UNIVERSITY OF BIRMINGHAM

HyDEX winter school

Water Electrolysis

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Electrolysis of water:

The electrolysis of water produces hydrogen gas at the cathode and oxygen gas at the anode.

Electrolysis : Basic Equations

- Water is separated into hydrogen and oxygen by applying an electrical potential:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \qquad \Delta H^0_{298K} = 286 \text{ kJ/mol}$$

- Steam can be used instead of liquid water:

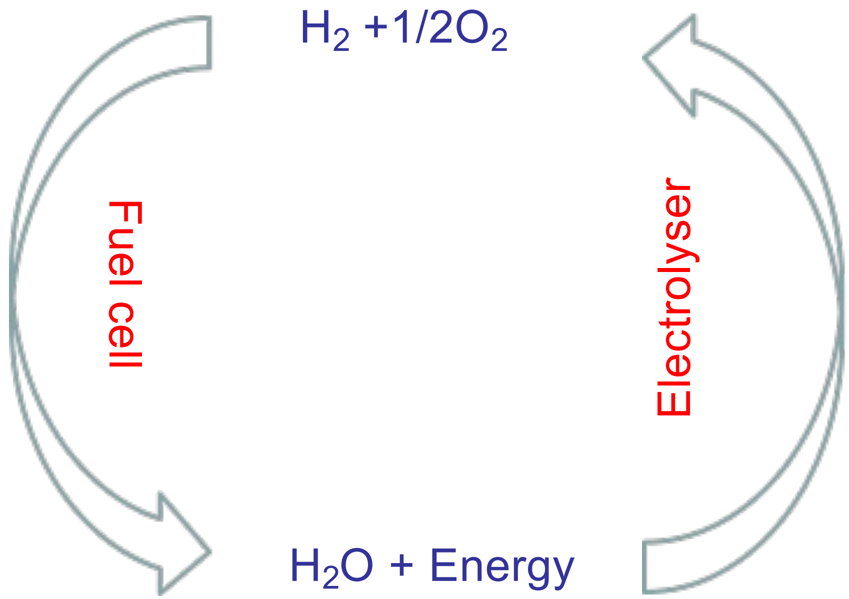
$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g) \qquad \Delta H^0_{298K} = 242 \text{ kJ/mol}$$

enthalpy of vaporization can be provided, for example, by waste heat

- Fuel cell: reverse reaction, hydrogen is oxidized to water, in the process 'generating' electricity:

$$2\,H_2(g) + O_2(g) \rightarrow 2H_2O\ (g/l)$$

The energy of the fuel

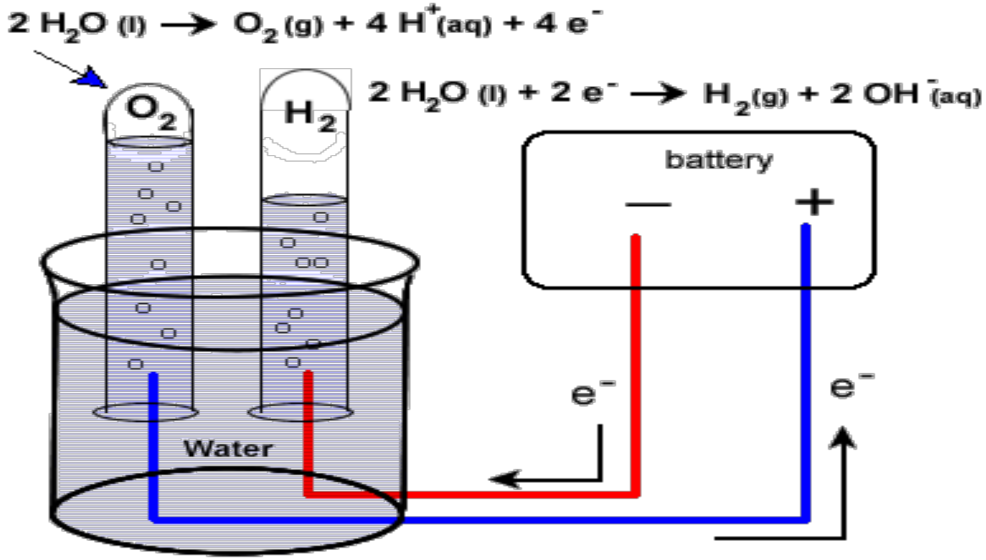


Round trip is like for a battery

What if the fuel is stored and used for another process?

What is the energy value of a fuel?

Electrolysis of water



Overall reaction: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

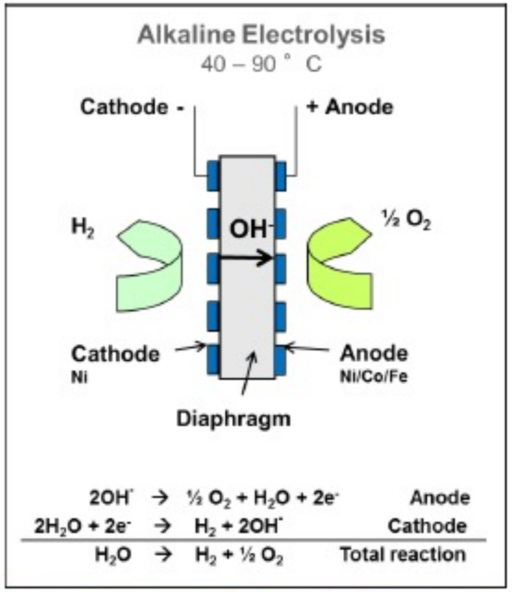
Acid:

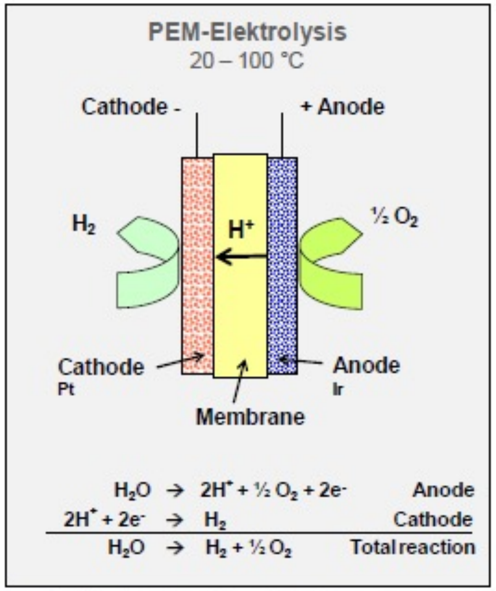
Reduction at cathode:	$4H^+(aq) + 4e^-$	$\rightarrow 2H_2(g)$
Oxidation at anode:	$2H_2O(l)$	$\rightarrow O_2(g) + 4H^+(aq) + 4e^-$

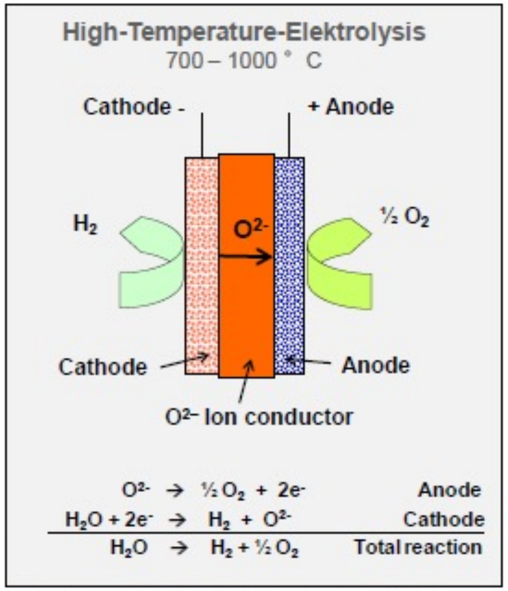
Base:

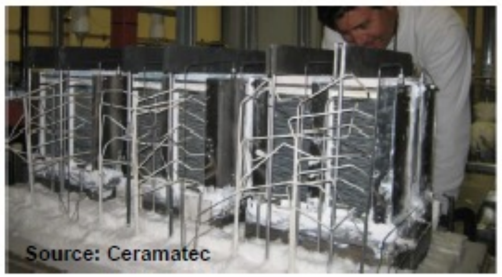
Cathode (reduction):	$4H_2O(l) + 4e^-$	$\rightarrow 2H_2(g) + 4OH^-(aq)$
Anode (oxidation):	$4OH^-(aq)$	$\rightarrow O_2(g) + 2H_2O(l) + 4e^-$

Electrolyser Types



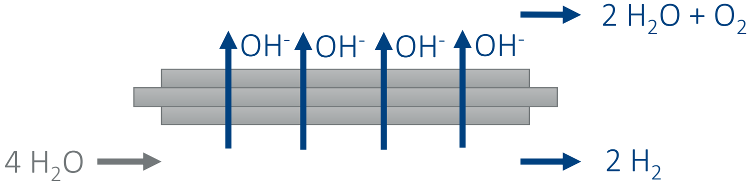






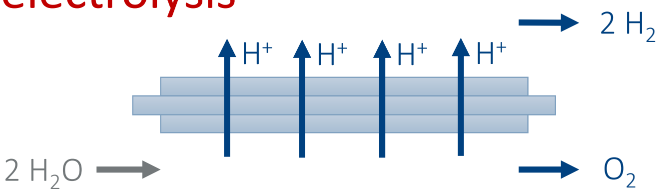
Electrolyser Types

Alkaline electrolysis



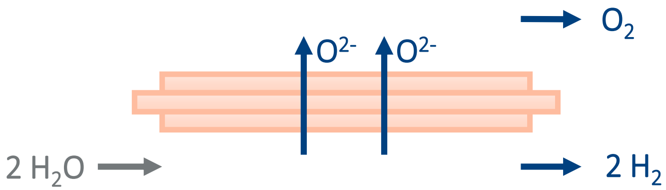
- Membrane permeable for hydroxide ions (OH^-)
- Efficiency: 55-70%$_{LHV}$ or 4.3-5.4 kWh/Nm^3
- Temperature: 60-90 °C
- Mature technology (>60 years in commercial applications)

PEM electrolysis



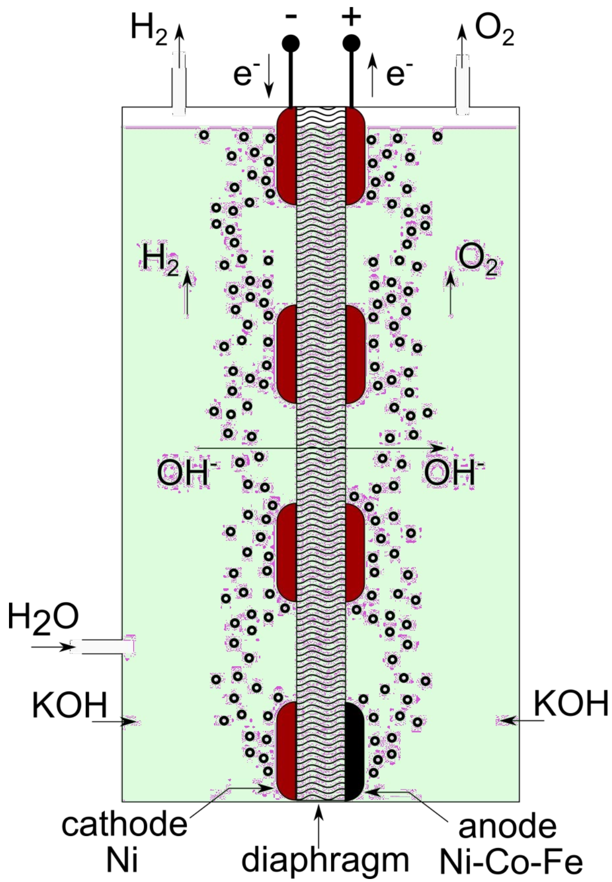
- Polymer Electrolyte-Membrane: permeable for protons (H^+)
- Efficiency: 50-65%$_{LHV}$ or 4.6-6.0 kWh/Nm^3
- Temperature: 70-90 °C
- Flexible operation from part to full load

High-temperature-electrolysis

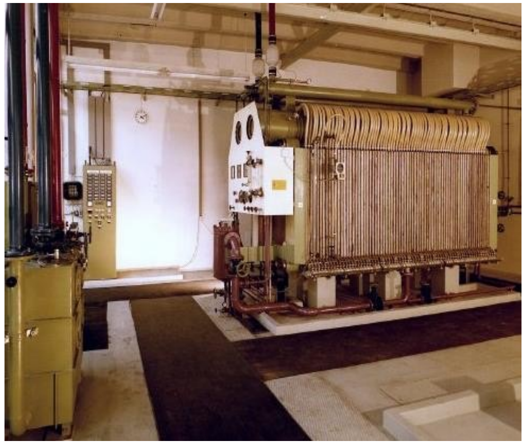


- Membrane permeable for oxide ions (O^{2-})
- Efficiency: 75-87%$_{LHV}$ or 3.4-4.0 kWh/Nm^3 (highest valued based on steam and ambient pressure)
- Temperature: 500-850 °C
- Less mature, promising economics

Alkaline water electrolysis



400 units in operation by 1902 (Anything else in history?)



BAMAG Elektrolyzer (atmospheric)

Source: Bamag

Lurgi High Pressure Elektrolyzer (32 bar)

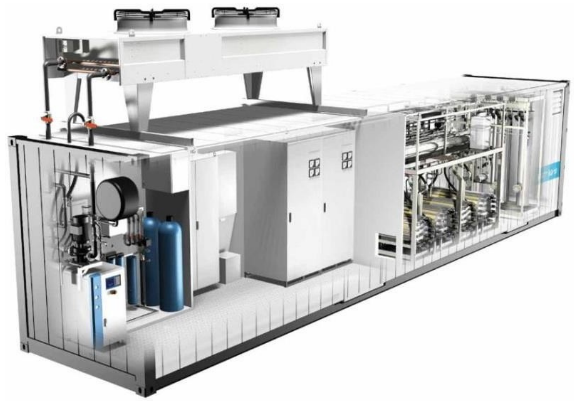
Source: Lurgi

Cell and stack design of alkaline water electrolysis

- State-of-the-art

Specifications	State-of-the-art
Cell temperature	60 – 80 °C
Cell pressure	< 30 bar
Current density	0,2 – 0,4 A/cm²
Cell voltage	1,8 – 2,4 V
Power density	< 1 W/cm²
Voltage efficiency	62 – 82 %
Spec. Energy consumption Stack	4,2 – 5,9 kWh/Nm³
Spec. Energy consumption System	4,5 – 7,0 kWh/Nm³
Low partial load range	20 – 40 %
Cell area	< 4 m²
H_2-Production rate/Stack/System	< 760 Nm³/h
Lifetime Stack	< 90.000 h
Degradation rate	< 3 µV/h
System life time inc. reassemblying	20 – 30 a

Source: NOW-Studie ‚Stand und Entwicklungspotenzial der Wasserelektrolyse zur Herstellung von Wasserstoff aus regenerativen Energien‘



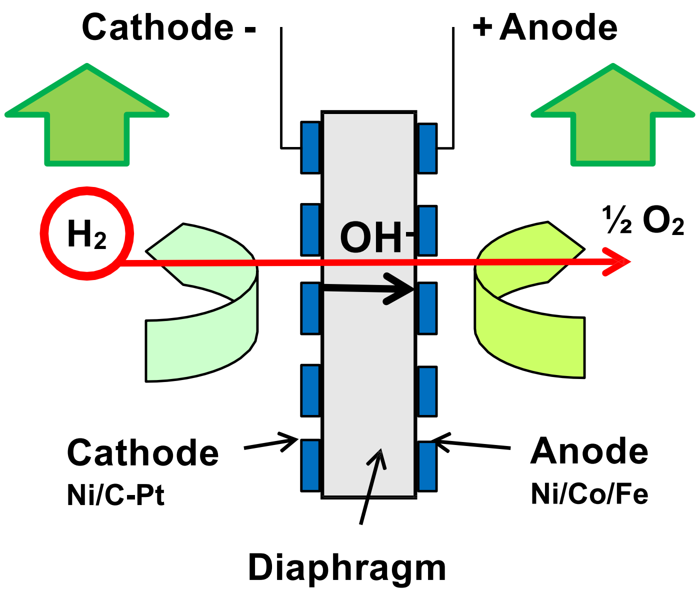
Hydrogenics HySTAT™-60 (60 Nm³/h; 5,5 kg/h;10 bar)

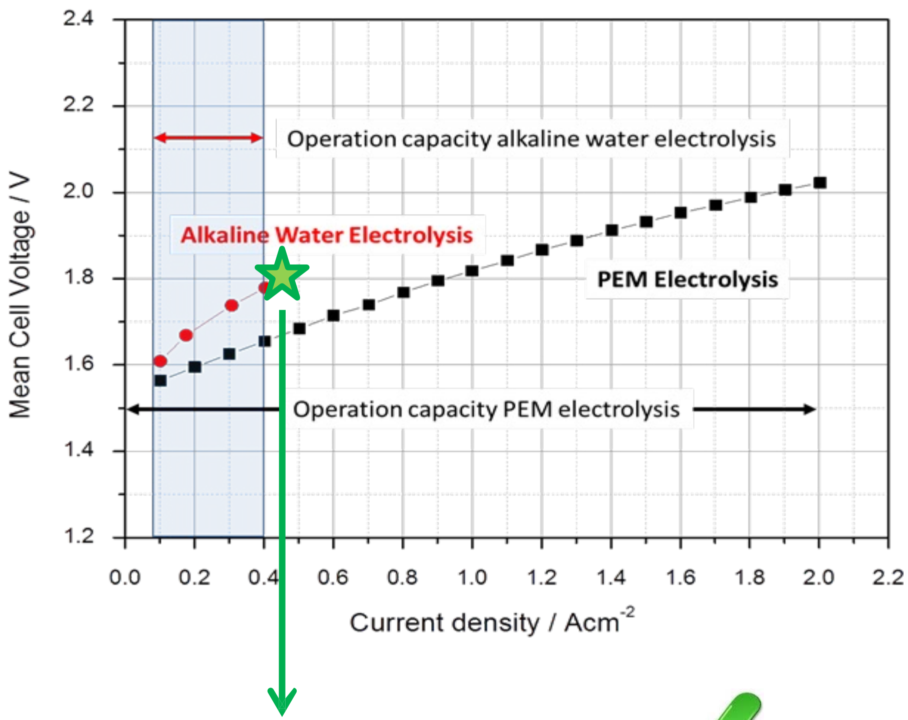
Lurgi Pressure Electrolyse (760 Nm³/h; 32 bar)

*bezogen auf HHV: 1,48 V

Materials and properties of alkaline water electrolysis

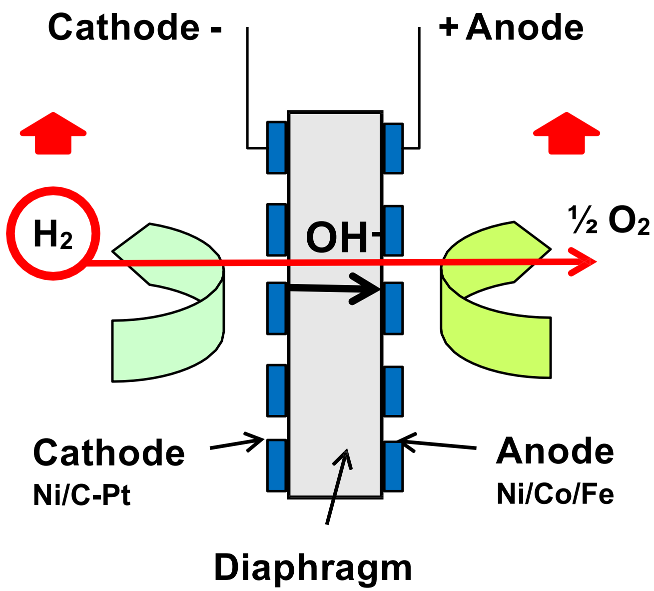
- Low partial load condition

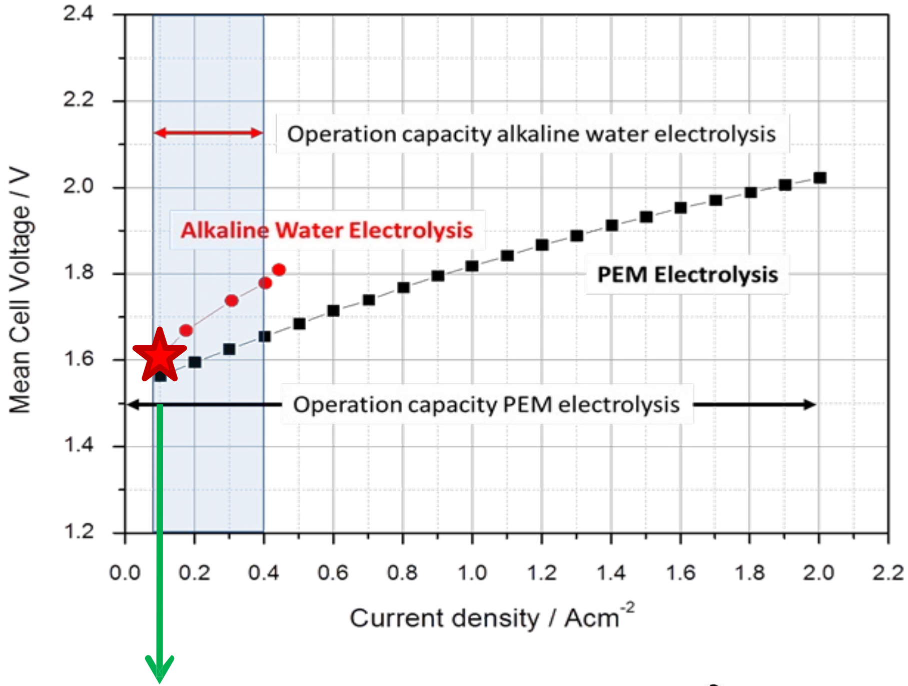




$[H_2]$ in O_2 is well under 2%
(no explosion risk!!!)

Materials and properties of alkaline water electrolysis
- Low partial load condition





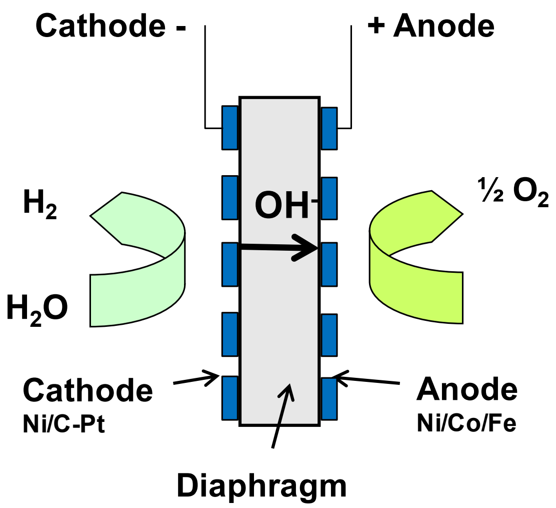
[H_2] in O_2 is reaches 2%
(explosion risk!!!)

Principles of PEM water electrolysis

- Alkaline electrolysis *vs.* PEM electrolysis

Alkaline Electrolysis

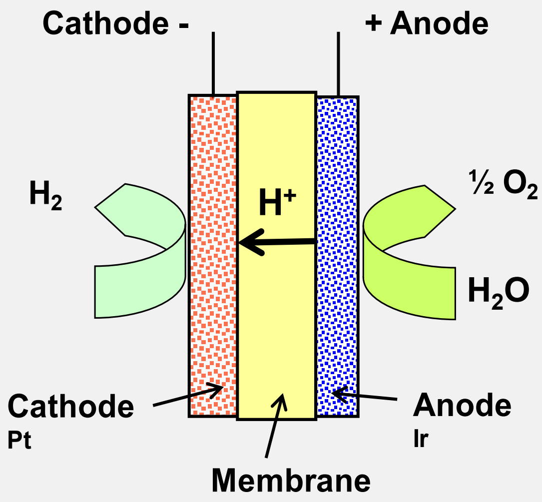
40 – 90 ° C



$2OH^-$	→	$\frac{1}{2} O_2 + H_2O + 2e^-$	Anode
$2H_2O + 2e^-$	→	$H_2 + 2OH^-$	Cathode
H_2O	→	$H_2 + \frac{1}{2} O_2$	Total reaction

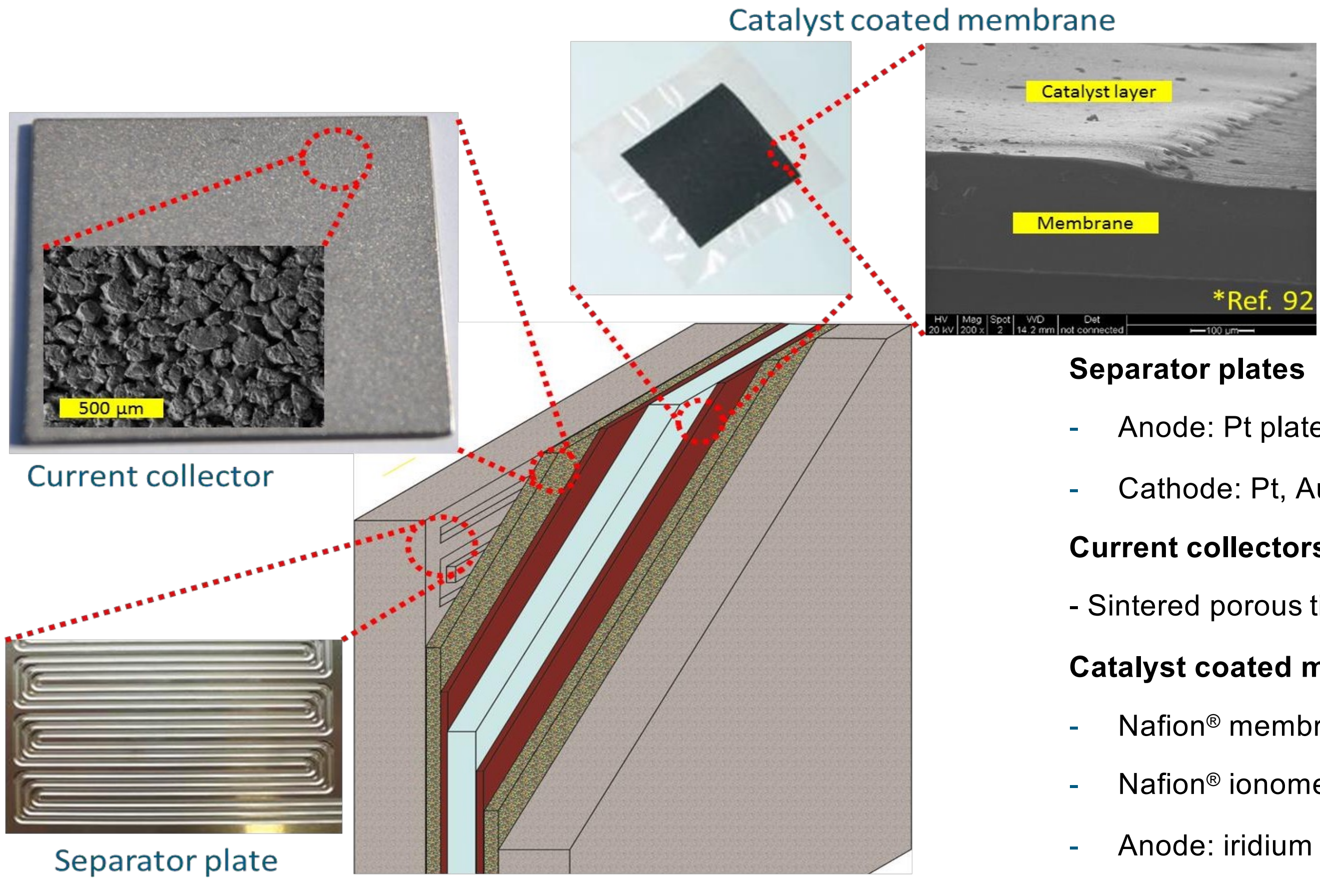
PEM-Elektrolysis

20 – 100 °C



H_2O	→	$2H^+ + \frac{1}{2} O_2 + 2e^-$	Anode
$2H^+ + 2e^-$	→	H_2	Cathode
H_2O	→	$H_2 + \frac{1}{2} O_2$	Total reaction

Cell and stack design of PEM water electrolysis



Separator plates

- Anode: Pt plated titanium
- Cathode: Pt, Au plated titanium

Current collectors

- Sintered porous titanium

Catalyst coated membrane (CCMs)

- Nafion® membrane
- Nafion® ionomer
- Anode: iridium oxide (IrO_2)
- Cathode: Pt/C

Cell and stack design of PEM water electrolysis
- State-of-the-art

Specifications	State-of-the-art
Cell temperature	50 – 80 ° C
Cell pressure	< 30 bar
Current density	0,6 – 2,0 A/cm²
Cell voltage	1,8 – 2,2 V
Power density	~ 4,4 W/cm²
Voltage efficiency*	67 – 82 %
Spec. Energy consumption Stack	4,2 – 5,6 kWh/Nm³
Spec. Energy consumption System	4,5 – 7,5 kWh/Nm³
Low partial load range	0 – 10 %
Cell area	< 300 cm²
H_2-Production rate pro Stack/System	bis 10 Nm³/h / 30 Nm³/h
Lifetime Stack	< 20.000 h
Degradation rate	< 14 µV/h
Lifetime system incl. reassemblying	10 – 20 a

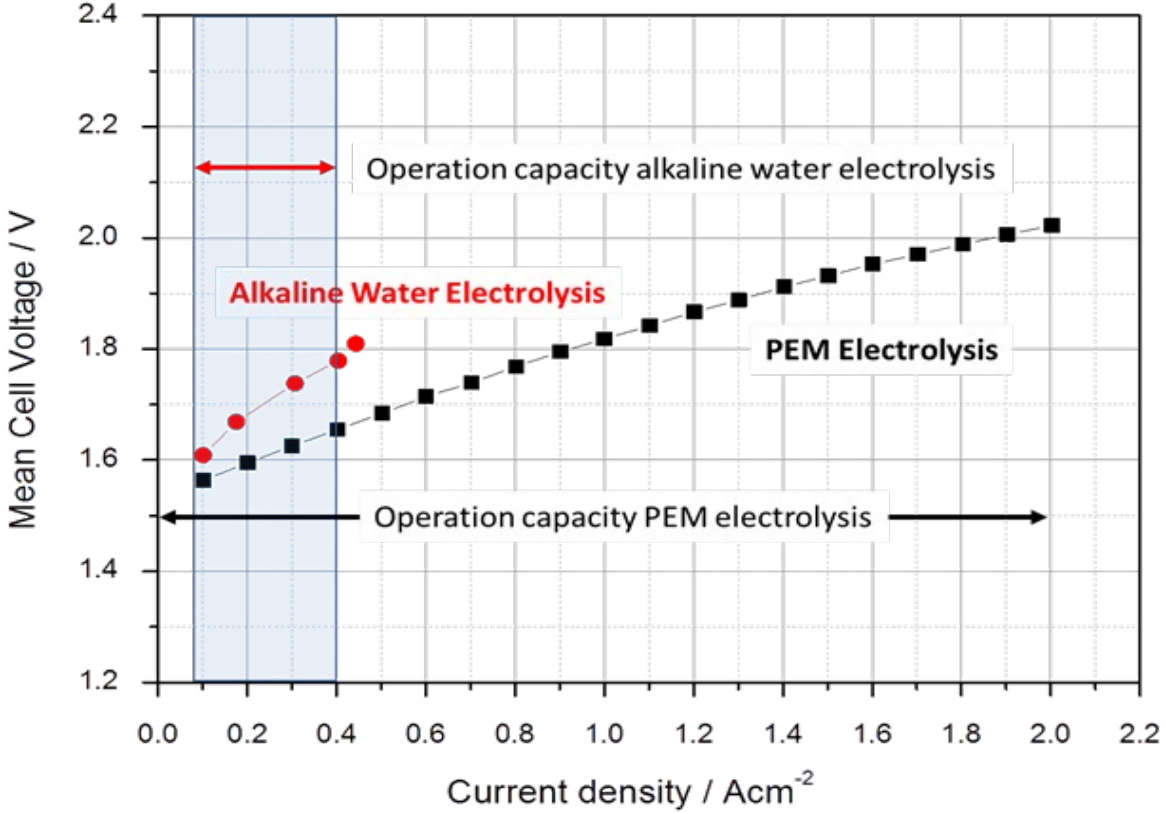
Source: NOW-Studie ‚Stand und Entwicklungspotenzial der Wasserelektrolyse zur Herstellung von Wasserstoff aus regenerativen Energien'

Quelle: Proton OnSite
PEM-Elektrolysestack
Einzelelektrodenfläche 213 cm²

Quelle: Proton OnSite
PEM-Elektrolyseur
Serie HOGEN C 30 Nm³/h

*bezogen auf HHV: 1,48 V

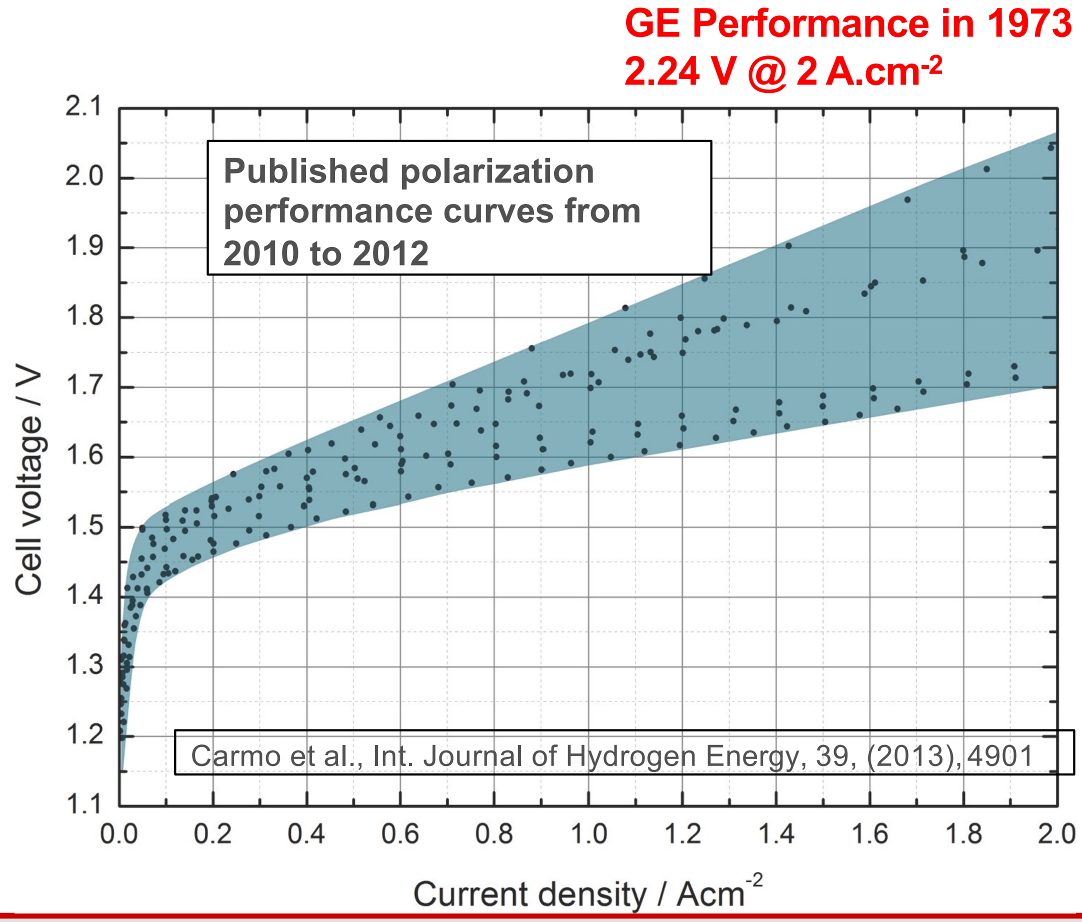
PEM water electrolysis *vs.* alkaline water electrolysis
- Current *vs.* voltage profiles



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.

Performance aspect: PEM water electrolysis

- Performance (polarization curves) found in the literature (lab scale)



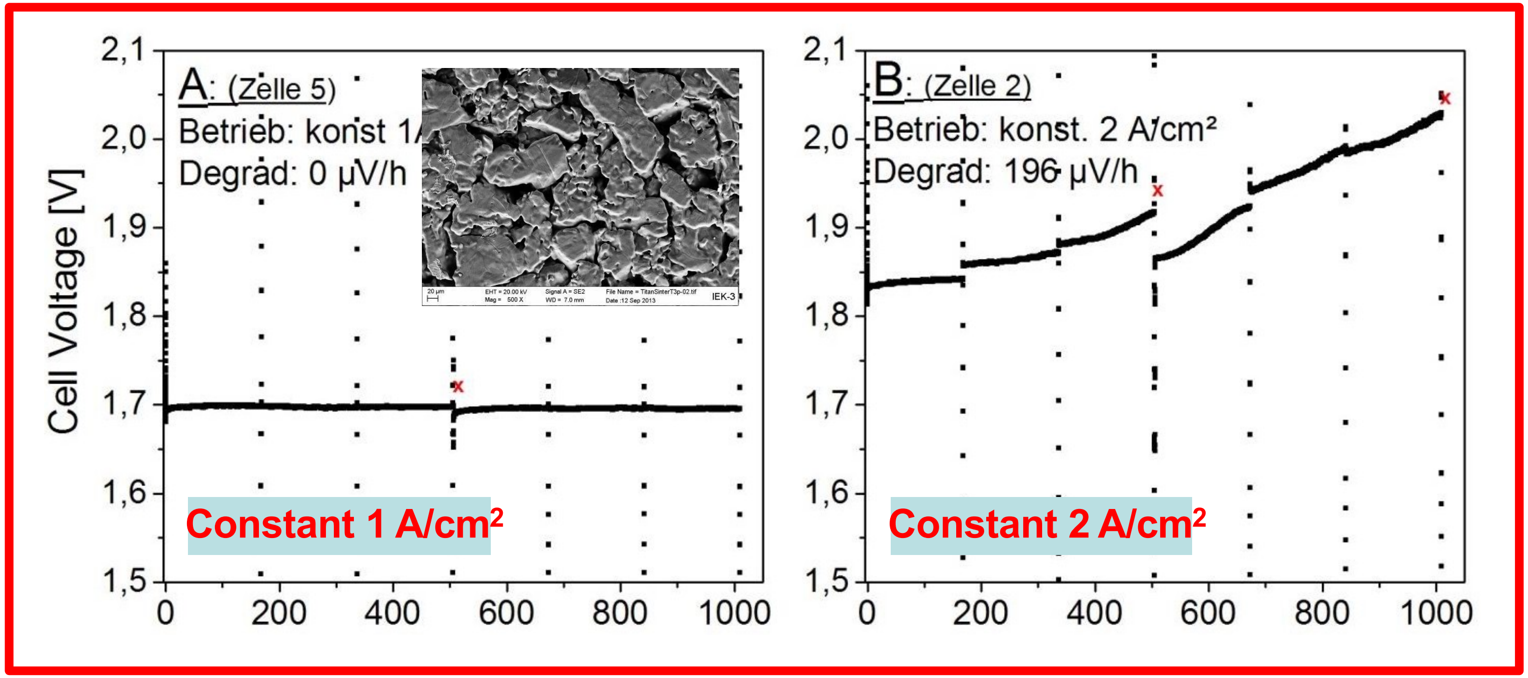
CCM example

- Nafion membrane 117
- Comercial catalysts:
  - IrO_2 AlfaAesar – 2.25 $mg_{Ir}cm^{-2}$
  - Pt/C J&M – 0.8 $mg_{Pt}cm^{-2}$
- Decal method

Titanium porous transport layers (PTLs)

- In-situ degradation tests (single cells)

Using uncoated titanium porous transport layers on the anode side



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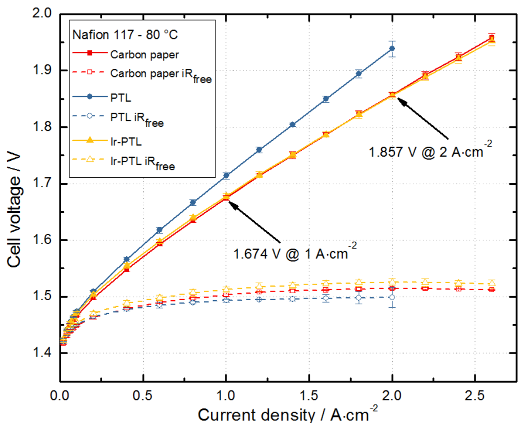
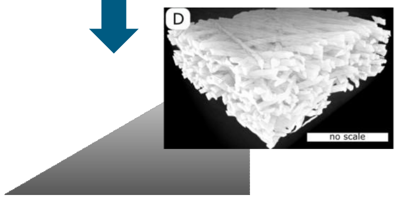
Porous Transport Layers (PTLs) for PEM Electrolyzers
- The challenge of a cost-effective PGM coating

Liu et al., Electrochemistry Comm. 97, 96, 2018.

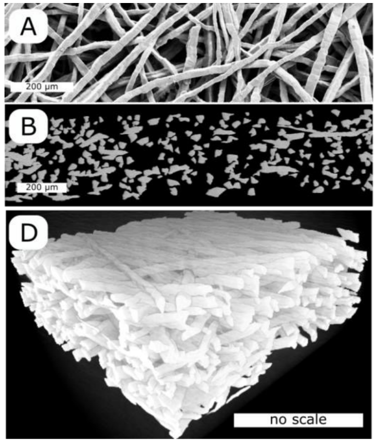
Porous Transport Layer (PTLs)
- PGM coatings
- Interface Resistance
- Durability



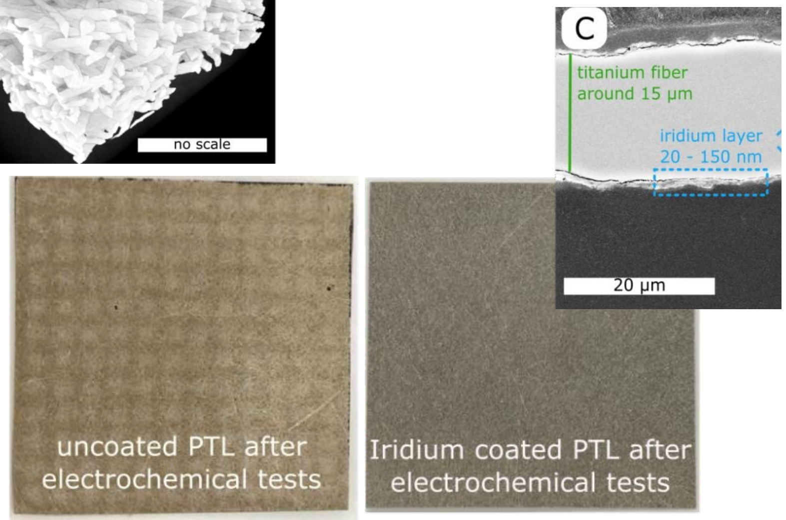


<300 cm²

Iridium sputtered PTL presenting performance results similar to carbon based PTL materials



Ti base felt from Bekaert®
- porosity: 76%
- 350 µm thick
- Less expensive than sintered PTLs
- good off-the-shelf tolerance



Mitglied der Helmholtz-Gemeinschaft

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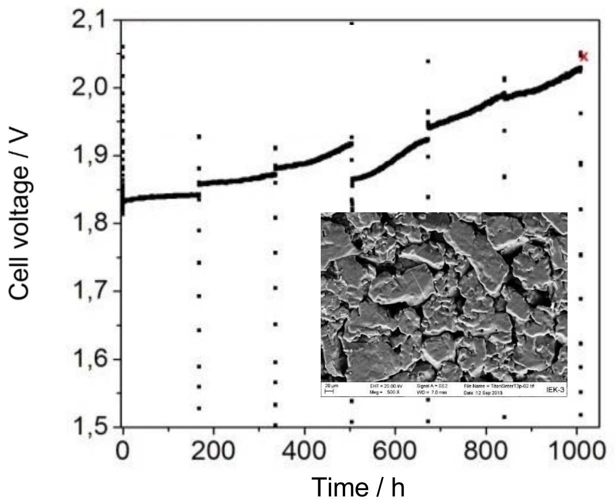
Titanium porous transport layers (PTLs)

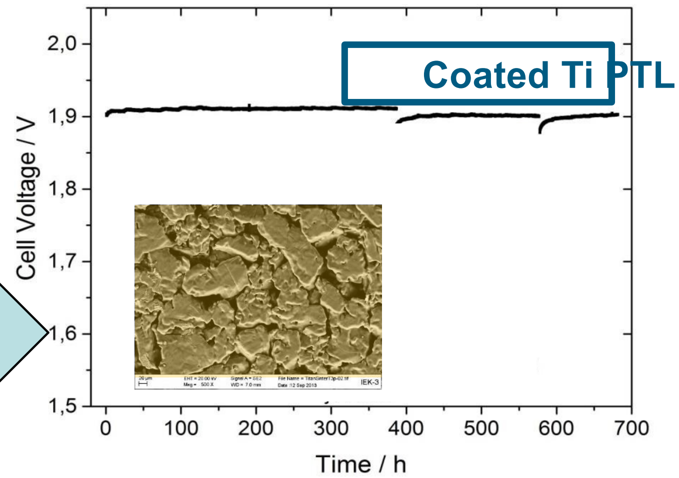
- In-situ degradation tests (single cells)

- Analysis of degradation behavior of MEA-components → severe degradation of titanium porous transport layers – TiO_2 passivation
- Coated porous transport layers → no detectable degradation after 700 h constant operation at 80 °C and ambient pressure



1000 hours at constant current of 2 A/cm² with a **degradation rate of ~ 200 µV/h**.

Coating
of porous
transport layer



700 hours at constant current of 2 A/cm² with **no measurable degradation rate**.

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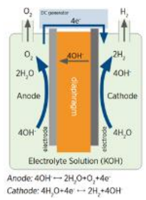
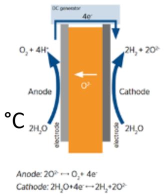
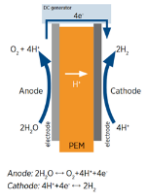
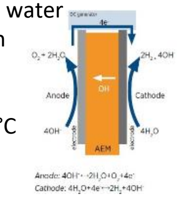
Electrolyser technology comparison

	Alkaline water Electrolyzer (AEL)	Solid Oxide Electrolyzer Cells (SOEC)	Proton Exchange Membrane Electrolyzer (PEM)	Anion Exchange Membrane Electrolyzer (AEM)
Technology	• AELs are using a liquid electrolyte • **Operating temperature:** 60-90 °C • **Pressure:** 1-40 bar 	• SOECs are using using a solid oxide or ceramic electrolyte • **Operating temperature:** 500-850 °C **Pressure:** 1-10 bar 	• PEMs are using a solid, ion-conducting electrolyte • **Operating temperature:** 70-90°C • **Pressure:** 1-40 bar 	• AEMs are using pure water or low-concentration alkaline solutions • **Operating temperature:** 30-60°C • **Pressure:** 1-40 bar 
Main features	Flexibility ●●○ Investment cost ●●● Operating cost ●●● TRL level* ●●●	Flexibility ●○○ Investment cost ●○○ Operating cost ●○○ TRL level* ●○○	Flexibility ●●● Investment cost ●○○ Operating cost ●●○ TRL level* ●●○	Flexibility ●●○ Investment cost ●○○ Operating cost ●○○ TRL level* ●○○
+	• **Well established and mature technology.** Sufficient dynamics for control power and energy market contribution • Best efficiency over 10 year operation due to low degradation (0.8 – 1.0 % per year) • Low feed water quality requirement	• High potential to be much more energy-efficient than the AEL and PEM electrolyzers • High materials availability	• **One of the most hyped electrolyzers on the market** • Dynamic response • Intermittent operation	• Low cost • High efficiency • Dynamic response
–	• Limited ability to operate at low loads / no intermittent usage • Produced H_2 needs additional purification	• **New technology, first commercial products have not yet shown maturity** • High cost (CAPEX and OPEX)	• Higher cost due to expensive materials (titanium, PGM catalysts, power supply) • 1.5 to 2-times the TCO of AEL • High feed water quality requirement • High degradation (1.1-1.2 % per year)	• **New technology, not mature, no high-power stacks available yet** • Lower durability compared to PEM electrolyzers

Source: BloombergNEF, McKinsey, FinH_2
Note: *TRL - Technology readiness level

HYDROGENITY
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