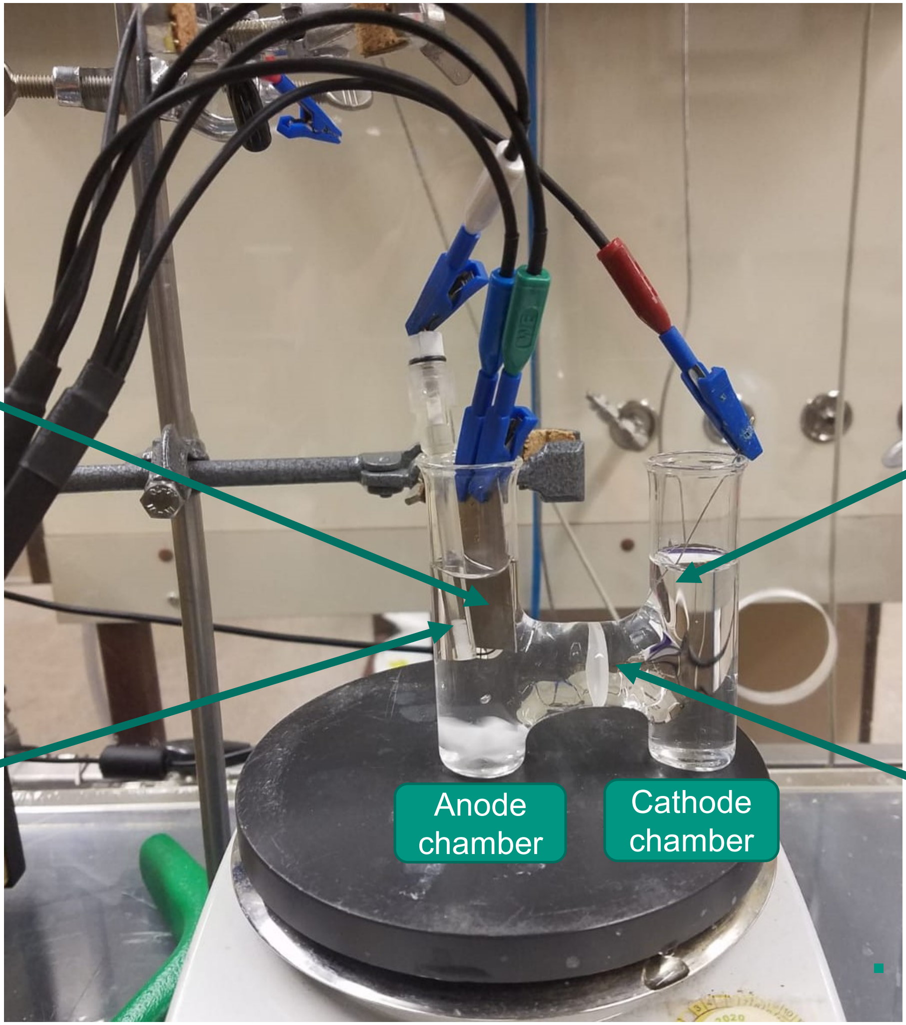
Summary fuel cells



Scheme for „privatized hydrogen economy“



Electrochemical biomass conversion



Working electrode
(Metal foil, here: Nickel)

Reference electrode
(Ag/AgCl)

Anode chamber

Cathode chamber

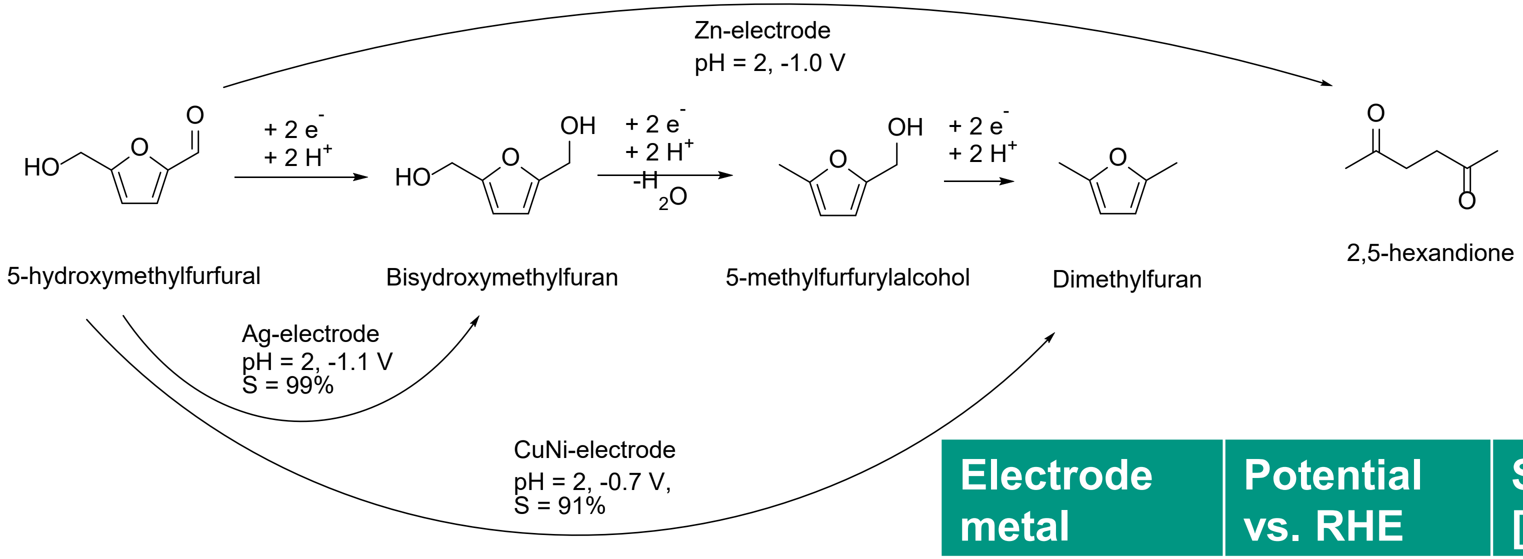
Counter electrode
(Pt-wire)

Seperator
(Membrane, Glas frit)

- Prevents reactants/products from diffusing to other chamber

Different electrodes promote different mechanism

- Reduction of HMF *via* various electrode metals

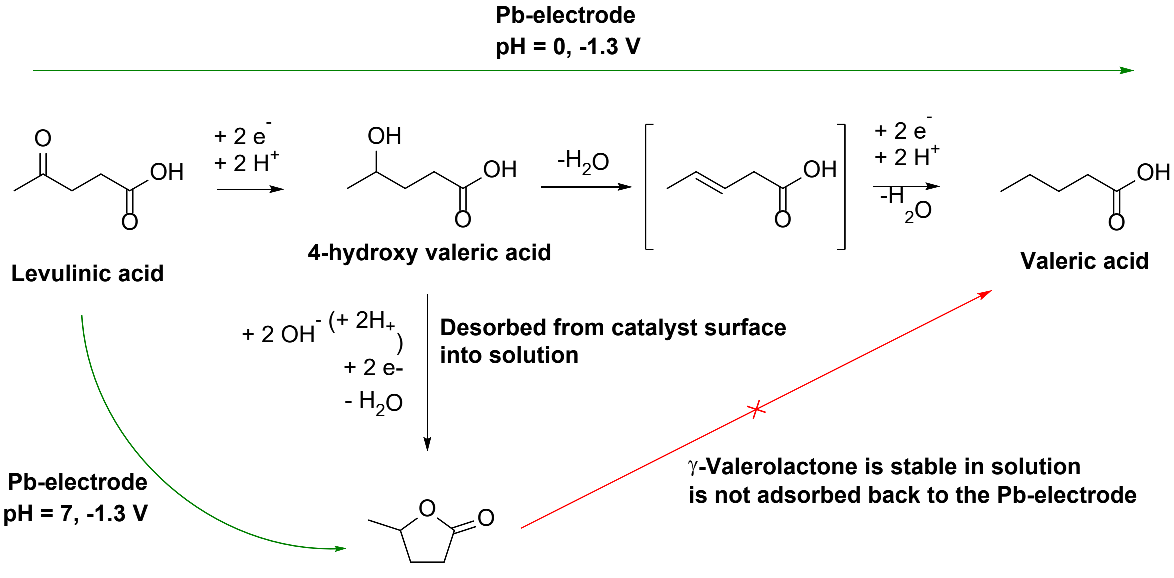


- Selectivity can further be controlled by choosing different potentials

Electrode metal	Potential vs. RHE	Selectivity [DMF]
Cu	-0.3 V	17.3%
Cu	-0.4 V	29.7%
Cu	-0.5 V	52.1%
Cu	-0.6 V	75.2%
Cu	-0.7 V	80.9%
Cu	-0.8 V	79.3%

Influence of pH on the mechanism

- Different selectivities based on pH

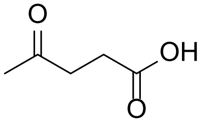


Desorbed from catalyst surface into solution

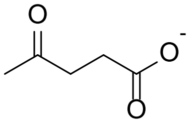
γ-Valerolactone is stable in solution is not adsorbed back to the Pb-electrode

γ-Valerolactone

At pH = 0 mostly protonated



At pH = 7 mostly unprotonated



- Anion less likely to adsorb to cathode, due to negative charge

→ Desorption right after the first step