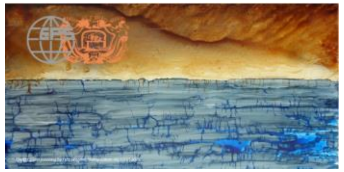
From electrolysers …..
….to fuel cells



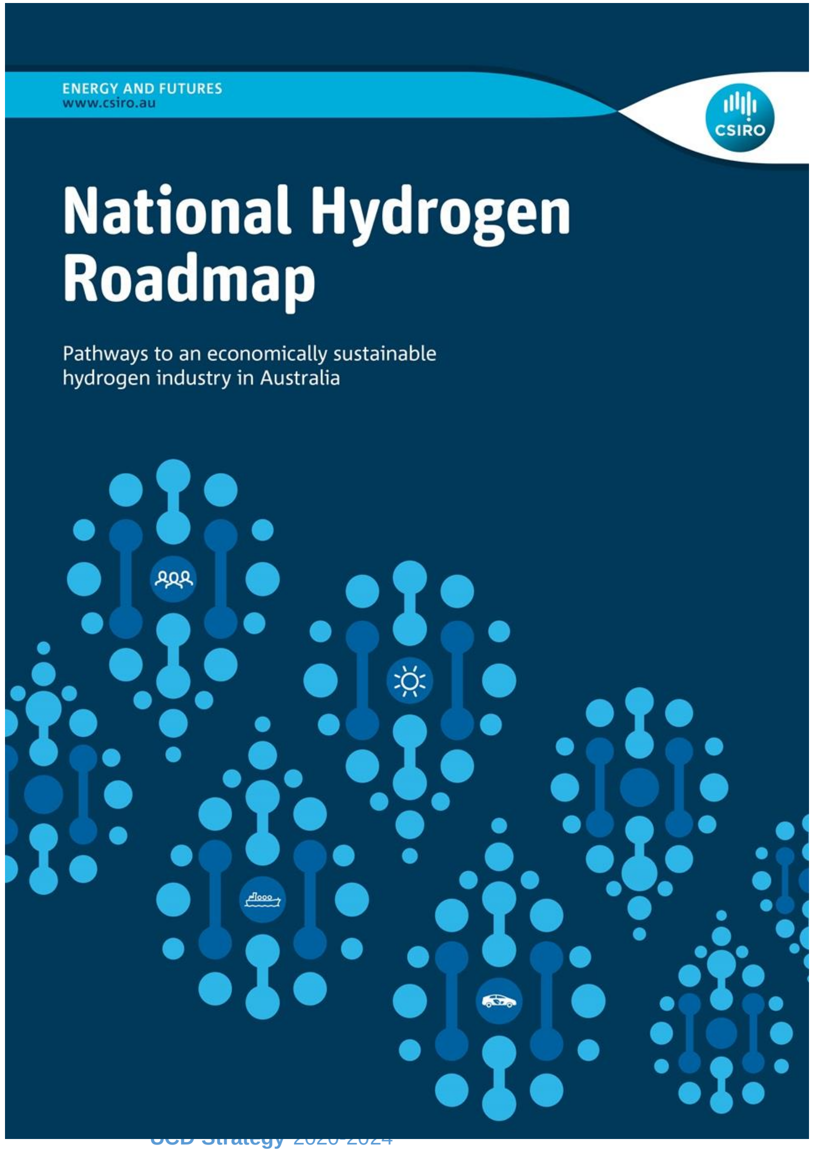
Assistant Professor
Maria Veronica Sofianos

Non compatible slides to colour blindness

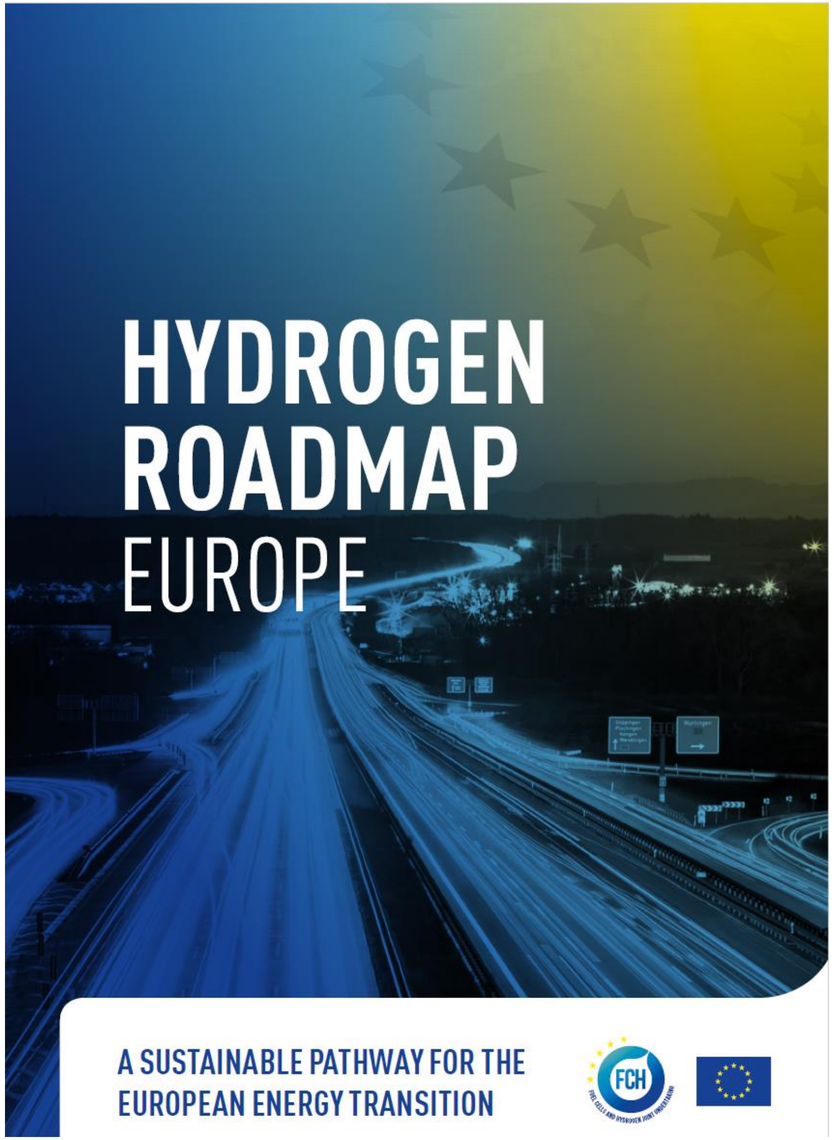
Lecture overview for first half

- Introduction of H_2
- Water electrolysis
- The role of the electrolyte
- Types of electrolysers
- The problems
- Research focus

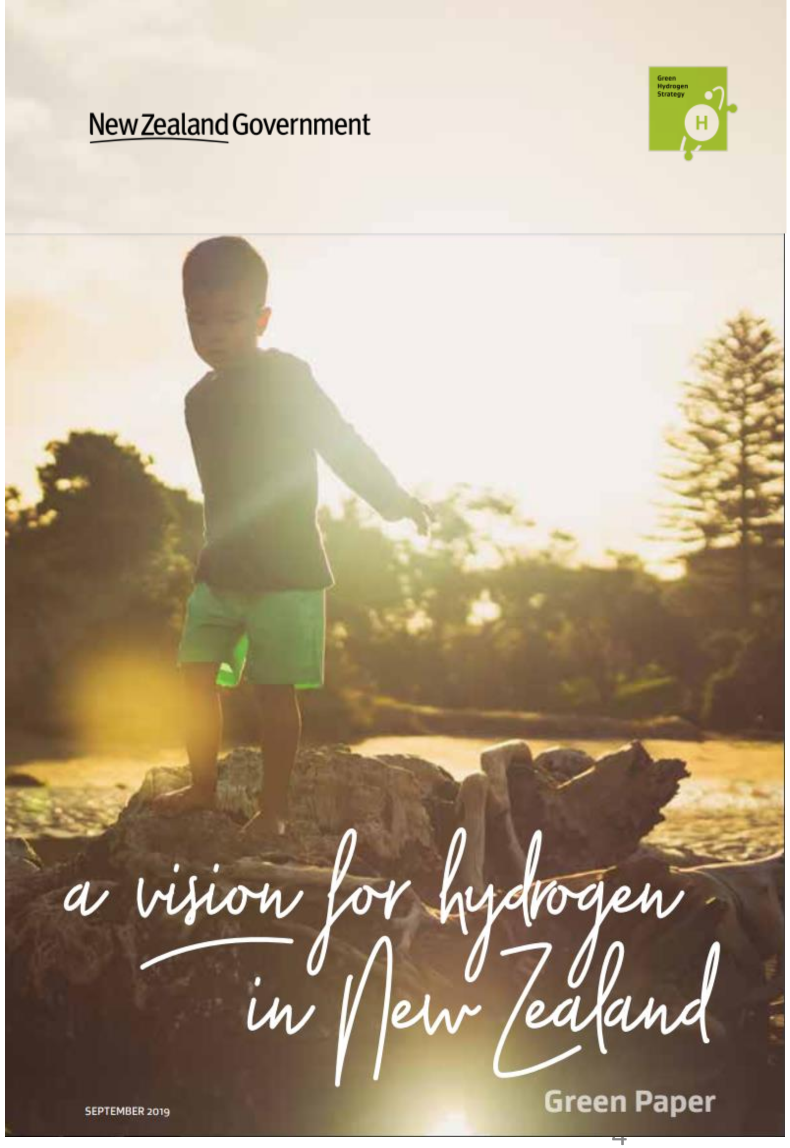
The Hydrogen roadmap rave



https://www.csiro.au/en/Do-business/Futures/Reports/Hydrogen-Roadmap



https://www.hydrogeneurope.eu/index.php/news/hydrogen-roadmap-europe-has-been-published



https://www.mbie.govt.nz/dmsdocument/6798-a-vision-for-hydrogen-in-new-zealand-green-paper

ACHIEVING DEEP DECARBONIZATION OF >80% OF CO_2 EMISSIONS REQUIRES HYDROGEN

Challenge

Hydrogen is the best or only choice for at-scale decarbonization of key segments, for example:

Achieving deep decarboni-zation

- H_2 TO DECARBONIZE THE GAS GRID
- FUEL CELLS/ SYNFUELS FOR HEAVY TRANSPORT AND LONG DISTANCES
- HIGH-GRADE HEAT FOR INDUSTRY & IN STEEL
- ULTRA-LOW-CARBON H_2 AS FEEDSTOCK, E.G., AMMONIA

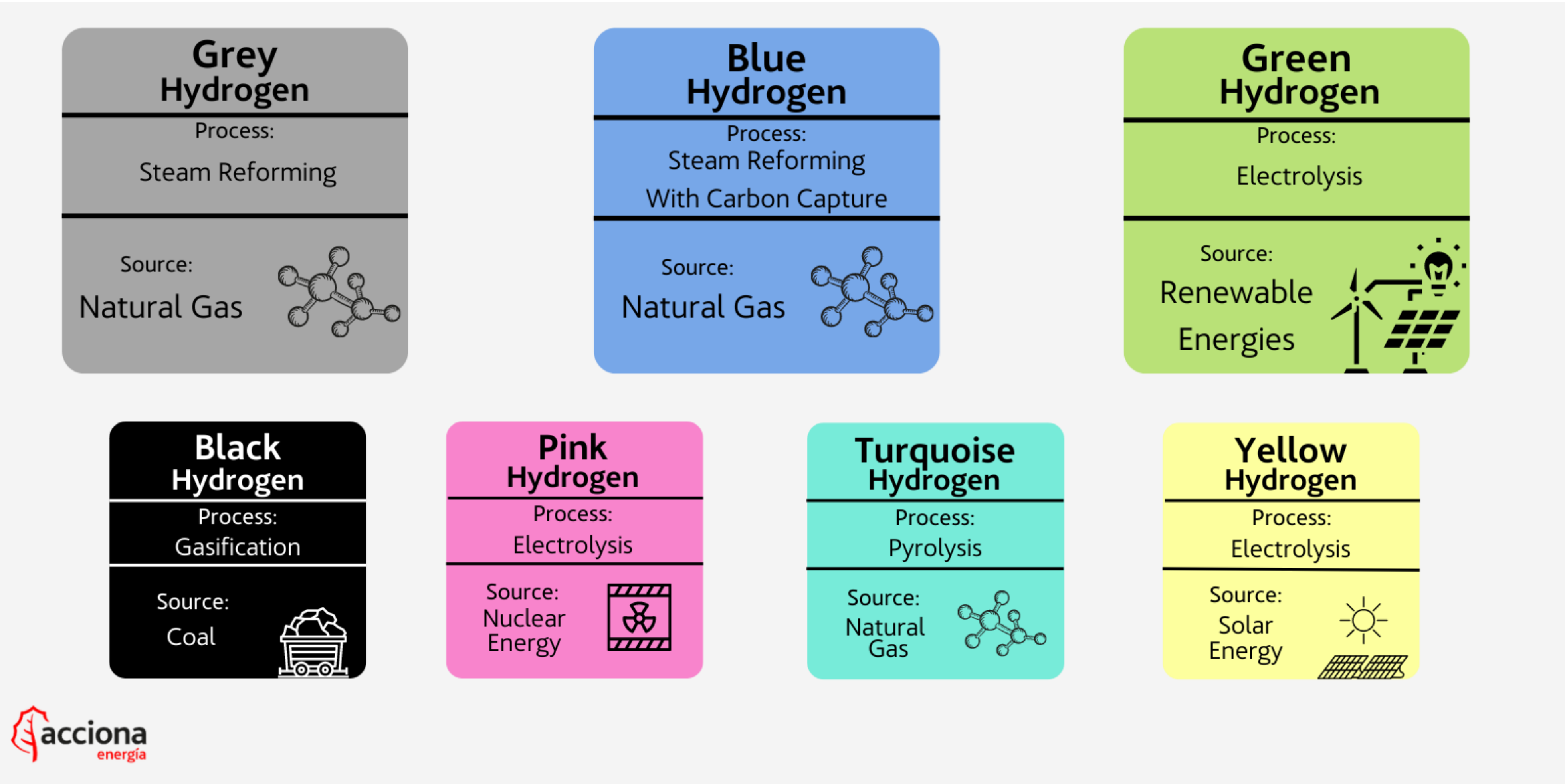
What is hydrogen? Where does it come from? …and its role in the energy sector…

- Hydrogen is the first element in the periodic table.
- It is the simplest and most abundant element in the universe (75% of all mass in the universe is hydrogen), but it rarely exists as a gas on Earth - it must be separated from other elements.
- Hydrogen is colorless and odorless.
- At atmospheric pressure, hydrogen is about 14 times lighter than air.
- The energy density of hydrogen is 120 MJ/kg
- It name comes from the Greek word ‘hydro’ and ‘genes’ that mean water-forming.

96% H_2 : steam-methane (from natural gas) reforming, which produces hydrogen and CO_2

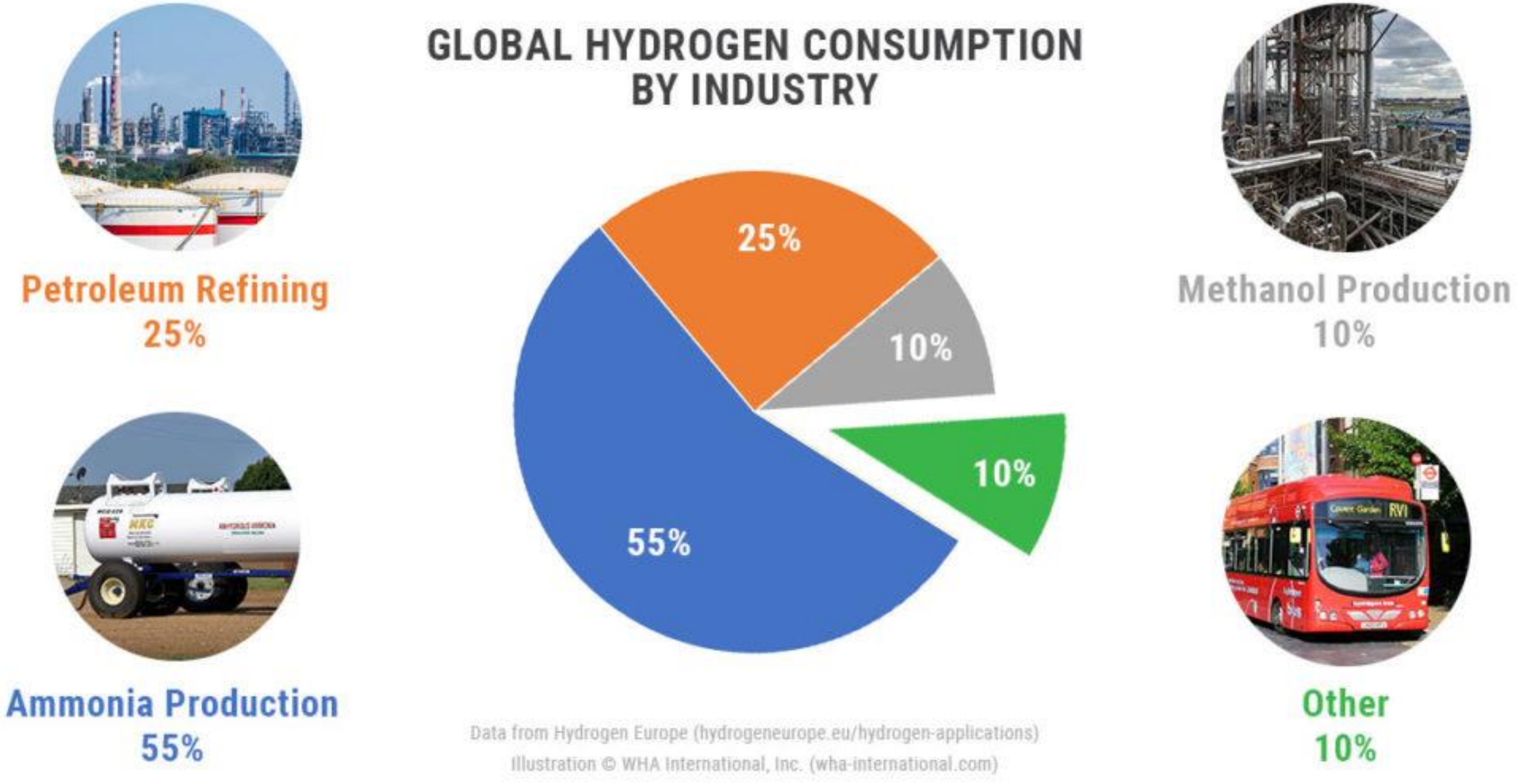
4% H_2 : using renewable energy to produce hydrogen by splitting water (electrochemically or photochemically)

The colour spectrum of hydrogen



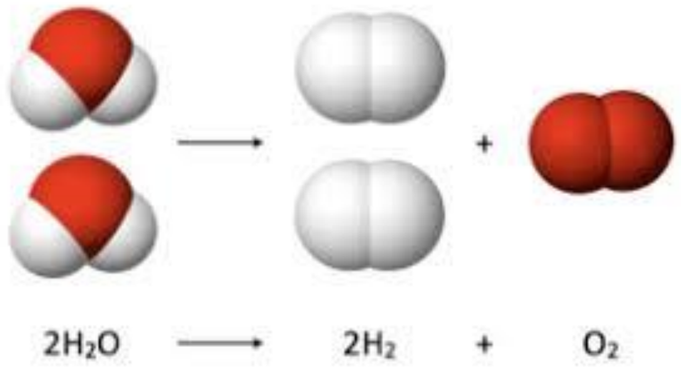
https://www.acciona.com.au/updates/stories/what-are-the-colours-of-hydrogen-and-what-do-they-mean/?_adin=02021864894

Where is hydrogen used?



https://wha-international.com/hydrogen-in-industry/

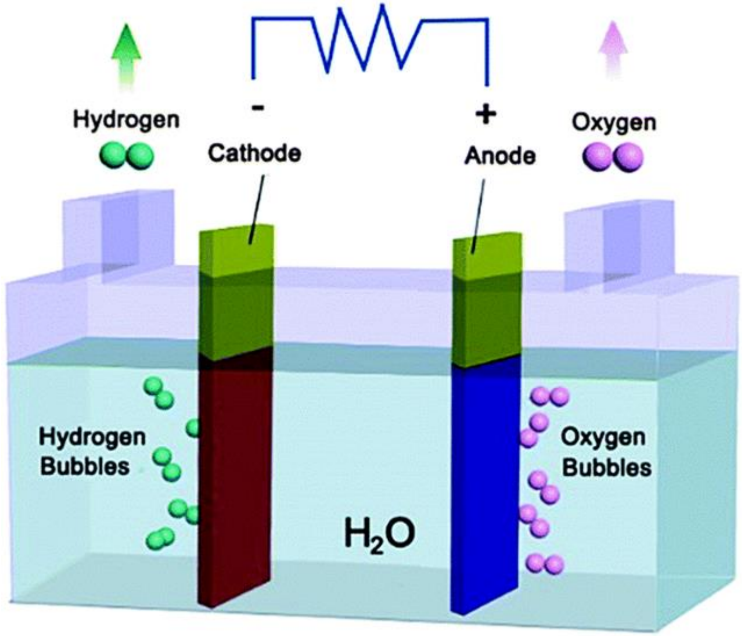
What is water electrolysis?



- Also known as electrochemical water splitting.

In simple terms: Splitting water into hydrogen and oxygen gas

In scientific terms: Water electrolysis is based on two half reactions: (i) the hydrogen evolution reaction (HER) at the cathode, and (ii) the oxygen evolution reaction (OER) at the anode.



Overall reaction: $H_2O \rightarrow H_2 + 1/2\ O_2$ $\Delta G_f = 229$ kJ/mol
HER: $2H^+ + 2e^- \rightarrow H_2$ $E^0 = 0.00$ V
OER: $2H_2O \rightarrow O_2 + 4e^- + 4H^+$ $E^0 = 1.23$ V

From: Chem. Soc. Rev. 2015, 44, 5148-5180

J. Mater. Chem. A, 2016,4, 11973-12000

The role of the electrolyte in water electrolysis

- The pH of the electrolyte will determine the mechanism of the reaction, both for the HER and OER.

pH < 7 Acidic electrolyte

HER:

(1) $H_3O^+ + e^- + * \rightarrow H^* + H_2O$, Volmer reaction

(2) $H^* + H_3O^+ + e^- \rightarrow H_2 + *$, Heyrovsky reaction

(3) $H^* + H^* \rightarrow H_2$, Tafel reaction

OER:

(1) $H_2O + * \rightarrow OH^* + H^+ + e^-$
(2) $OH^* \rightarrow O^* + H^+ + e^-$
(3) $O^* + H_2O \rightarrow {}^*OOH + H^+ + e^-$
(4) ${}^*OOH \rightarrow * + O_2 + H^+ + e^-$
(5) $O^* + O^* \rightarrow O_2$

pH = 7 Neutral electrolyte

HER:

(1) At low cathodic overpotentials, $H* + H_3O^+ + e^- \rightarrow H_2 + *$

(2) At high cathodic overpotentials, $H* + H_2O + e^- \rightarrow H_2 + OH^-$

OER:

(1) $2H_2O + * \rightarrow OH^* + H_2O + e^- + H^+$
(2) $OH^* + H_2O \rightarrow O^* + H_2O + e^- + H^+$
(3) $O^* + H_2O \rightarrow {}^*OOH + e^- + H^+$
(4) ${}^*OOH \rightarrow O_2 + e^- + H^+$

pH > 7 Alkaline electrolyte

HER:

(1) $H_2O + e^- + * \rightarrow H* + OH^-$, Volmer reaction

(2) $H* + H_2O + e^- \rightarrow H_2 + OH^-$, Heyrovsky reaction

(3) $H* + H* \rightarrow H_2$, Tafel reaction

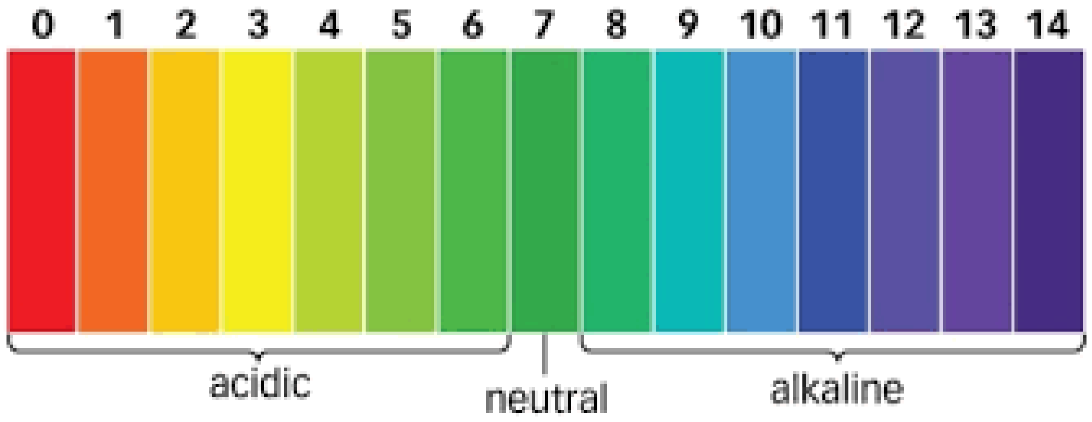
OER:

(1) $OH^- + * \rightarrow OH^* + e^-$
(2) $OH^* + OH^- \rightarrow O^* + H_2O + e^-$
(3) $O^* + OH^- \rightarrow *OOH + e^-$
(4) ${}^*OOH + OH^- \rightarrow * + O_2 + H_2O + e^-$
(5) $O^* + O^* \rightarrow O_2$

* stands for the catalyst surface, H^* is the adsorbed hydrogen intermediate, OH^*, O^* and ${}^*OOH$ are the adsorbed oxygen intermediates.

Types of electrolysers

- The pH of the electrolyte defines the type of the electrolyser.



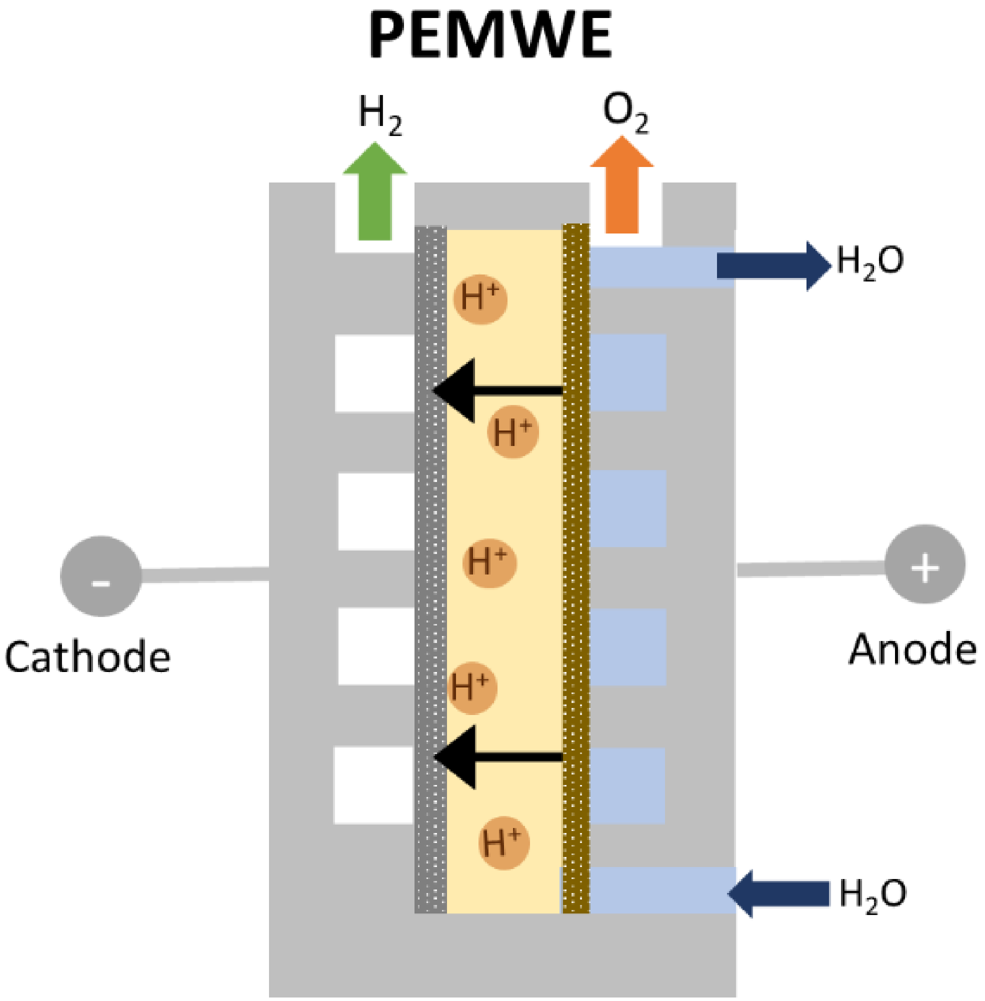
1. Proton exchange membrane water electrolyser (PEMWE) **pH < 7 Acidic electrolyte**

2. High-temperature water electrolysers **pH = 7 Neutral electrolyte**

3. Alkaline water electrolyser (AWE) **pH > 7 Alkaline electrolyte**

4. Anion exchange membrane water electrolyser (AEMWE) **pH > 7 Alkaline electrolyte**

Proton exchange membrane water electrolyser (PEMWE)

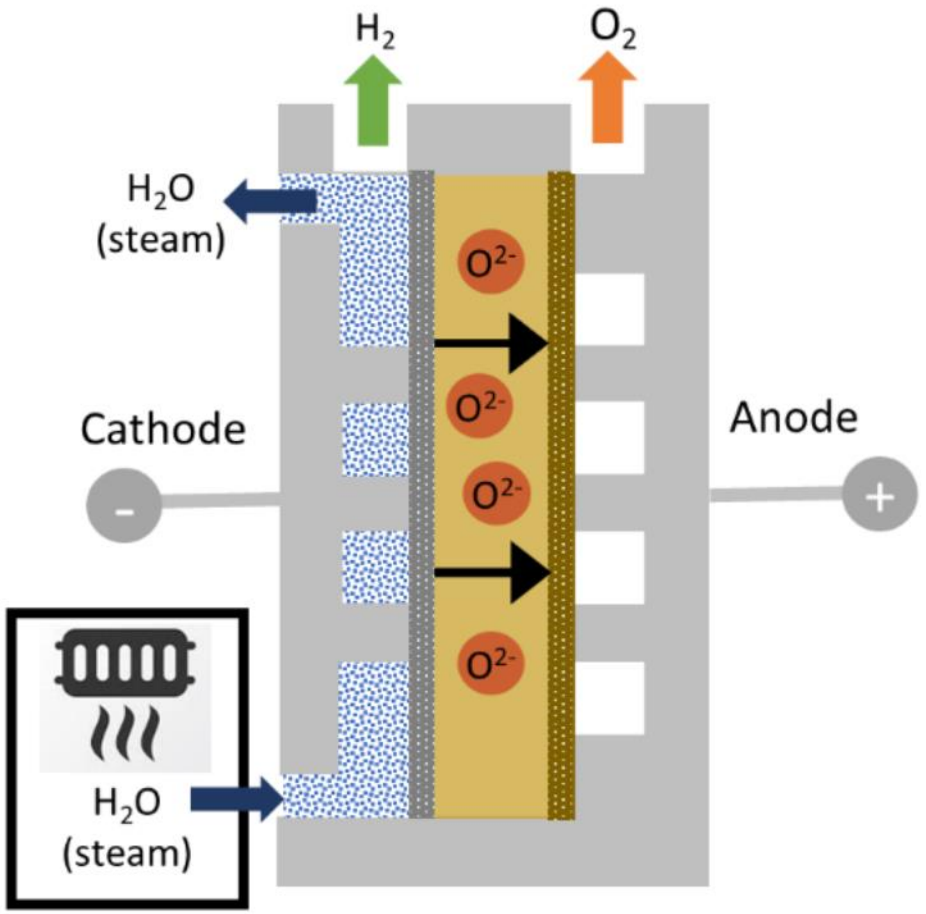


A proton exchange membrane water electrolyser (PEMWE) consists of:

1. a solid acid electrolyte polymer sandwiched between the anode and cathode.
2. In most cases, water is only fed to the anode.
3. Catalyst material on the anode: Iridium or Ruthenium oxide
4. Catalyst material on the cathode: Platinum
5. Cell temperature: 50-80°C
6. Stack pressure: <30 bar
7. Current density: 0.6-10.0 A/cm^2
8. Cell voltage: 1.75-2.20 V
9. Power density: to 4.4 W/cm^2
10. Cell voltage efficiency: 57-80%
11. System hydrogen production rate: 30 Nm^3/h
12. Lifetime stack: <20,000 h
13. Acceptable degradation rate: <14 μV/h
14. System lifetime: 10-20 y

https://doi.org/10.1038/s41560-020-0550-8

High-temperature water electrolysers

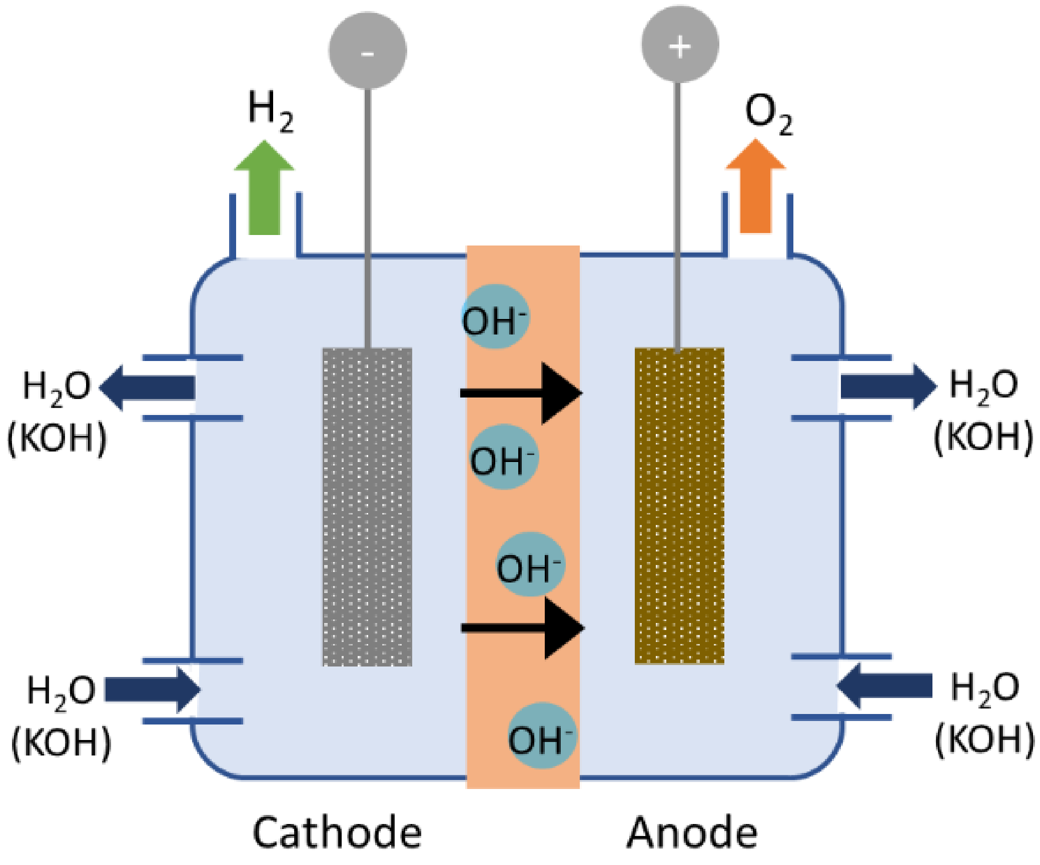


In a High-temperature water electrolysers, water evaporates and transports to the cathode as steam to produce H_2 while a solid oxide or ceramic membrane transports O^{2-} to the anode.

1. Catalyst material on the anode: Sr-based and Co-based perovskites, such as (La, Sr)(Co, Fe)O3 and La0.8Sr0.2MnO3−δ
2. Catalyst material on the cathode: Ni-cermets
3. Cell temperature: 700 - 1000 °C
4. Stack pressure: 10-60 bar
5. Current density: 1 A/cm^2
6. Cell voltage: 1.3-1.5 V
7. Cell voltage efficiency: >90%

https://doi.org/10.1038/s41560-020-0550-8

Alkaline water electrolyser (AWE)

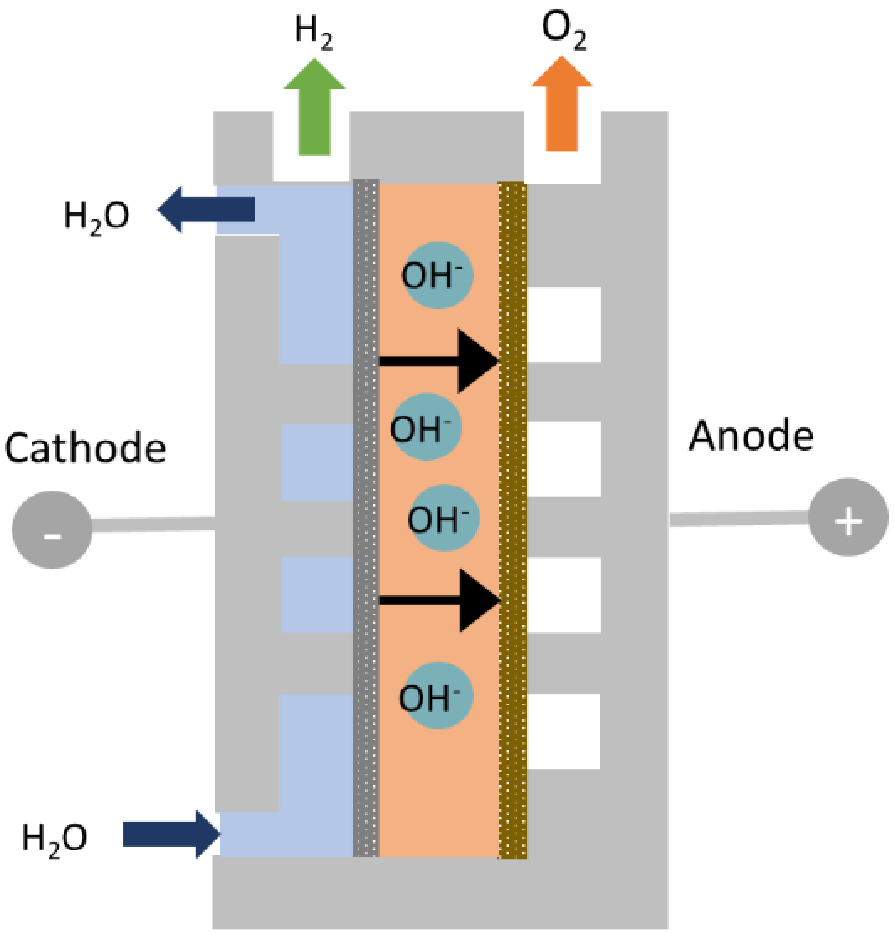


An alkaline water electrolyser (AWE) operates as a 2-compartment cell in which a liquid alkaline electrolyte (typically 20–30% KOH) is pumped around both sides and a porous diaphragm allows hydroxyl ion (OH^-) migration while preventing gas crossover.

1. Catalyst material on the anode: Ni/Co/Fe
2. Catalyst material on the cathode: Ni/C-Pt
3. Cell temperature: 60-80°C
4. Stack pressure: <30 bar
5. Current density: 0.2-0.4 A/cm^2
6. Cell voltage: 1.8-2.4 V
7. Power density: to 1 W/cm^2
8. Cell voltage efficiency: 52-80%
9. System hydrogen production rate: 760 Nm^3/h
10. Lifetime stack: <90,000 h
11. Acceptable degradation rate: <3 µV/h
12. System lifetime: 20-30 y

https://doi.org/10.1038/s41560-020-0550-8

Anion exchange membrane water electrolyser (AEMWE)

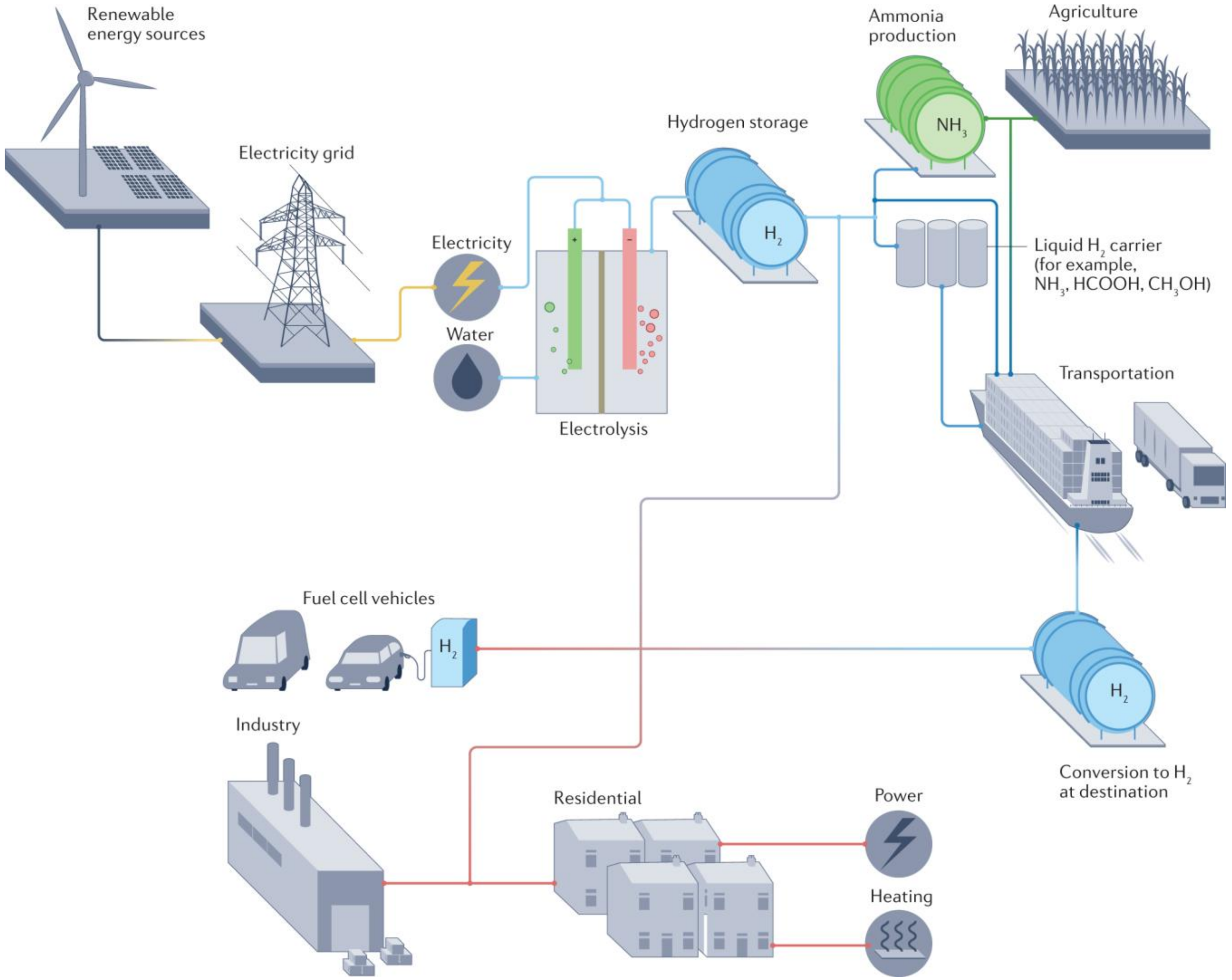


An anion exchange membrane water electrolyser (AEMWE) sandwiches an OH^- transporting membrane between the anode and cathode. Water is supplied to the cathode in this example, however it is also possible to supply water to the anode or both sides.

1. Catalyst material on the anode: Ni, Fe, Co, Mn, Cu
2. Catalyst material on the cathode: Ni, Fe, Co, Mn, Cu
3. Cell temperature: >60 °C
4. Stack pressure: 15-30 bar
5. Current density: 1 A/cm^2
6. Cell voltage: 1.57-1.8 V
7. Cell voltage efficiency: 75%

https://doi.org/10.1038/s41560-020-0550-8

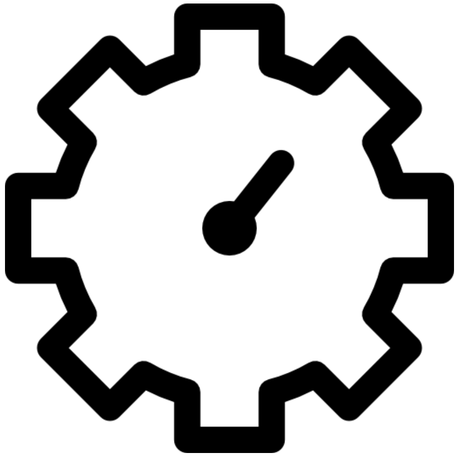
Where can we find electrolysers?



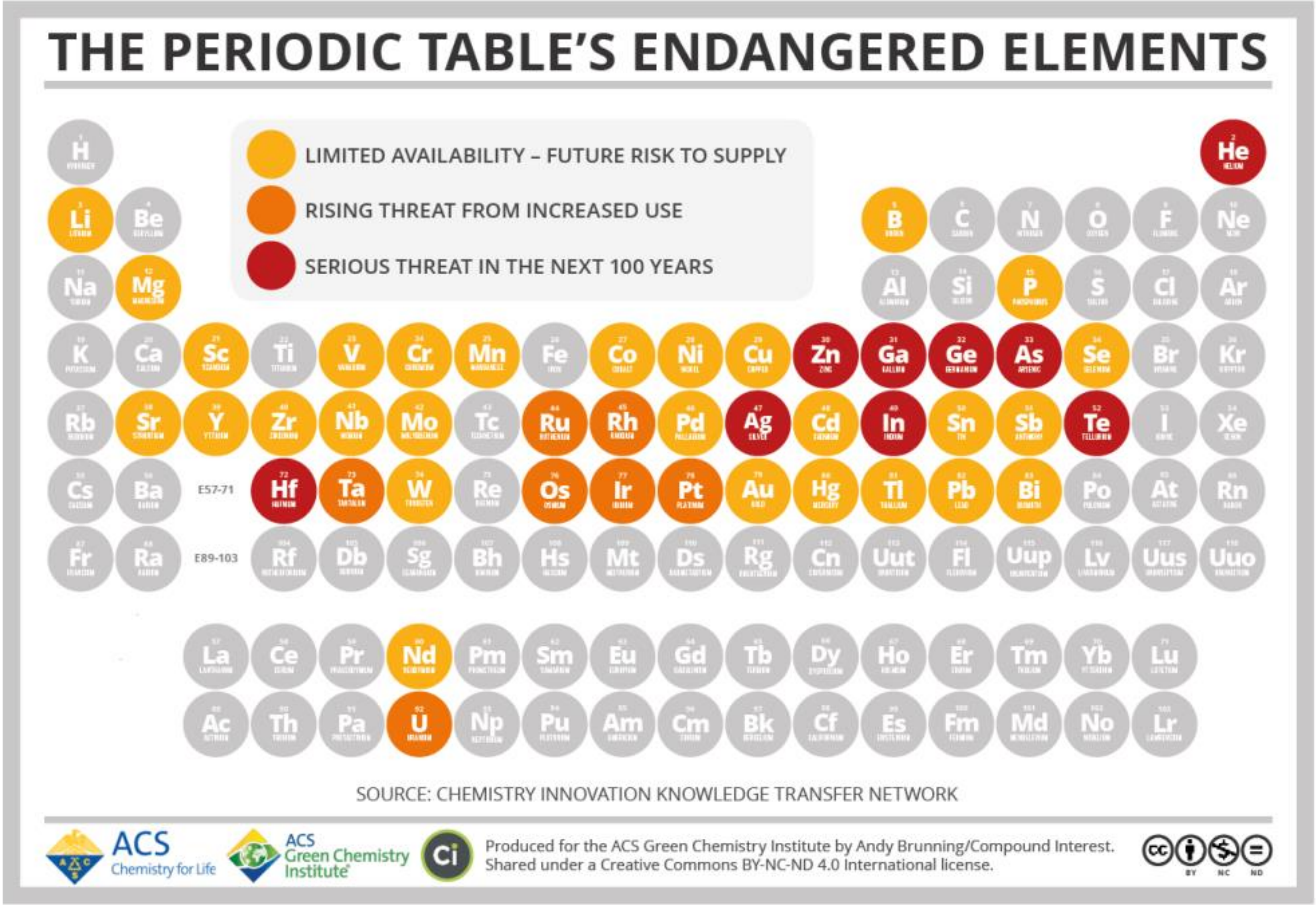
https://doi.org/10.1038/s43586-022-00164-0

What is the problem with electrolysers then?

Since electrolysis requires electricity to break down the water, it can cost over 50% more than hydrogen produced through fossil fuel processes.



The efficiency of current commercial electrolysers is at 70-80%, but this number needs to keep increasing if it is to compete with fossil fuels.


THE PERIODIC TABLE'S ENDANGERED ELEMENTS
LIMITED AVAILABILITY – FUTURE RISK TO SUPPLY
RISING THREAT FROM INCREASED USE
SERIOUS THREAT IN THE NEXT 100 YEARS
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba E57-71 Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra E89-103 Rf Db Sg Bh Hs Mt Ds Rg Cn Uut Fl Uup Lv Uus Uuo
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
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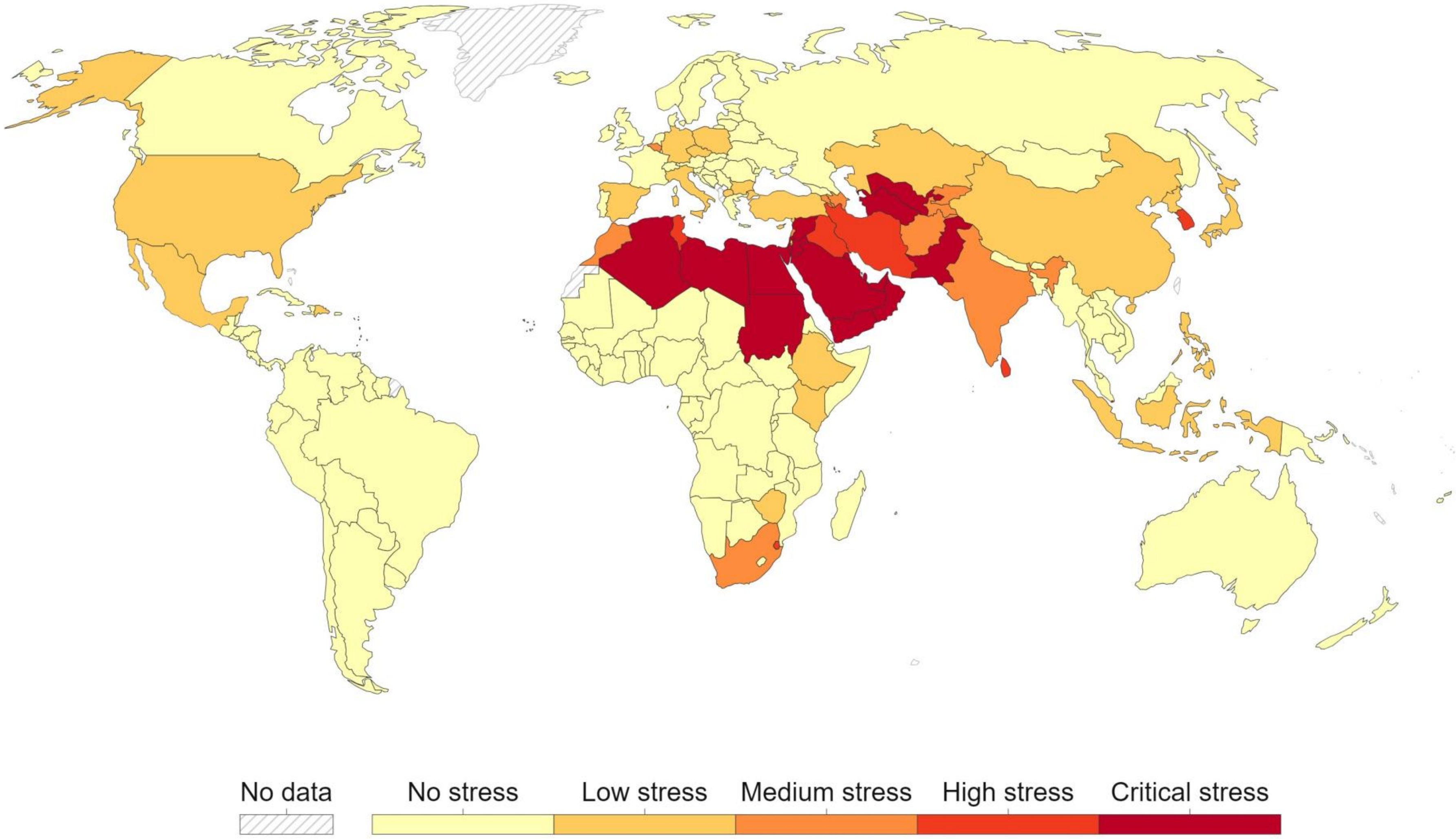
BY NC ND

Freshwater withdrawals as a share of internal resources, 2019

Our World in Data

Annual freshwater withdrawals refer to total water withdrawals from agriculture, industry and municipal/domestic uses. Withdrawals can exceed 100% of total renewable resources where extraction from nonrenewable aquifers or desalination plants is considerable.



Source: Food and Agriculture Organization of the United Nations

Alternative water sources for electrolysers?

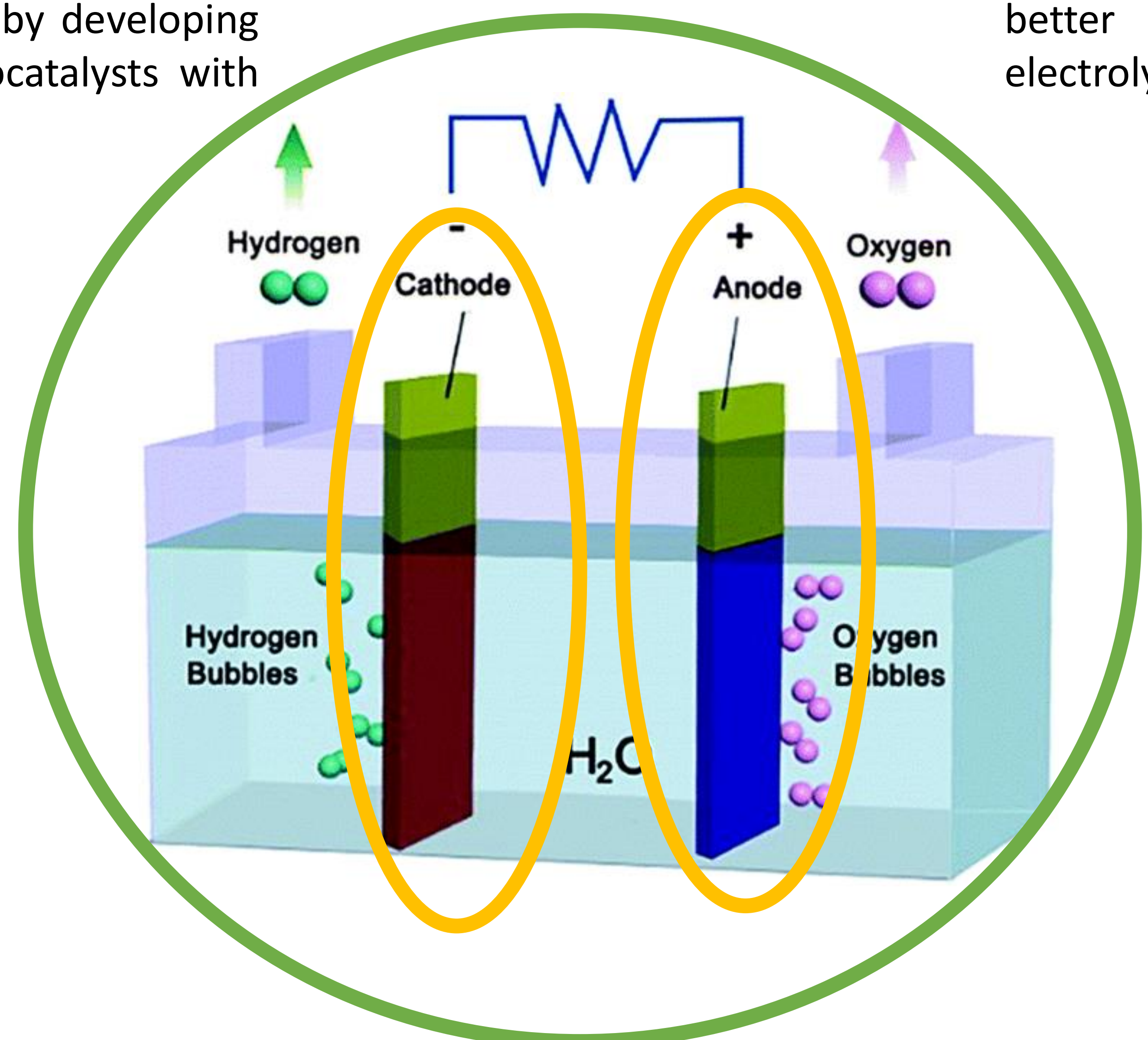
https://bgr.com/science/revolutionary-invention-transforms-seawater-into-hydrogen-fuel/

https://scitechdaily.com/vast-amounts-of-valuable-energy-nutrients-water-lost-in-worlds-wastewater/

Current research focus

1. Reducing the cost of electrode material (electrocatalysts) by developing new cost effective electrocatalysts with high efficiencies.

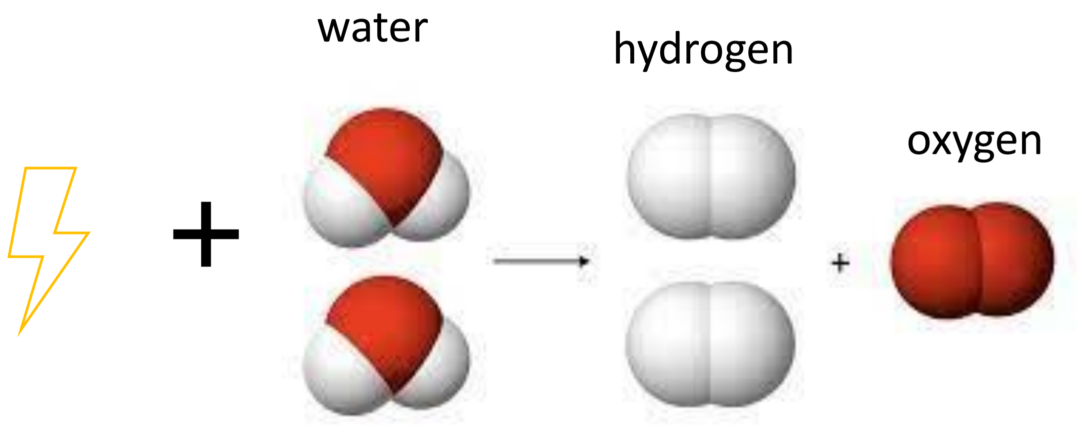
2. New electrolysers designs in order to better facilitate the needs of water electrolysis.

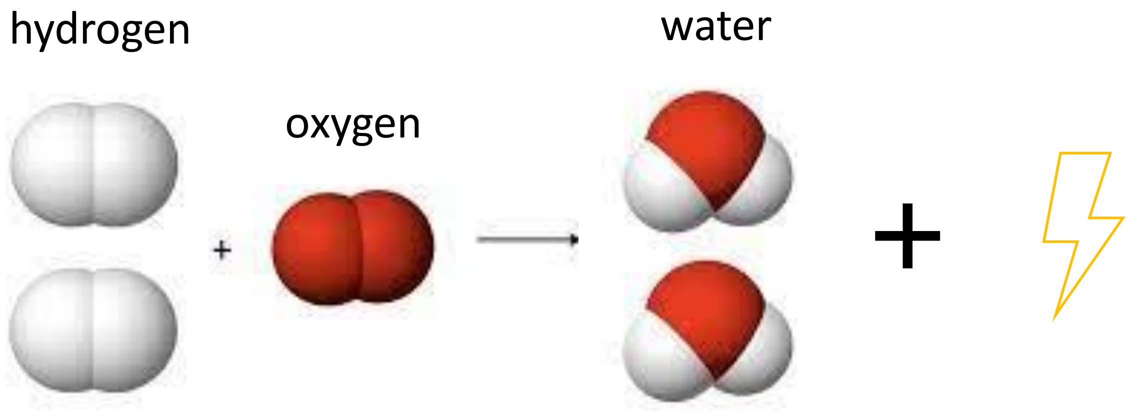


Lecture overview for second half

Electrolysers vs fuel cells → Hydrogen fuel cells → Types of fuel cells → Reversible fuel cells → The problems → Research focus

Electrolysers vs Fuel cells





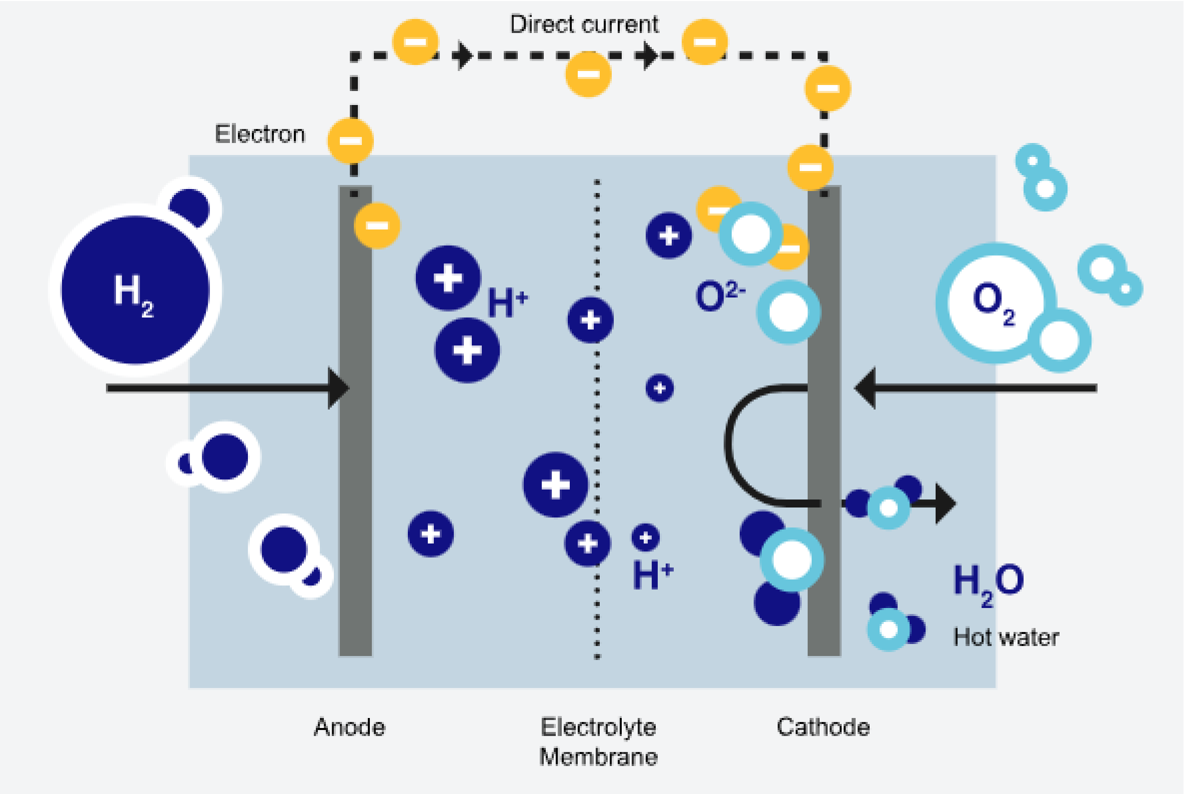
Hydrogen fuel cells

- A hydrogen fuel cell is an electrochemical cell that uses a spontaneous redox reaction to produce current that can do work.

The net reaction is exothermic.

Combining the 2 half cell potentials for the electrochemical reaction gives a positive cell potential.

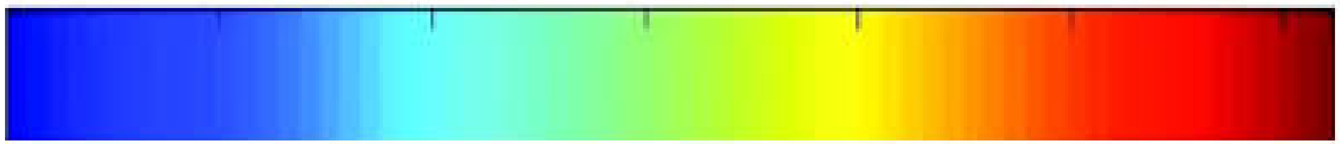
$H_2 + 1/2O_2 \rightarrow H_2O$ $\Delta G_f = -229$ kJ/mol
$H_2 \rightarrow 2H^+ + 2e^-$ $E_0 = 0.00$ V
$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$ $E_0 = -1.23$ V



https://www.tuev-nord.de/en/company/energy/hydrogen/hydrogen-fuel-cell/

Types of fuel cells

➢ The operating temperature of the fuel cell defines its type.

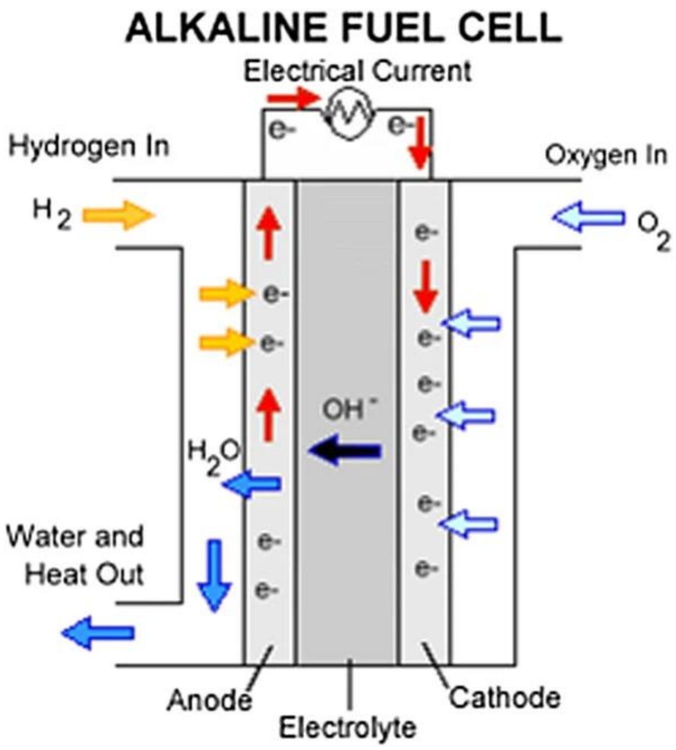


Low temperature

High temperature

1. Alkaline fuel cell (AFC), low temperature 20-90 °C
2. Proton-exchange membrane fuel cell (PEMFC), low temperature 20-80 °C
3. Direct methanol fuel cell (DMFC), low temperature 20-130 °C
4. Phosphoric acid fuel cell (PAFC), medium temperature 160-220 °C
5. Molten carbonate fuel cell (MCFC), high temperature 620-660 °C
6. Solid oxide fuel cell (SOFC), high temperature 800-1000 °C

Alkaline fuel cell (AFC)



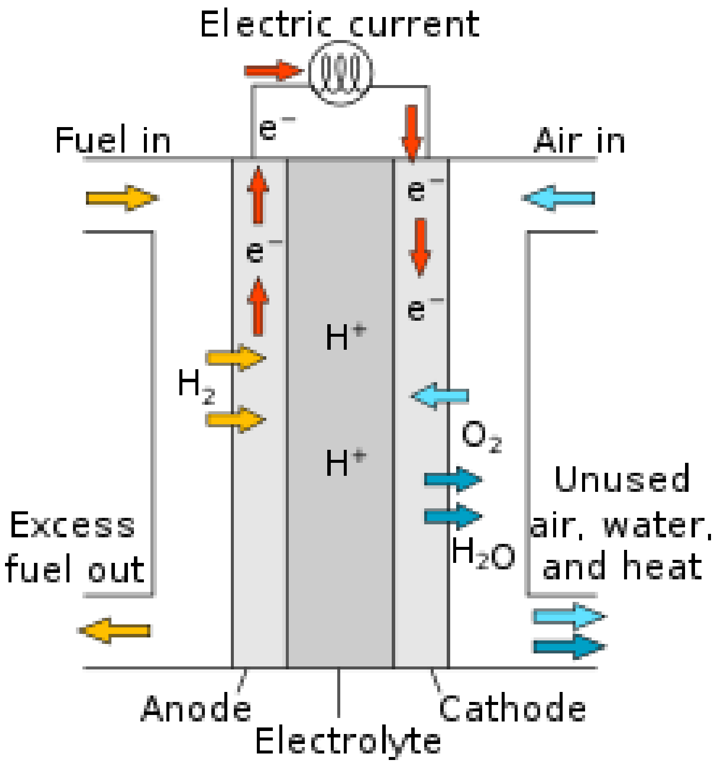
https://sustainablechemicalprocesses.springeropen.com/articles/10.1186/2043-7129-1-16/figures/4

Alkaline fuel cells were one of the first fuel cell technologies developed, and they were the first type widely used in the U.S. space program to produce electrical energy and water on-board spacecraft.

1. Anode gas: hydrogen
2. Cathode gas: oxygen
3. Electrolyte: potassium hydroxide solution (KOH)
4. Working temperature: 20 °C - 90 °C
5. Performance range: Up to 100 kW
6. Cell efficiency: 60 % - 70 %

Anode reaction: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
Cathode reaction: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Overall reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

Proton-exchange membrane fuel cells (PEMFC)



https://en.wikipedia.org/wiki/Proton-exchange_membrane_fuel_cell

Proton-exchange membrane fuel cells, also known as polymer electrolyte membrane (PEM) fuel cells, are a type of fuel cell being developed mainly for transport applications, as well as for stationary fuel-cell applications and portable fuel-cell applications.

PEMFCs generate electricity and operate on the opposite principle to PEM electrolysis, which consumes electricity. They are a leading candidate to replace the aging alkaline fuel-cell technology, which was used in the Space Shuttle.

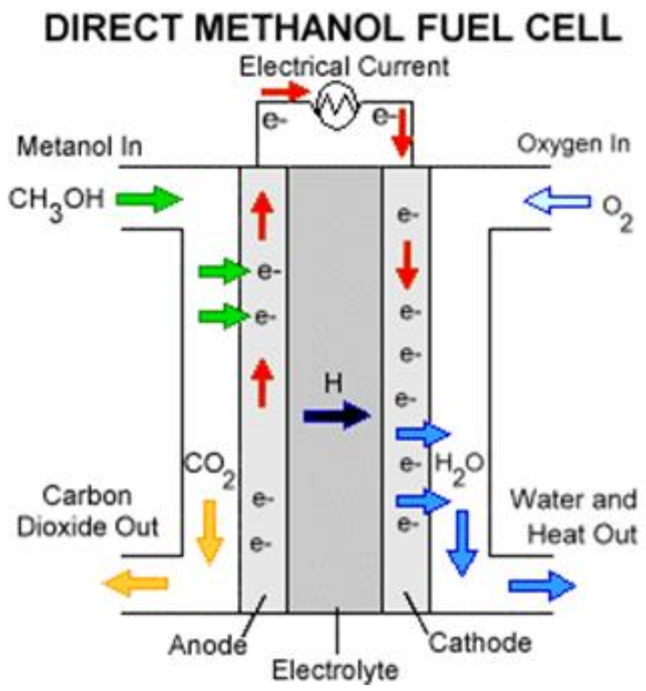
1. Anode gas: hydrogen
2. Cathode gas: air oxygen
3. Electrolyte: polymer membrane
4. Working temperature: 20 °C - 80 °C
5. Performance range: Up to 500 kW
6. Cell efficiency: 50 % - 70 %

Anode reaction: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode reaction: $½O_2 + 2H^+ + 2e^- \rightarrow H_2O$

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

Direct Methanol Fuel Cell (DMFC)



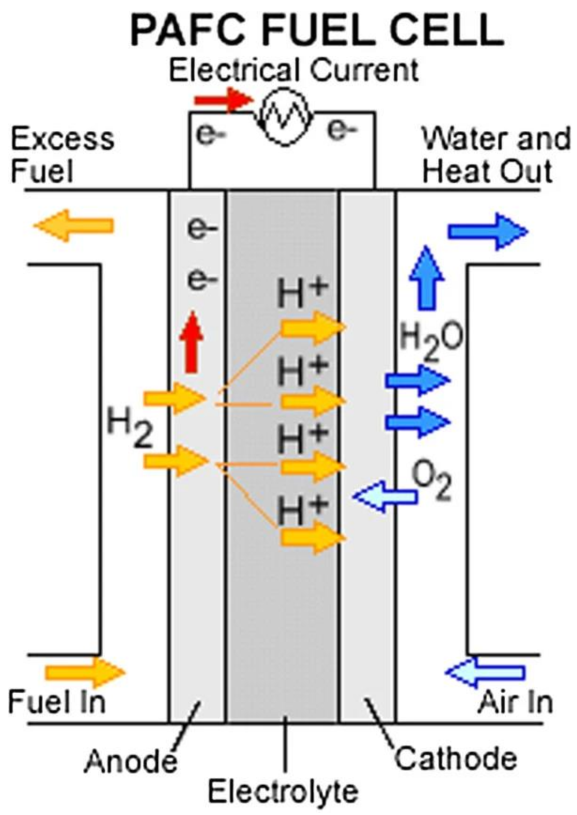
http://derekcarrsavvy-chemist.blogspot.com/2017/03/redoxii-fuel-cells.html

Direct-methanol fuel cells or DMFCs are a subcategory of proton-exchange fuel cells in which methanol is used as the fuel. Their main advantage is the ease of transport of methanol, an energy-dense yet reasonably stable liquid at all environmental conditions.

1. Anode gas: methanol
2. Cathode gas: air oxygen
3. Electrolyte: polymer membrane
4. Working temperature: 20 °C - 130 °C
5. Performance range: Up to 100 kW
6. Cell efficiency: 20 % - 30 %

Anode reaction: $CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$
Cathode reaction: $3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
Overall reaction: $CH_3OH + 3/2O_2 \rightarrow 2H_2O + CO_2$

Phosphoric Acid Fuel Cell (PAFC)



https://en.wikipedia.org/wiki/Phosphoric_acid_fuel_cell

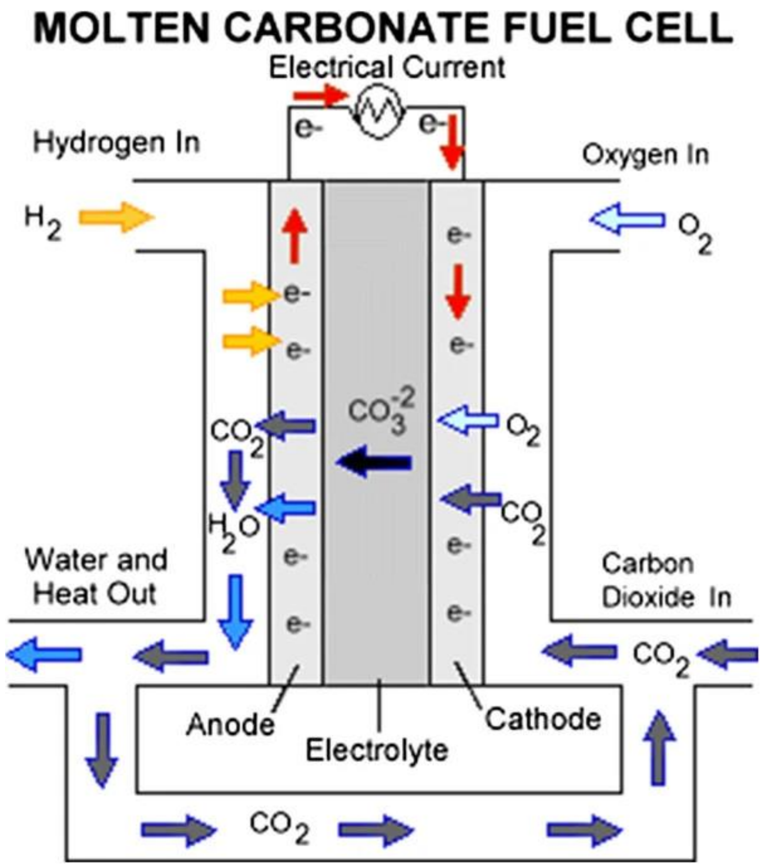
Phosphoric acid fuel cells (PAFC) are a type of fuel cell that uses liquid phosphoric acid as an electrolyte. They were the first fuel cells to be commercialized. Developed in the mid-1960s and field-tested since the 1970s, they have improved significantly in stability, performance, and cost. Such characteristics have made the PAFC a good candidate for early stationary applications.

1. Anode gas: hydrogen, natural gas or biogas
2. Cathode gas: air oxygen
3. Electrolyte: phosphoric acid
4. Working temperature: 160 °C - 220 °C
5. Performance range: Up to 10 MW
6. Cell efficiency: 55 %

Anode reaction: $H_2 \rightarrow 2H^+ + 2e^-$
Cathode reaction: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Overall reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

https://sustainablechemicalprocesses.springeropen.com/articles/10.1186/2043-7129-1-16/figures/4

Molten Carbonate Fuel Cell (MCFC)



https://sustainablechemicalprocesses.springeropen.com/articles/10.1186/2043-7129-1-16/figures/3

https://en.wikipedia.org/wiki/Molten_carbonate_fuel_cell#External_links

Molten carbonate fuel cells (MCFCs) were developed for natural gas, biogas (produced as a result of anaerobic digestion or biomass gasification), and coal-based power plants for electrical utility, industrial, and military applications.

MCFCs are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic matrix of beta-alumina solid electrolyte (BASE).

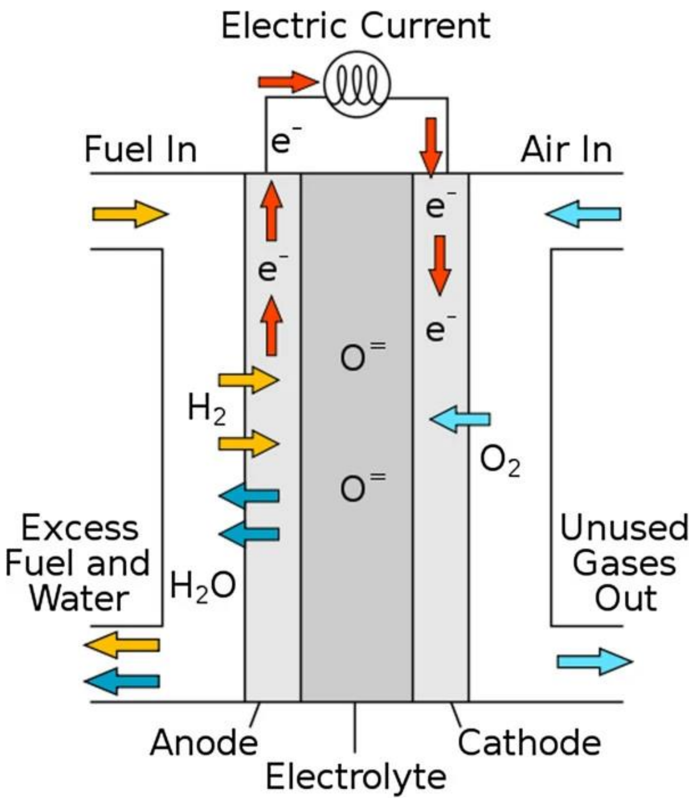
1. Anode gas: natural gas, coal gas or biogas
2. Cathode gas: air oxygen
3. Electrolyte: alkali carbonate melting
4. Working temperature: 620 °C - 660 °C
5. Performance range: up to 100 MW
6. Cell efficiency: 65 %

Anode reaction: $H_2 + CO_3^{2-} \rightarrow CO_2 + H_2O + 2e^-$

Cathode reaction: $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$

Overall reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

Solid Oxide Fuel Cell (SOFC)



https://sustainablechemicalprocesses.springeropen.com/articles/10.1186/2043-7129-1-16#Fig4

Solid oxide fuel cells are a class of fuel cells characterized by the use of a solid oxide material as the electrolyte to conduct negative oxygen ions from the cathode to the anode. The electrochemical oxidation of the hydrogen, carbon monoxide or other organic intermediates by oxygen ions occurs on the anode side.

Anode gas: natural gas, coal gas or biogas
Cathode gas: air oxygen
Electrolyte: yttrium-stabilised zirconium oxide
Working temperature: 800 °C - 1000 °C
Performance range: Up to 100 MW
Cell efficiency: 60%-65 %

Anode reactions: $H_2 + O_2^- \rightarrow H_2O + 2e^-$

$CO + O_2^- \rightarrow CO_2 + 2e^-$

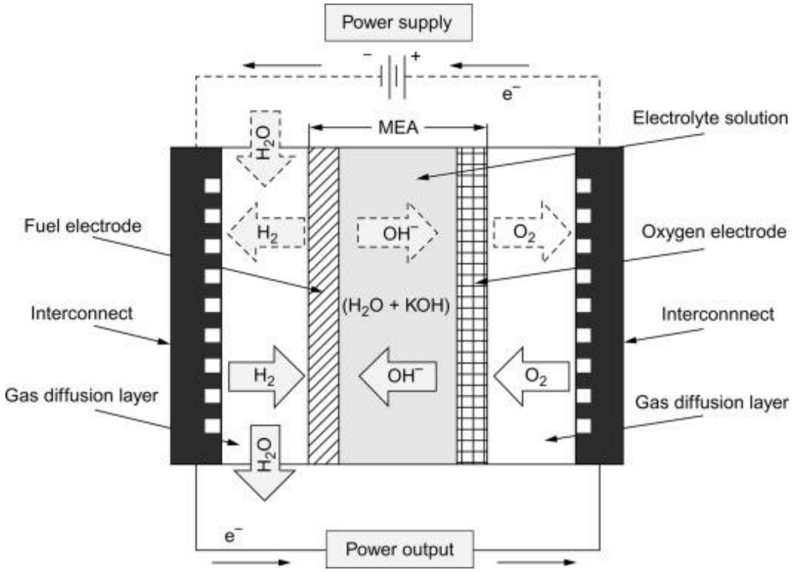
Cathode reaction: $O_2 + 4e^- \rightarrow 22^-$

Overall reaction: $H_2 + O_2 + CO \rightarrow H_2O + CO_2$

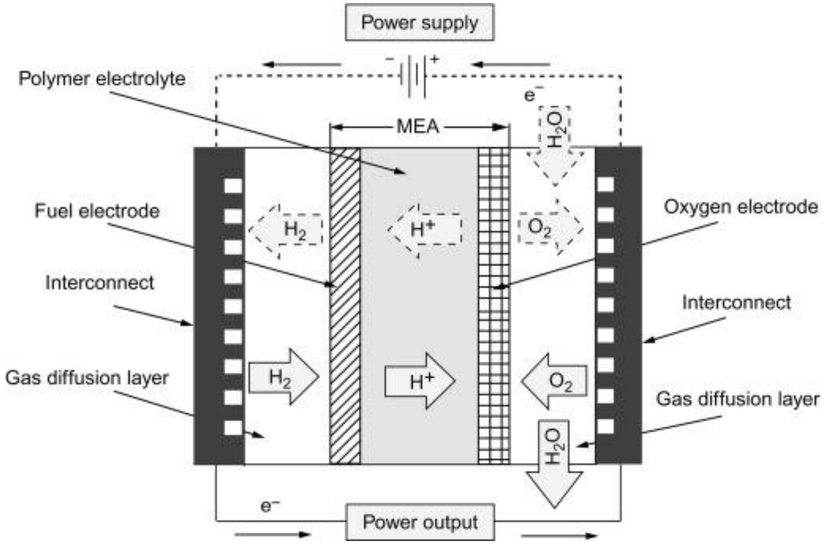
Reversible or regenerative fuel cell

Reversible fuel cells operate like batteries and may be one solution to the problem of storing electricity generated by variable resources. Reversible fuel cells (RFCs) offer a solution to producing fuel through the use of surplus electricity and reconverting this into electricity using the same device. In autonomous systems with surplus energy during periods of high solar radiation in summer, an RFC system can in electrolysis mode produce hydrogen and oxygen, which are then stored in tanks. If there is a lack of energy, the unit is fed with the stored gases operating in fuel cell mode to produce electricity

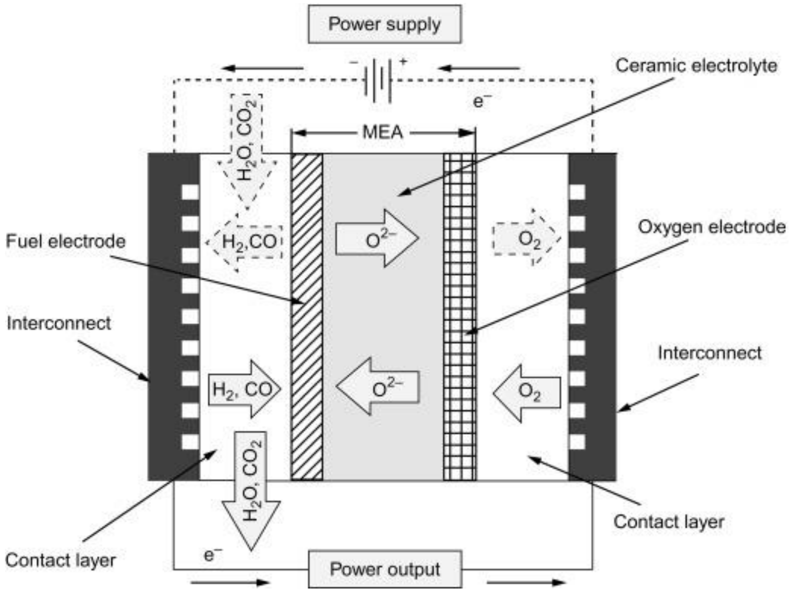
Reversible alkaline fuel cell (RAFC)



Reversible polymer electrolyte fuel cell (RPEFC)



Reversible solid oxide fuel cell (RSOFC)



https://doi.org/10.1016/B978-1-78242-363-8.00005-0

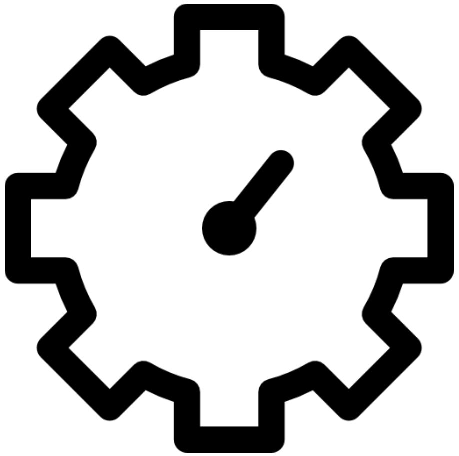
Where can we find fuel cells?

- Fuel Cell (FC) Stack
- FC Backup Power
- FC Forklifts
- FC Cars
- FC Buses
- FC Prime Power
- Hydrogen Infrastructure

https://www.plugpower.com/fuel-cell-applications-101-where-are-fuel-cells-used-today/

What is the problem with fuel cells then?

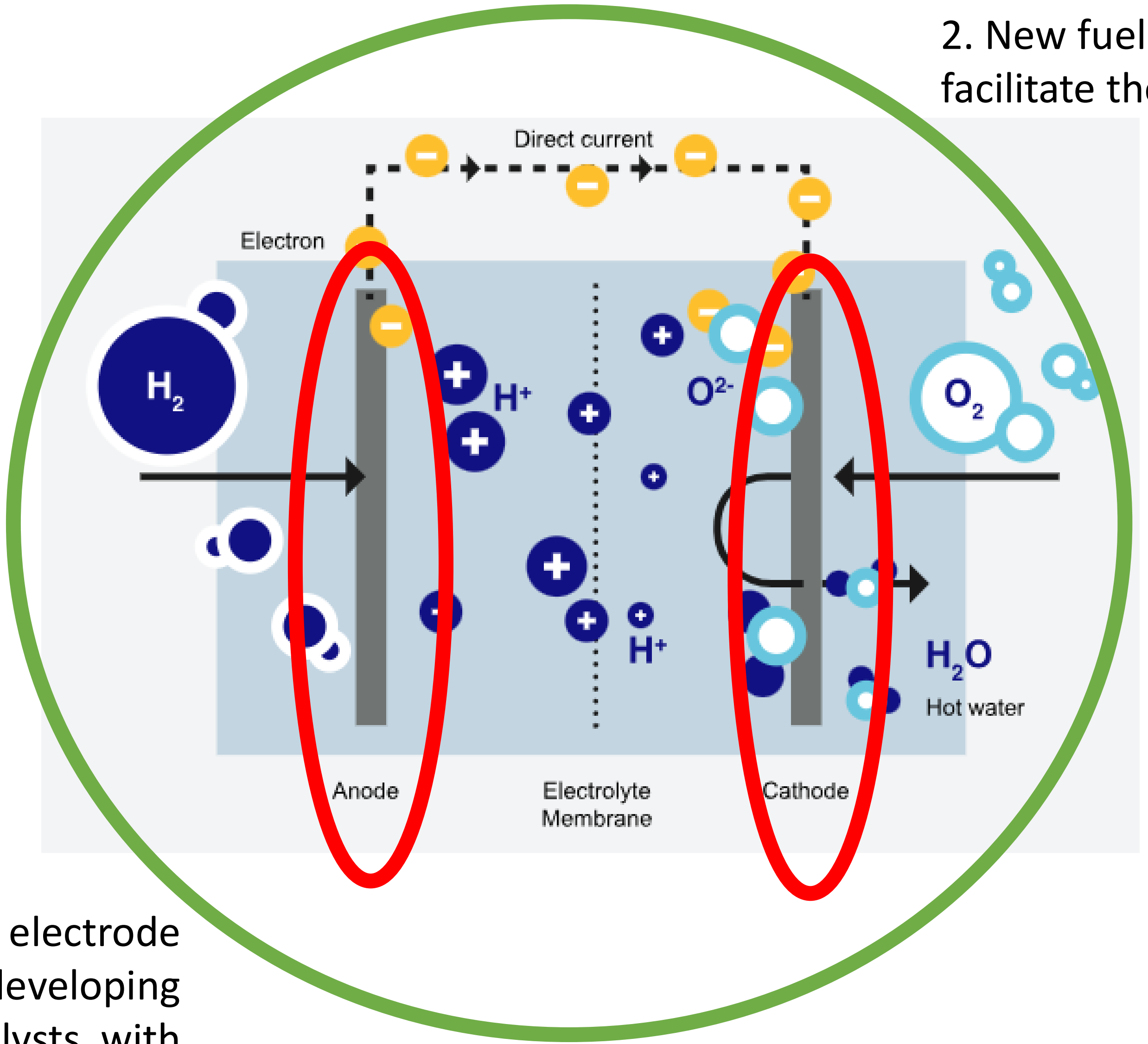
High costs related to the manufacturing of fuel cells, especially the electrocatalysts, and the production of hydrogen used in fuel cells are the main obstacles for this technology to flourish.



The efficiency of current commercial fuel cells is at maximum 70%, making it not efficient enough to compete or even overtake fossil fuels.

Current research focus

2. New fuel cell designs in order to better facilitate the needs of water electrolysis.



1. Reducing the cost of electrode material (electrocatalysts) by developing new cost effective electrocatalysts with high efficiencies.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danke
謝謝
ngiyabonga
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kia ora
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welalin
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спасибі
blagodaram
dank je
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