Catalysis for Energy Storage

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All course materials via Moodle
Password (if needed): energy

Chapter I. Introduction

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- Hydrogen economy
- Electrolyzers

I. Information related to course structure

Pre-requisite:
Coordination chemistry;
Organometallic chemistry;
basic electrochemistry

Focus of class (learning outcome):
Mechanism;
Broad overview;
Problem solving;
Critical analysis;

Teaching/Learning:
Lectures;
Slides – Ask questions if you don't understand;
Exercises;
Reading papers and analyze them

Why read papers :
Real-life learning involves learning from literature
Primary literature tells you what is happening now
(text book is a summary of old knowledge)
Primary literature is «raw» and need analysis
Not everything published is already proven; need critical analysis

More on papers :

Encounter state-of-the-art research;
Understand the scientific background (echo the course material);
Acquaint typical scientific methods;
Analyze how data are processed and how hypotheses are tested;
Learn how conclusions are formulated;
Critical reading and thinking.

In other words, this part of the class prepares you for future research as a PhD student in a lab, or working in an industrial environment, where you need to find a solution yourselves

Note: paper is part of lecture materials and some exam questions are based on papers

Ok, some words about exams:

Written exams during semester.
One mid-term; one Final (last week)

Check last year's exam for reference

Exam is not about memorizations.

Exam tests:

1. Major knowledge points, major methods, techniques, etc. (30%)
2. Mechanistic analysis (60%)
3. Case study (10%)

The scope of this course:

Renewable energy production and storage through water splitting or CO_2 reduction; context.

Catalysis for these reactions.

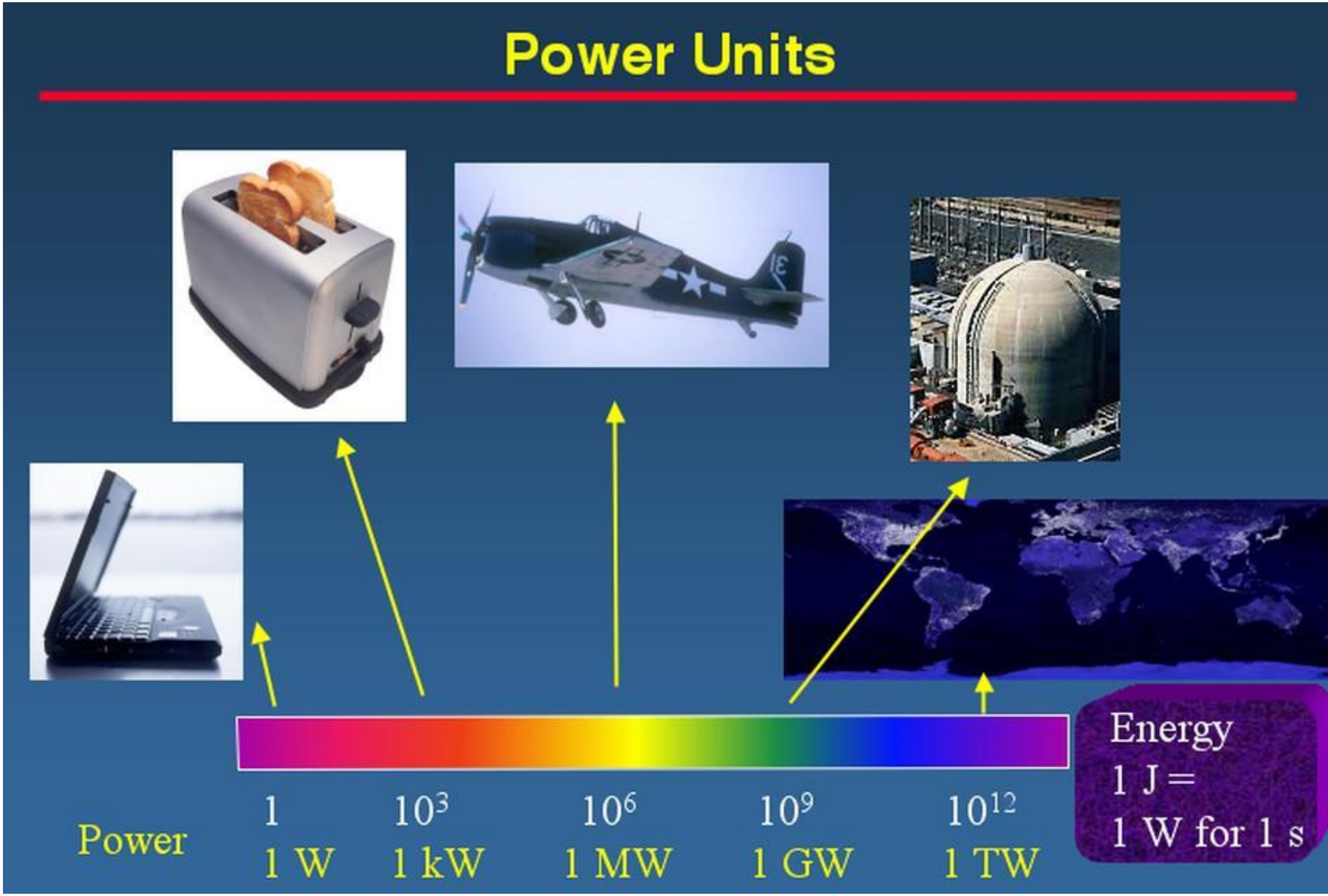
Different types of catalysts: homogeneous, enzymatic, and heterogeneous.

Mechanisms of catalysis.

Examples of contemporary research.

Discussion on industrial relevance.

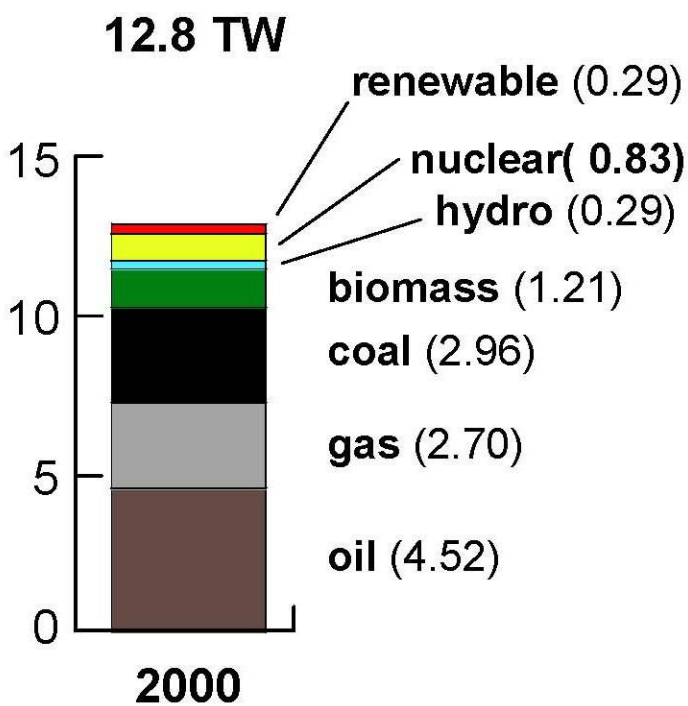
II. Renewable energy perspective

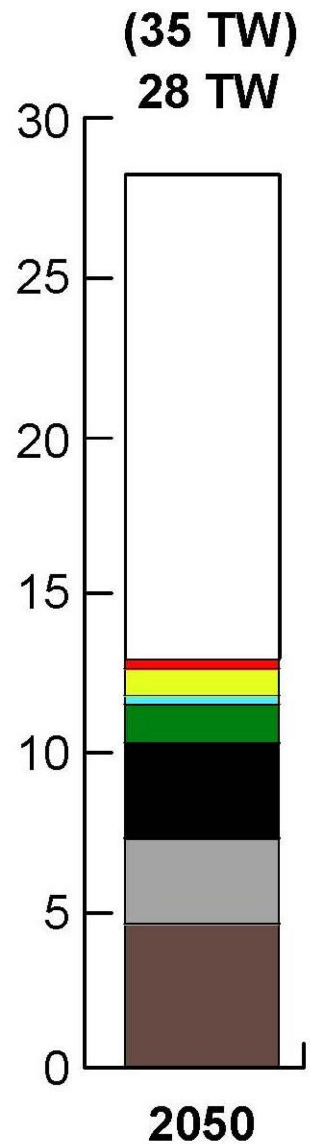

Power Units
Power
1
1 W
10³
1 kW
10⁶
1 MW
10⁹
1 GW
10¹²
1 TW
Energy
1 J =
1 W for 1 s

Lewis slide

Energy: the Present and the Future

World Energy Assessment (WEA) and the Inter-governmental Panel on Climate Change (IPCC) data, Lewis/Nocera slides





$$E = N \times (GDP/N) \times (E/GDP)$$

N: the global population, 6.1 billions in 2001, 0.9% yearly increase, 9.4 billions in 2050

GDP/N: the globally averaged gross domestic product (GDP) per capita, 7500 USD in 2001, 1.4% yearly increase, 15000 USD in 2050

E/GDP: the globally averaged energy intensity, 0.29 W/($\$yr^{-1}$) in 2001, 0.8%yearly decrease, to 0.20 W/($\$yr^{-1}$) in 2050

E: world energy comsuption, 13.5 TW in 2001, 1.5% yearly increase, 27 TW in 2050

By year 2050,
20-30 TW of energy supply
should be CO_2 emission free
To reach the 2^oC warming cap

How to Get That Much Carbon-Less Energy

- Improve efficiency and energy conservations

➢ Decarbonization and carbon sequestration

➢ Carbon-neutral and/or renewable energy sources

Renewable Energy Resources

Solar
1.2×10^5 TW at Earth surface
600 TW practical

energy gap
~ 14 TW by 2050
~ 33 TW by 2100

Wind
2-4 TW extractable

Biomass
5-7 TW gross
all cultivatable
land not used
for food

Tide/Ocean Currents
2 TW gross

Hydroelectric
4.6 TW gross
1.6 TW technically feasible
0.9 TW economically feasible
0.6 TW installed capacity

Geothermal
12 TW gross over land
small fraction recoverable

Nuclear Power Station

Fission: the problem of scaling

10 TW = 10,000 new 1 GW reactors

•a new reactor every other day for the next 50 years

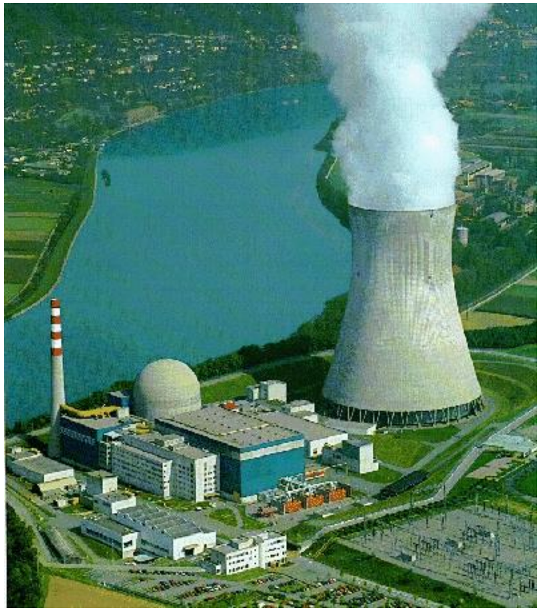
•currently there are 500 reactors

•proven reserve and resources of U are 3.4 and 17 million metric tons respectively

•enough to run for 6-30 years at 10 TW

•Need to mine U from seawater

•Safety and proliferation



Leibstadt plant, CH

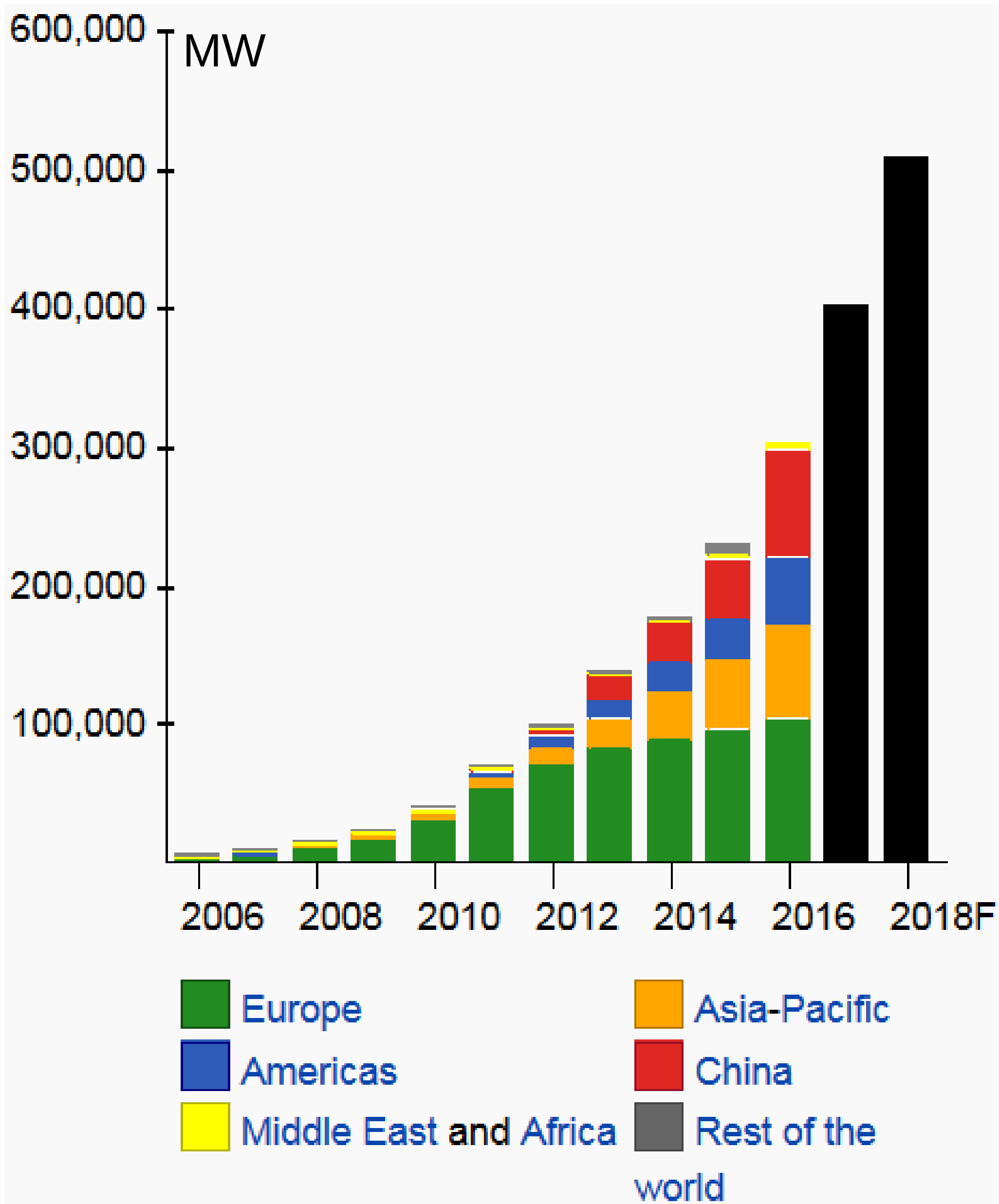
Fusion: puting a sun on the earth

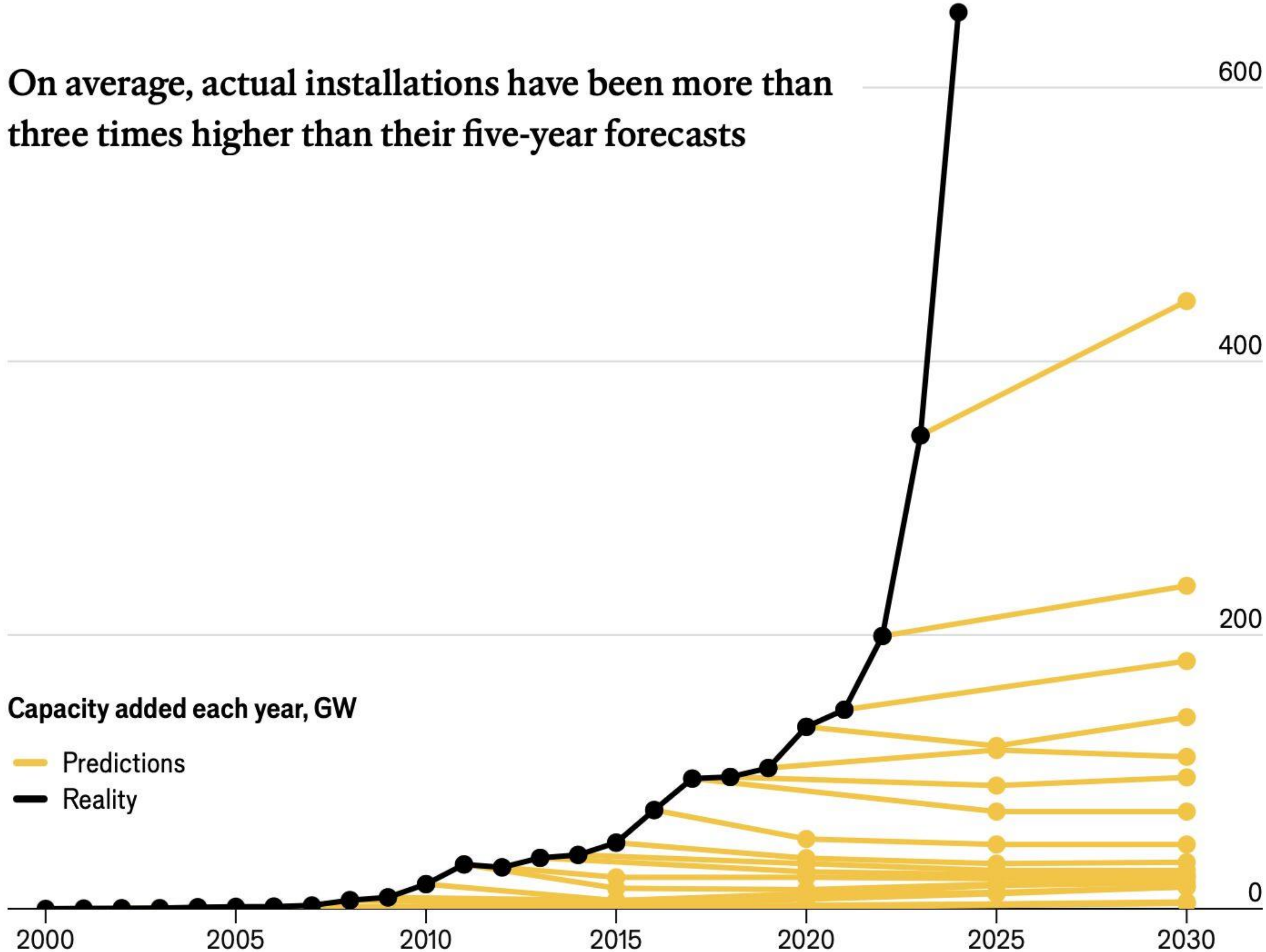
•30 years to know if it will work?

•another 30 years to make it work?

So solar energy is the ultimate energy source
And we have the technology for photovoltaics

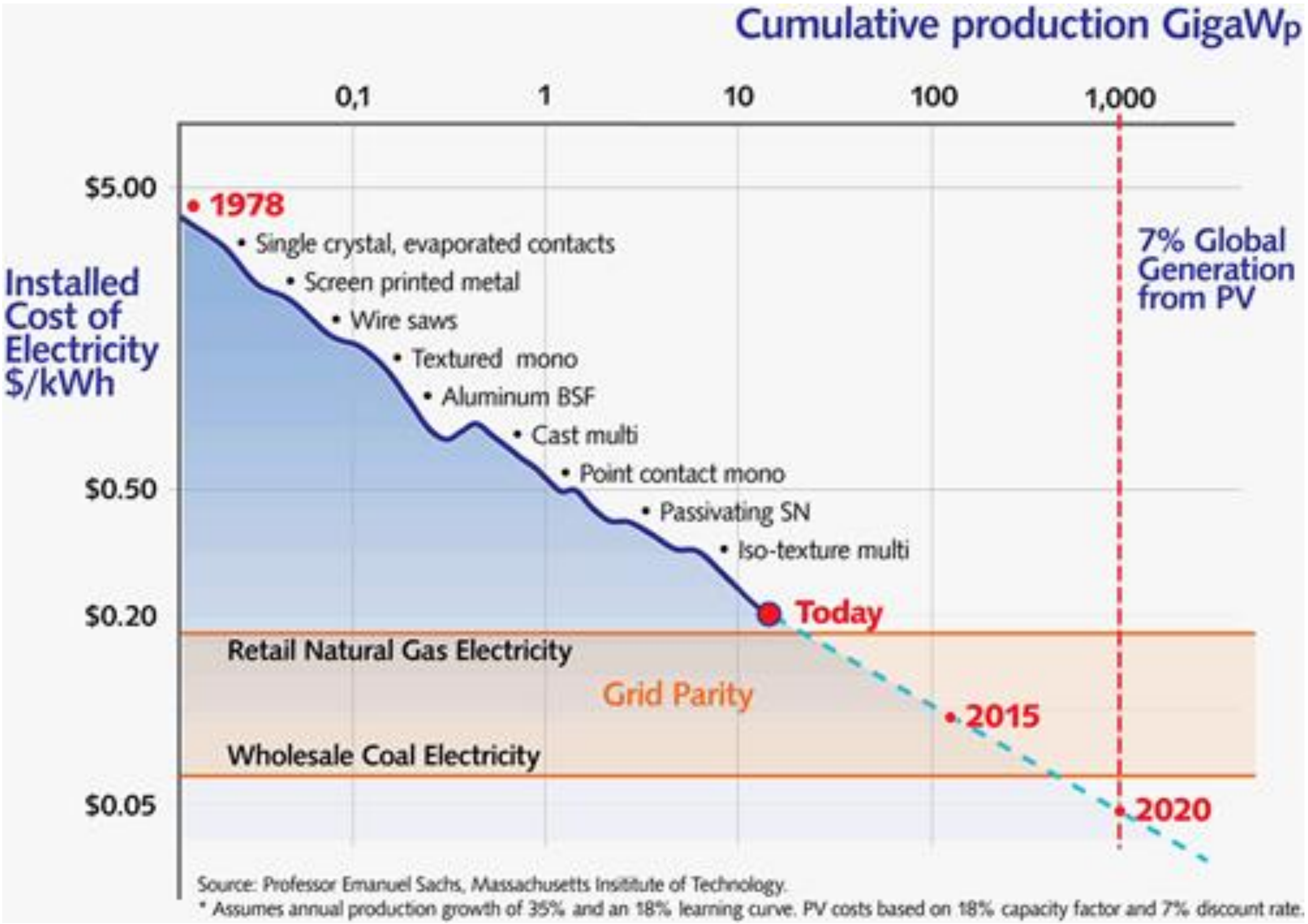
Cumulative Capacity of PV

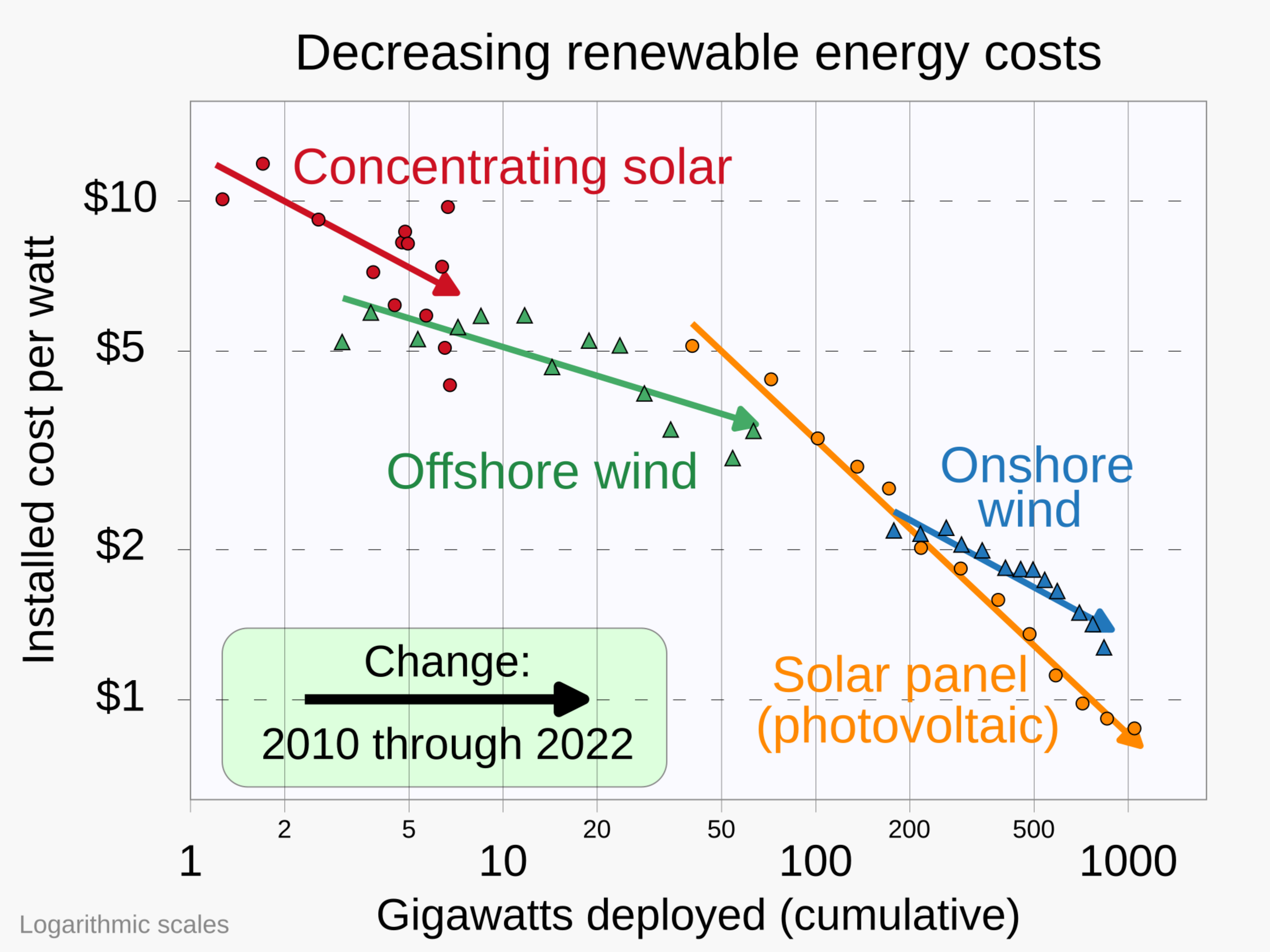


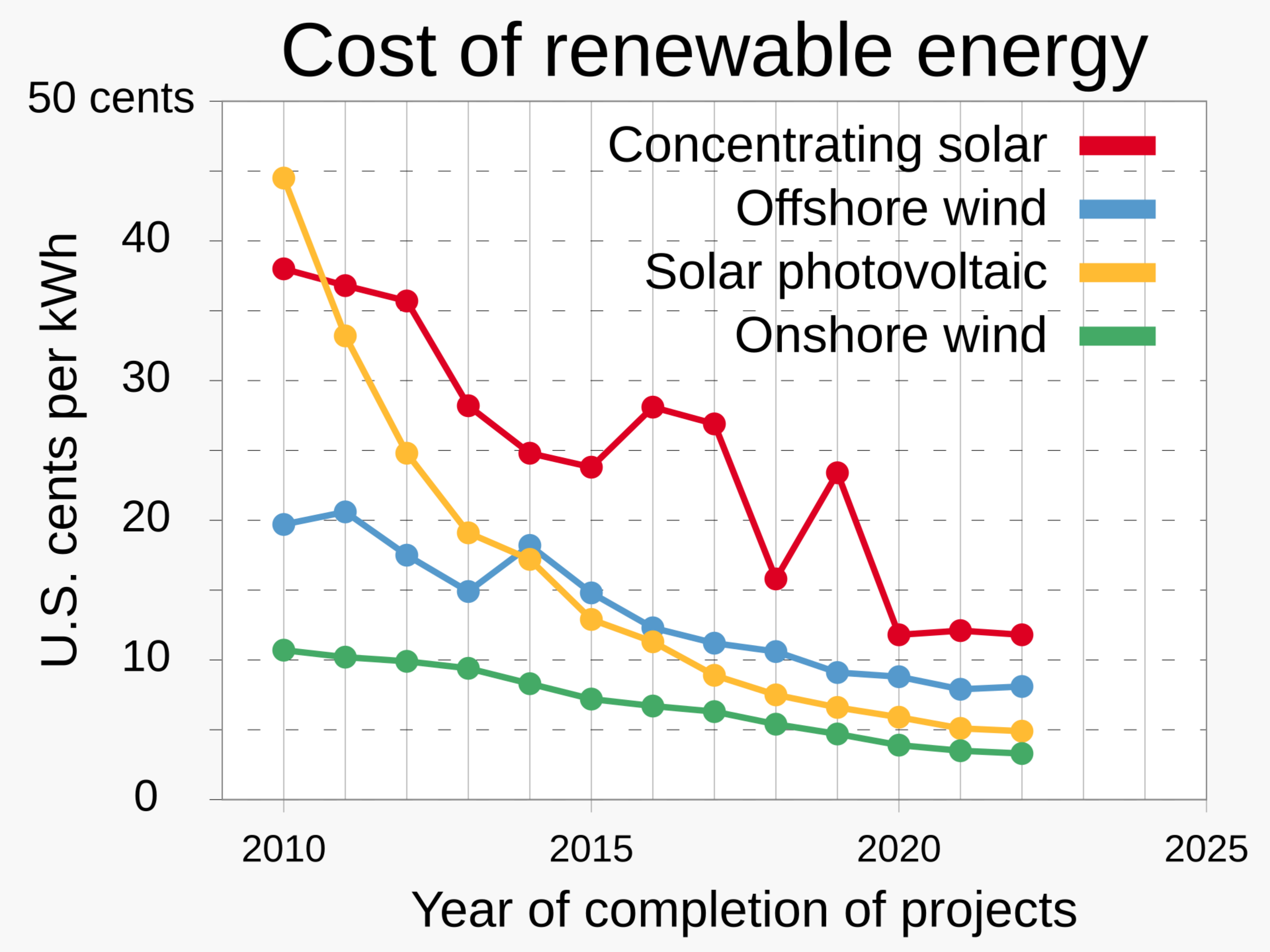


Sources: IEA; Energy Institute; BloombergNEF

Solar Parity is a reality, driven by tech progress




Decreasing renewable energy costs
Concentrating solar
Offshore wind
Onshore wind
Solar panel (photovoltaic)
Change:
2010 through 2022
Installed cost per watt
$10
$5
$2
$1
1
2
5
10
20
50
100
200
500
1000
Gigawatts deployed (cumulative)
Logarithmic scales

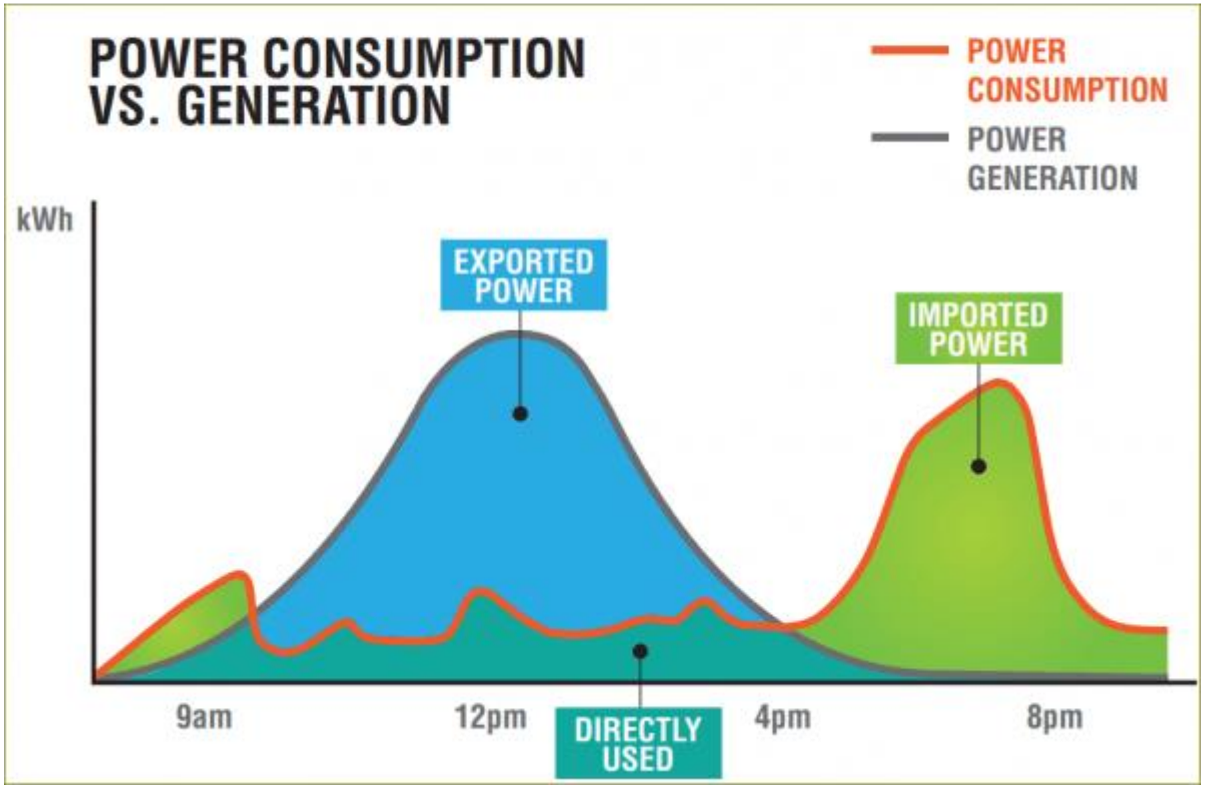

Cost of renewable energy
50 cents
40
30
20
10
0
U.S. cents per kWh
Concentrating solar
Offshore wind
Solar photovoltaic
Onshore wind
2010
2015
2020
2025
Year of completion of projects

Conclusion:

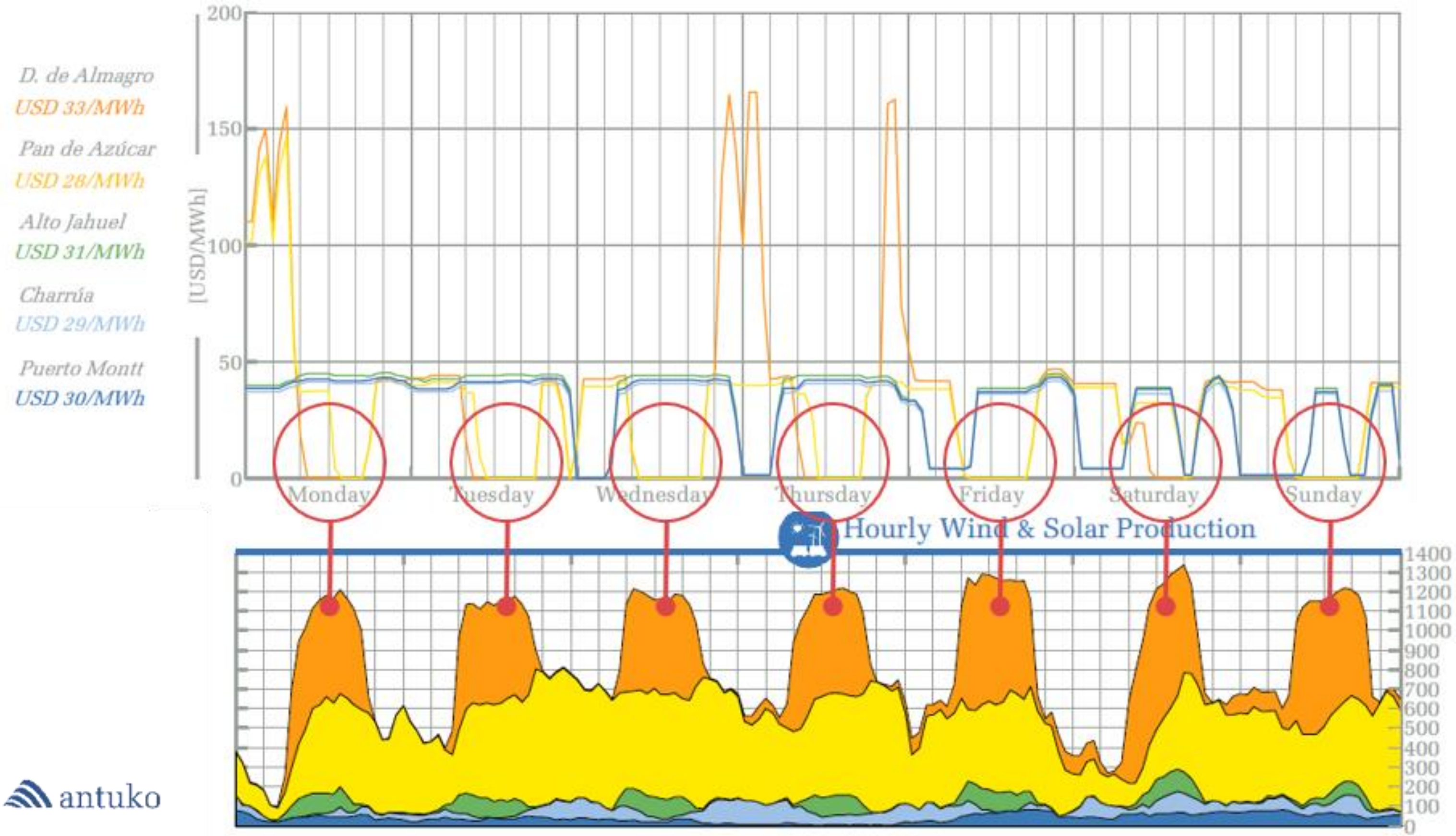
- Renewable energy, particualrly solar, is already cost competitive, and has the capacity to meet worlds' need.

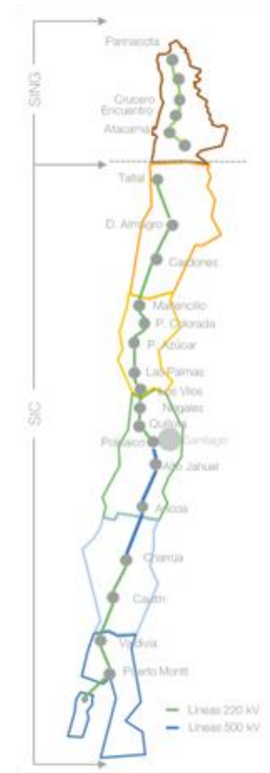
III. Energy storage options

Solar Energy is Intermittant



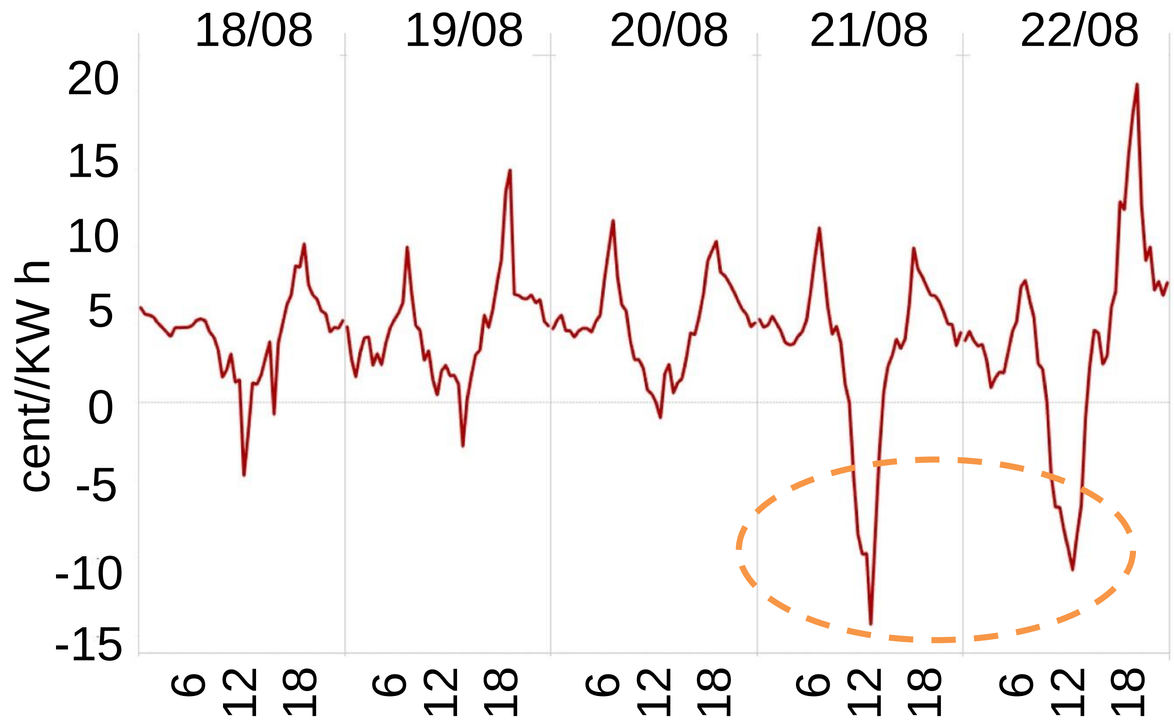
When sun shines, wind blows, electricity price is very low …





Sometime solar farms have to pay you to use their electricity

This is bad!



Spot price of electricity, Queensland, 2019
(> 40% renewables)

- ✓ If you can use electricity for anything, please use it. It is the cheapest and most efficient option.
- But not all energy need can be met by electricity, and storing electricity for a long time is a problem.

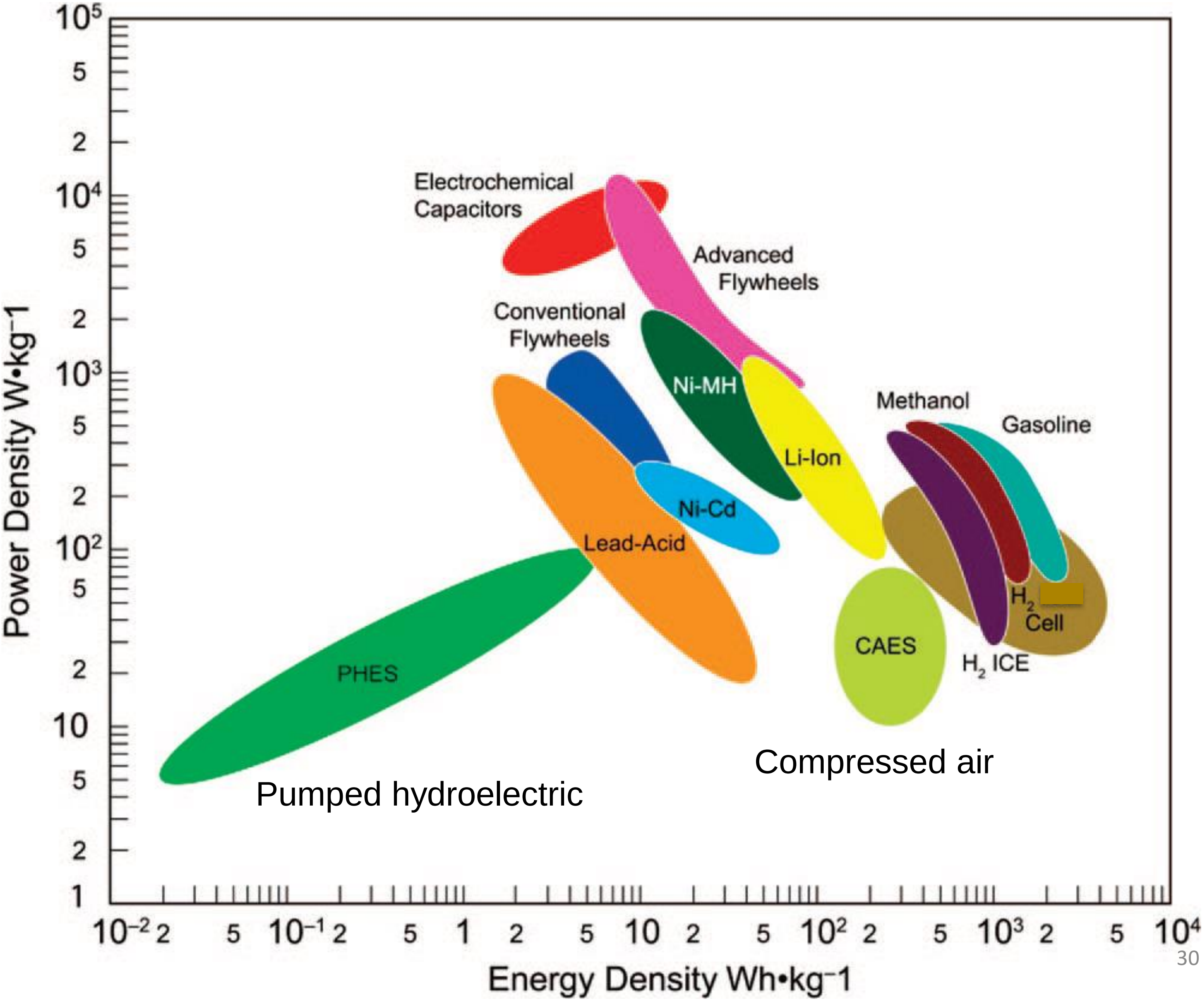
Many Energy Storage Options Exist

If we have made plenty solar electricity ... how do we store it?

Stationary Energy Storage

Decentralized	Centralized
Compressed Air (cylinders) (S-CAES)	Pumped Hydroelectric (PHES)
Small Flywheel (S-FES)	Flywheel (FES)
Batteries	Compressed Air (CAES)
Supercapacitor	Superconducting Magnetic (SMES)
Renewable Fuels	Solar Thermal

Above energy storage systems are classified for their most easily adapted implementation. Technology advances can result in category realignment


Power Density W•kg−1
Energy Density Wh•kg−1
Electrochemical Capacitors
Advanced Flywheels
Conventional Flywheels
Ni-MH
Li-Ion
Ni-Cd
Lead-Acid
PHES
CAES
Methanol
Gasoline
H2 Cell
H2 ICE
Compressed air
Pumped hydroelectric

Li ion battery is energy density is too low (not to mention the capacity and cost)

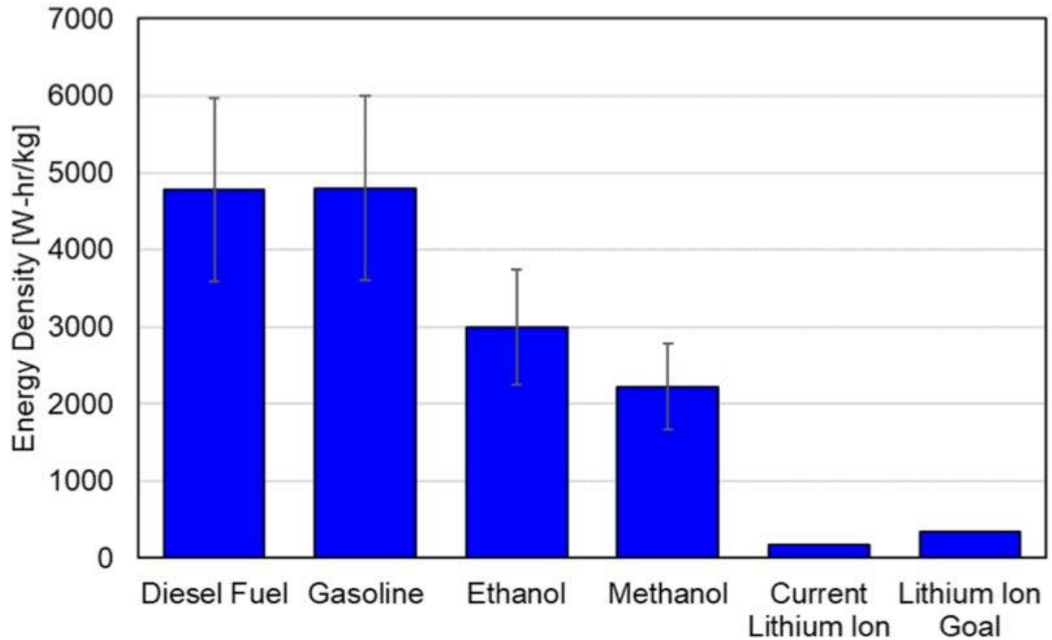
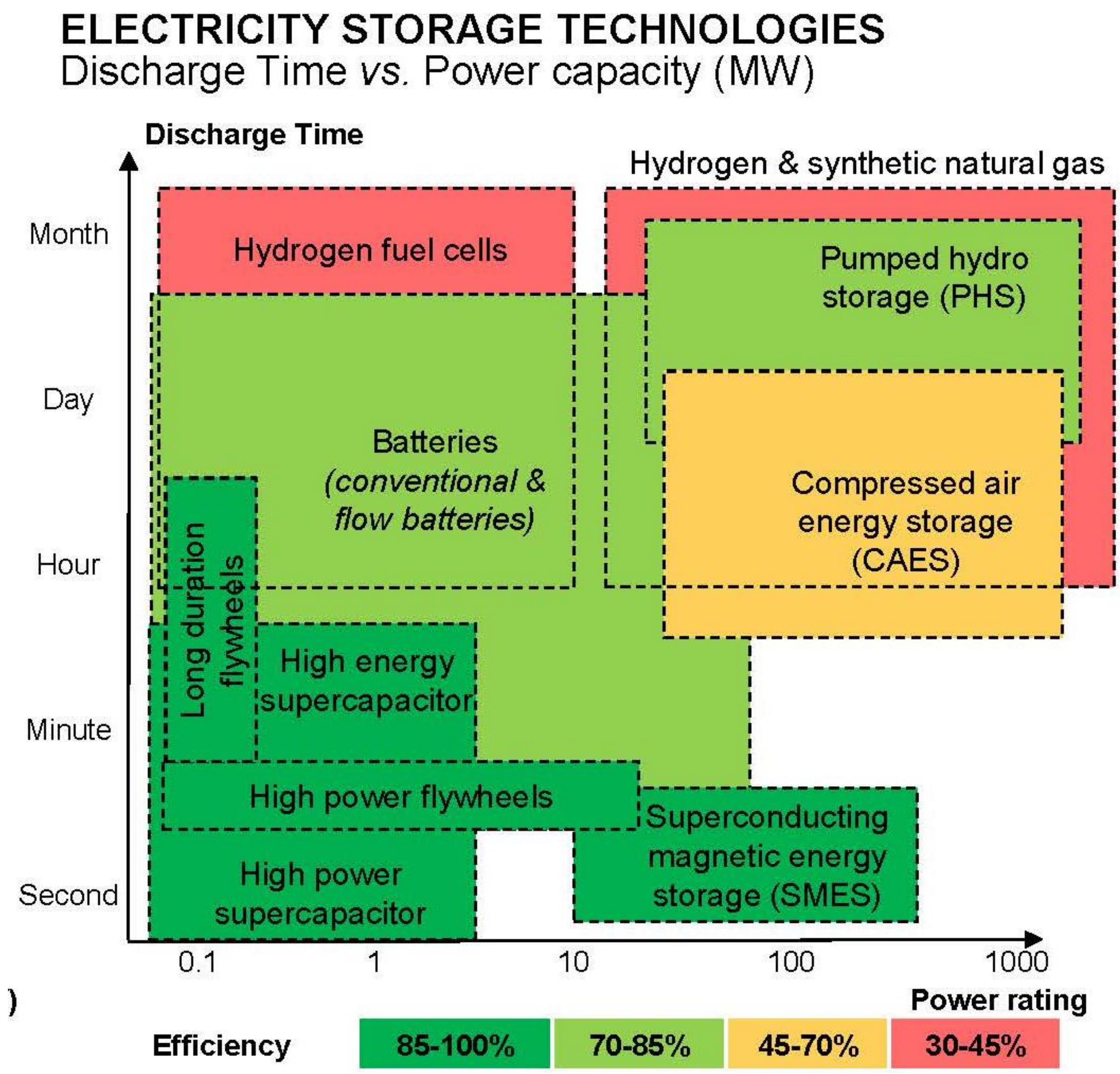


Figure 4. Useable energy density of several fuels and lithium ion batteries.



ELECTRICITY STORAGE TECHNOLOGIES
Discharge Time vs. Power capacity (MW)
Discharge Time
Hydrogen & synthetic natural gas
Month
Day
Hour
Minute
Second
Hydrogen fuel cells
Pumped hydro storage (PHS)
Batteries (conventional & flow batteries)
Compressed air energy storage (CAES)
Long duration flywheels
High energy supercapacitor
High power flywheels
Superconducting magnetic energy storage (SMES)
High power supercapacitor
0.1
1
10
100
1000
Power rating
)
Efficiency
85-100%
70-85%
45-70%
30-45%

In our course we focus on the method of energy storage via the production of chemical fuels using electricity, which should be ultimately supplied by solar (and to a less degree wind) energies.

This storge method is an irreplacable part of the solutions to renewable energy storage: **long storage duration**; **large capacity** (up to total energy concumptions); **high energy density**.

The method is not perfect but we have to accept it: low efficiency (batteries: 85%; fuel cells: 50%; internal engine: 20%).

The technologies are still in development phase for large-scale implementation.

Conclusion:

- Storage of renewable electricity is key to their widespread uses.
- Different storage options needed to be pursued, each has strength and weakness.
- For long-duration, high-density, high-capacity storage, synthetic fuels including hydrogen can play an important role.

IV. Hydrogen economy

Some fuel producing reactions

Water splitting: $2\,H_2O \xrightarrow{\text{energy}} 2\,H_2 + O_2$

CO_2 reduction:

$$2CO_2 \xrightarrow{\text{energy}} 2\,CO + O_2$$

$$2CO_2 + 2H_2O \xrightarrow{\text{energy}} 2\,HCOOH + O_2$$

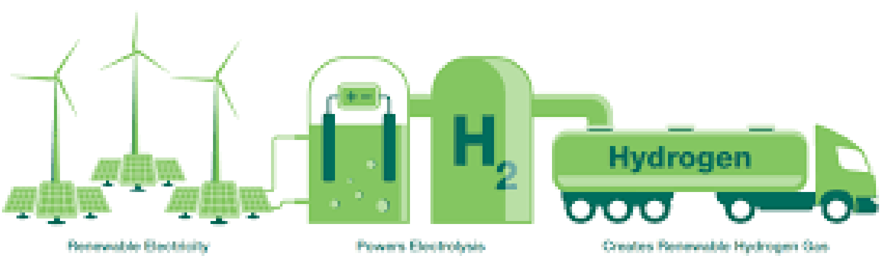
$$CO_2 + H_2O \xrightarrow{\text{energy}} HCOH + O_2$$

$$2CO_2 + 4\,H_2O \xrightarrow{\text{energy}} 2\,H_3COH + 3\,O_2$$

$$CO_2 + 2\,H_2O \xrightarrow{\text{energy}} H_4C + 2\,O_2$$

Hydrogen economy: the use of hydrogen as an energy carrier; in principle no carbon is involved.

Technical components: hydrogen production, storage, and use



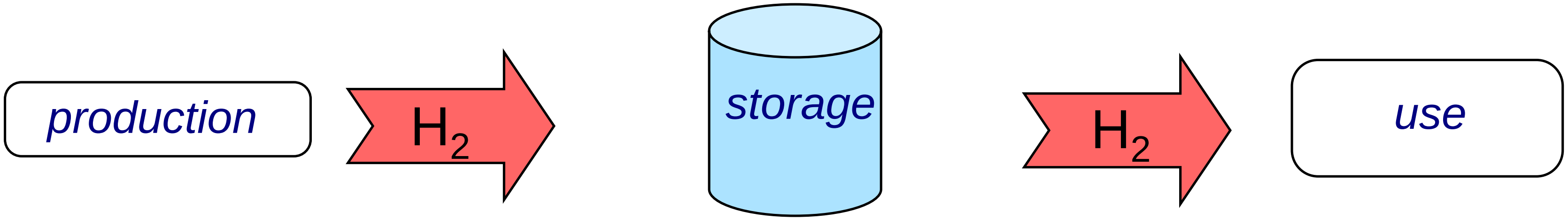
production *storage* *use*

The water splitting reaction we will discuss in detail in the class is the «cleanest» «green» way of producing hydrogen.

But let’s see some brief introduction about hydrogen storage and use.

IV-A. Hydrogen storage

Hydrogen Storage



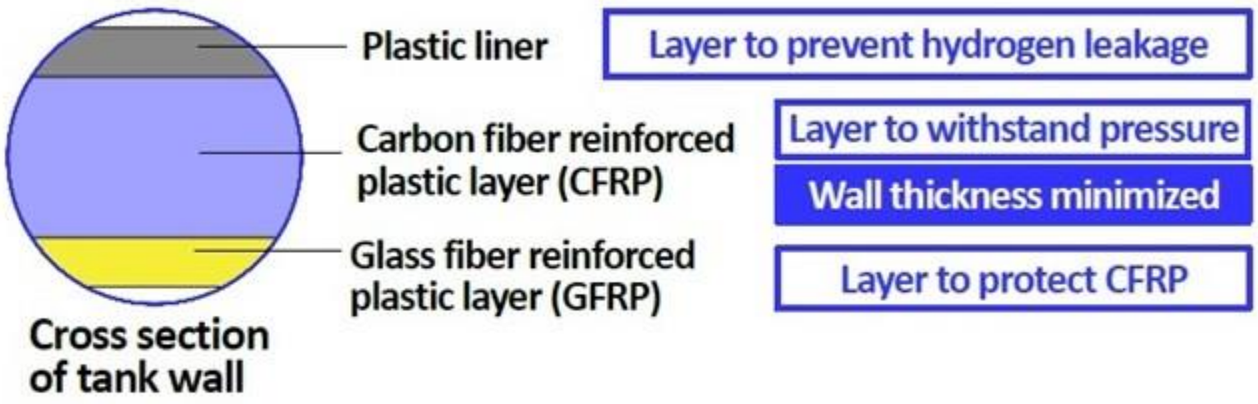
H_2 is the lightest gas, RT, 1atm. density: 0.0000899 g/cm^3
(1/14 of air, 1/11120 of water)

The most challenging H_2 storage task is for transportation

- minimum volume and weight specifications
- supply enough hydrogen to enable a 480-km (300-mi) driving range (5-10 kg H_2)
- charge/recharge near room temperature
- provide H_2 at rates fast enough for fuel cell locomotion of cars, trucks, and buses
- safety

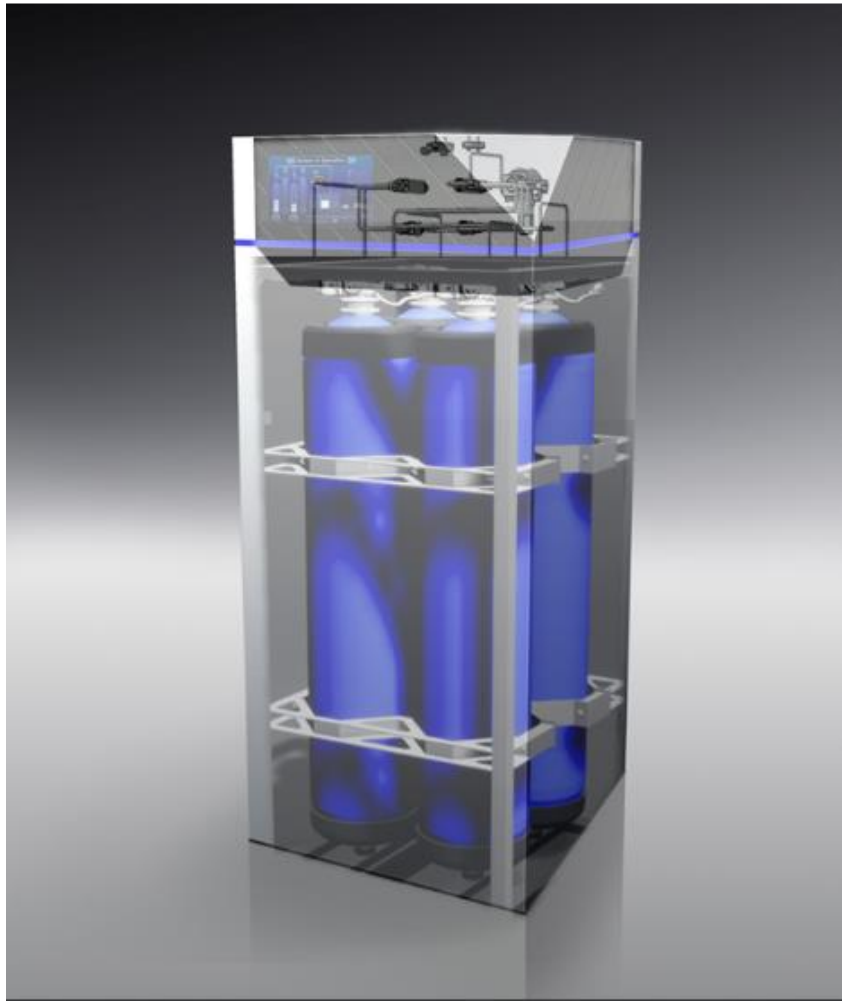
State of the art; High pressure

Toyota Mirai, 3 tanks
Composite plastics
650 km range, 5.6 kg H_2, 700 atom.

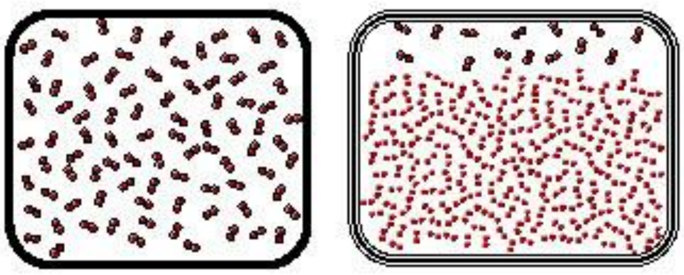


High-tech carbon composites satisfy pressure and safety requirements

H_2 tanks in Mirai cars can be adapted for other uses



Hydrogen Storage Options



High Pressure Gas Tanks

- Low volmetric density:
10,000-psi (700 atm.) pressure
0.030 kg/L, 4.4 MJ/L
- < 6 kWh/kg H_2 to get to 700 atm.
(15% H_2 energy)
Theoretically 1.4 kWh/kg to get from 20 to 700 atm

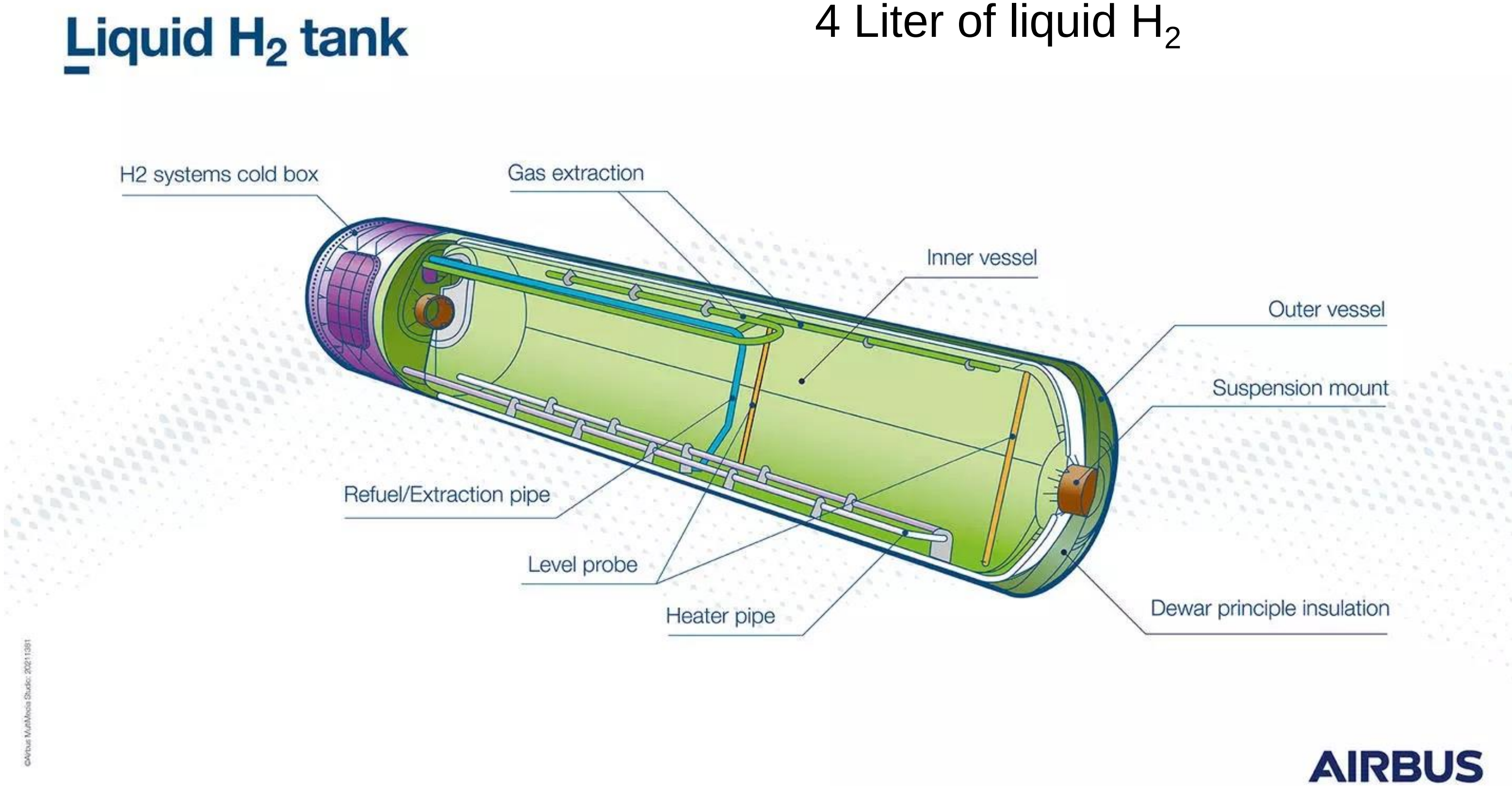
Liquid H_2 Tanks

- Low volmetric density:
0.070 kg/L, 8.4 MJ/L
- H_2 evaporate 1% per day
- Boiling Point: -252.87 °C
- Today 10 kWh/kg H_2 to liquefy
(30% H_2 energy)
Theoretically 4 kWh/kg H_2 to liquidify

Even higher density can be achieved by Liquid H_2, but more energy demanding.
Airbus project:

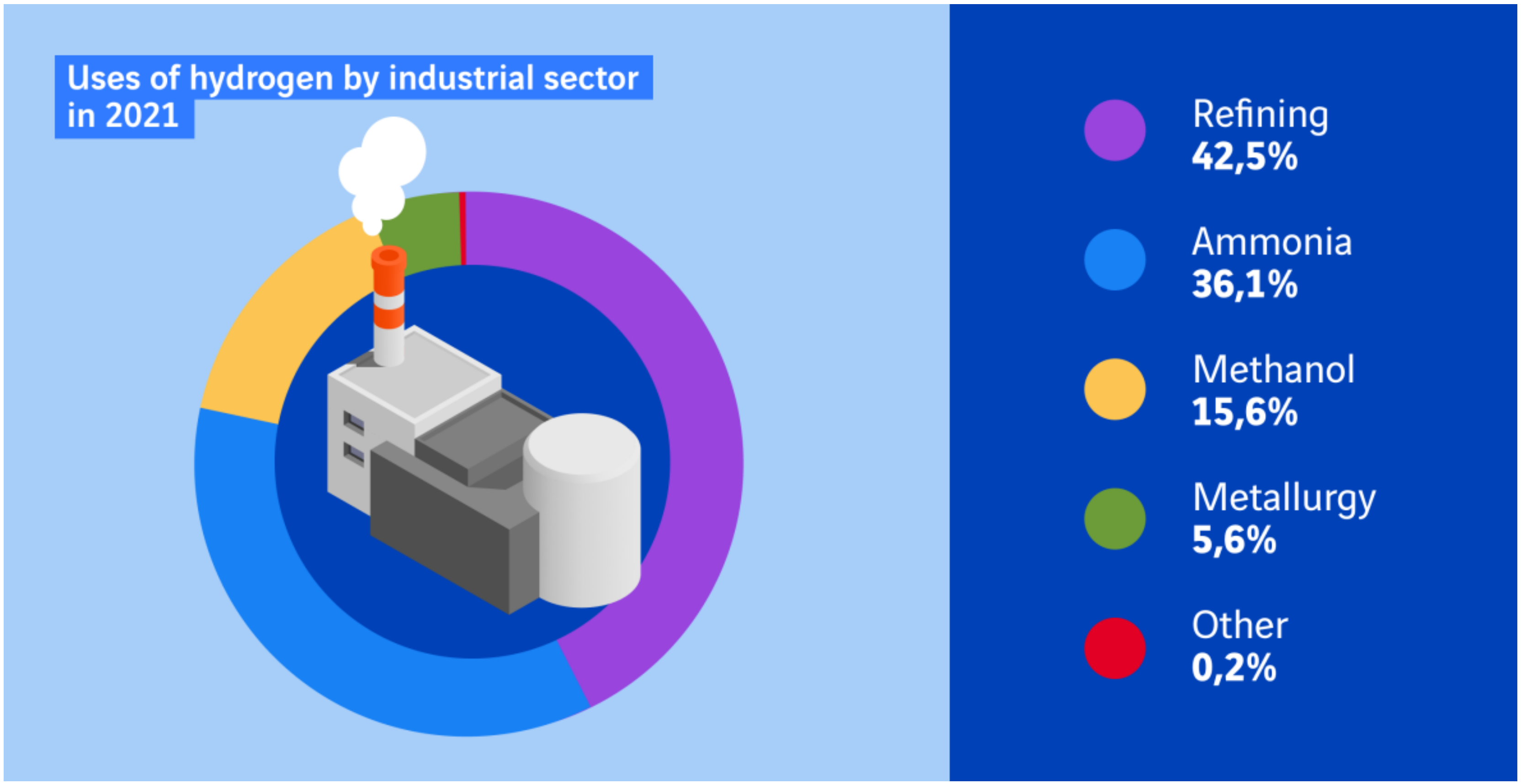
One liter of kerosene (jet) fuel:

3000 Liter of H_2 at 1 atm. RT
6 Liter of H_2 at 700 atm. (Mpa)
4 Liter of liquid H_2

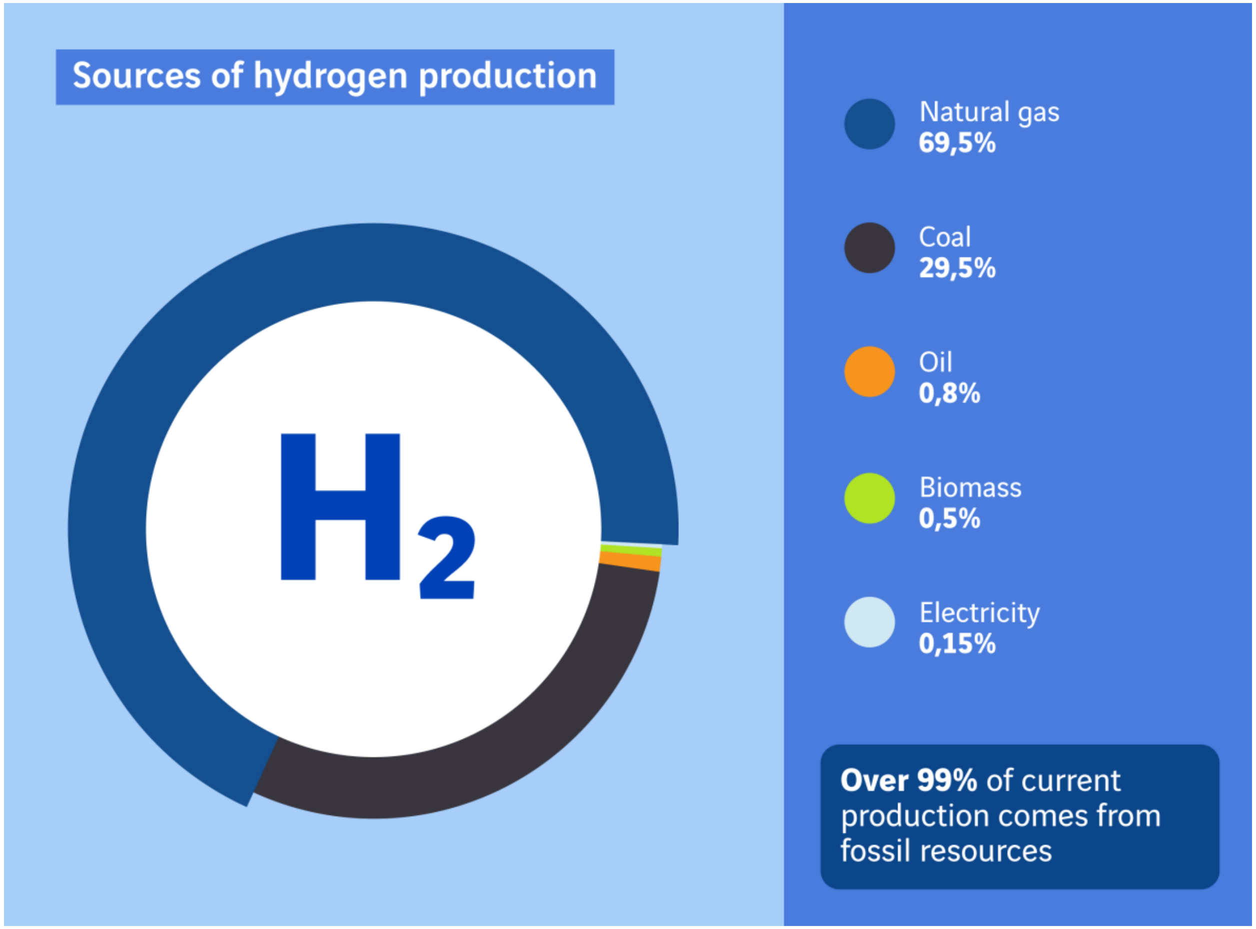


IV-B. Hydrogen use

Hydrogen is widely used today



Today's hydrogen is not "green"



In 2022, **100M** tonnes, **160B** USD

Fossil-based H_2 production, 3% global CO_2 emission

Need green H_2

Green Hydrogen has many uses for decarbonization

ammonia

steel

methanol

Energy storage

Transportation

H_2 for Transportation – Fuel Cells

1. C-less

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

fossile fuels

$$C(coal) + O_2(g) \rightarrow CO_2(g)$$

$$C_nH_{2n+2}\ (oil) + (3n+1)/2O_2(g) \rightarrow nCO_2(g) + (n+1)H_2O(l)$$

$$CH_4\ (gas) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

2. More efficient:

fuel cell: 83% (theory), 50-60% (practice)
conbustion engine (Carnot): 60% (theory), 20-25% (practice)

3. Less polluting

No NO_x, SO_x, etc. as in combustion engines

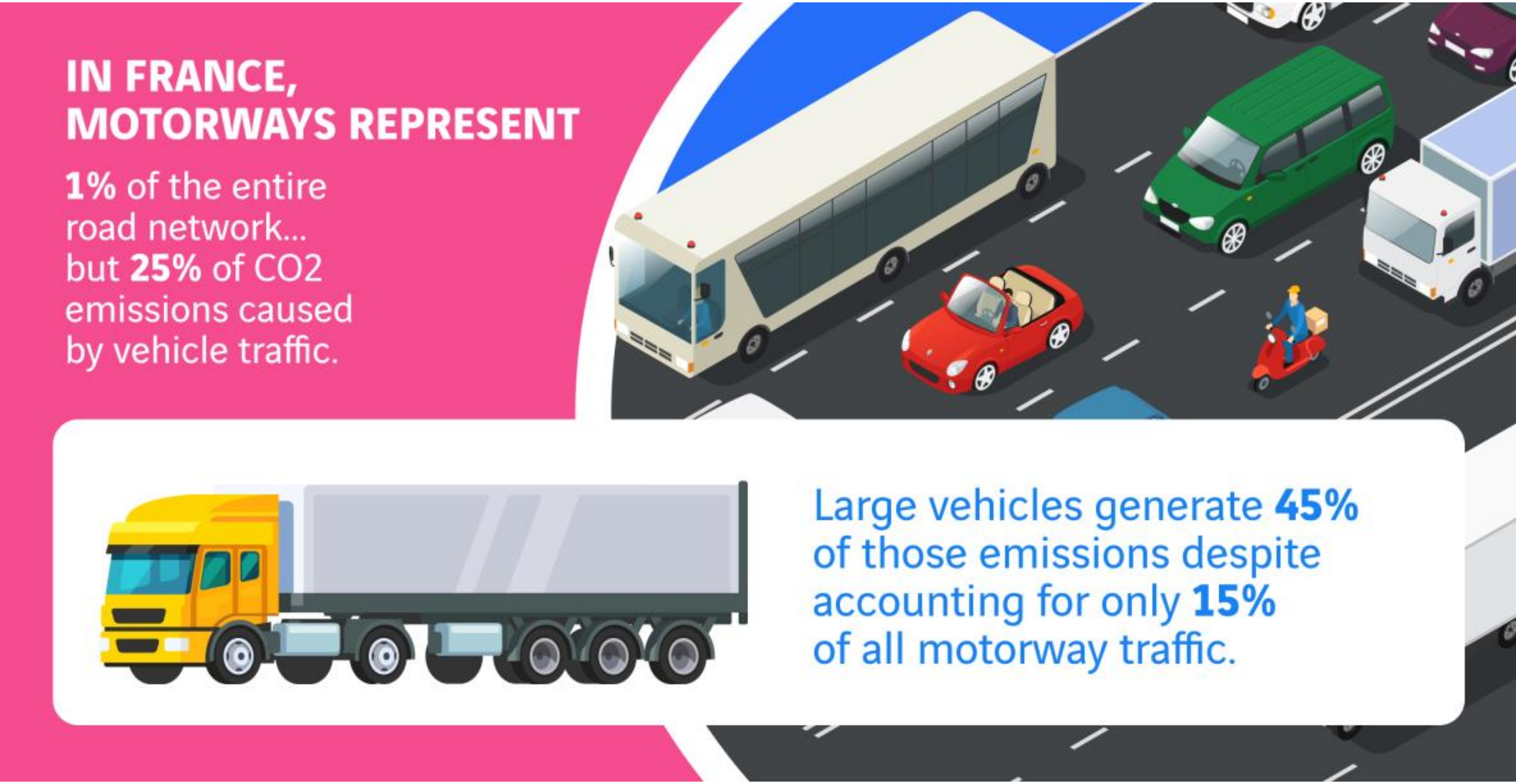
Make more sense for heavy duty, long haul: trucks; ships; planes where electric is not a good option (battery has low energy density and long charging time)

State of the art fuel cells

Proton Exchange Membrane Fule Cells (PEMFCs)

Toyota: 320 cell stack; 120 kW output
Efficiency: 60%
Price: 300 CHF per kW

Heavy duty vehicles are an opportunity for H_2

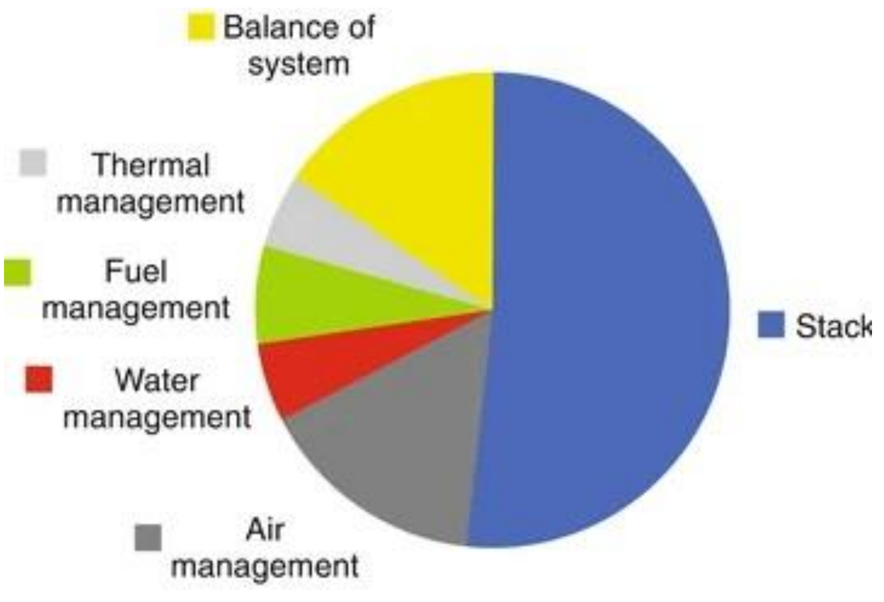


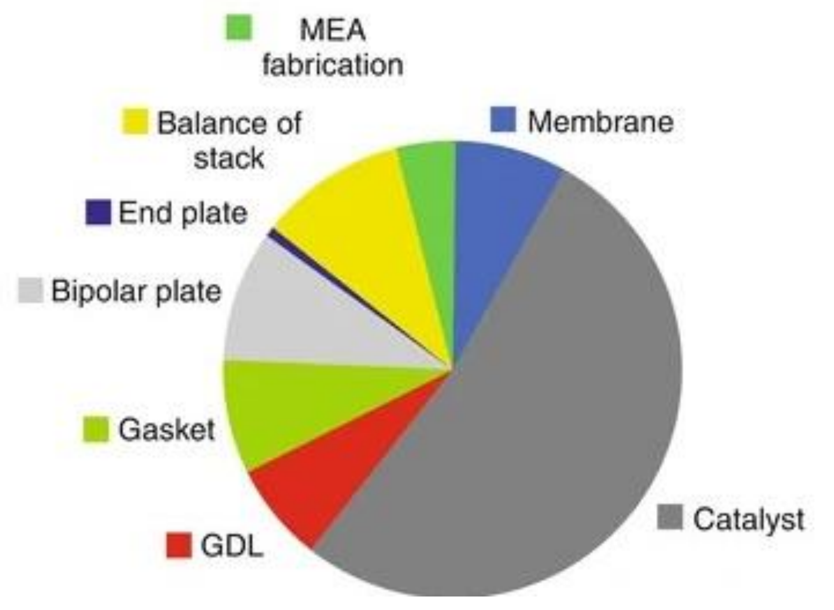
Why fuel cell so expensive?

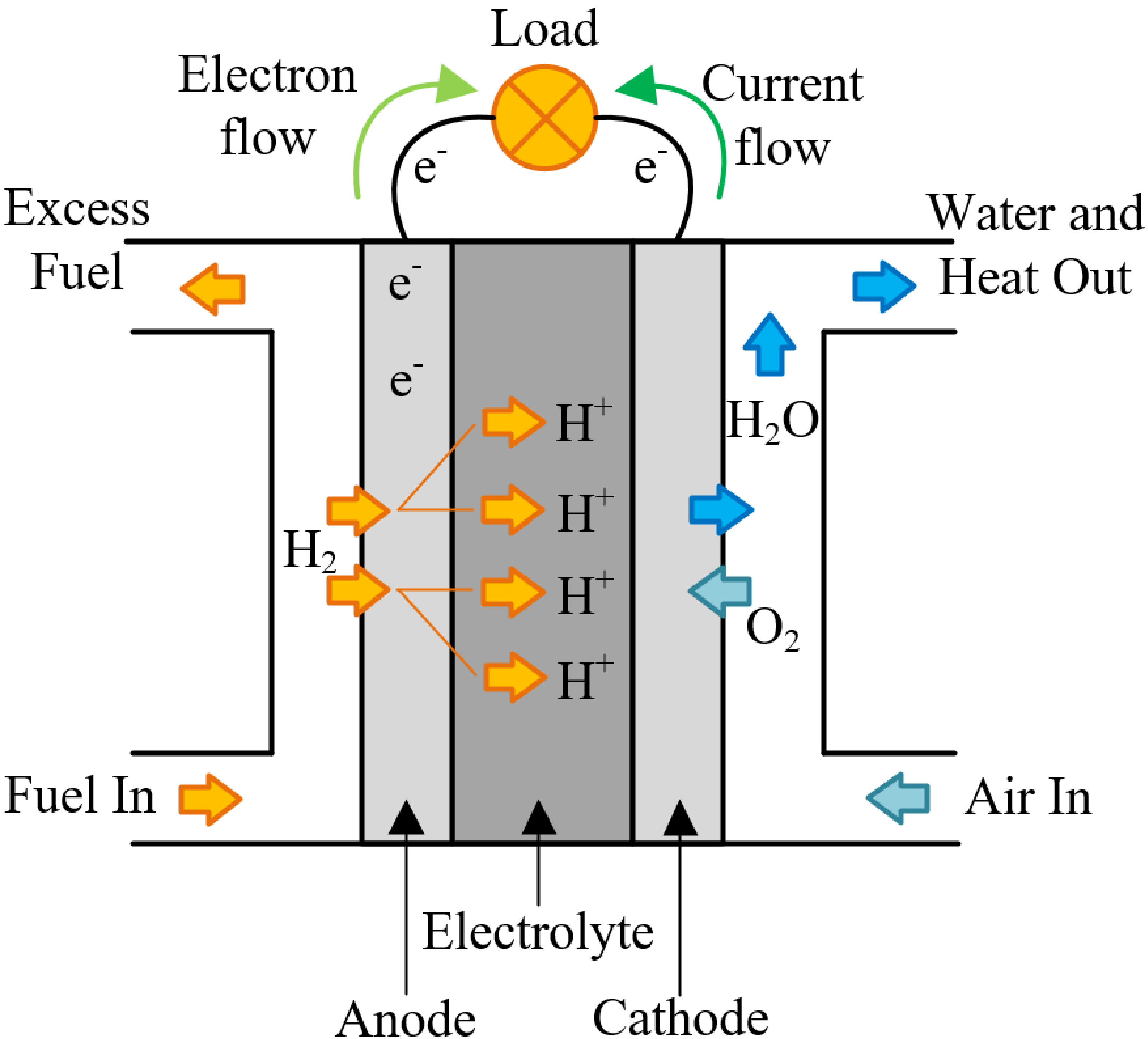
1. Catalysts (Pt)

2. Bipolar plate (Ti, to be acid resistent)

More than 50% cost due to stack.
More than 50% stack cost due to catalysts





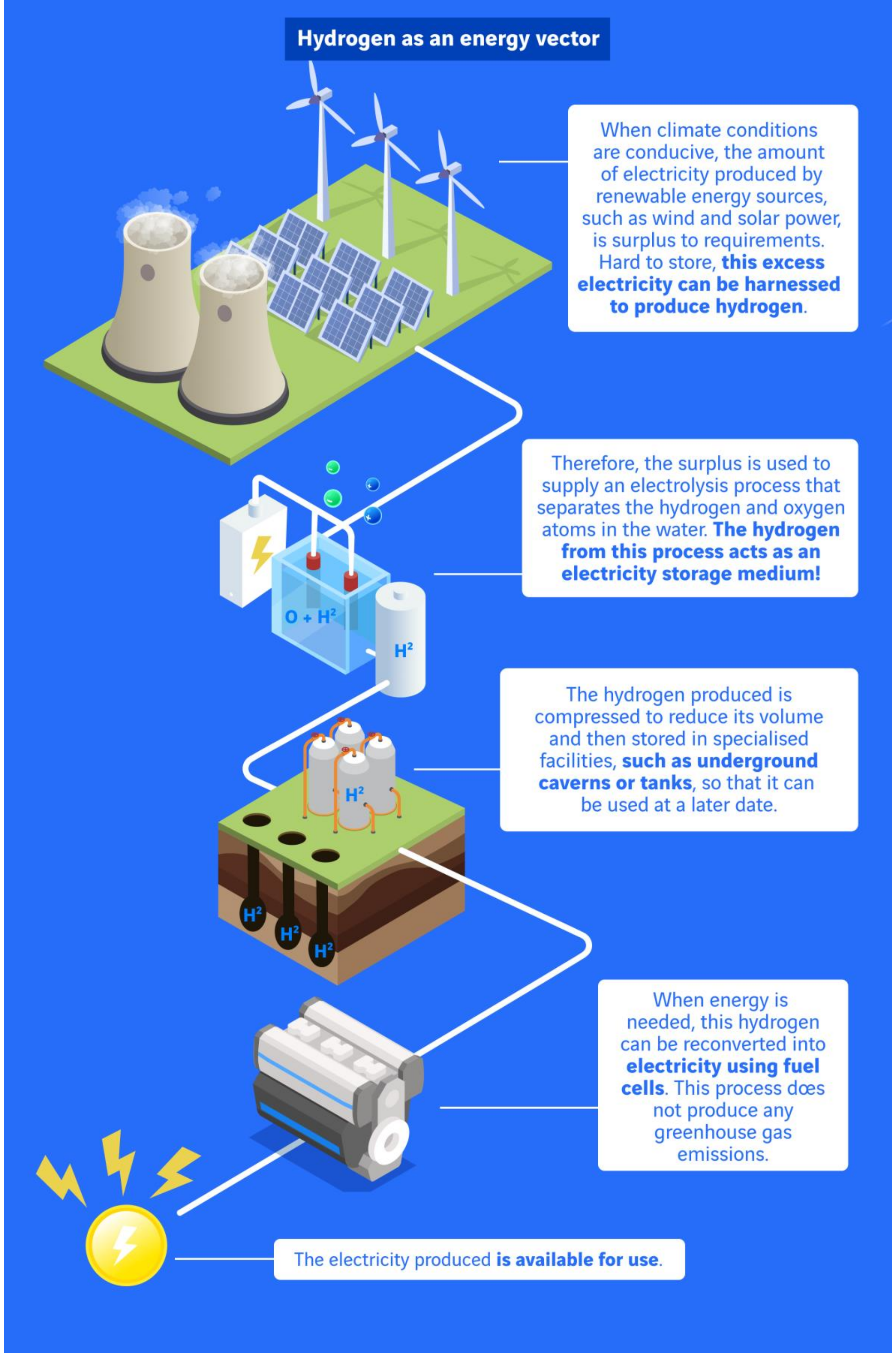


Load
Electron flow
Current flow
e-
e-
Excess Fuel
Water and Heat Out
e-
e-
H+
H+
H+
H+
H2
H2O
O2
Fuel In
Air In
Electrolyte
Anode
Cathode

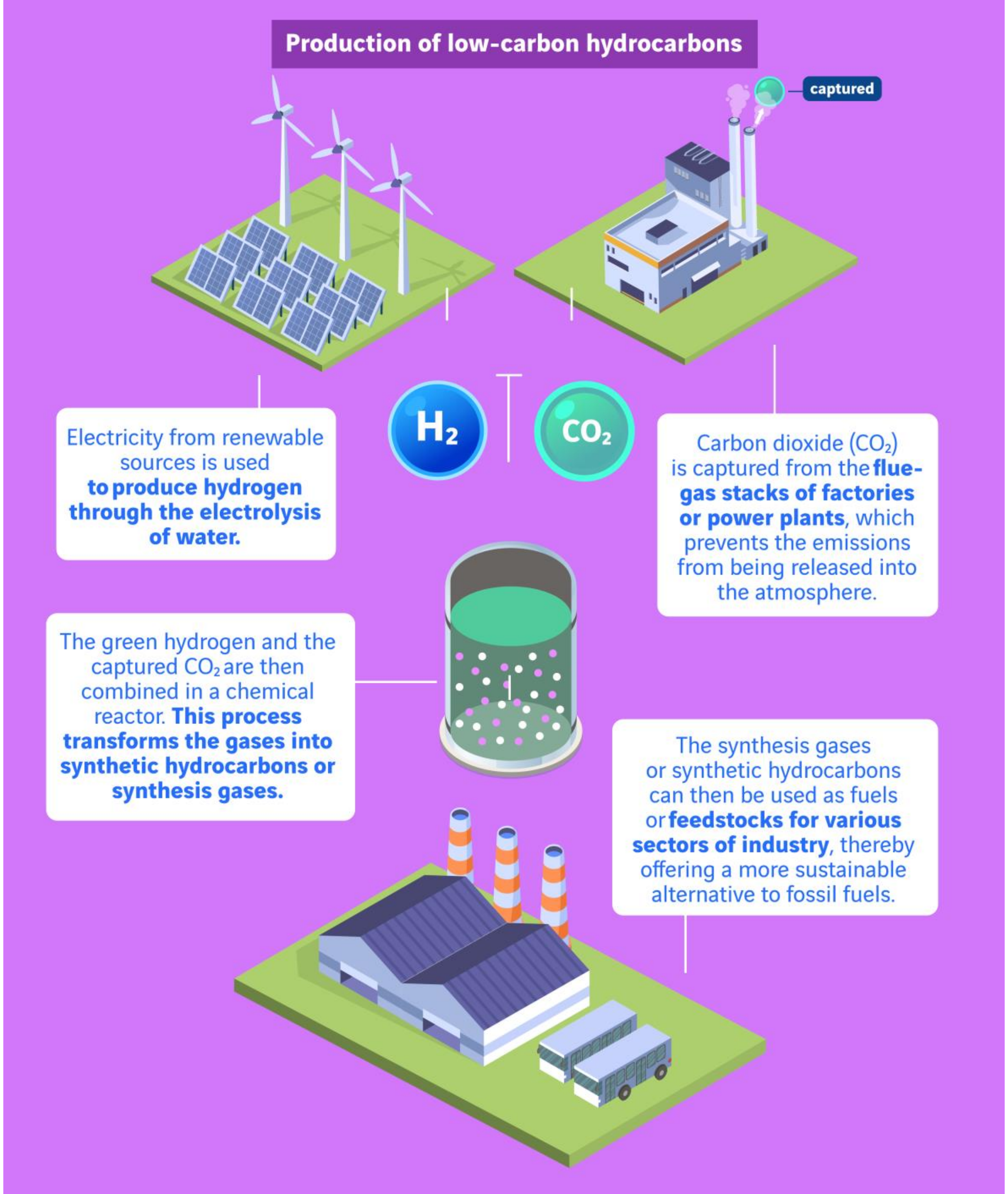
H_2 side (anode)	H_2	$\rightarrow$	$2\ H^+ + 2\ e^-$
O_2 side (cathode)	$O_2 + 4\ H^+ + 4\ e^-$	$\rightarrow$	H_2O
Overall reaction	$2\ H_2 + O_2$	$\rightarrow$	$2\ H_2O$

The hydrogen oxidation and oxygen reduction in acidic medium requires Pt-based catalysts

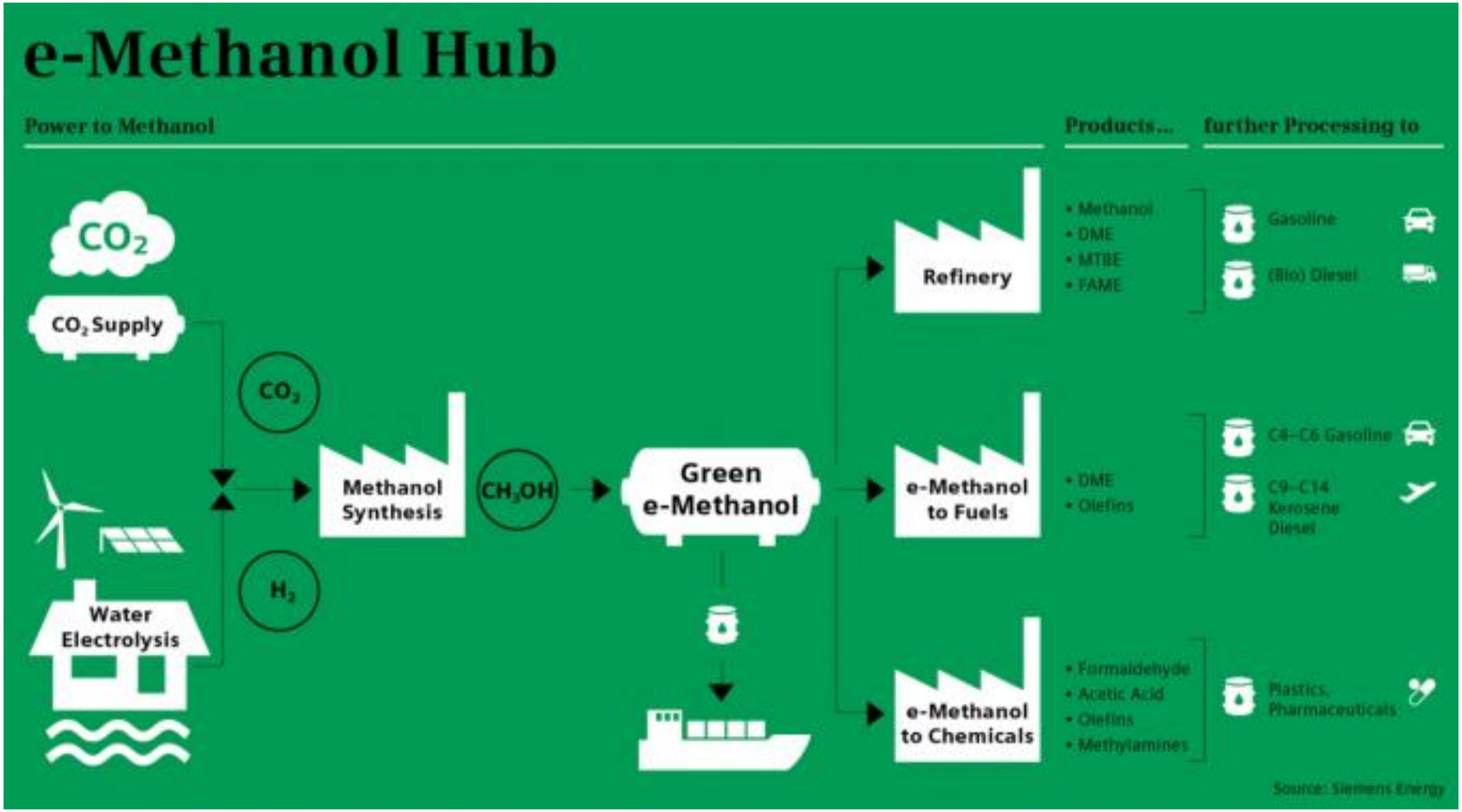
Platinum-group-metal-free fuel cells can potentially decrease greatly the cost of fuel cells.



Hydrogen as an energy vector
When climate conditions are conducive, the amount of electricity produced by renewable energy sources, such as wind and solar power, is surplus to requirements. Hard to store, **this excess electricity can be harnessed to produce hydrogen**.
Therefore, the surplus is used to supply an electrolysis process that separates the hydrogen and oxygen atoms in the water. **The hydrogen from this process acts as an electricity storage medium!**
$O + H^2$
H^2
The hydrogen produced is compressed to reduce its volume and then stored in specialised facilities, **such as underground caverns or tanks**, so that it can be used at a later date.
When energy is needed, this hydrogen can be reconverted into **electricity using fuel cells**. This process dœs not produce any greenhouse gas emissions.
The electricity produced **is available for use**.


Production of low-carbon hydrocarbons
captured
Electricity from renewable sources is used **to produce hydrogen through the electrolysis of water.**
H_2
CO_2
Carbon dioxide (CO_2) is captured from the **flue-gas stacks of factories or power plants**, which prevents the emissions from being released into the atmosphere.
The green hydrogen and the captured CO_2 are then combined in a chemical reactor. **This process transforms the gases into synthetic hydrocarbons or synthesis gases.**
The synthesis gases or synthetic hydrocarbons can then be used as fuels or **feedstocks for various sectors of industry**, thereby offering a more sustainable alternative to fossil fuels.

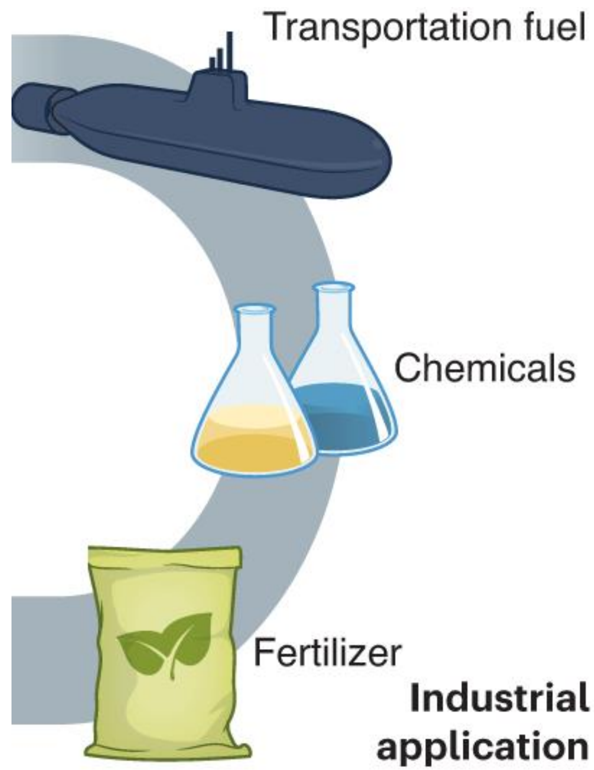
Green H_2 to green methanol

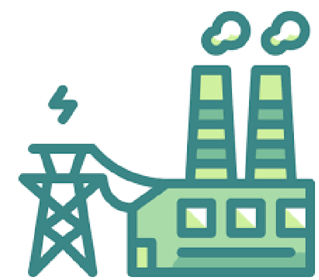


Green H_2 to green ammonia

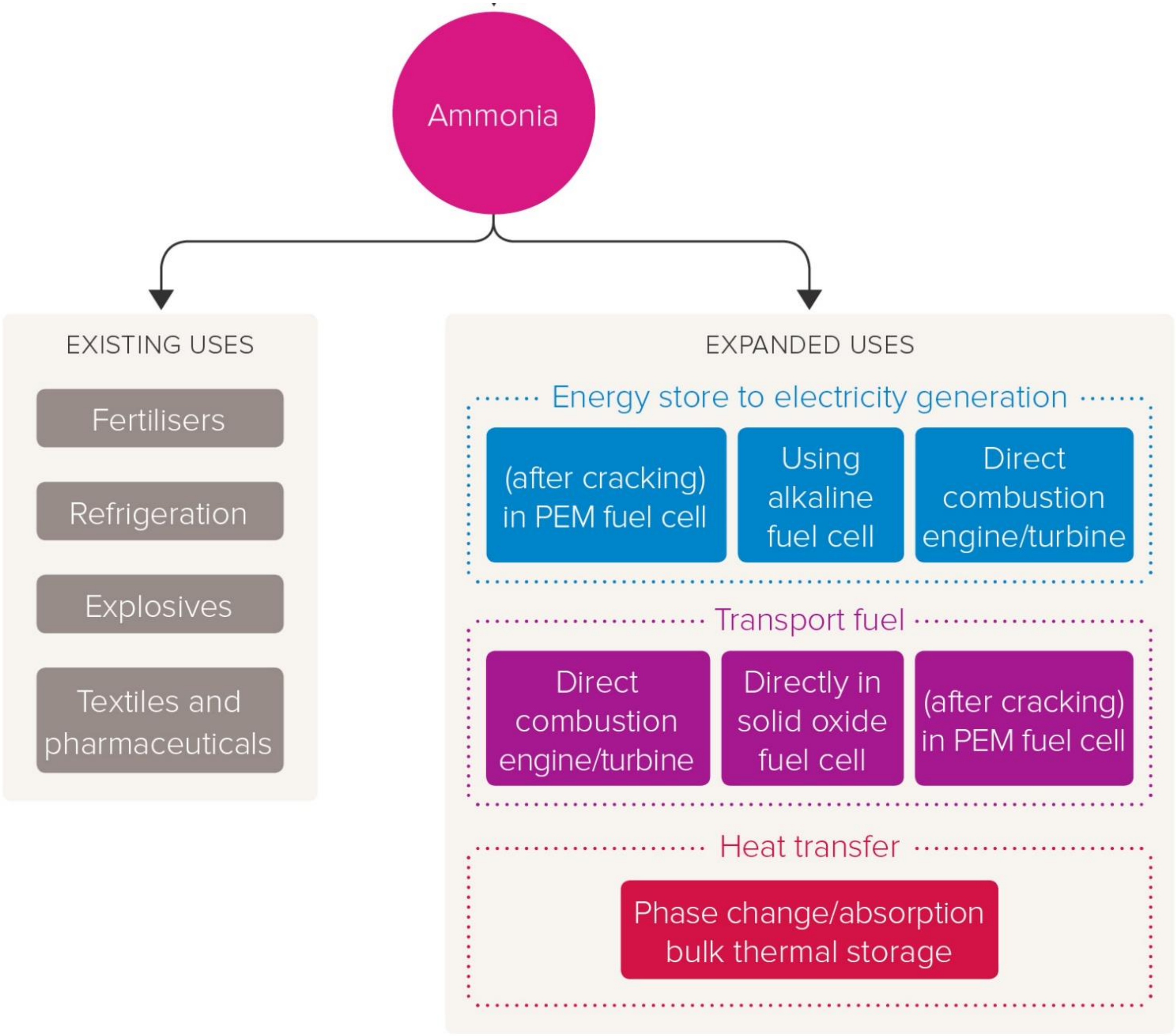
green ammonia

$H_2 + N_2 = NH_3$

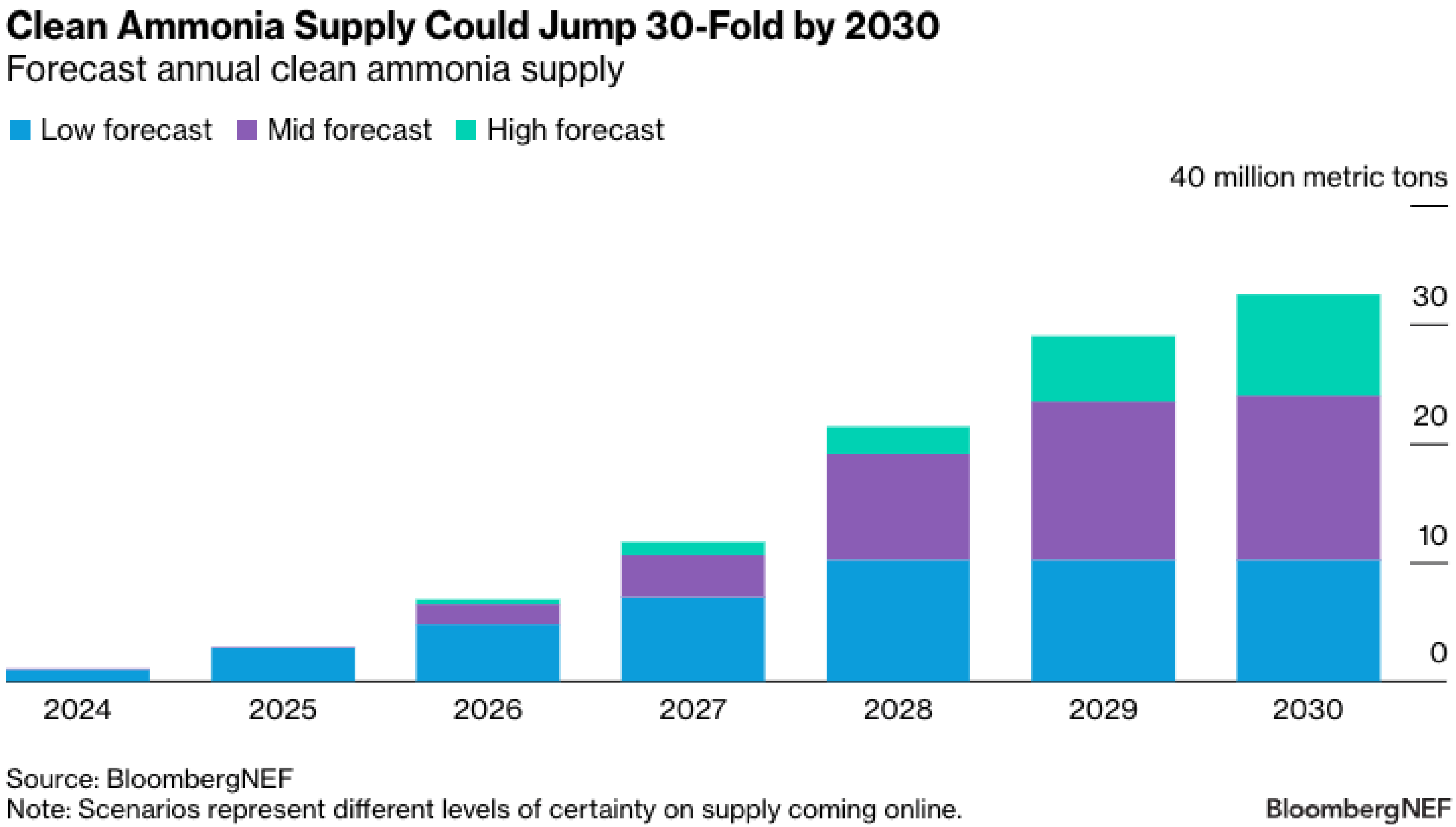


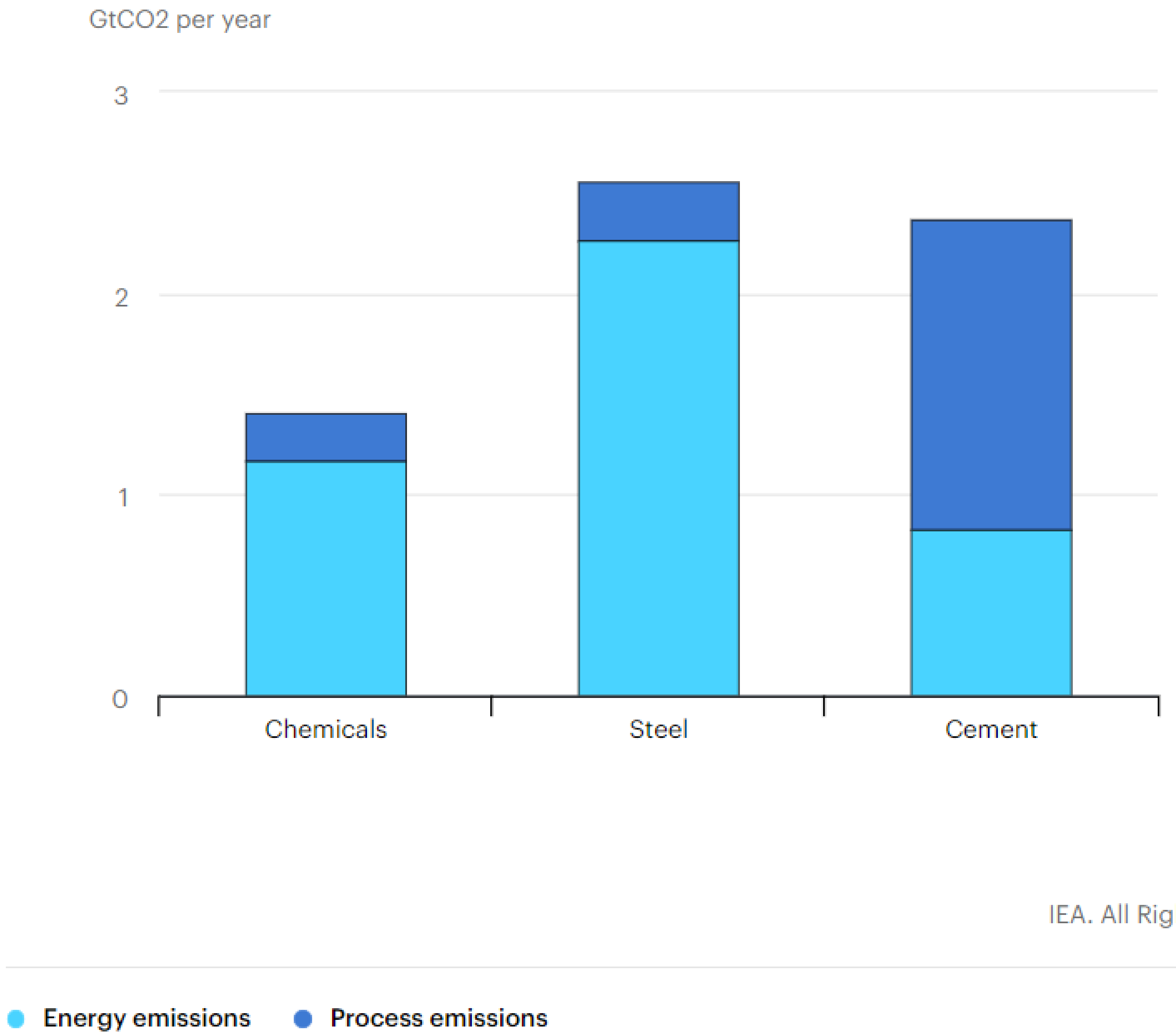


power generation

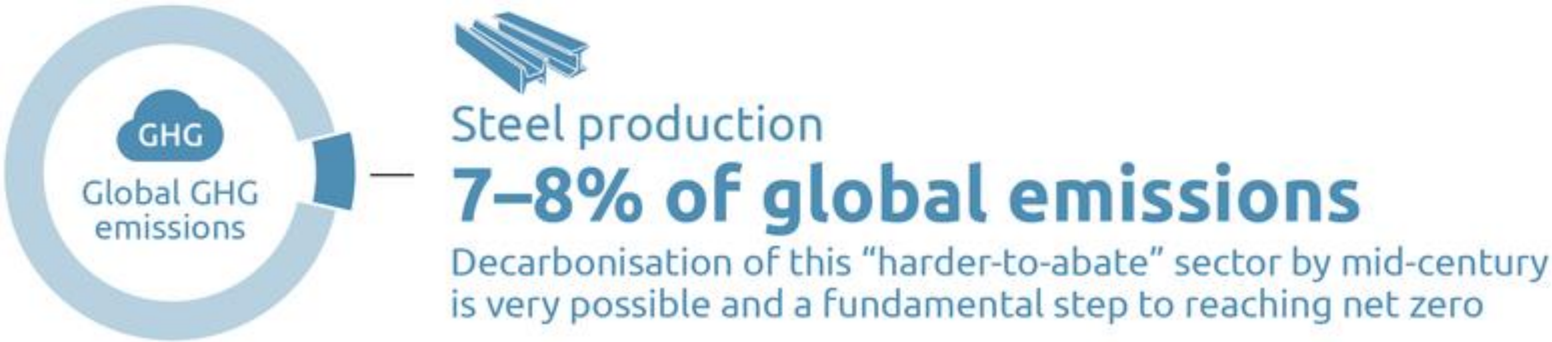


Ammonia
EXISTING USES
Fertilisers
Refrigeration
Explosives
Textiles and pharmaceuticals
EXPANDED USES
Energy store to electricity generation
(after cracking) in PEM fuel cell
Using alkaline fuel cell
Direct combustion engine/turbine
Transport fuel
Direct combustion engine/turbine
Directly in solid oxide fuel cell
(after cracking) in PEM fuel cell
Heat transfer
Phase change/absorption bulk thermal storage


Clean Ammonia Supply Could Jump 30-Fold by 2030
Forecast annual clean ammonia supply
Low forecast
Mid forecast
High forecast
40 million metric tons
30
20
10
0
2024
2025
2026
2027
2028
2029
2030
Source: BloombergNEF
Note: Scenarios represent different levels of certainty on supply coming online.
BloombergNEF



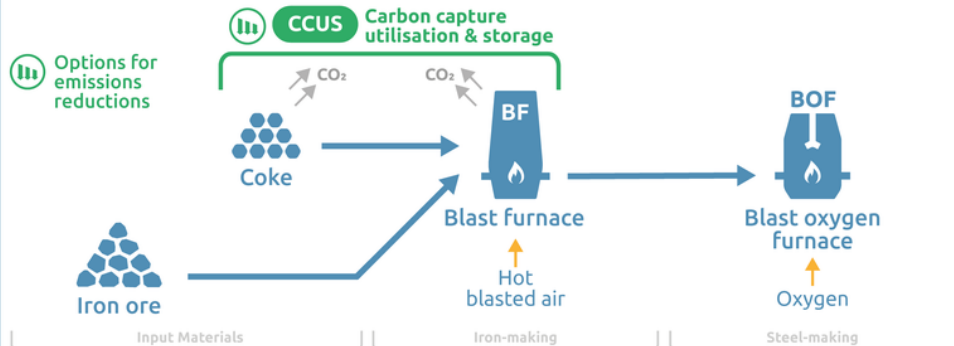
GtCO2 per year
3
2
1
0
Chemicals
Steel
Cement
Energy emissions
Process emissions



Green H_2 to green steel

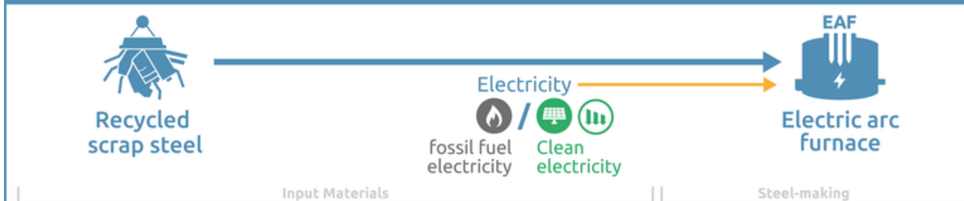
GREENING MAIN STEEL PRODUCTION METHODS USED TODAY

Basic oxygen BF-BOF process — Blast furnace to blast oxygen furnace — 71%



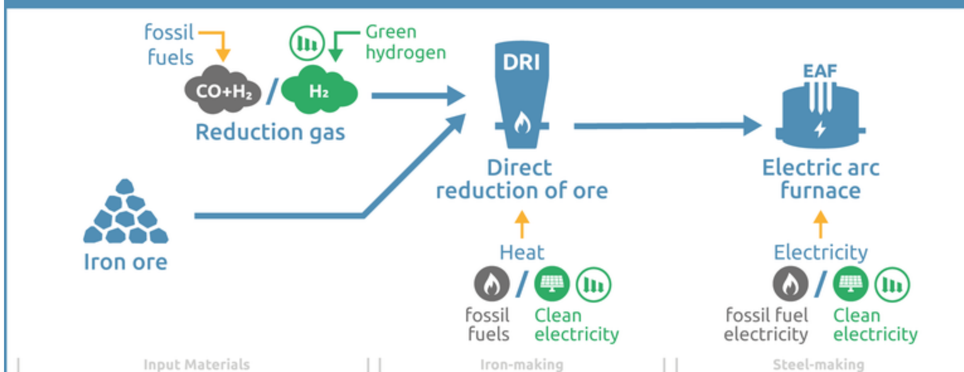
BF-BOF is the most carbon-intensive and energy-intensive route. Deep emission reductions can be achieved through rebuilding with CCUS, which has limited applications in the steel sector.

Scrap-EAF process — Recycled scrap steel to electric arc furnace — 22%



Scrap-EAF is one of the cleanest and most cost-effective routes and can be significantly decarbonised if powered by clean electricity. Availability of scrap steel is a constraint.

DRI-EAF process — Direct reduction to electric arc furnace — 7%



DRI-EAF's emissions footprint depends on the reduction gas used, and can be further decarbonised with green hydrogen as the reduction gas as well as using clean electricity throughout the process. It requires a higher grade of iron ore than BF-BOF route.

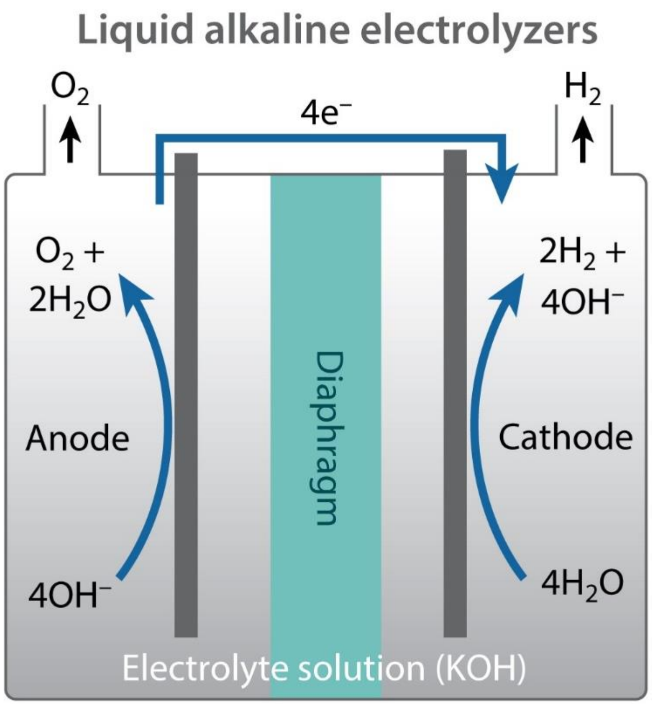
Conclusion:

- Green H_2 is a key enabler to net zero, having many applications, and especially important for hard to abate fields such as fertilizer, steel, and long haul transportations.
- Production, storage, and use of green H_2 are still work in progress, with good initial solutions.

$$2\,H_2O \xrightarrow{\text{Green Electricity}} 2\,\mathbf{H_2} + O_2$$

V. Electrolyzers – the production of green H_2

Paint point analysis of current electrolyzers



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

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

Ayers K, et al. 2019.
Annu. Rev. Chem. Biomol. Eng. 10:219–39

1st Generation Alkaline Electrolyzers

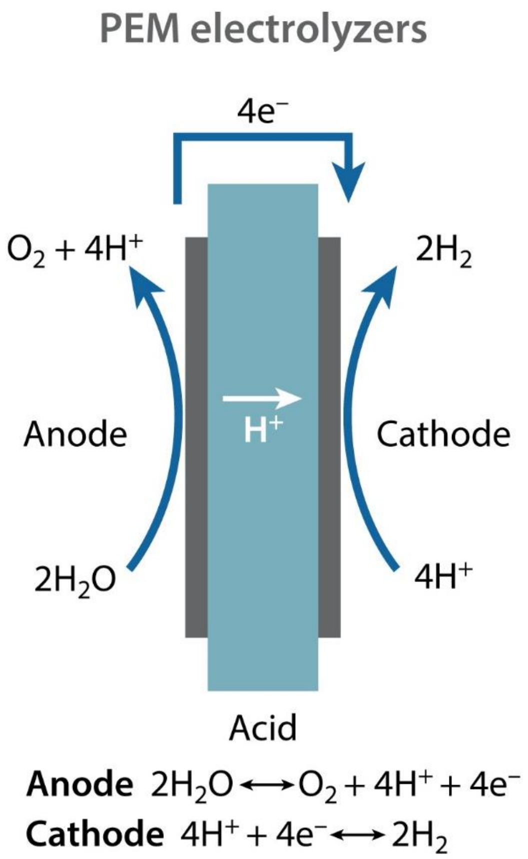
- Lost cost catalysts and hardware (Steel, Ni)
- high resistance (liquid electrolyte)
- low current density (0.4 A/cm^2)

Large footprint; high maintenance

- Porous separator between anode and cathode, prone to H_2 crossover – designed for constant input
- Changes of loads leads to H_2 cross over
- Slow response

Not fit for intermittent solar/wind

Paint point analysis of current electrolyzers



2nd Generation Acidic PEM Electrolyzers

- PEM = proton exchange membrane
- Low resistance (membrane conduction)
- high current density (1-3 A/cm^2)

Small footprint; low maintenance

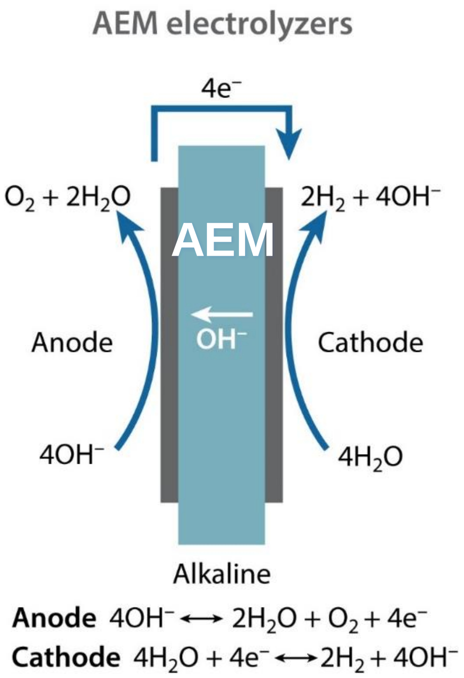
- Membrane separation of anode and cathode, low H_2 crossover
- Fast response

Fit for solar/wind

- Strong acidic, very corrosive - Require Pt, Ir catalysts and high cost Ti hardware

High Cost and Not scalable

AEM (anion exchange membrane) electrolyzer's potentials



Alkaline working conditions

- Precious metal-free catalysts (Ni, Fe)
- Low cost hardware (Ni, Fe)

→ Inexpensive and Scalable

Membrane technology

- Low resistance → High current density

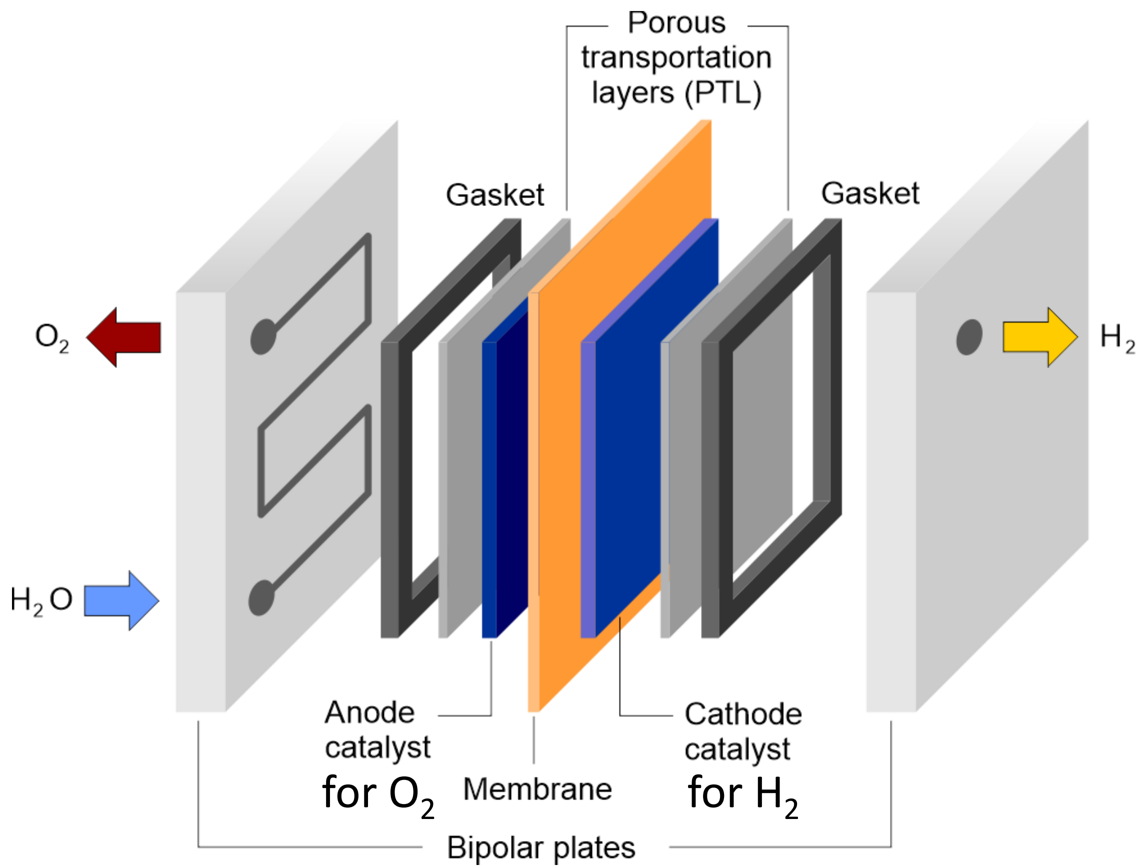
→ Small footprint

- Separation of H_2 and O_2 by membrane

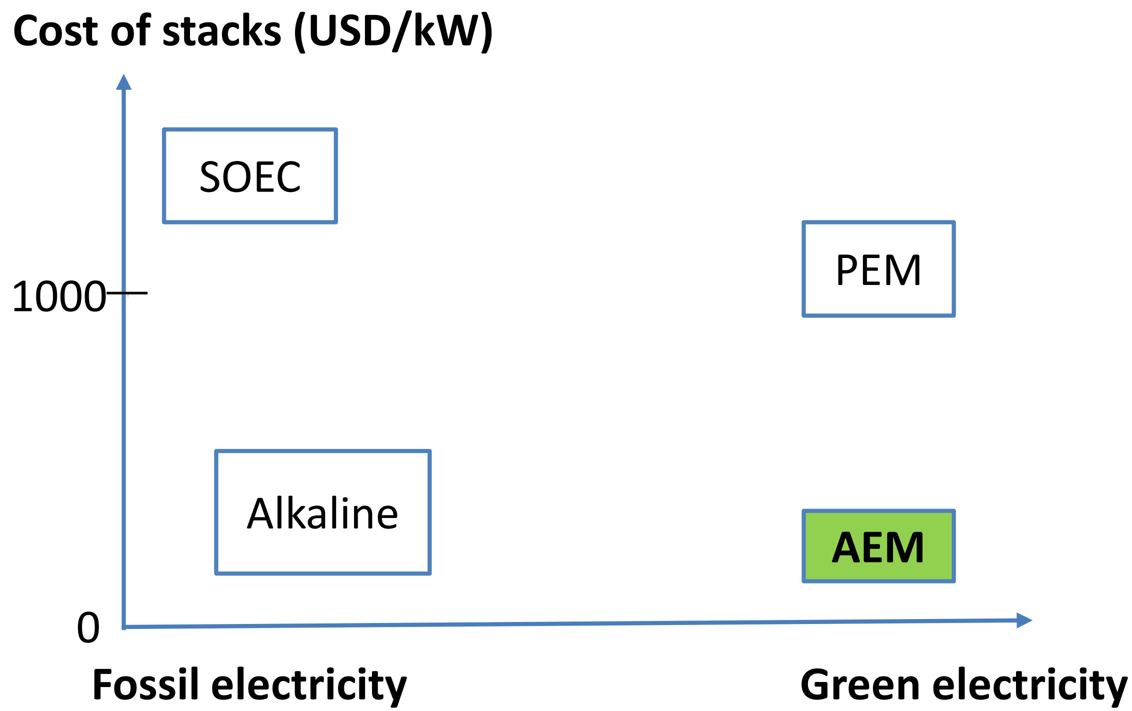
→ Low H_2 crossover due to load change

→ Compatible with intermittent wind/solar

AEM electrolyzer’s cell



AEM is the most viable green H_2 production technology



Problem: AEM (anion exchange membrane) electrolyzer is undeveloped **due to lack of suitable materials, including membranes and catalysts**

Conclusion:

- Green H_2 can be made via water electrolyzers. But current alkaline electrolyzers are not suitable for intermittant green electricity, and current PEM electrolyzers are not scalable.
- AEM electrolyzer is a promising technology, but needs development in membrane and catalysts to make it applicable.