Fuel cells and hydrogen energy

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Outline

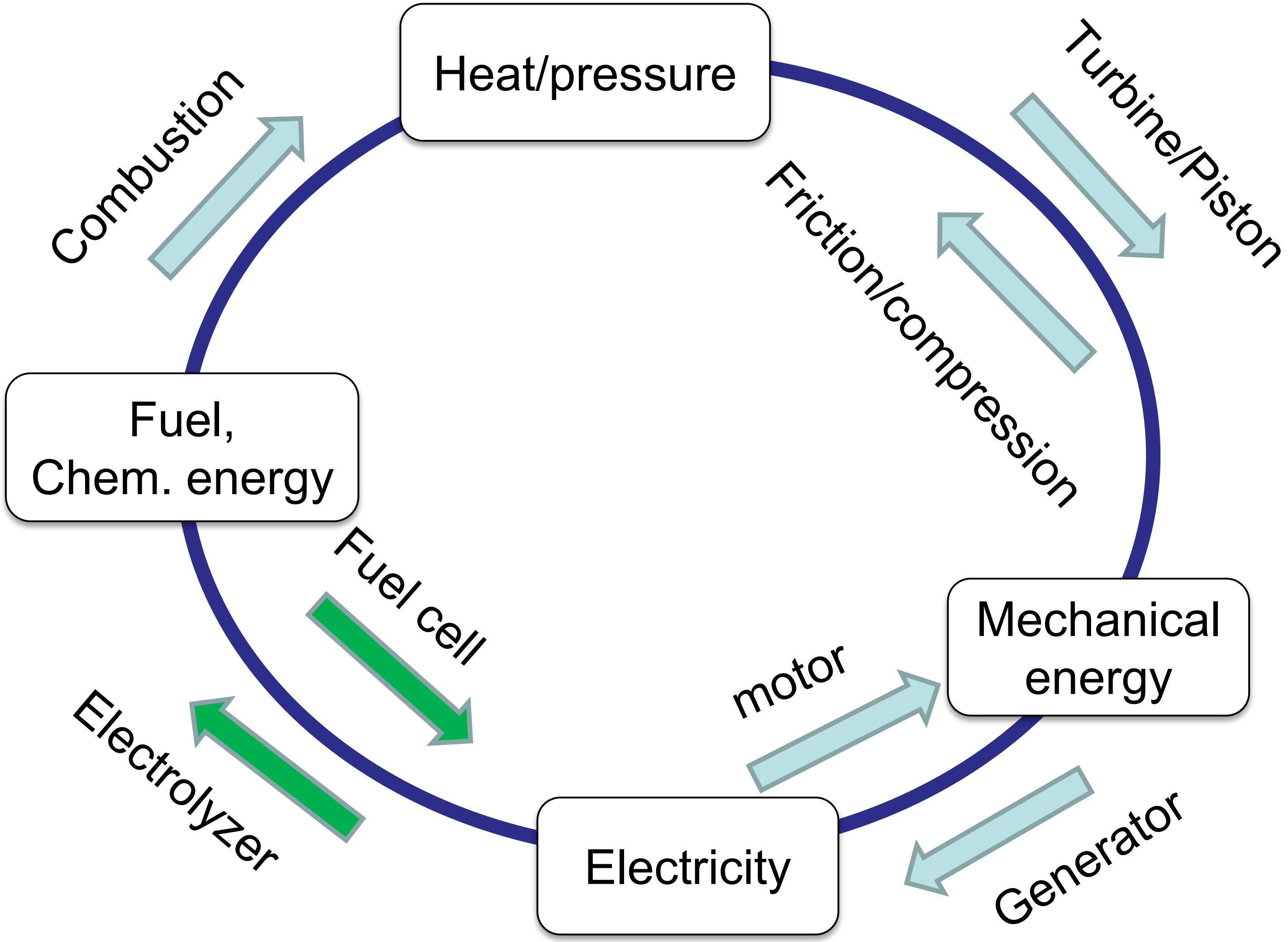
- The fuel cell – working principle and components
- Energy conversion by fuel cells
- Types of fuel cells
- Hydrogen as an energy carrier
- Hydrogen storage
- State of implementation
- Hydrogen for energy transmission

Learning objectives

- Explain the **main principles** of a fuel cell
- Outline the characteristics of the **most common types** of fuel cell (AEC, PEMEC, DMFC, PAFC, MCFC and SOFC)
- Explain the **function of the components in a stack** (electrodes, catalysts, electrolyte, bipolar plates)
- Explain the shape of **a polarization curve**
- Calculate the **current, voltage, electrical power and thermal power** of a fuel cell stack with given dimensions and number of cells, at a given working point (voltage an current density)
- Calculate the **electrical conversion efficiency** and the heat evolved at a given cell voltage
- Outline the concept of **hydrogen as an energy carrier**
- Explain the principles of the different **ways to store hydrogen**
- Evaluate **advantages and disadvantages of hydrogen** as fuel in different applications

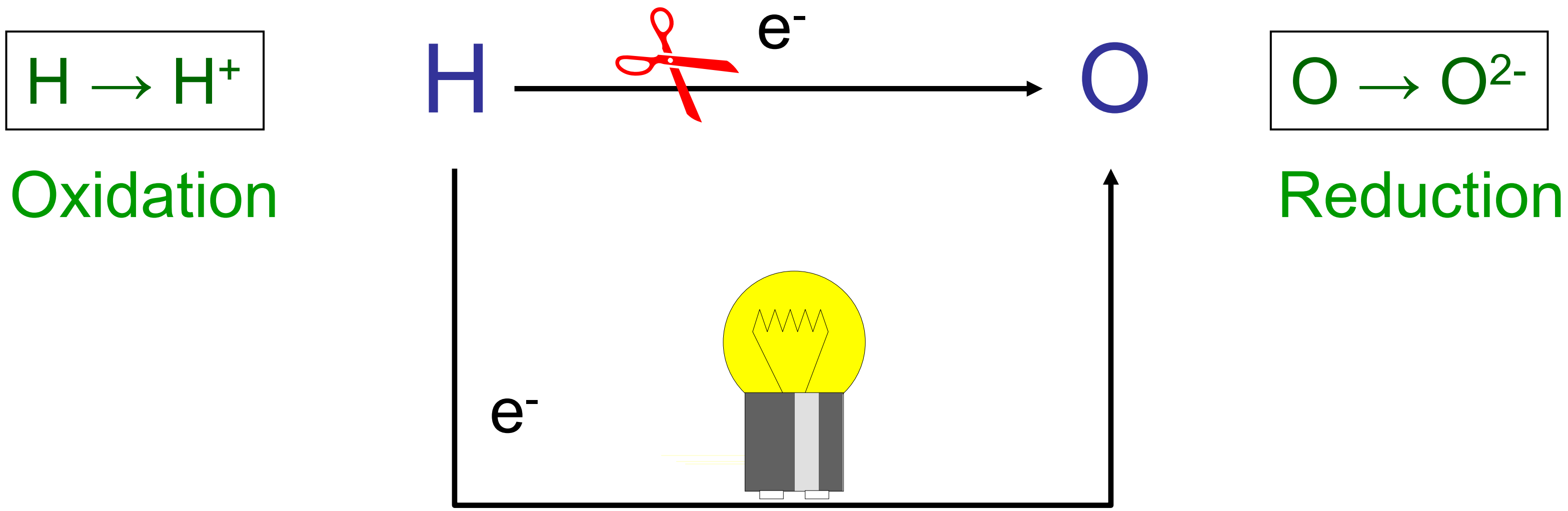
The fuel cell.
Working principle and components

Conversion - fuel to work

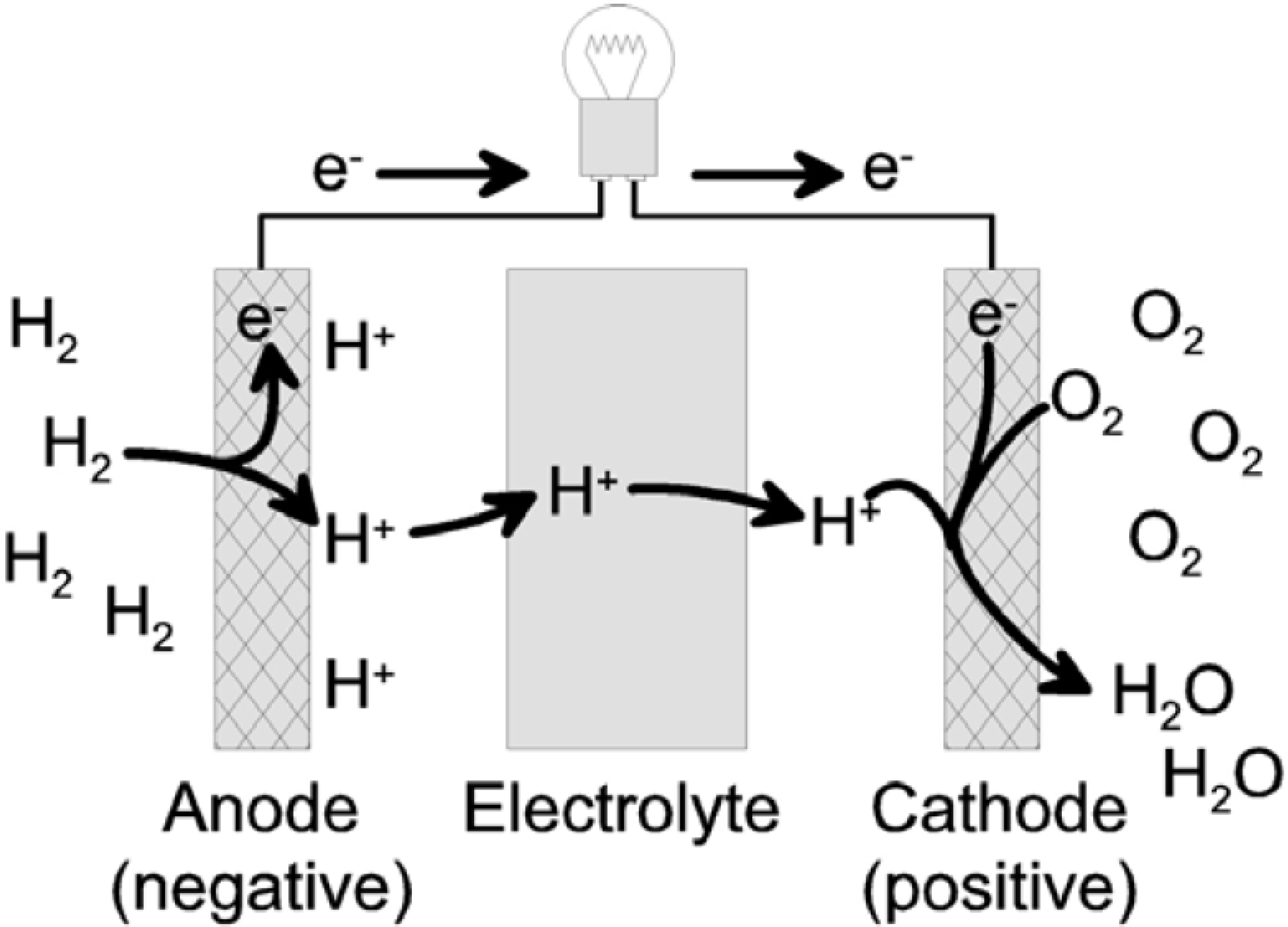


Extracting the work

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$



The fuel cell with proton conducting electrolyte



Electrode reactions

Proton conducting electrolyte

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $\underline{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$

Total: $2H_2 + O_2 \rightarrow 2H_2O$

Oxide ion conducting electrolyte

Anode: $2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^-$

Cathode: $\underline{O_2 + 4e^- \rightarrow 2O^{2-}}$

Total: $2H_2 + O_2 \rightarrow 2H_2O$

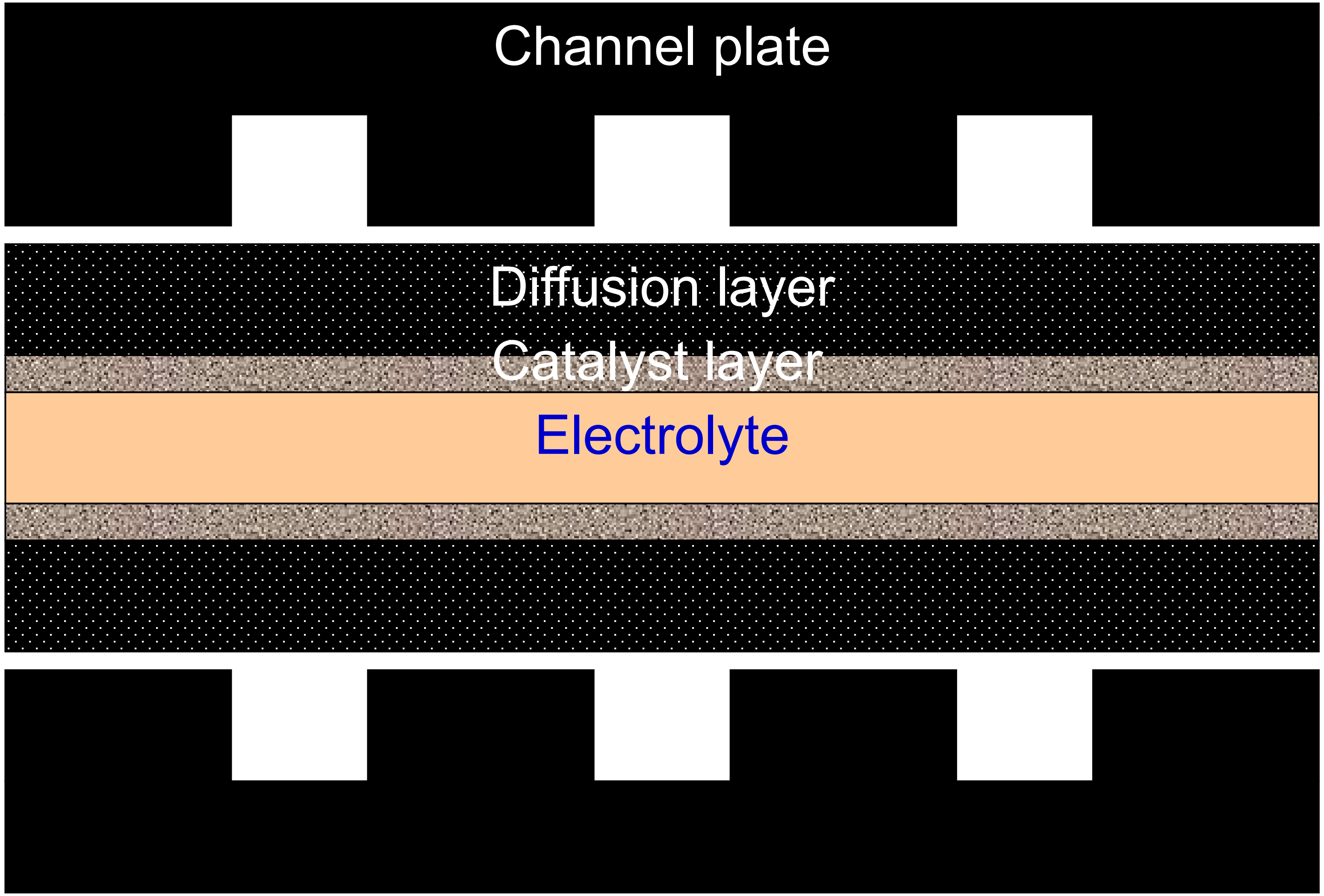
Hydroxide ion conducting electrolyte

Anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

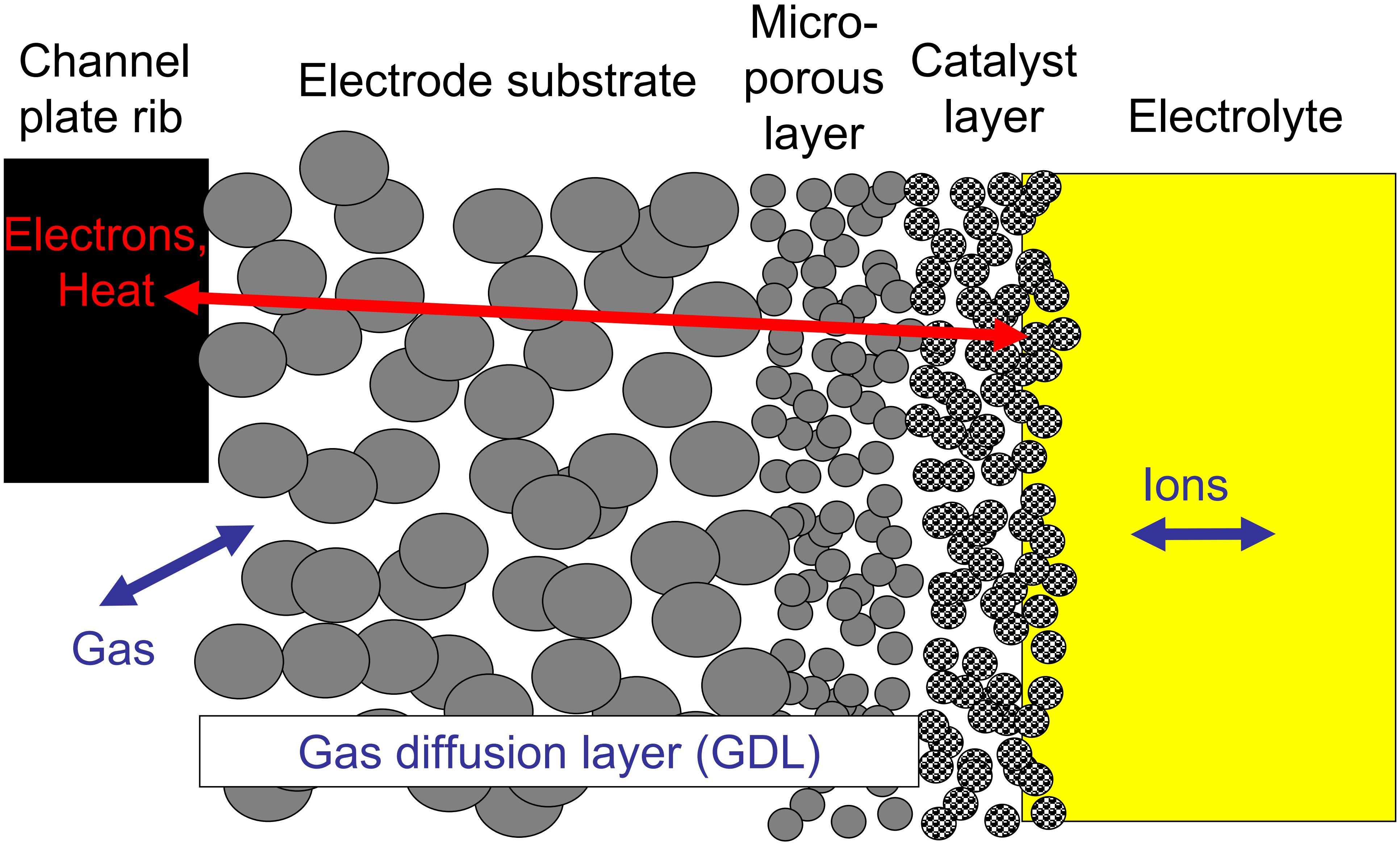
Cathode: $\underline{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-}$

Total: $2H_2 + O_2 \rightarrow 2H_2O$

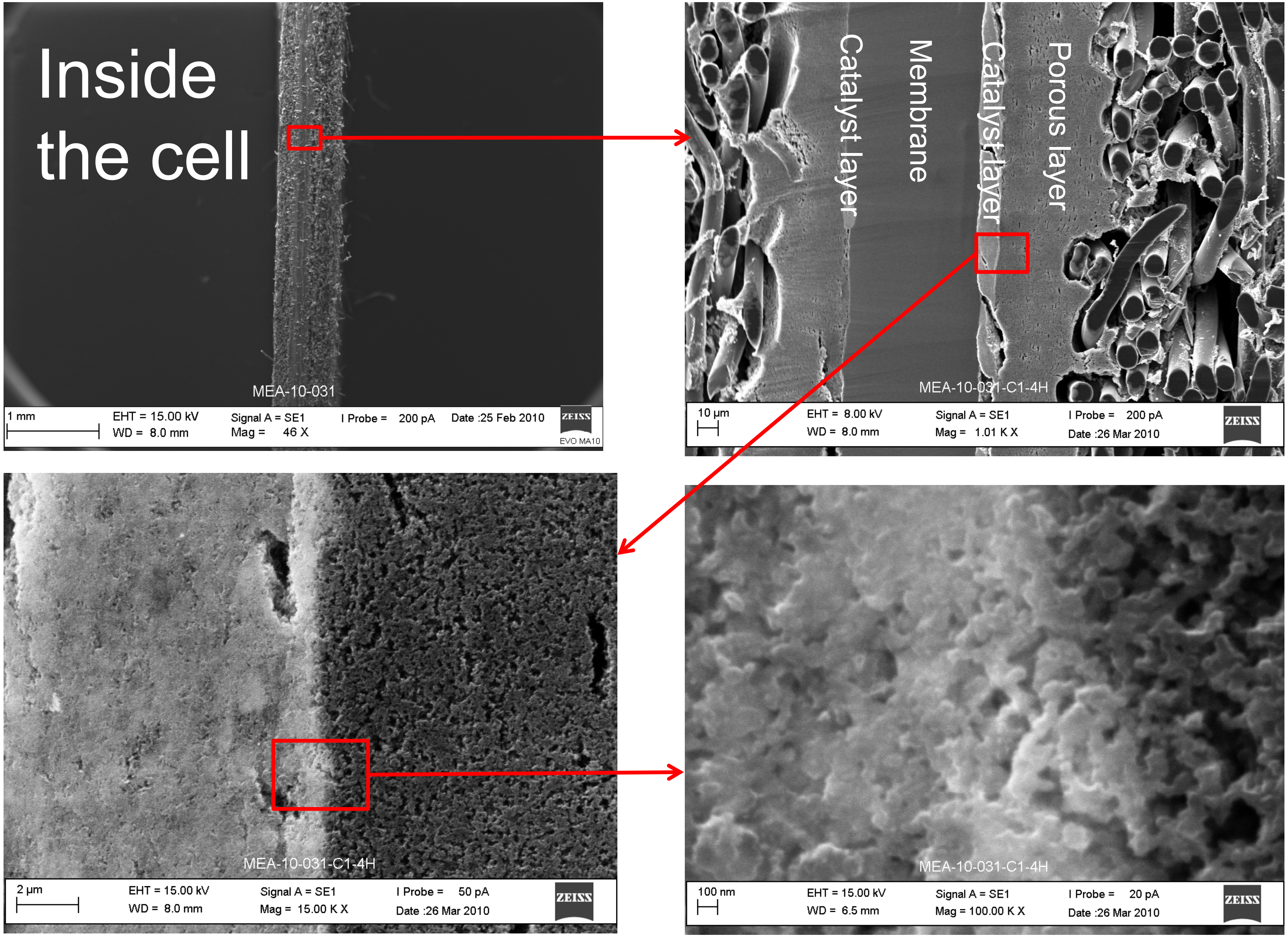
The single cell



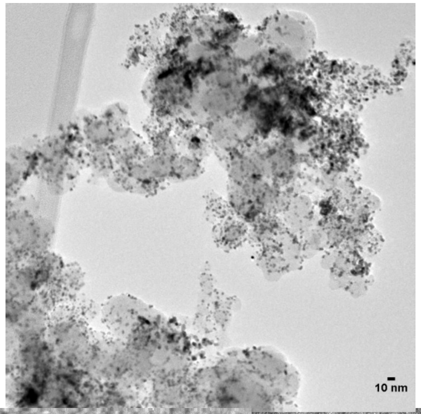
Electrode structure and transport processes



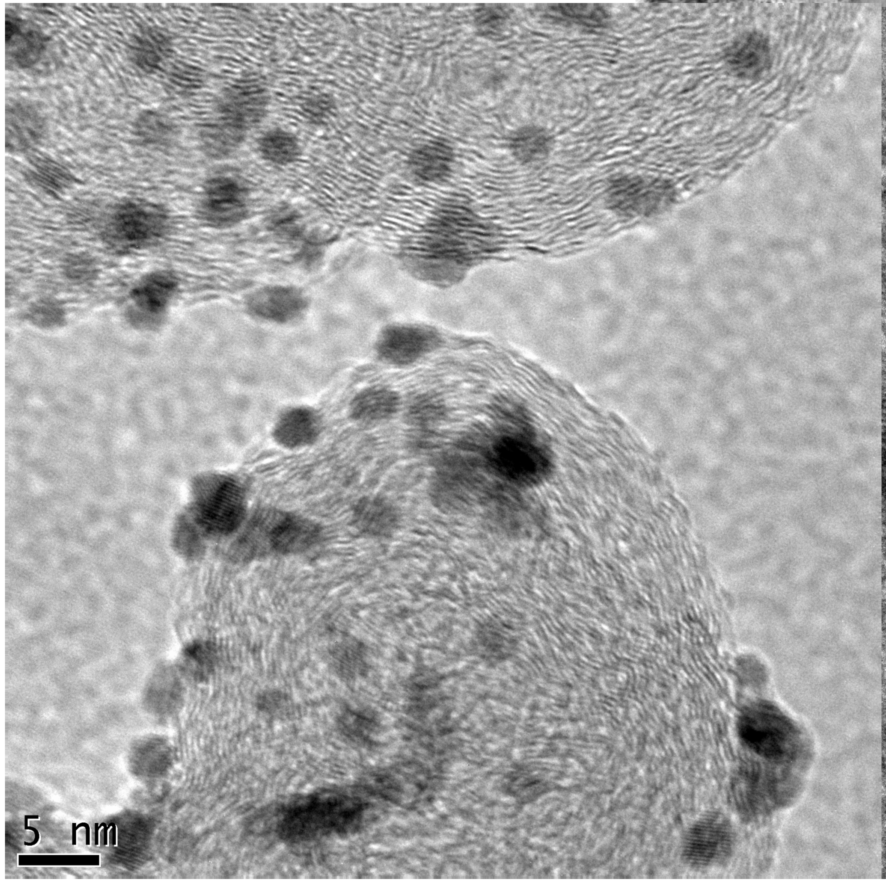
Inside the cell

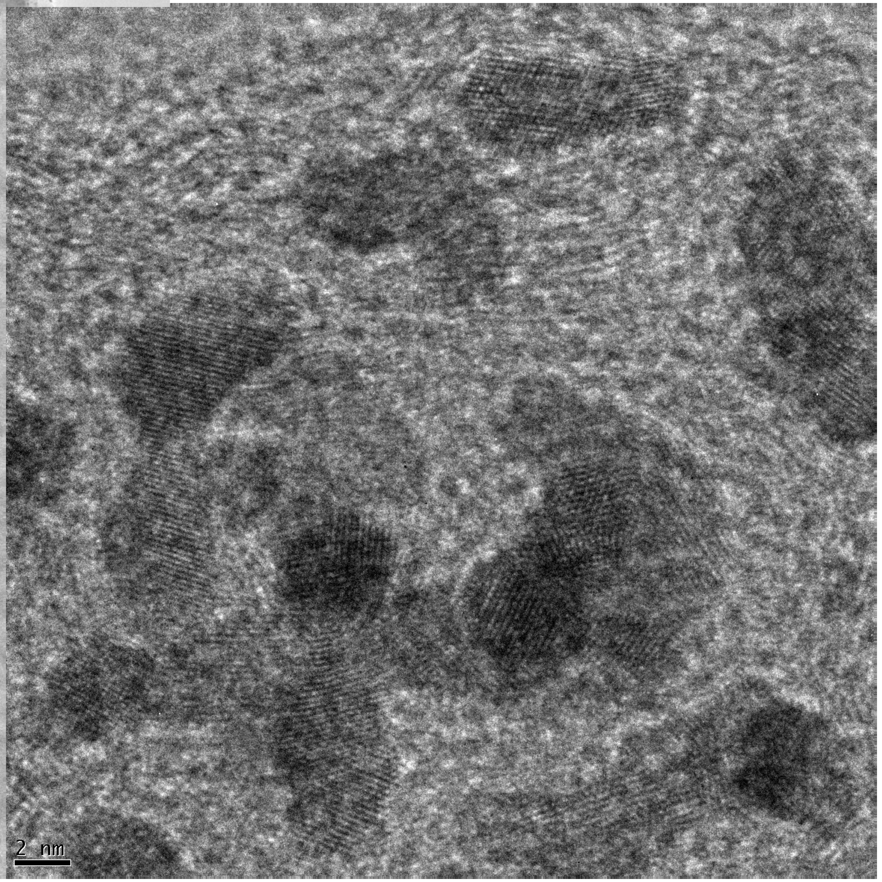


Catalyst

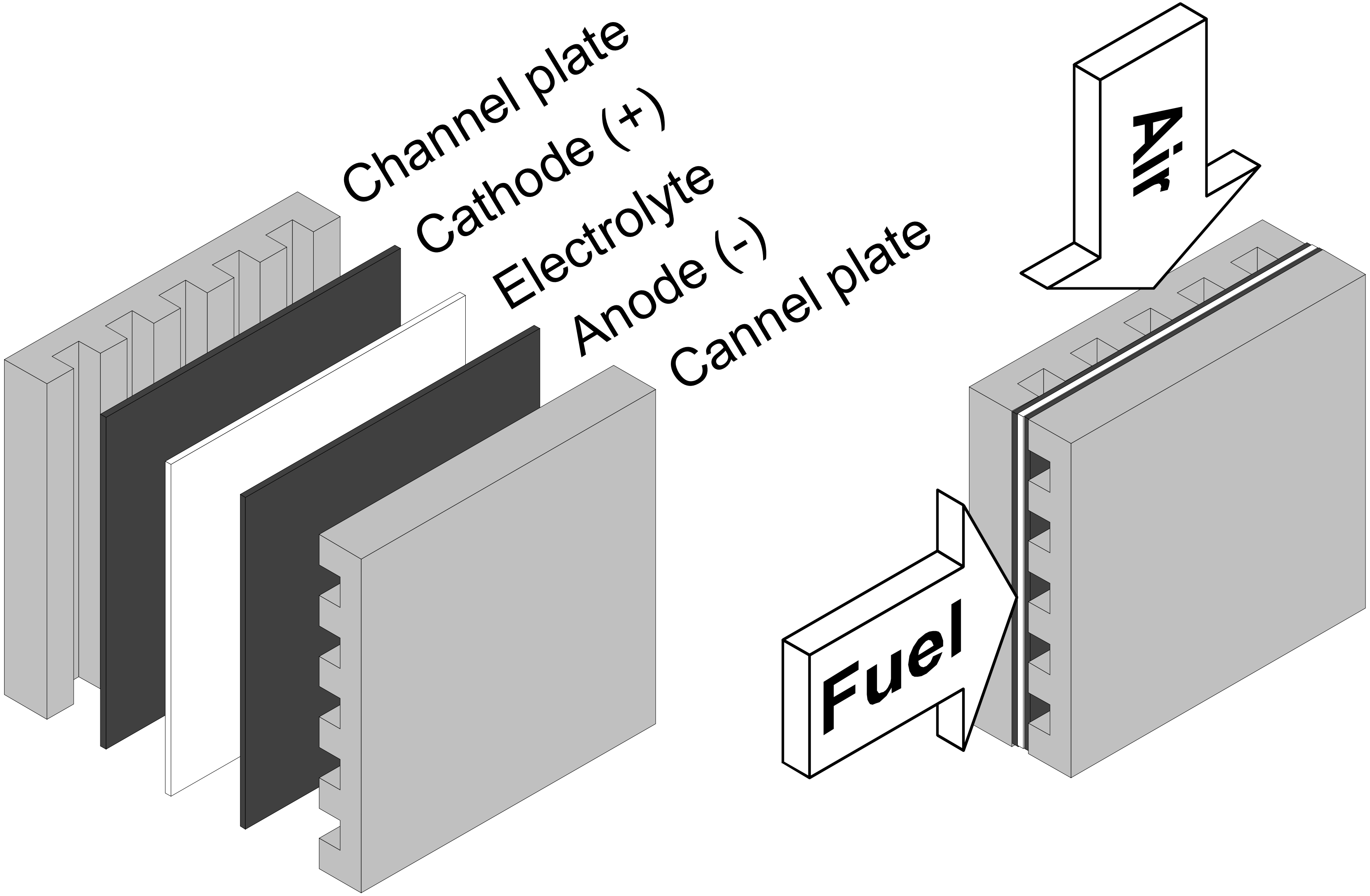


Platinum nanoparticles on carbon

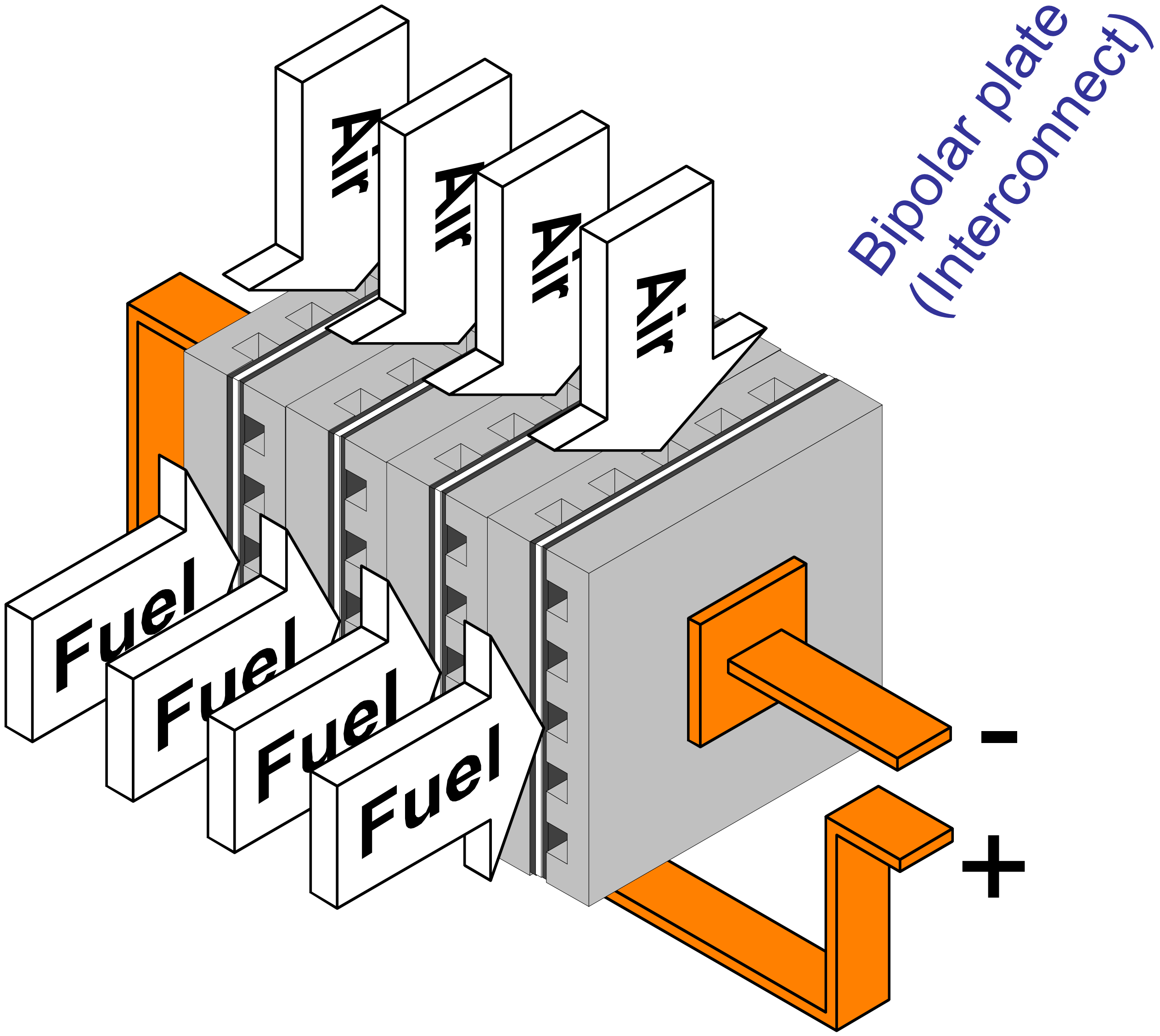


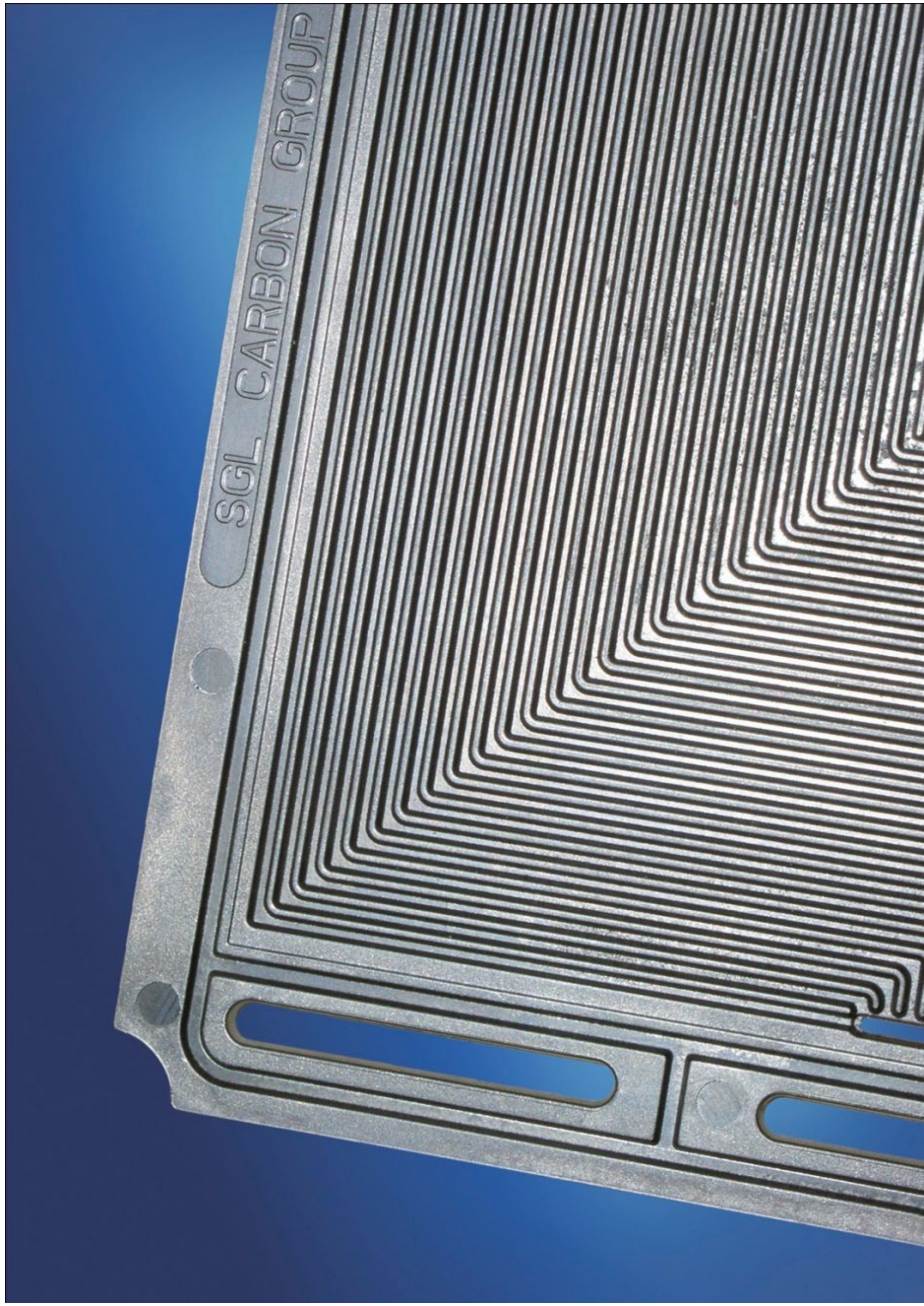


The single cell

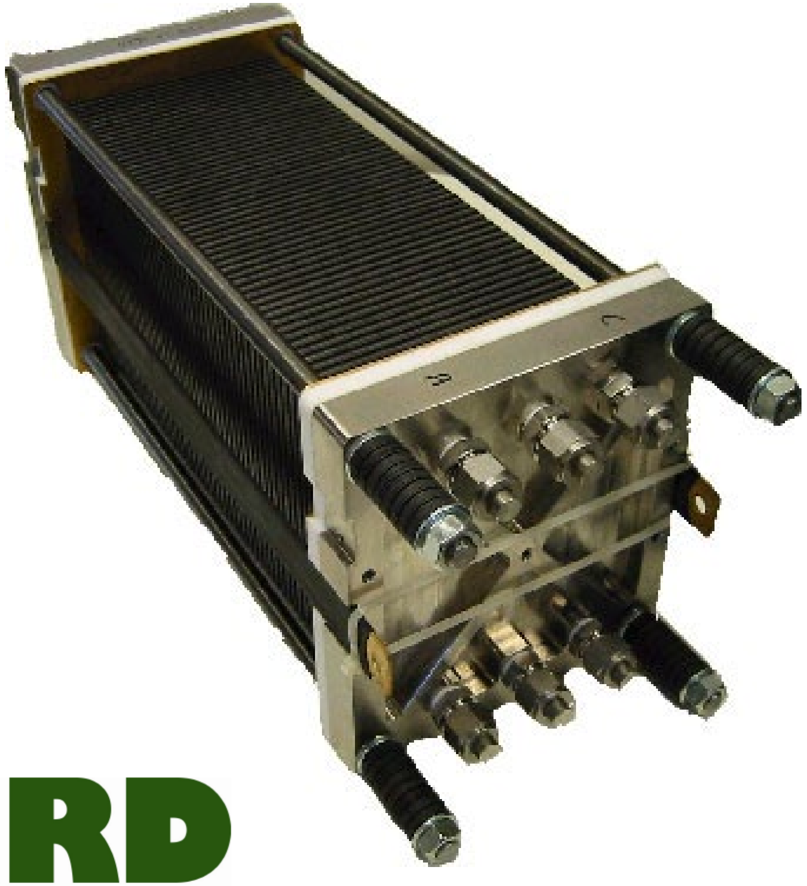


Stacking


Air
Air
Air
Air
Fuel
Fuel
Fuel
Fuel
-
+
Bipolar plate
(Interconnect)

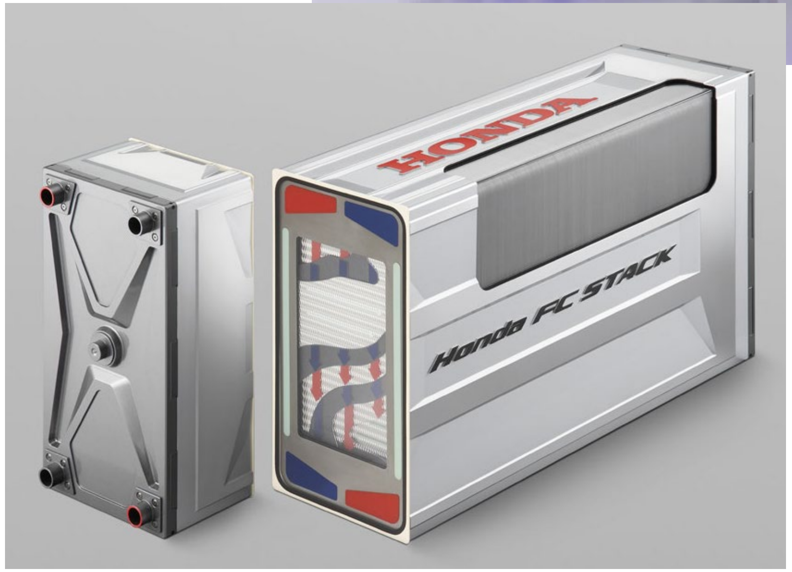

SGL CARBON GROUP

Fuel cell stacks

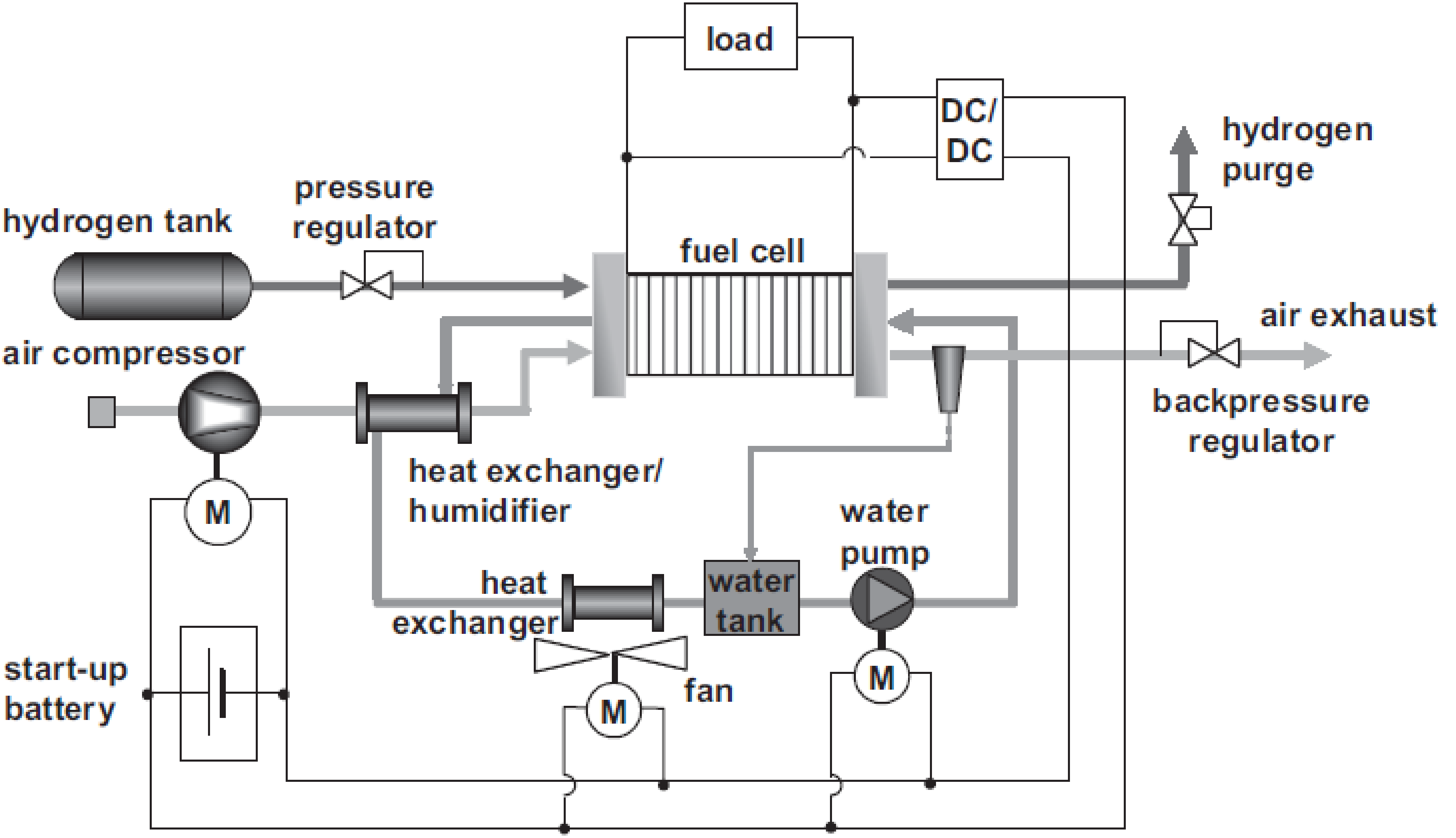


IRD
Fuel Cell Technology

Modern automotive stacks

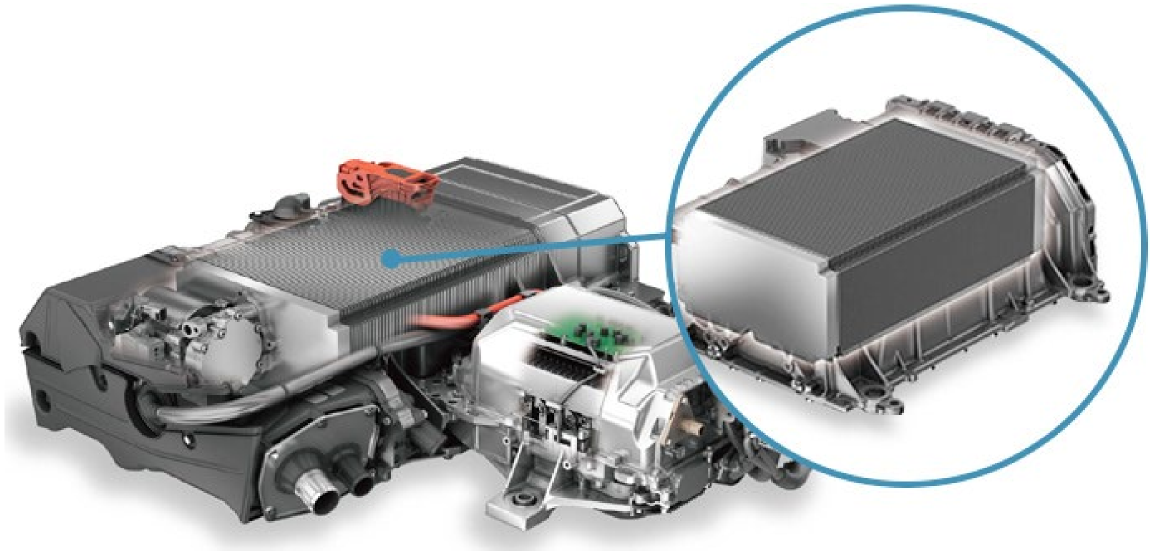


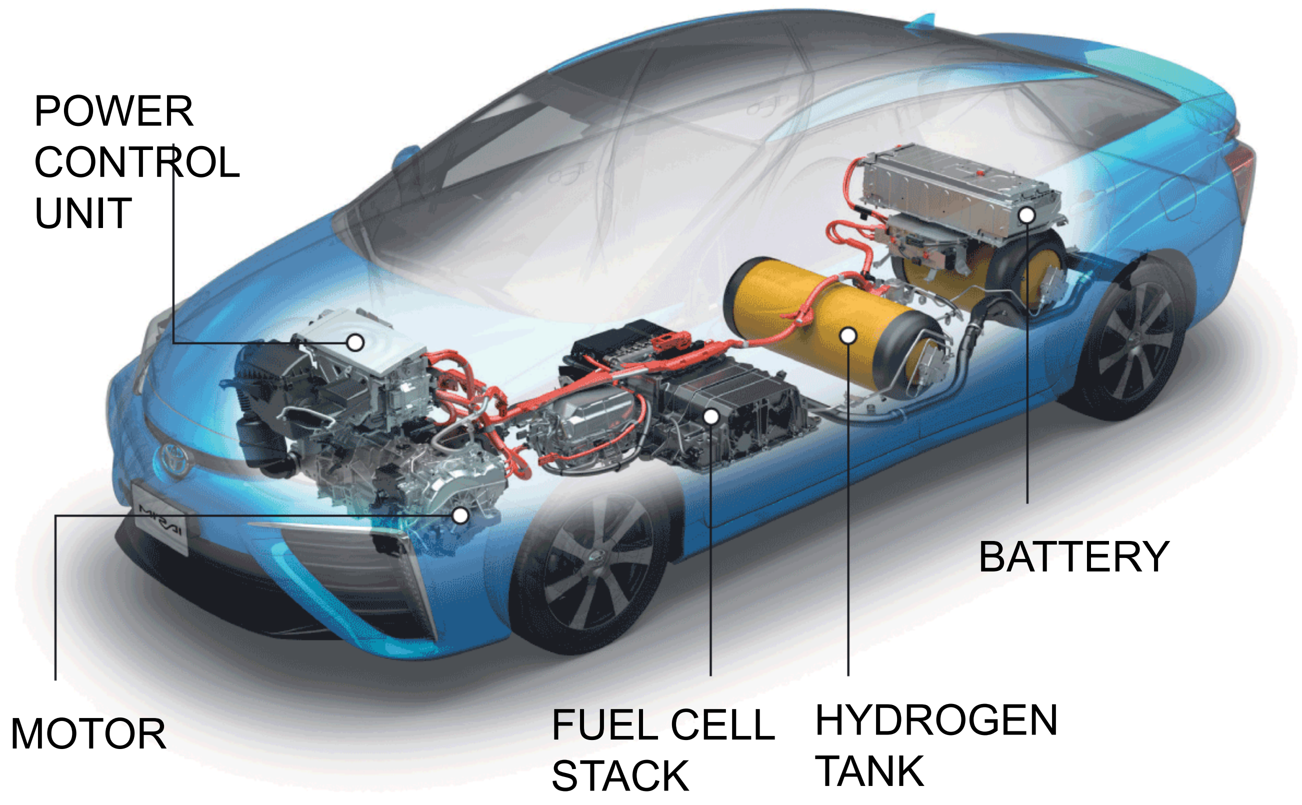
The complete system – balance of plant



PEM fuel cells : theory and practice / Frano Barbir. – 2nd ed. Academic Press

Toyota Mirai from 2015





Maximum output	114 kW (155 hp)
Volume power density	3.1 kW/L (global top level)
Number of cells in one stack	370 cells (single-line stacking)

Energy conversion by fuel cells

The available energy and maximum efficiency, η

Carnot efficiency:
(any heat engine)

$$\eta_{\text{carnot}} = \frac{T_{\text{high}} - T_{\text{low}}}{T_{\text{high}}}$$

Maximum fuel cell efficiency:

$$\eta_{\text{fuel cell}} = \frac{\Delta G(T)}{\Delta H°}$$

The available energy and maximum efficiency

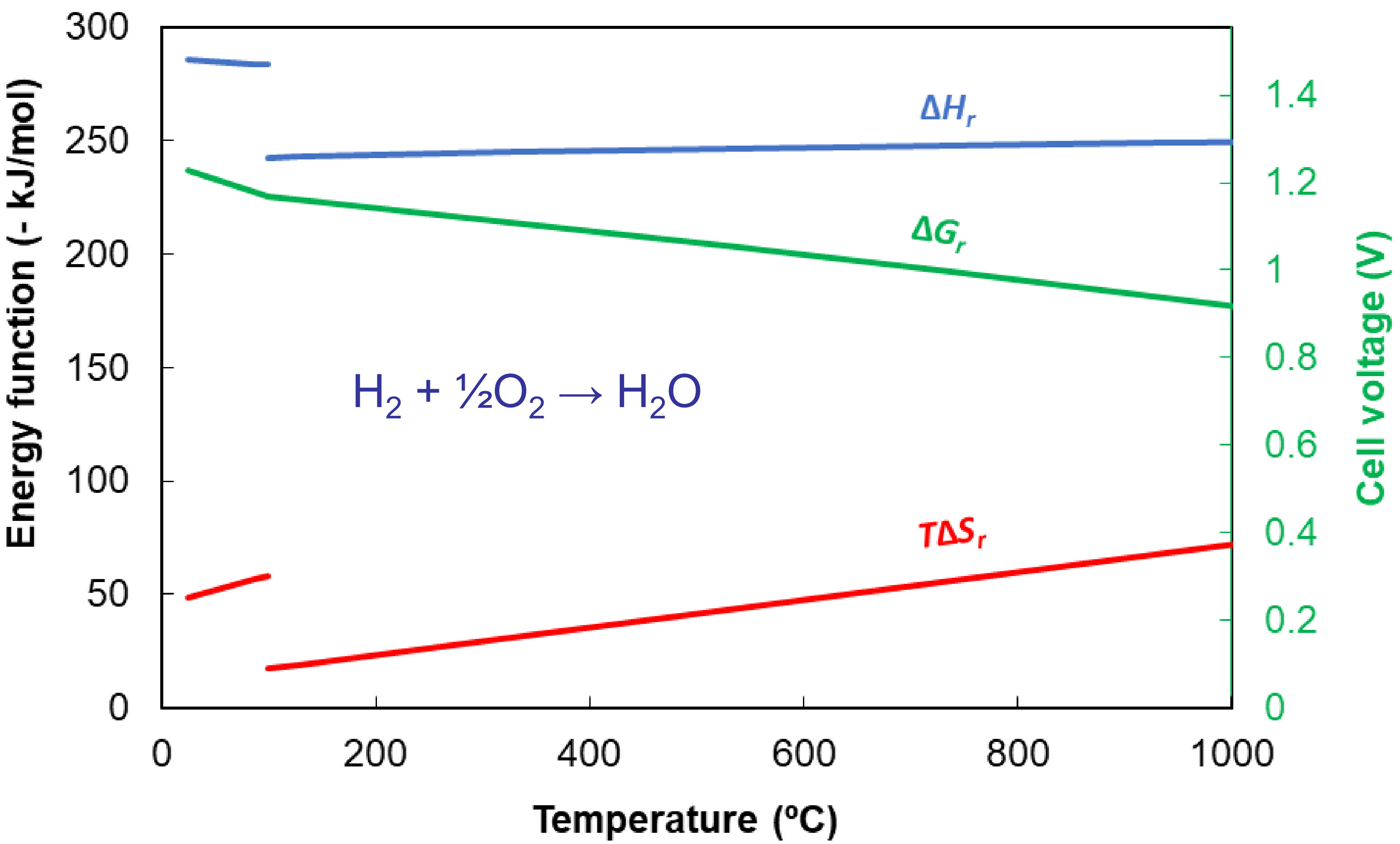
(25 °C, all at 1 bar)	HHV based	LHV based
Reaction	$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$	$H_2(g) + ½O_2(g) \rightarrow H_2O(g)$
ΔH_r^0	-285.8 kJ/mol	-241.8 kJ/mol
ΔG_r^0	-237.1 kJ/mol	-228.6 kJ/mol
η_{max} $(\Delta G_r^0/\Delta H_r^0)$	83 %	98 %

$$\left(\eta = \frac{What\ you\ get}{What\ you\ pay}\right)$$

The theoretical cell voltage

Max. cell voltage: $E = \frac{-\Delta G}{nF} = 1.23\text{V}$ (at 25ºC, 1 bar)

ΔG: Gibbs Free Energy
n: No. of electrons in reaction
F: Faraday's constant (the charge of 1 mole electrons, 96,485 C mol^{-1})



The maximum work efficiency

$$\left(\eta = \frac{What\ you\ get}{What\ you\ pay}\right)$$

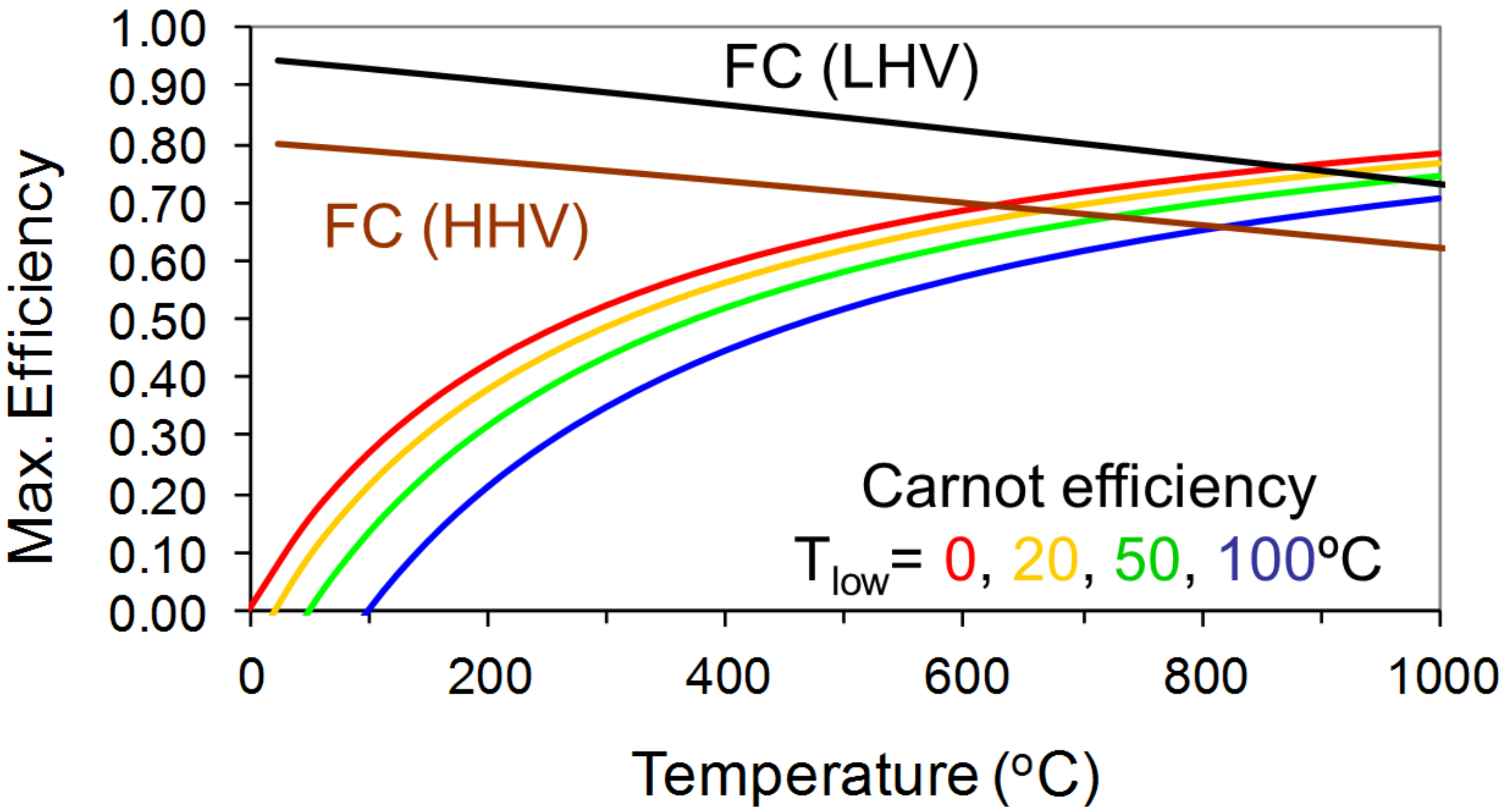
Carnot efficiency:
(any heat driven engine)

$$\eta_{carnot} = \frac{T_h - T_c}{T_h}$$

Maximum fuel cell efficiency:

$$\eta_{FC} = \frac{\Delta G^o(T)}{\Delta H^o}$$

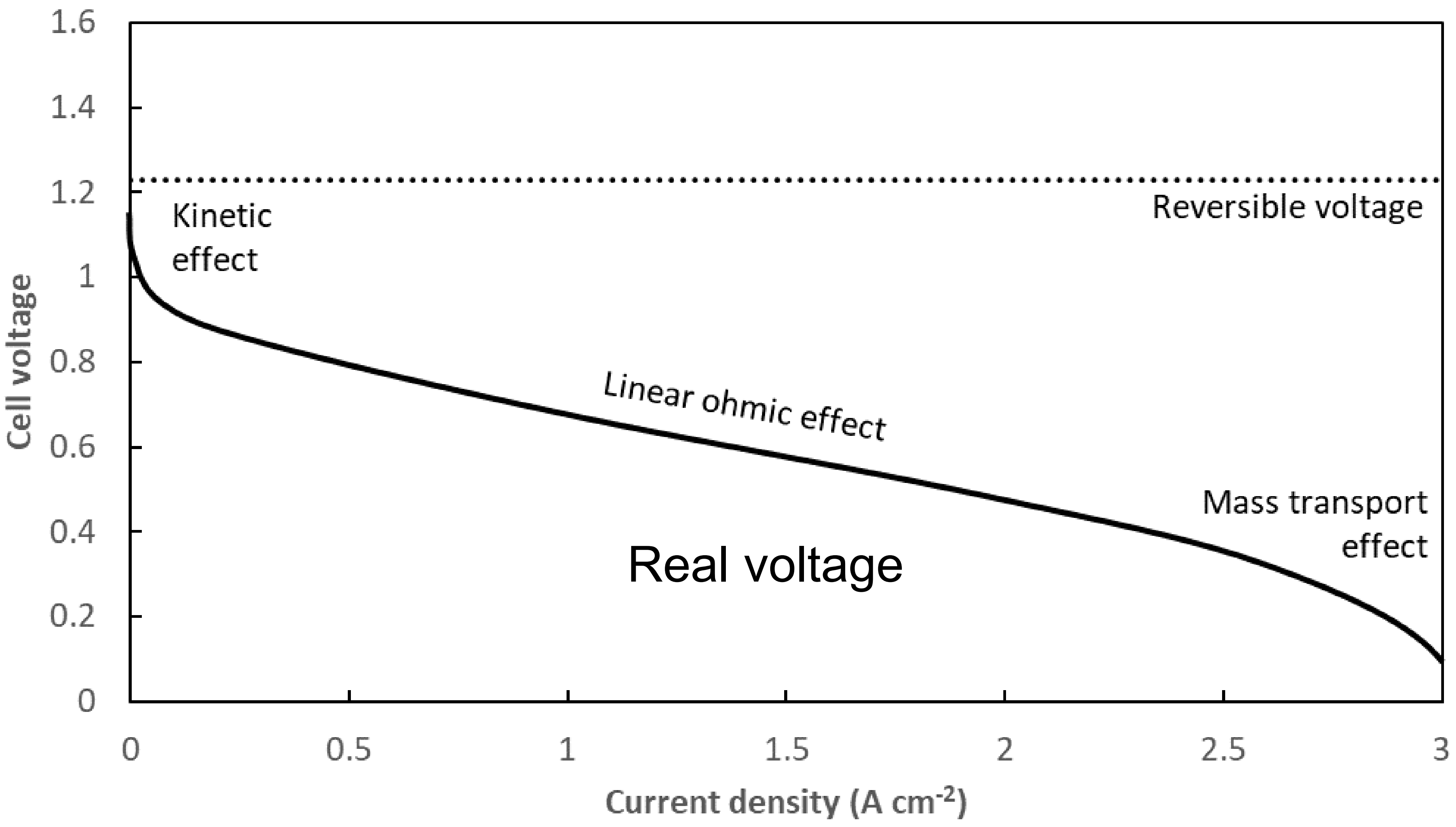
ΔG is maximum work related to a fuel



Thermodynamics versus kinetics

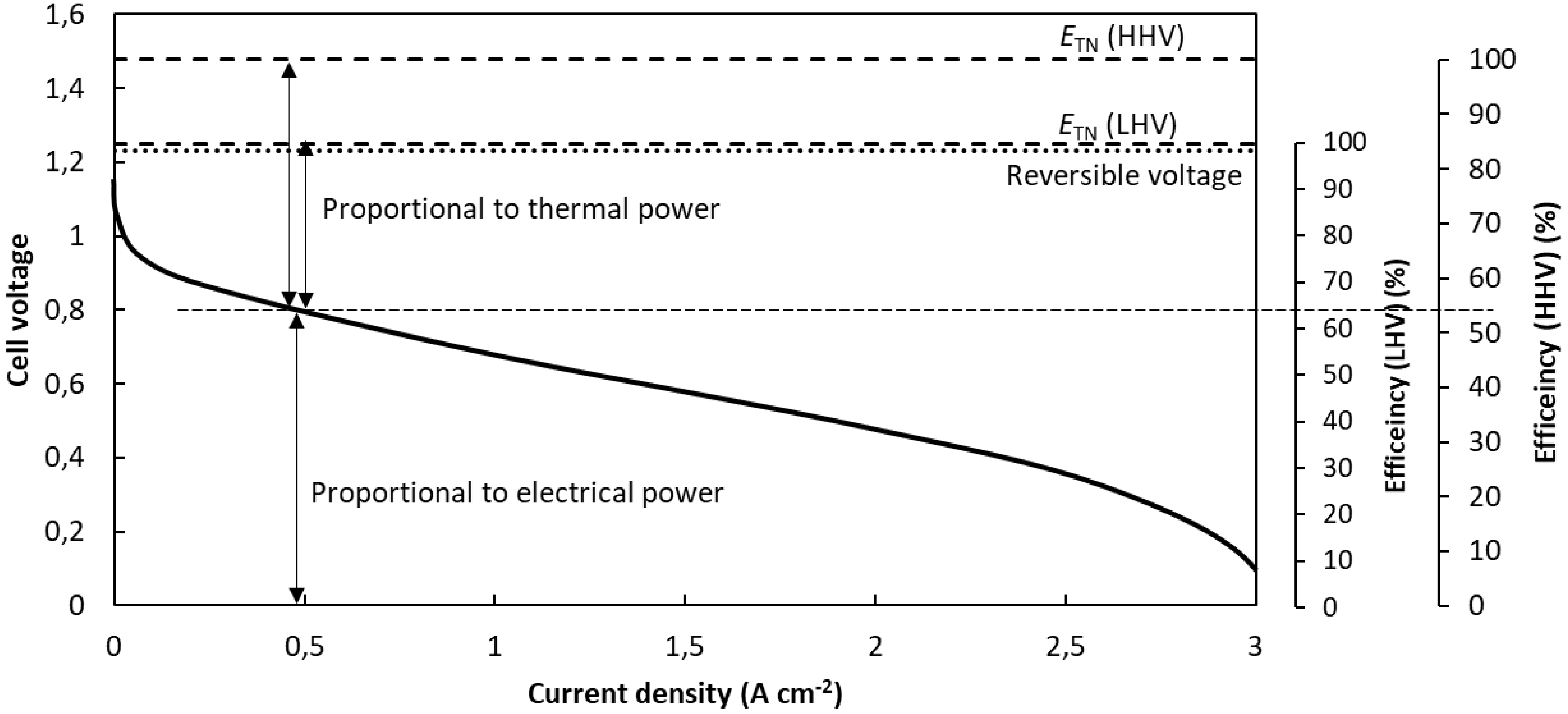
Thermodynamics	Kinetics
• Ideal case • The most efficient physically possible • No resistance anywhere • No demand for high rate • Infinitely slow • Reversible processes	• The real world • Processes slowed by resistance • Finite reaction rates needed • Incomplete reaction or side reactions • Irreversible processes
What is ultimately possible theoretically	What is possible in reality
Thermodynamics can only be improved by changing the chemistry, the temperature or the gas pressures	Kinetics can be improved by a proper catalyst, increased gas pressure and temperature

The fuel cell polarization curve (real cell voltages)



Efficiency and heat evolved

$$E_{whatever} = \frac{Energy}{Charge} = \frac{HHV\ or\ LHV\ or\ \Delta G\ \ or\ \Delta H}{nF}$$



Types of fuel cells

Types of fuel cells

Type	Abrev	Temp	Electrolyte	Ion conducted
		Low temperature systems		
Alkaline FC	AFC	60-80°C	aq. KOH	OH^-
Polymer FC	**PEMFC**	**60- 80°C**	**Polymer**	**H^+**
Direct methanol FC	DMFC	60- 80°C	Polymer	H^+
Phosphoric acid FC	PAFC	200°C	H_3PO_4	H^+
		High temperature systems		
Molten carbonate FC	MCFC	650°C	Molten salt	CO_3^{2-} (carbonate)
Solid oxide FC	**SOFC**	**700-900°C**	**Ceramic**	**O^{2-}**

PEMFC

Proton Exchange Membrane Fuel Cell

or

Polymer Electrolyte Membrane Fuel Cell

PEM fuel cell

Cathode: Platinum on carbon

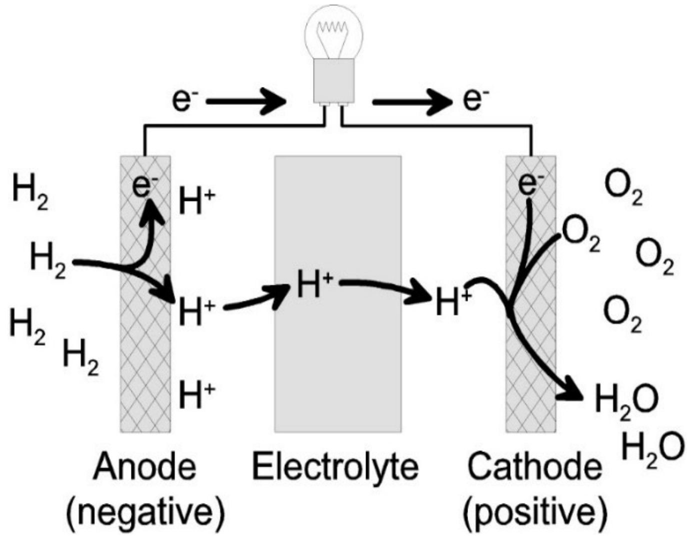
$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Electrolyte: H^+ conducting polymer

Perfluorosulfonic acid (e.g., Nafion)

Anode: Platinum on carbon

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



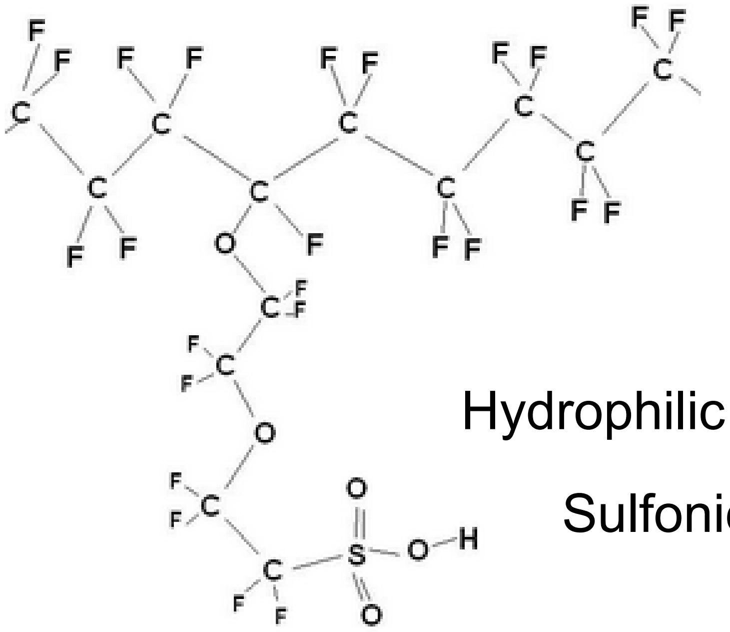
Advantages:

- High power density
- Good dynamic capability
- Well-established
- Most common type

Disadvantages:

- Depends on Pt for the catalysts
- Water management
- Fuel crossover
- Cost

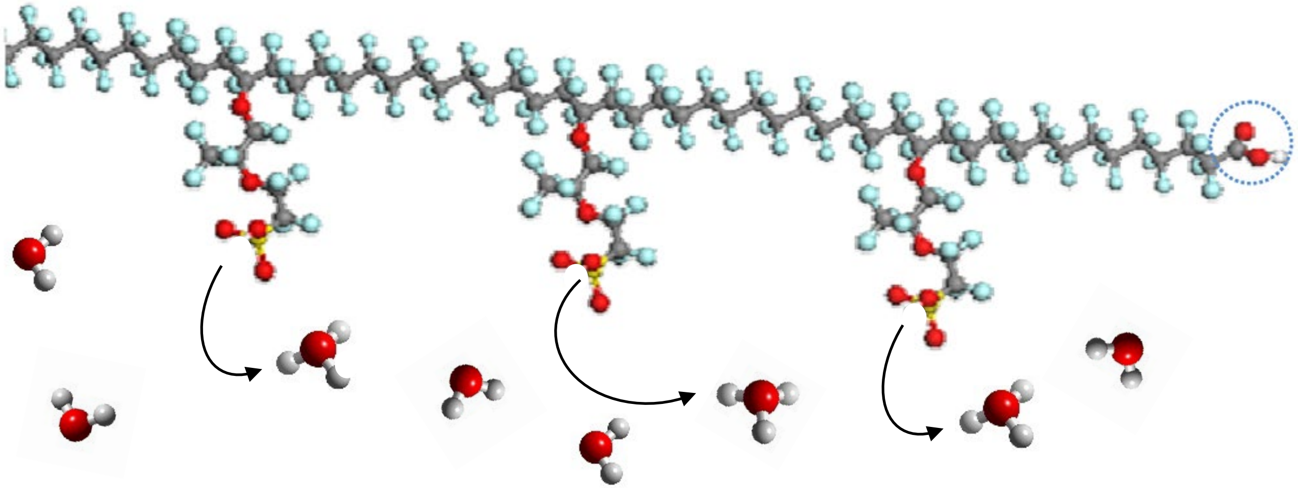
Proton conduction in polymer



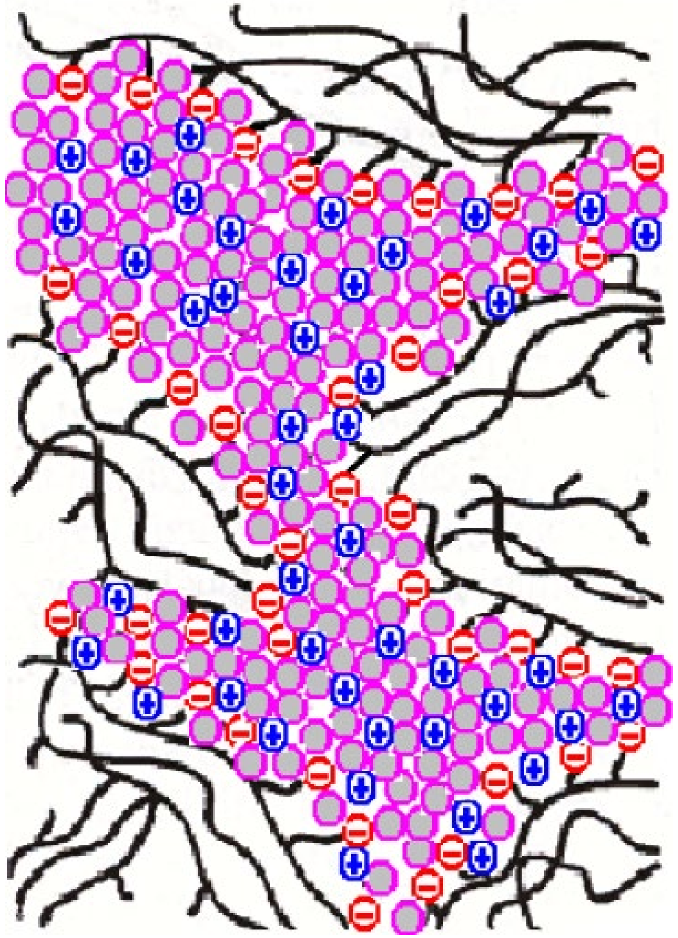
Hydrophobic backbone

Hydrophilic side chains

Sulfonic acid



Hydrophobic backbone



Perfluorosulfonic acid, PFSA

Early milestones with PEMFC

2002

NECAR 5

DaimlerChrysler

First FCV across USA

San Francisco -
Washington, D.C.

2004

HydroGen3

GM/Opel

10,000 km in Europe

Direct methanol fuel cell (DMFC)

(*A special PEMFC*)

Anode: $CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$

Cathode: $1.5O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

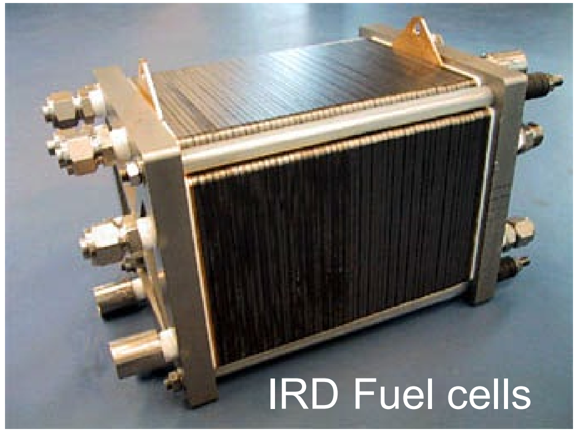
Electrolyte: Ion conducting polymer (e.g., Nafion)
Catalysts: Noble metals (Pt and Pt-Ru alloys)

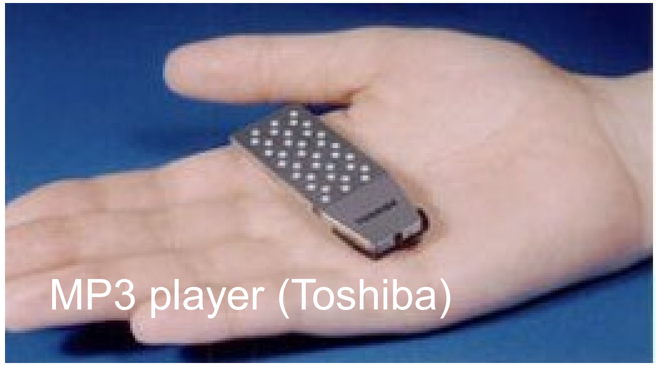
Advantages:

- Liquid fuel
- Easy and fast fuelling
- Easy and compact fuel storage

Disadvantages:

- Low efficiency
- Fuel crossover
- Expensive catalyst (10 x Pt amount)
- Methanol poisonous





SOFC

Solid Oxide Fuel Cell

Solid oxide fuel cell (SOFC)

Cathode: Ceramic: e.g., $La_{1-x}Sr_xMnO_3$ (conductive, catalytic)

$O_2 + 2e^- \rightarrow O^{2-}$

Electrolyte: Ceramic: Yttrium stabilized zirconia (YSZ)

O^{2-} conductor (700-900ºC)

Anode: Ceramic: YSZ with nickel

$O^{2-} + H_2 \rightarrow H_2O + 2e^-$

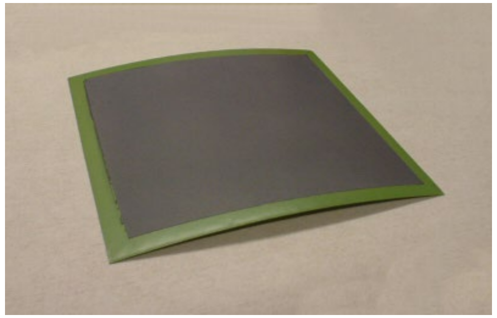
Sealing: Soft glass

Advantages:

- High efficiency
- Many fuels (H_2, CO, organics)
- High value of heat

Disadvantages:

- Still under development
- Difficult to manufacture large cells
- Not suited for start/stop



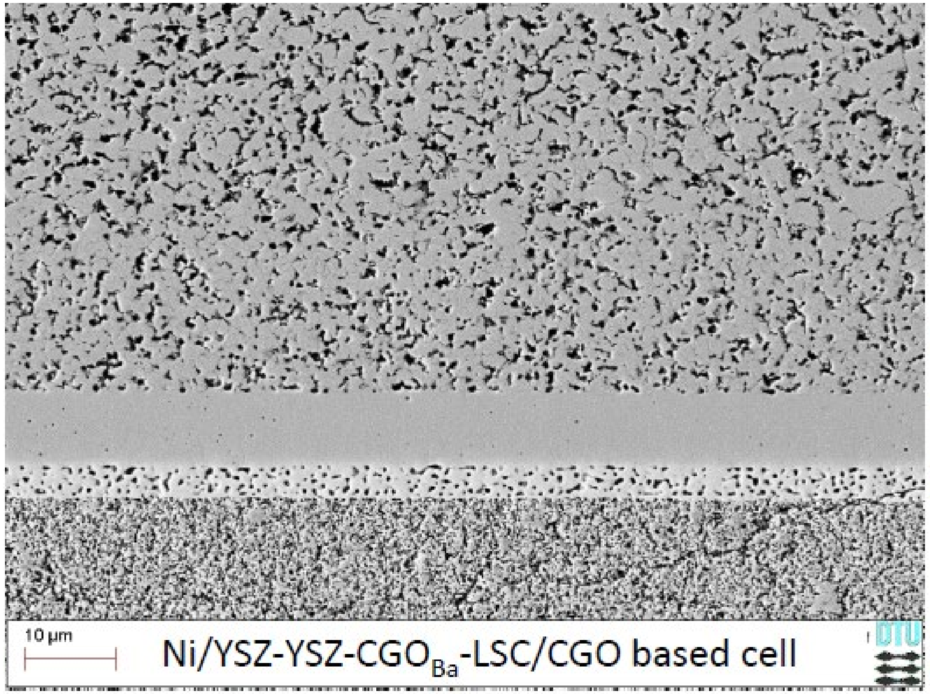
Single cell DTU

20 kW power unit

TOPSOE FUEL CELL
RETHINKING ENERGY

Solid oxide fuel cell (SOFC)

Made of advanced ceramic materials



Ni/YSZ support layer

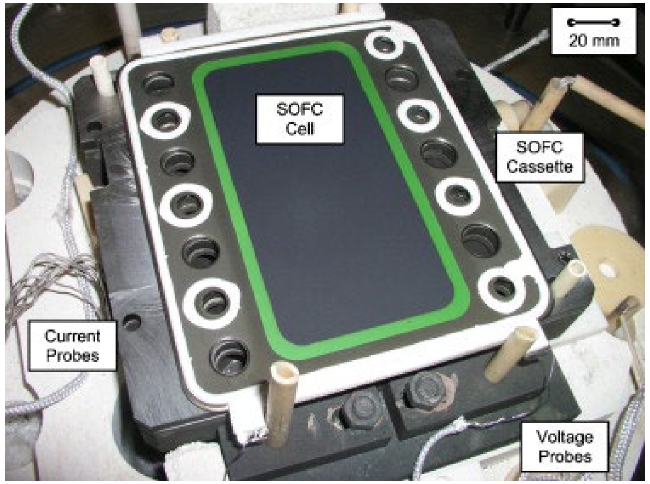
Ni/YSZ electrode

YSZ electrolyte

CGO barrier layer

LSC/CGO electrode

Ref. Brodersen, Hauch, Chen and Hjelm, Patent no.: WO201702935 (2017)



Research Center Jülich

AFC: Alkaline Fuel Cell

PAFC: Phosphoric Acid Fuel Cell

MCFC: Molten Carbonate Fuel Cell

Alkaline fuel cell (AFC)

Cathode: Pt, Ag or metal oxides on Ni

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

Electrolyte: Aqueous KOH (ca. 30 w%)

Anode: Pt or Ni on Ni

$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Advantages:

- Less expensive materials
  Non-noble catalysts (Ni, oxides, others)
- Lower O_2 overvoltage
- Fast start-up

Disadvantages:

- Carbonization by CO_2. CO_2 from air:
  $CO_2 + 2K^+ + 2OH^- \rightarrow K_2CO_3$

Phosphoric acid fuel cell (PAFC)

Cathode: Pt on carbon

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

Electrolyte: Phosphoric acid (H_3PO_4)

in a SiC (Silicon carbide) matrix (200ºC)

Anode: Pt on carbon

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

Advantages:

- Early development
- Tolerance to CO (a few pct.) from methane reformer

Disadvantages:

- High O_2 overvoltage (moderate efficiency)
- Liquid electrolyte
- Acid depletion

Early commercial fuel cell units

Combined heat and power

200 – 400 kW units by UTC running on natural gas via reformer

Molten carbonate fuel cell (MCFC)

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

Electrolyte: Molten salt, Li-Na-K carbonate
CO_3^{2-} conductor (650ºC)

Anode: Ni-Cr or Ni-Al alloy
$CO_3^{2-} + H_2 \rightarrow H_2O + CO_2 + 2e^-$

Advantages:
- Many fuels (H_2, CO, organics)
- High value of heat

Disadvantages:
- CO_2 circuit
- Corrosive electrolyte
- Not suited for start/stop
- Only large systems

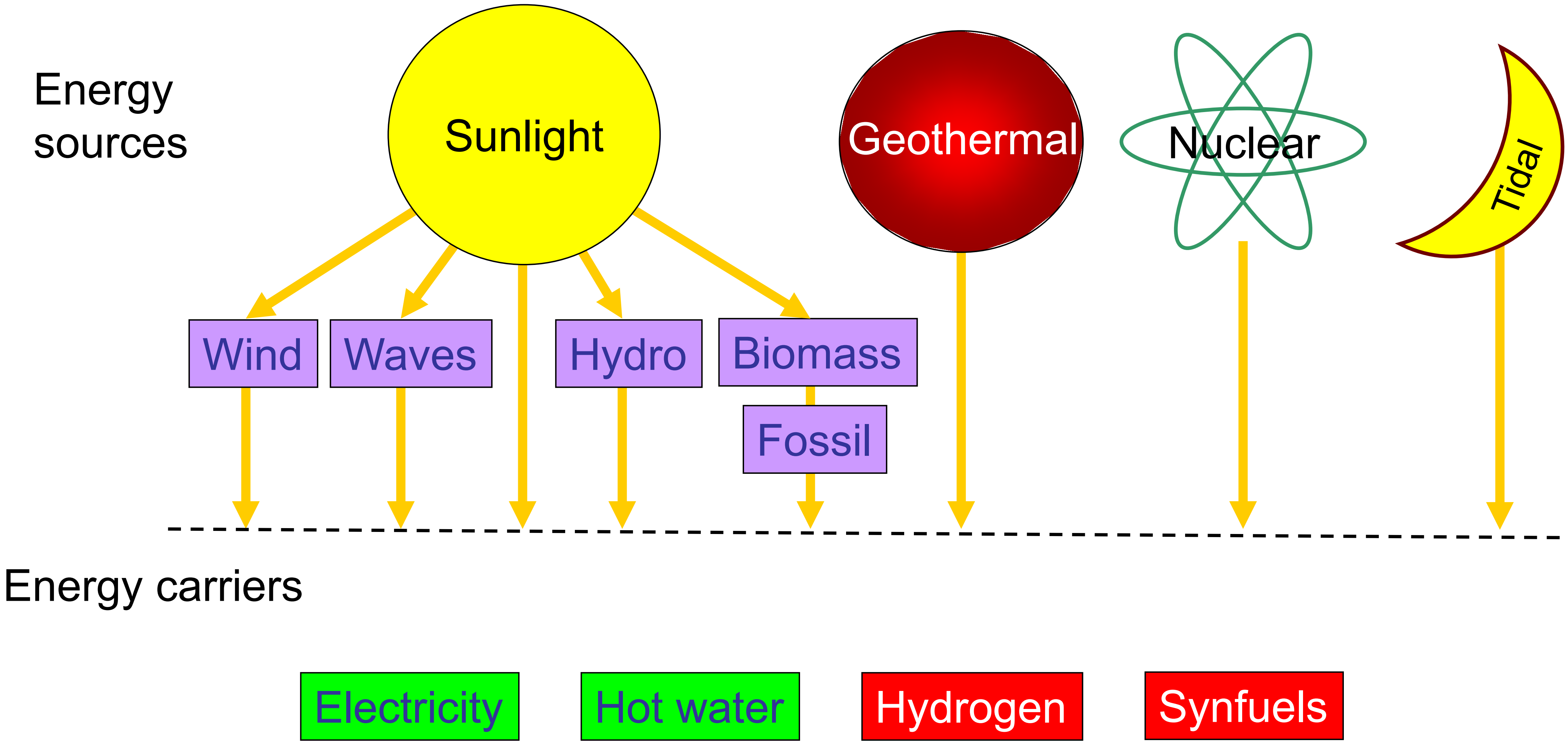
Applications by type

Type	Typical applications	Typical power rating	Fuel	Share
AFC	Space or applications with pure oxygen. Potential for Pt elimination	1-100 kW	H_2	Very limited
PEMFC	Transport and portable applications, auxiliary power + micro-CHP	1 W – 200 kW	H_2	Most common fuel cell. Increasing in number
DMFC	Portable, battery chargers	< 1 kW	Methanol	Very limited
PAFC	Stationary CHP on natural gas	100-400 kW	H_2, CH_4 (by reforming)	Have peaked Larger stationary CHP Decreasing importance
MCFC	Power plants	1-10 MW	H_2, CO, CH_4	Limited
SOFC	Medium to large scale. Stationary, CHP. Potential for powering plants and ships	1 kW – 1 MW	H_2, CO, CH_4, NH_3	Early markets, Increasing

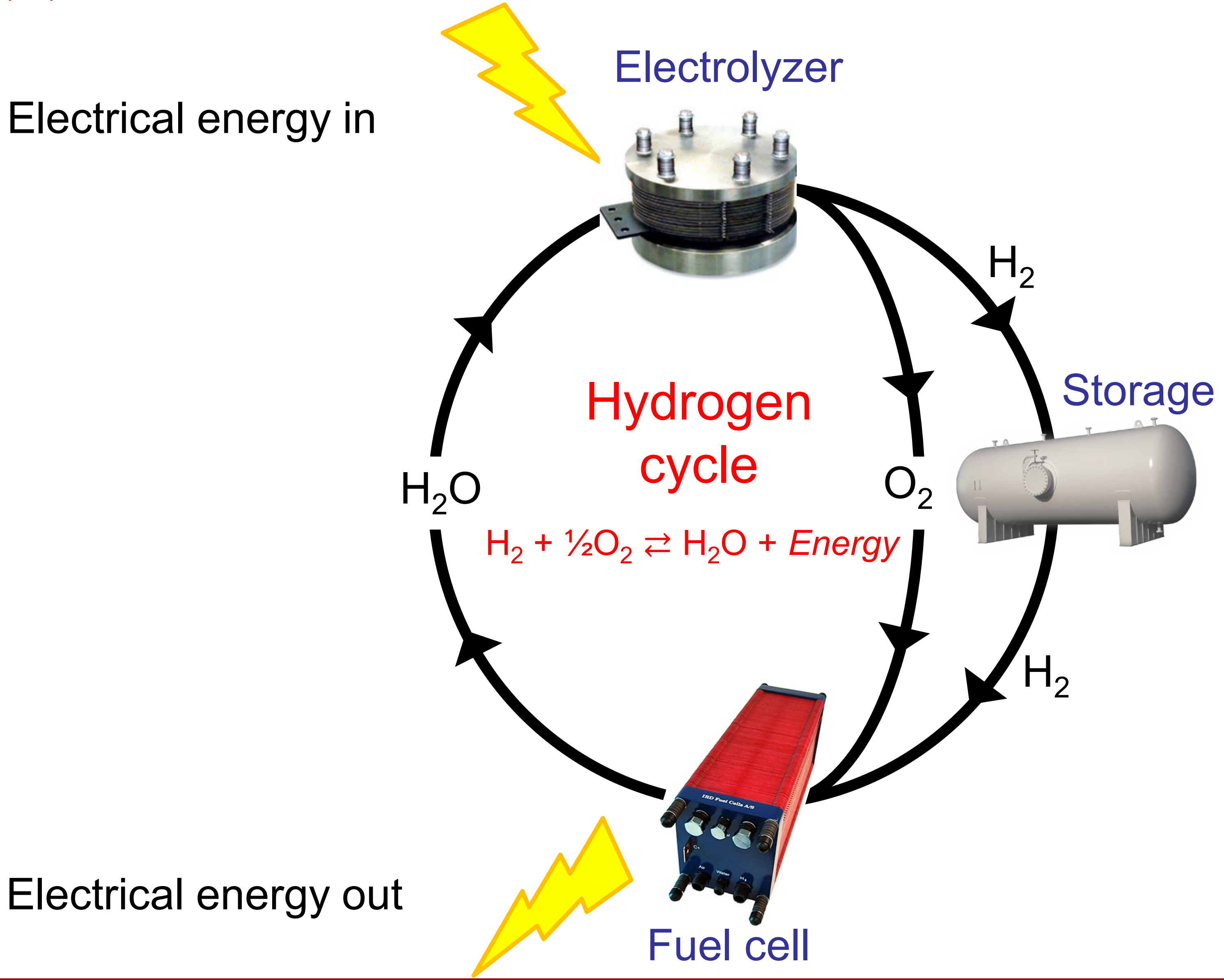
CHP: combined heat and power

Hydrogen as an energy carrier

Hydrogen - another energy carrier



Hydrogen as an energy carrier

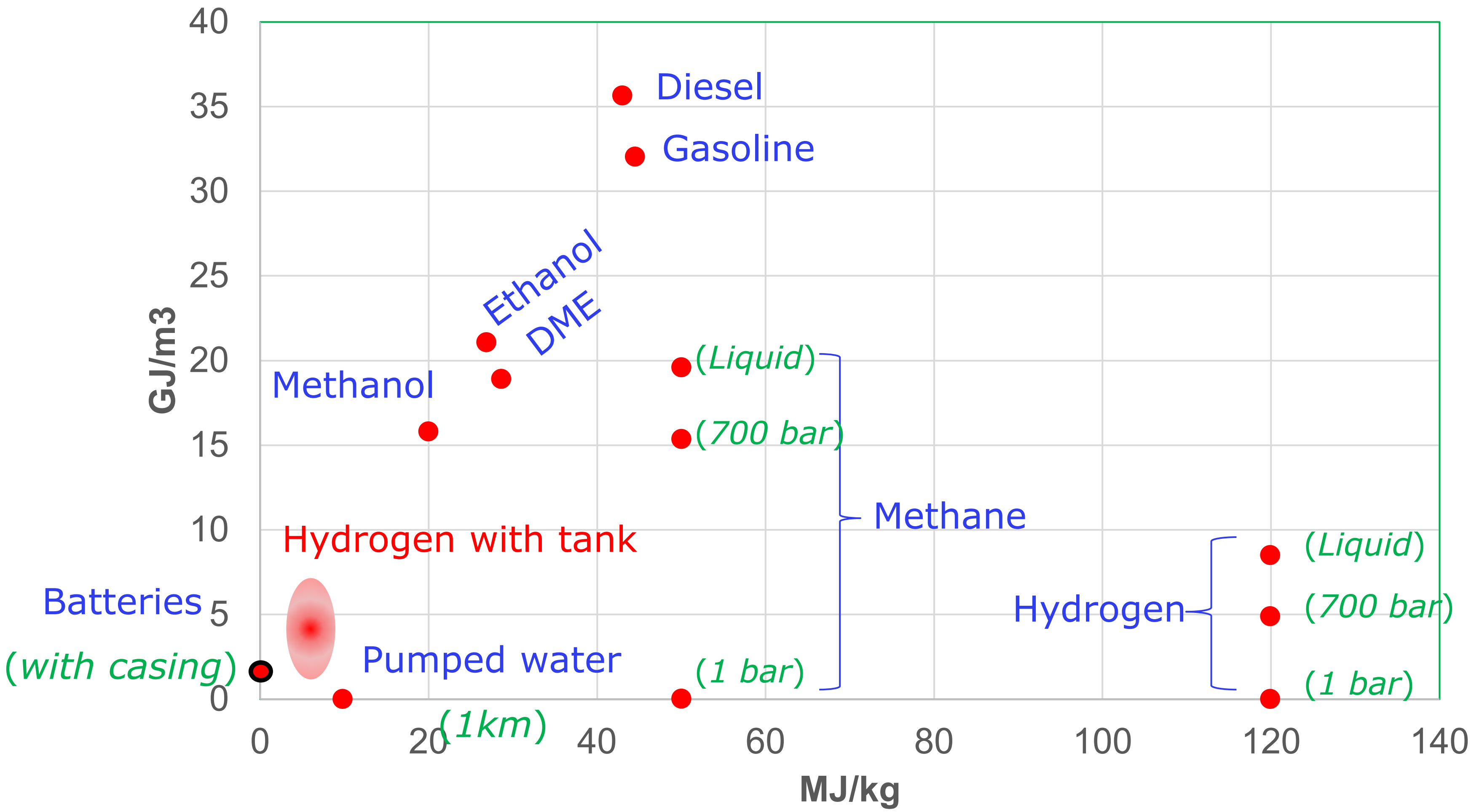


Hydrogen

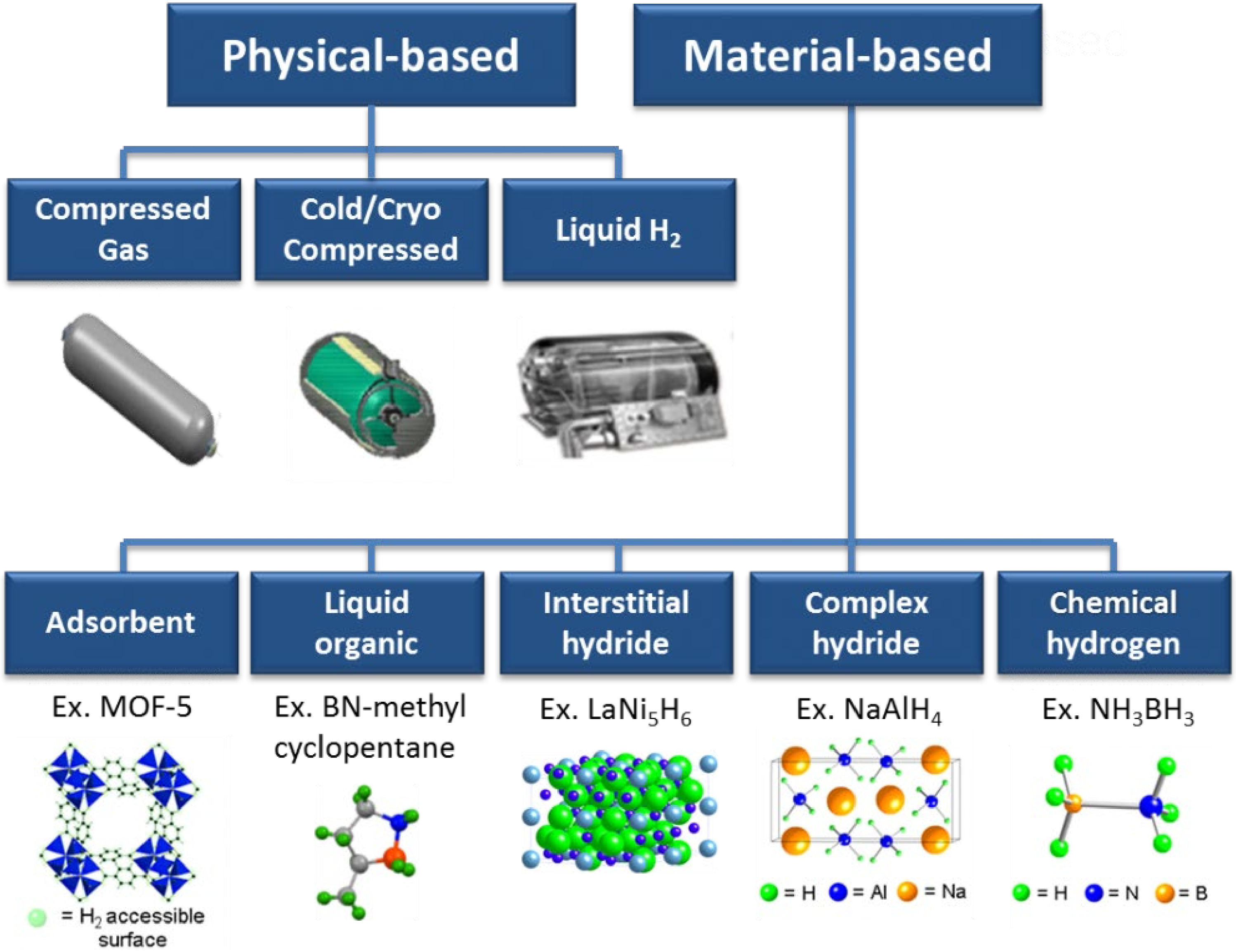
- The lightest fuel (hmm…)
- Highly abundant
- No geographic limitations
- Non-toxic
- Non-corrosive
- Zero emission
- Simple production
- Well described
- The hydrogen society

Hydrogen storage

Energy storage density (without container)



Ways of storing hydrogen



http://energy.gov/eere/fuelcells/hydrogen-storage

Ways of storing hydrogen

Compressed	Liquid	Adsorbed	Absorbed	Chemical compounds
200-700 bar	20 K	large surface	Metal hydrides	Organics, NH_3 Metal hydrides

Physical storage

Easy access

Chemical storage

Decomposition

Reforming

Compression, fibre tanks

Steel containers (standard 200 bar)

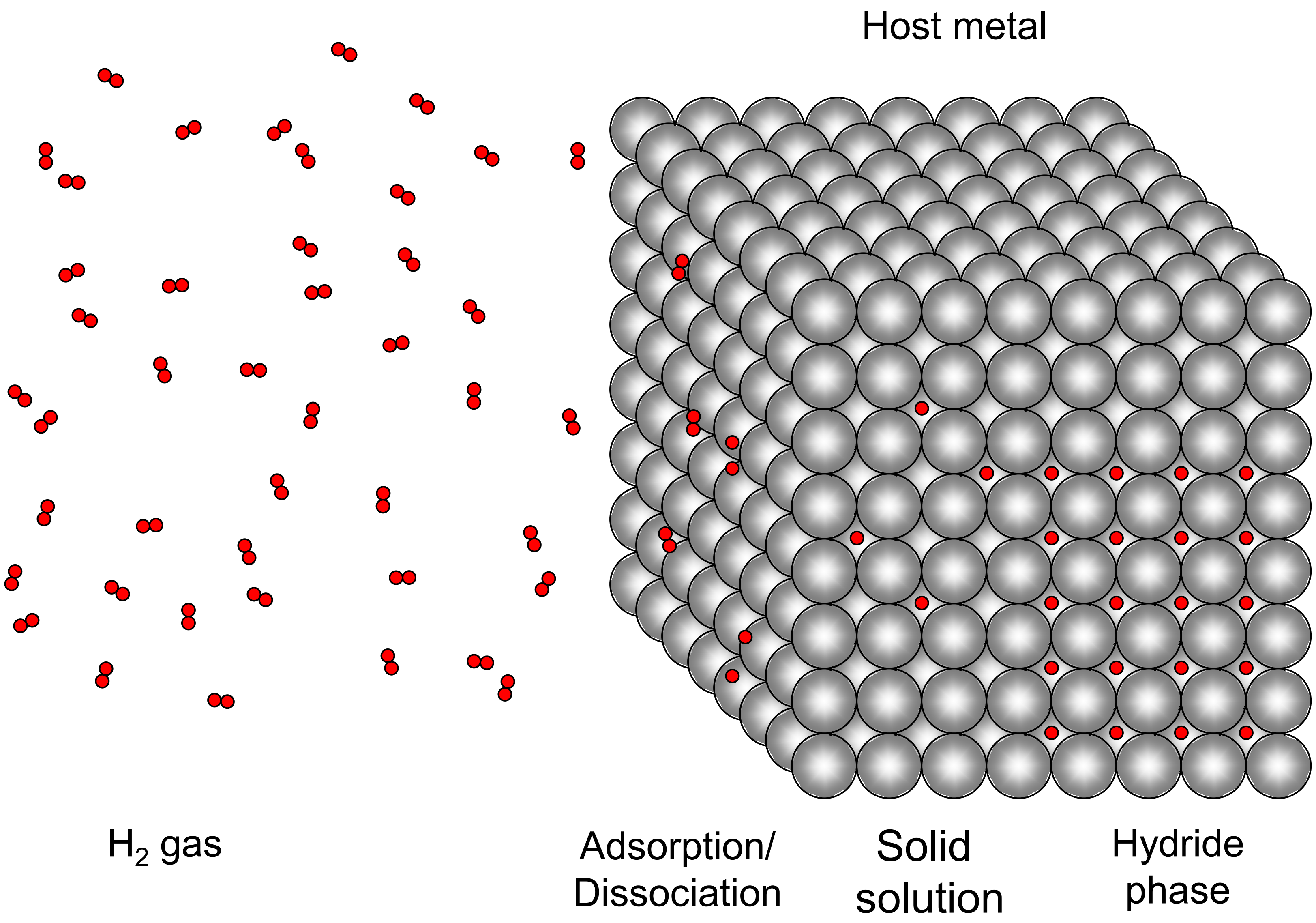
Fibre composites (up to 700 bar - or more)

Liquid hydrogen

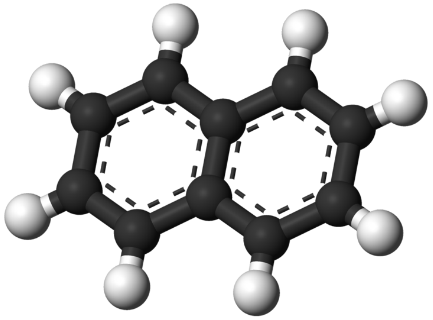
Advantages
Denser that compressed gas
Liquid fuelling
Keeps cold by evaporation

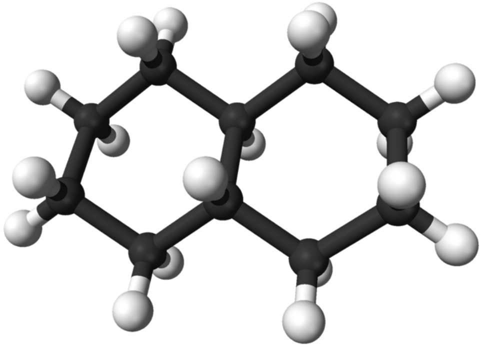
Disadvantages
Expensive
Energy to cooling and condensation
Self discharge
Safety

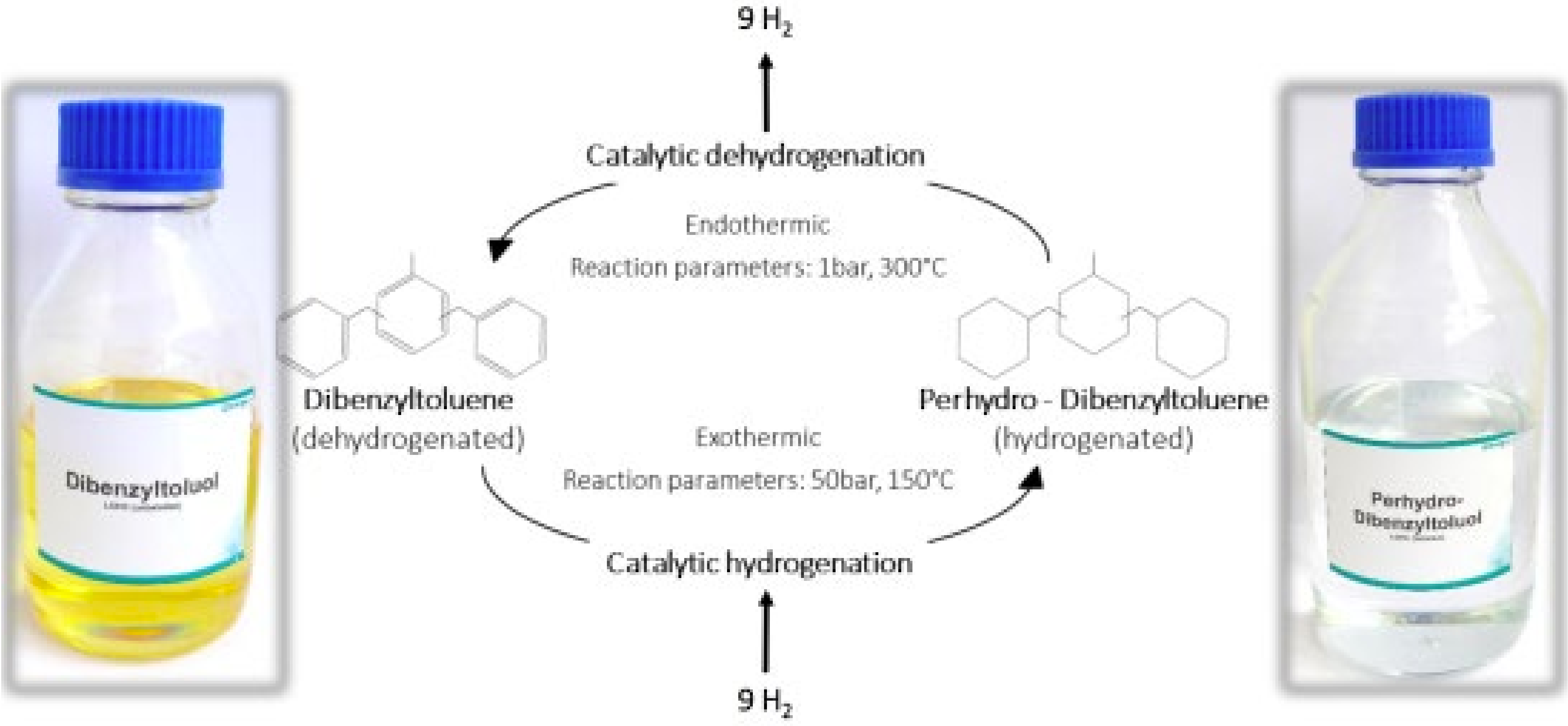
Hydride formation (interstitial hydride)



Liquid organic hydrogen carriers (LOHC)







hydrogenious
LOHC TECHNOLOGIES

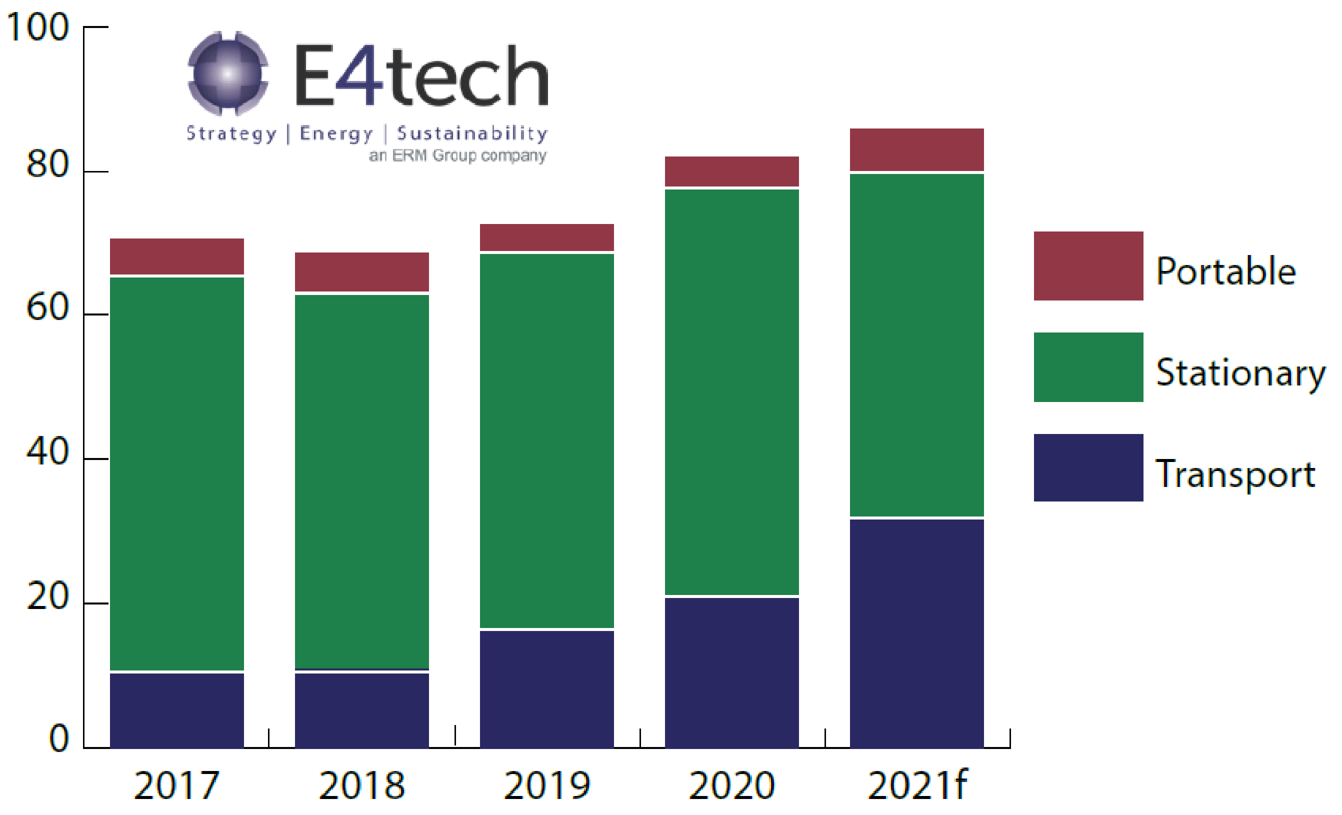
Overview of hydrogen storage

Method	Pros	Cons	State of implementation
High pressure	Practical. Quite high energy density. Easy access.	Energy for compression. Safety. Cost of cylinder	**Standard (almost exclusively)**
Liquid	High energy density. Liquid fuelling. Potential for large scale transportation of energy.	Energy for liquefaction. Boil-off. Cost of tank	Only demo
Adsorbed	Potential for higher storage density than high pressure	Only dense at 77 K.	Not practical
Metal hydride	Low equilibrium pressure. Tailoring pressure.	High mass of host material and tank. Large heat of reaction. Cost.	Only demo
Liquid organic (LOHC)	Liquid. Easy to transfer. Potential for large scale transportation of energy.	Heat of reaction. Cost.	Only demo
Synthetic fuels	Liquid. High energy density. Existing infrastructure.	Energy loss on conversion	In progress (Power-to-X)

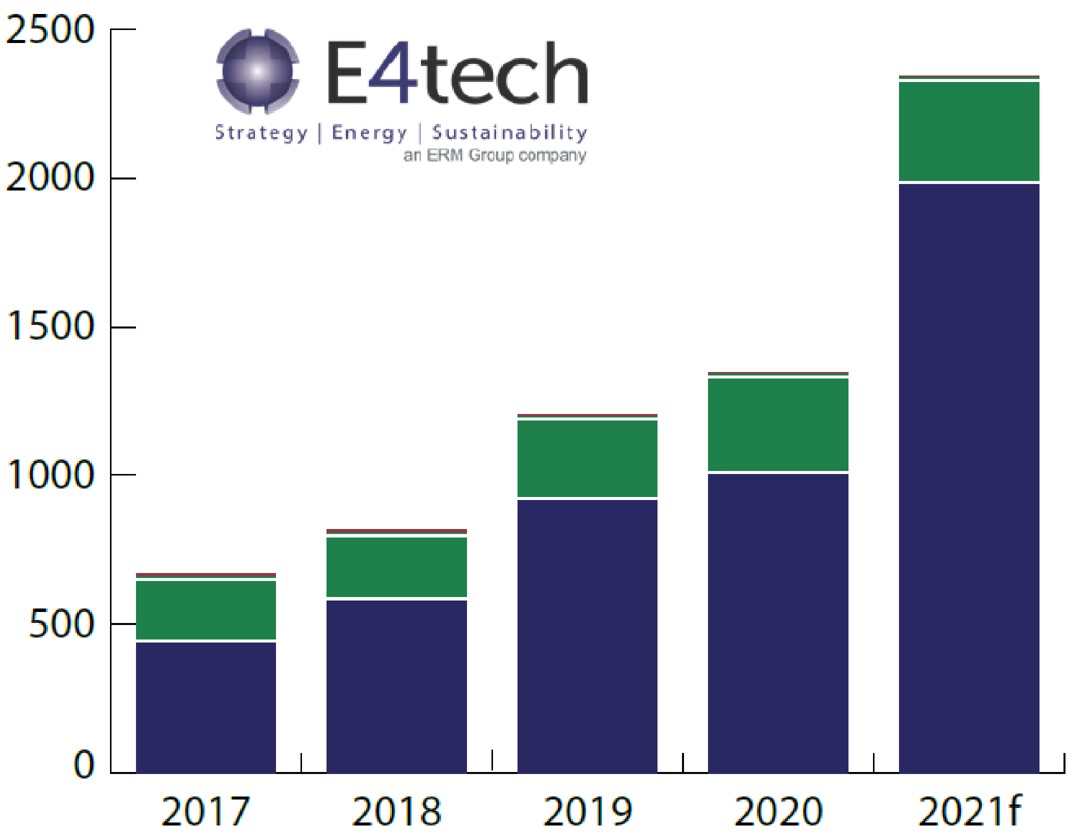
State of fuel cell implementation

Shipment of fuel cells (by application)

Shipments by application 2017 - 2021 (1,000 units)



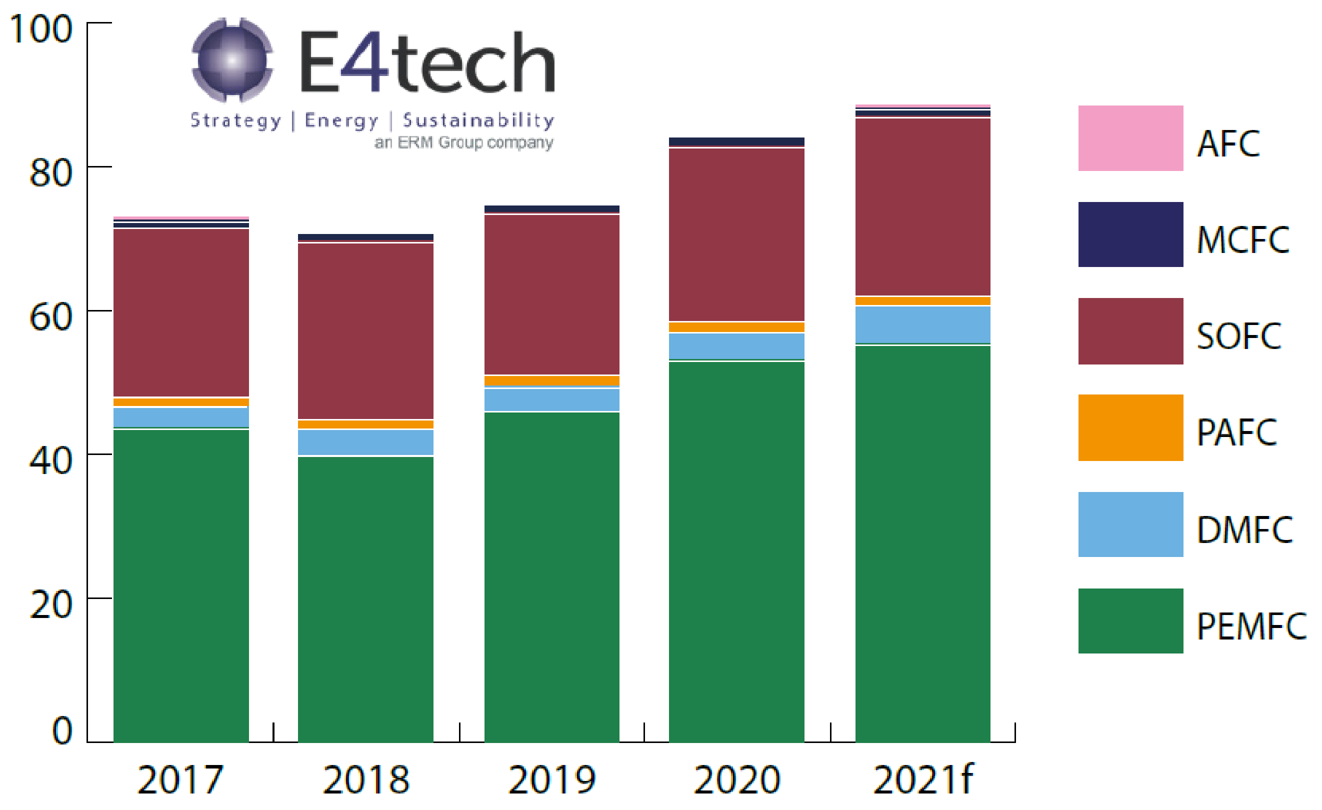
Megawatts by application 2017 - 2021



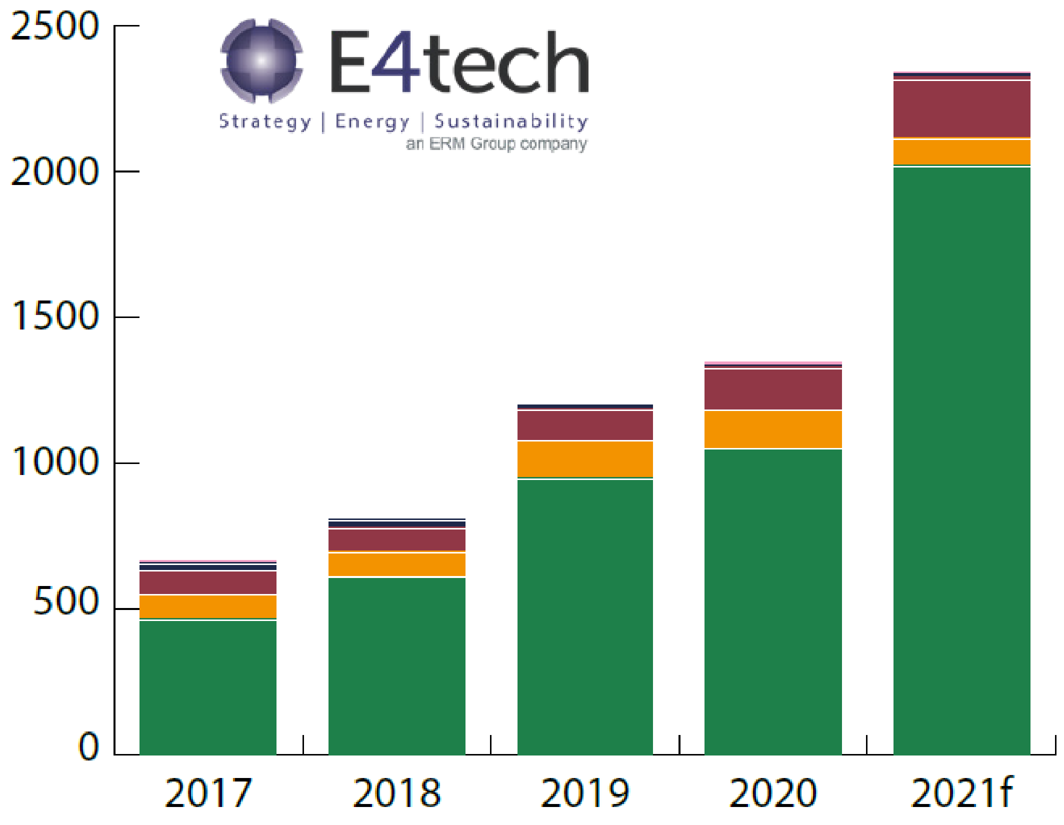
www.FuelCellIndustryReview.com

Shipment of fuel cells (by type)

Shipments by fuel cell type 2017 - 2021 (1,000 units)



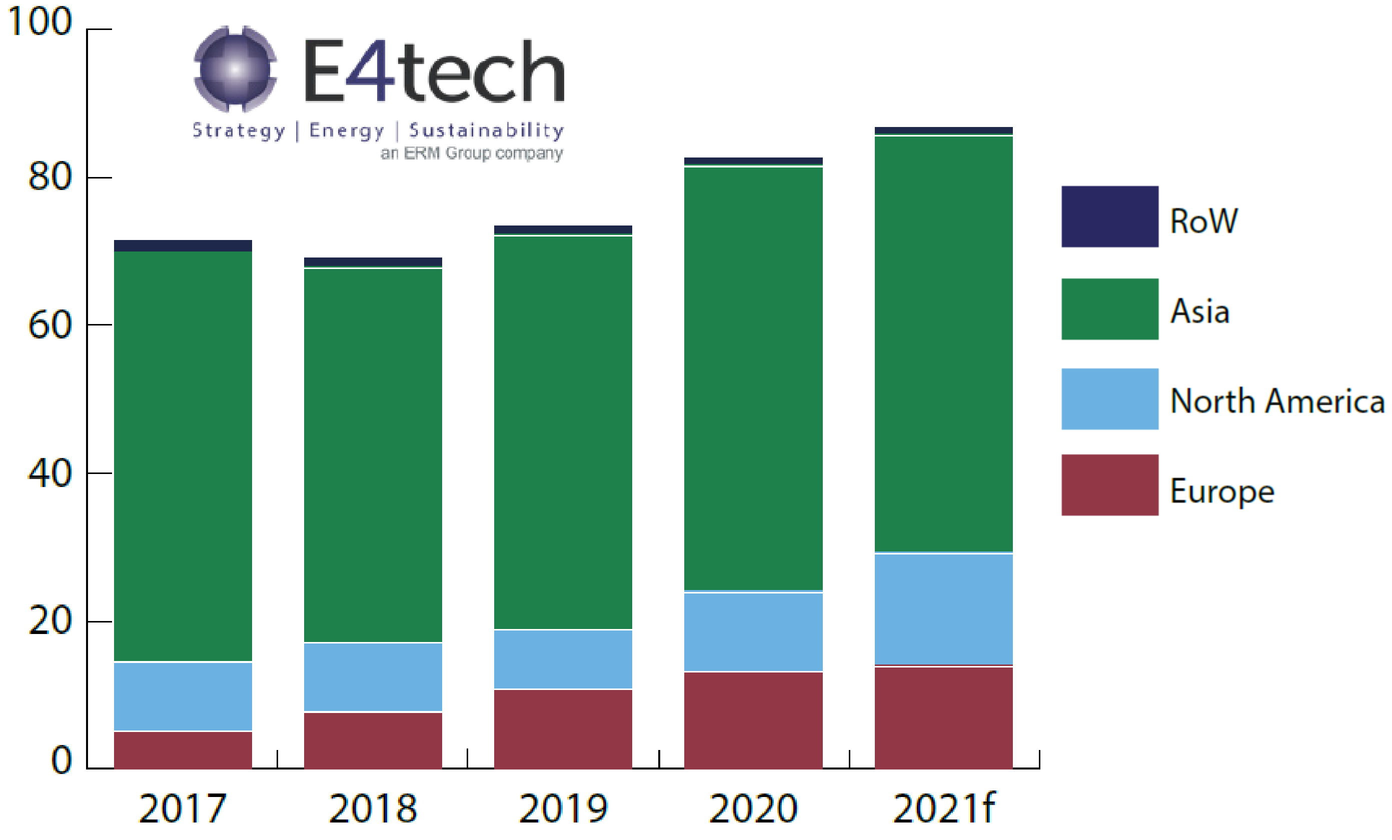
Megawatts by fuel cell type 2017 - 2021



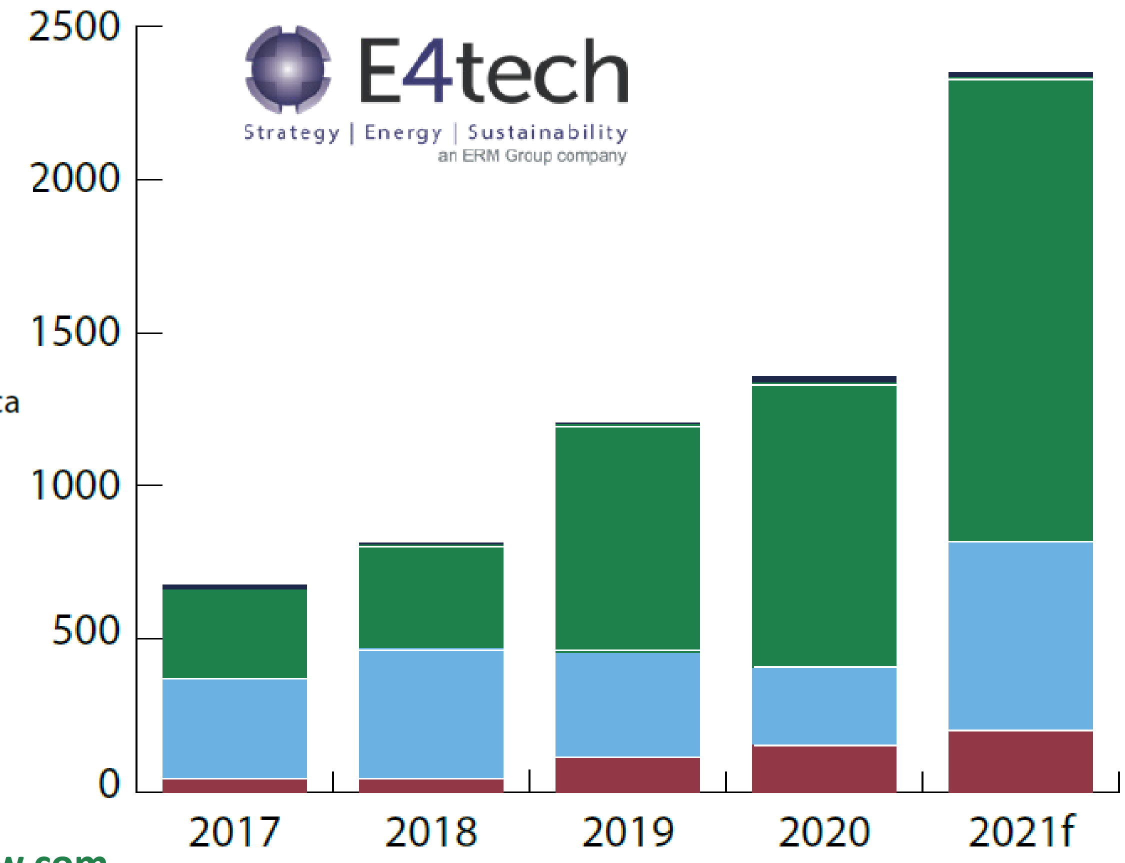
www.FuelCellIndustryReview.com

Shipment of fuel cells (by country)

Shipments by region of adoption 2017 - 2021 (1,000 units)



Megawatts by region of adoption 2017 - 2021



www.FuelCellIndustryReview.com

(RoW = Rest of the World)

Status for FC vehicles (a few years back)

Hyundai ix35
594 km
160 km/t
100 kW/136 hp
700 bar
0,95 kg/100km

First roll out
(15 in CPH 2013)

Toyota Mirai
658 km
178 km/t
114 kW/154 hp
700 bar
0,76 kg/100km

Honda Clarity
~ 600 km
200 km/t
100 kW/130 hp
700 bar

Later models

Hyundai Nexo 2018

Toyota Mirai 2020

Honda clarity 2018

Toyota Crown 2023

BMW NEXT FCEV concept car

Mercedes Benz Plug-in hybrid

Grove fuel cell car (China)

Taxi companies, DRIVR (Copenhagen area)

Taxi company with green cars
Hybrid or fuel cell vehicles
+100 FCV
Drivr.com

Dutch fuel cell taxis

2023 all hydrogen fuelling station were closed by Everfuel

The battle with the batteries

Driving range	√	√
Efficiency	÷	√
Fuelling time	√	÷
Emissions	√	√
Weight	(√)	(√)
Infrastructure	÷	÷
Home charging	÷	√
Apartment charging	√	÷

Changing focus for hydrogen vehicles

Fuel cell trucks

Hyundai: 1,600 trucks for Switzerland

Nikola: 13,000 pre-orders (800 trucks for Anheuser-Busch)

Hyundai X2 Xcient.
2 Nexo stacks: 190 kW
7 pressure tanks 35 kg H_2
400 km

Hyundai ships first tucks to Switzerland, July, 2020

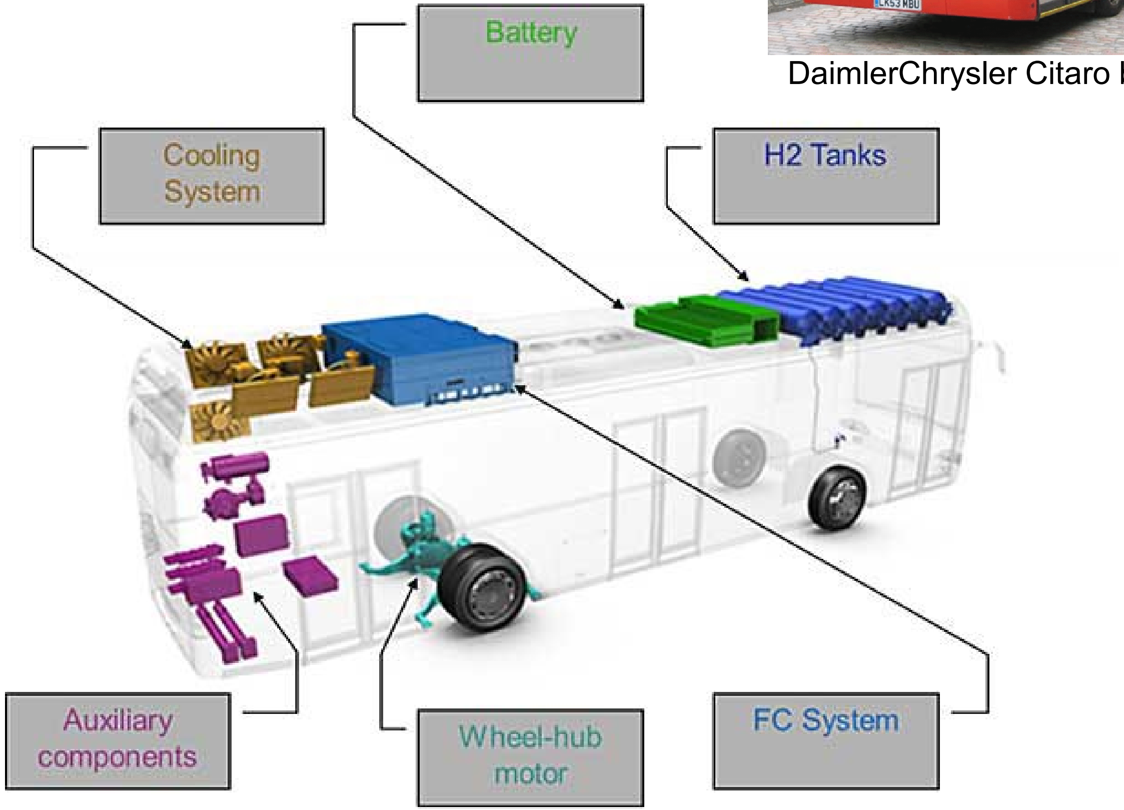
Nikola truck. Up to 750 kW (1000 hp)

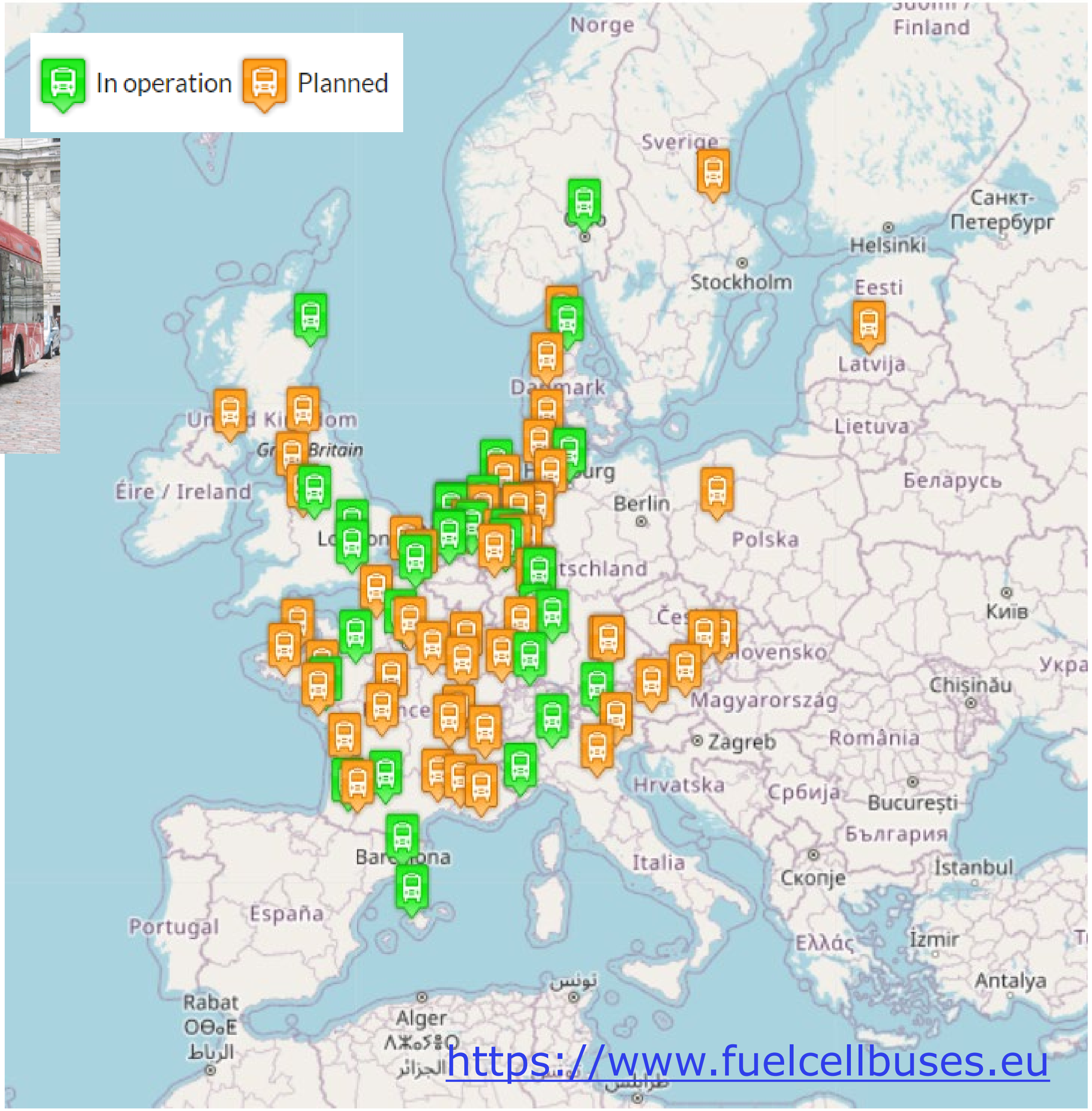
Fuel cell busses

Fuel cell busses have been around for a long time.

Many projects

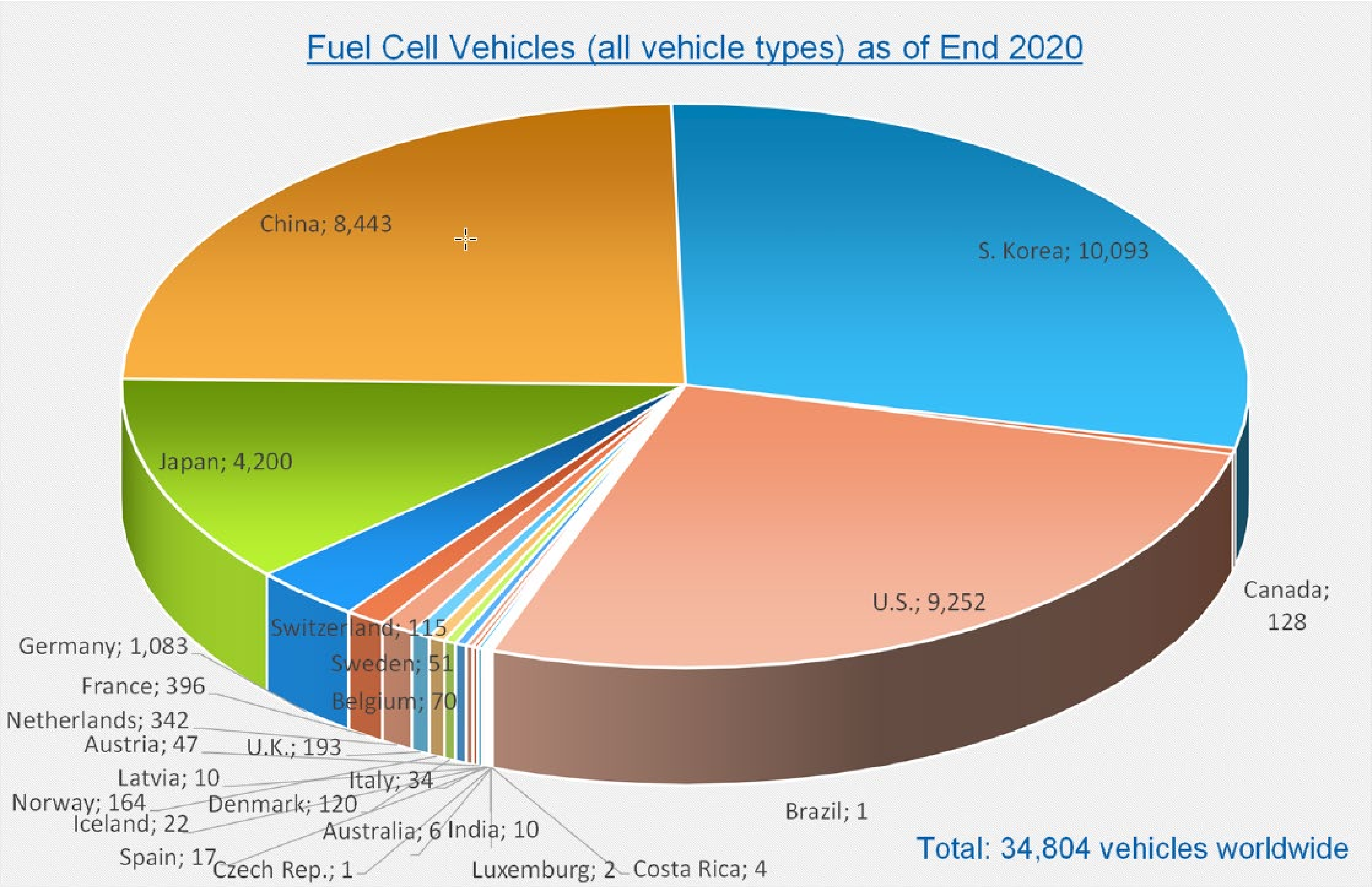
DaimlerChrysler Citaro bus





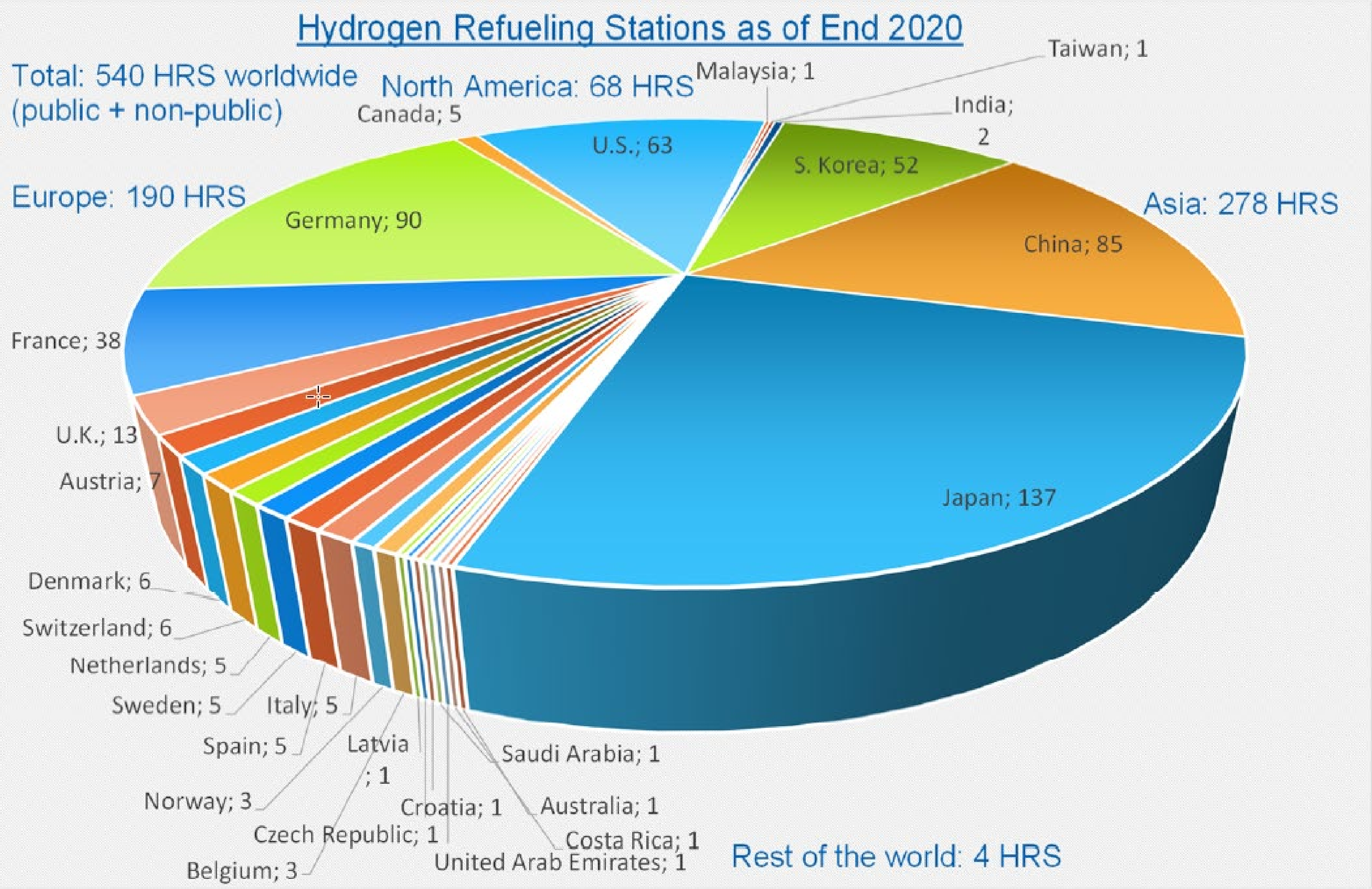
https://www.fuelcellbuses.eu

Deployment of fuel cell vehicles

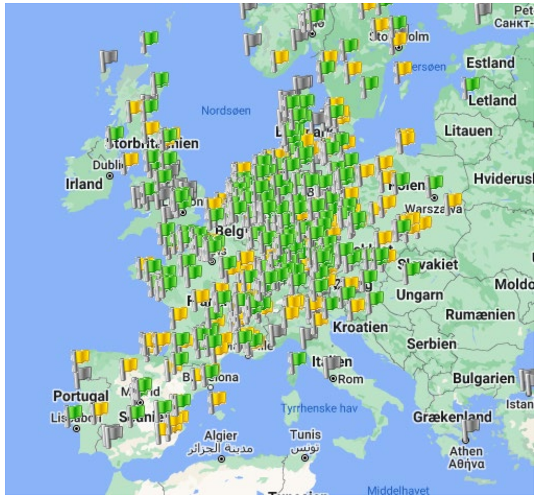


Deployment Status of Fuel Cells in Road Transport: 2021 Update. Schriften des Forschungszentrums Jülich
Reihe Energie & Umwelt / Energy & Environment Band / Volume 542

Deployment of fuel cell vehicles



Maps on www.h2stations.org



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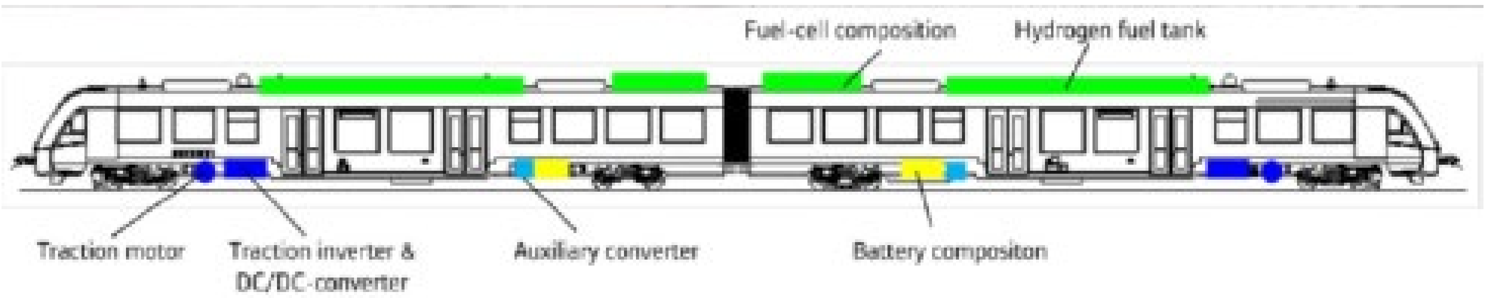
Trains



Alstom hydrogen/fuel cells train. Salzgitter, Lower Saxony, Germany 2018.

Hydrogen powered FC forklifts

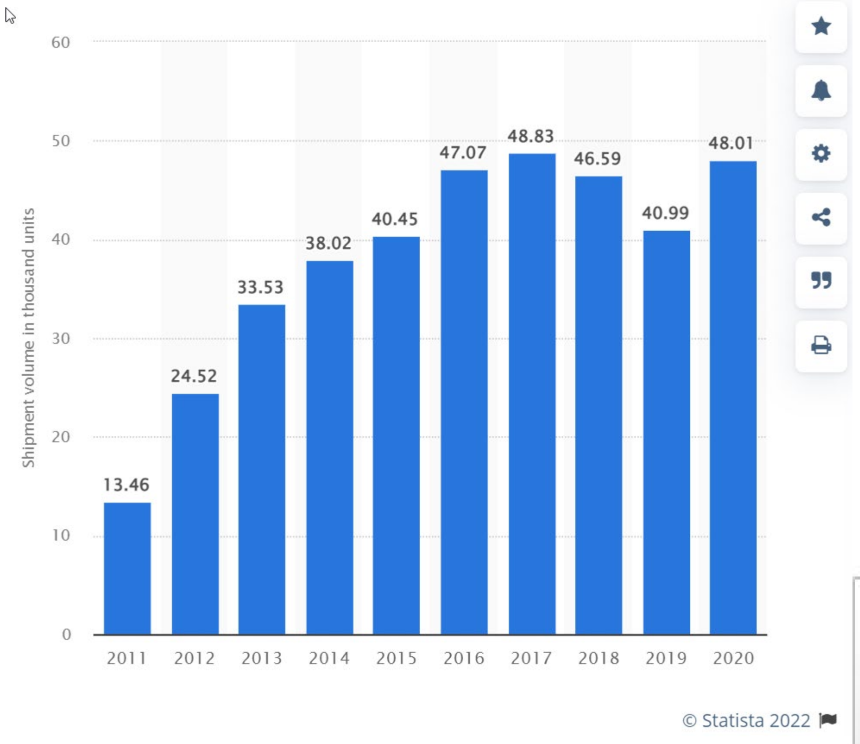
The forklift is the most successful fuel cell vehicle to date.

Work continuously, no extended battery charging

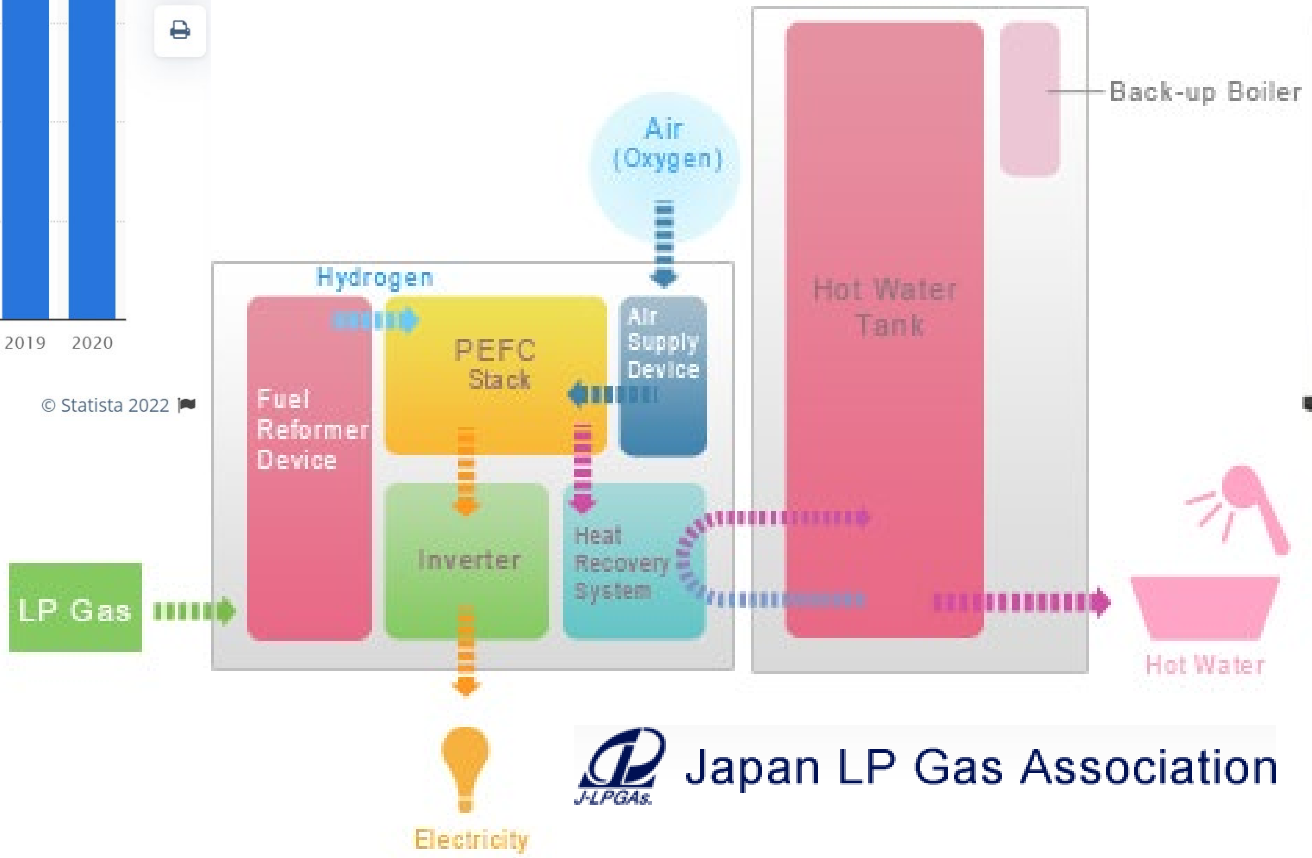
30,000 units, in North America. (Amazon and Walmart)

Hyster N-ZR forklift

Status for micro-CHP in Japan



Japan:
ENE-FARM programme from 2009.
+400.000 units installed.
Most PEMFC and some SOFC



Panasonic µCHP
700W_e, 1000 W_h

Airbus hydrogen powered aircrafts

Concept 2020

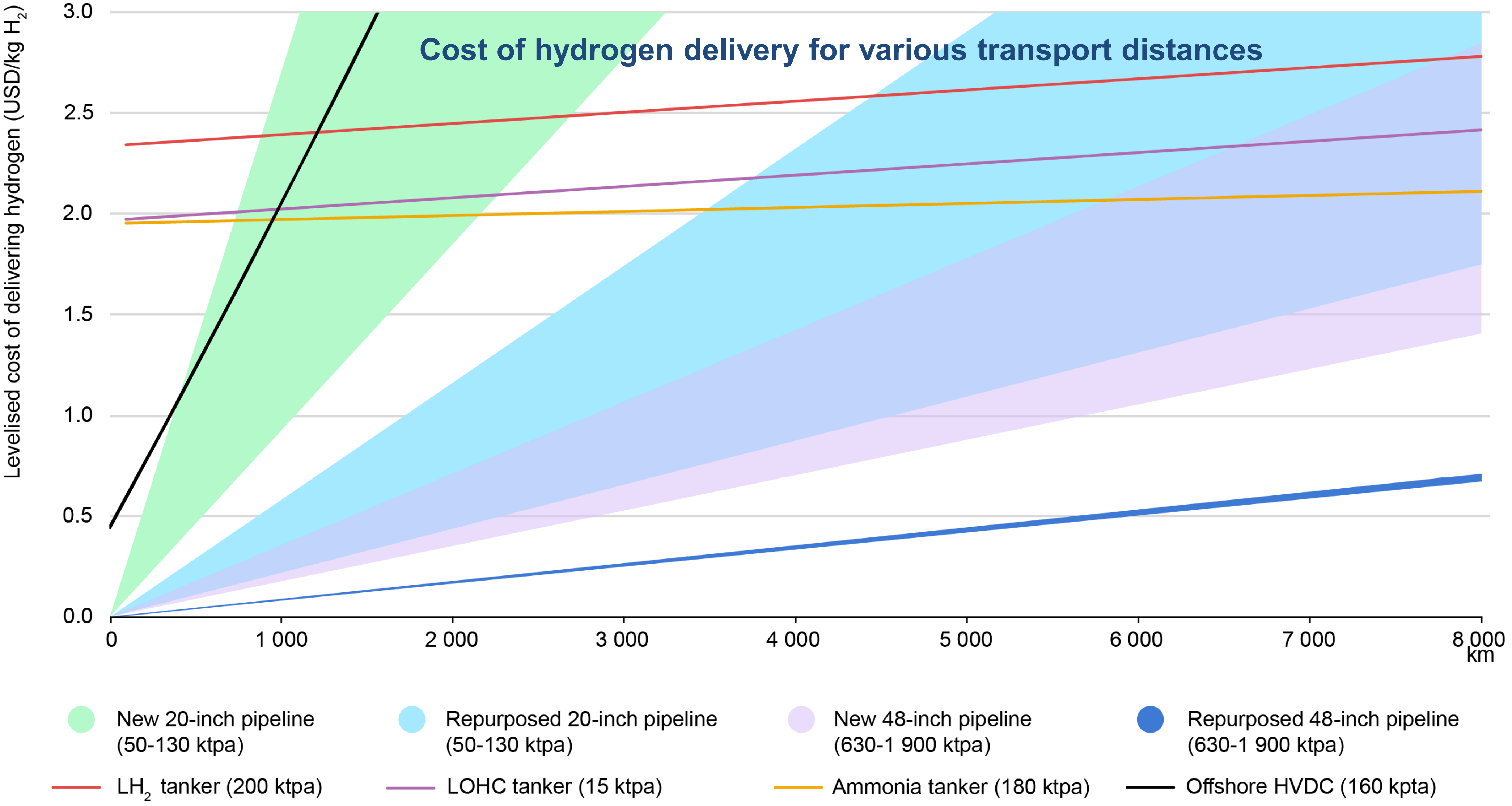
Test flights 2025

Flights 2035

Hydrogen for energy transmission

Long distance transport of hydrogen (2030)

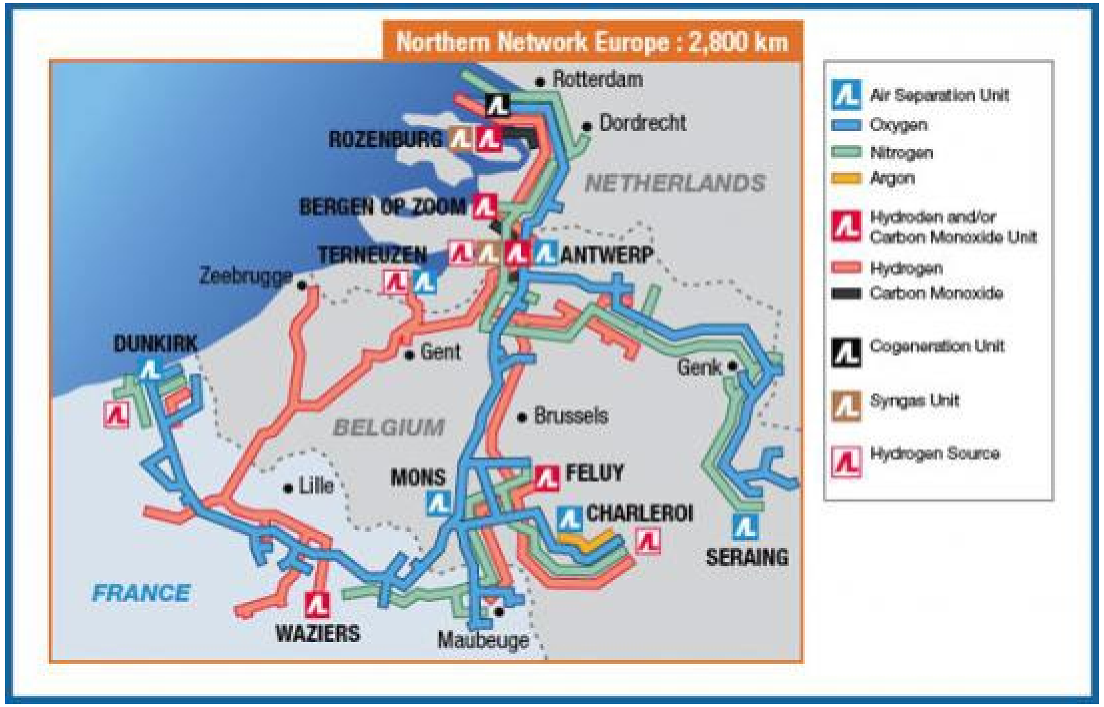
Levelised costs of delivering hydrogen by pipeline and by ship as LH2, LOHC and ammonia carriers, and electricity transmission, 2030

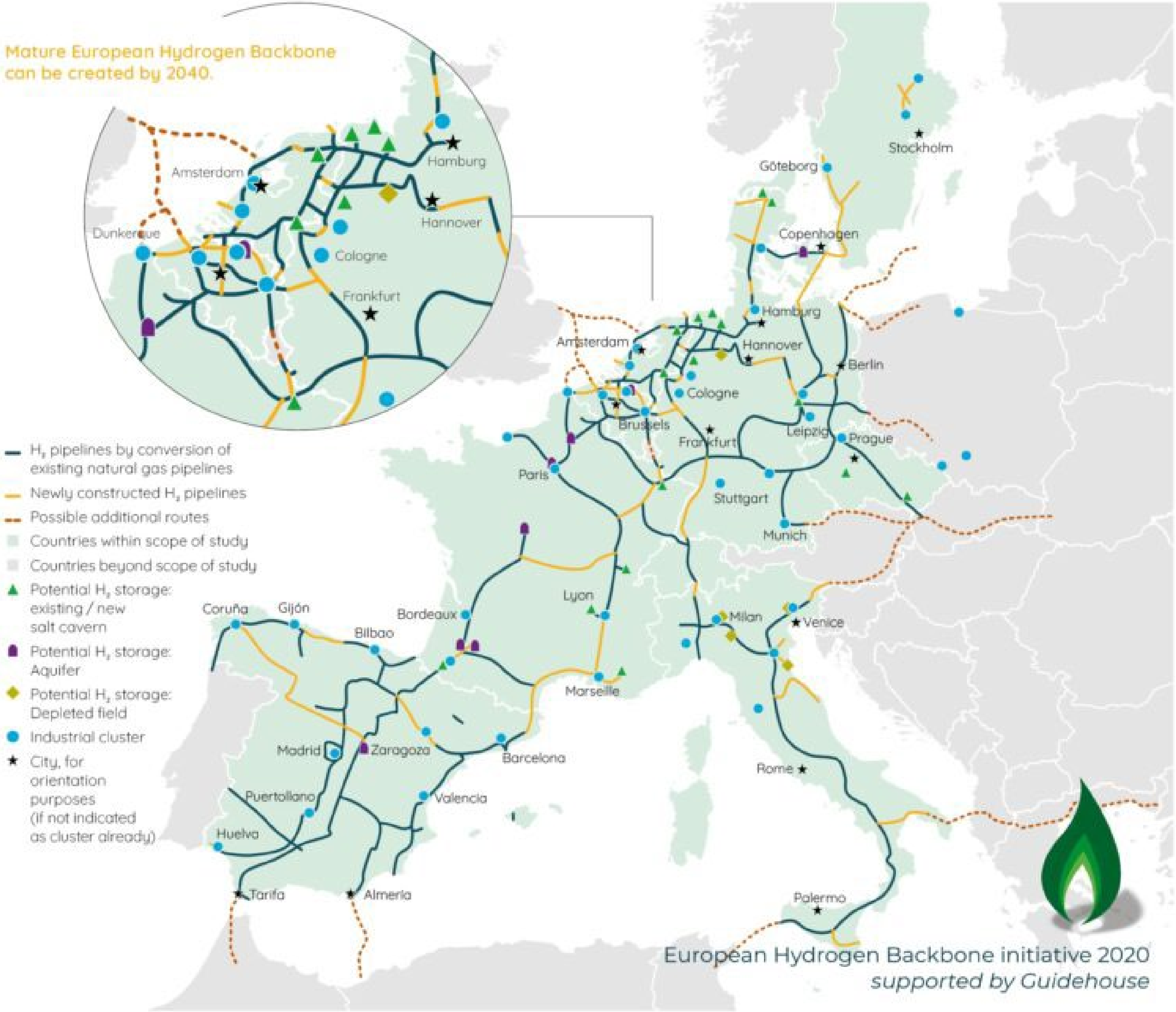


Global Hydrogen Review 2022

Hydrogen pipelines

Plans for 40,000 km in Europe by 2040.
Very little in place today

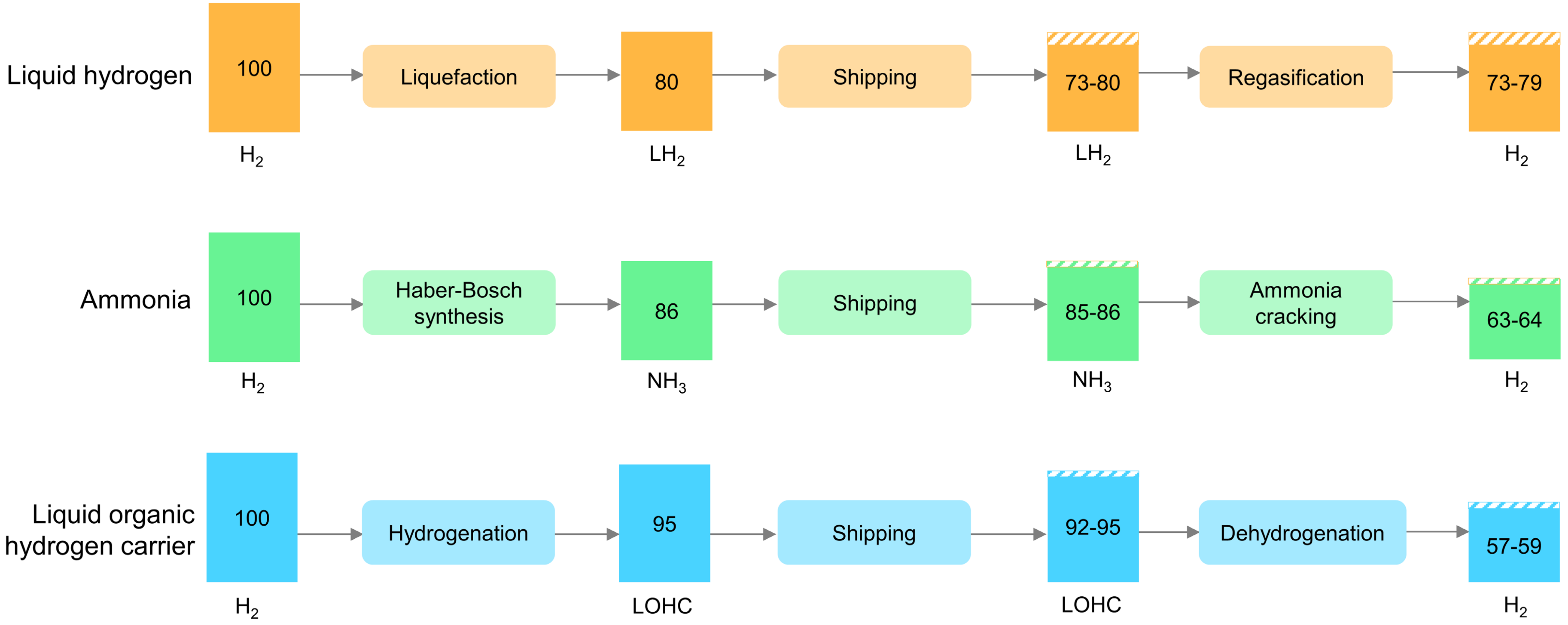




Belgium/Netherlands a hydrogen-pipeline network (Air Liquide) 900 kms, running from Rotterdam (NL). 70-100 bar.

www.fuelcellbuses.eu/wiki/concept-hydrogen-refueling-station/pipeline

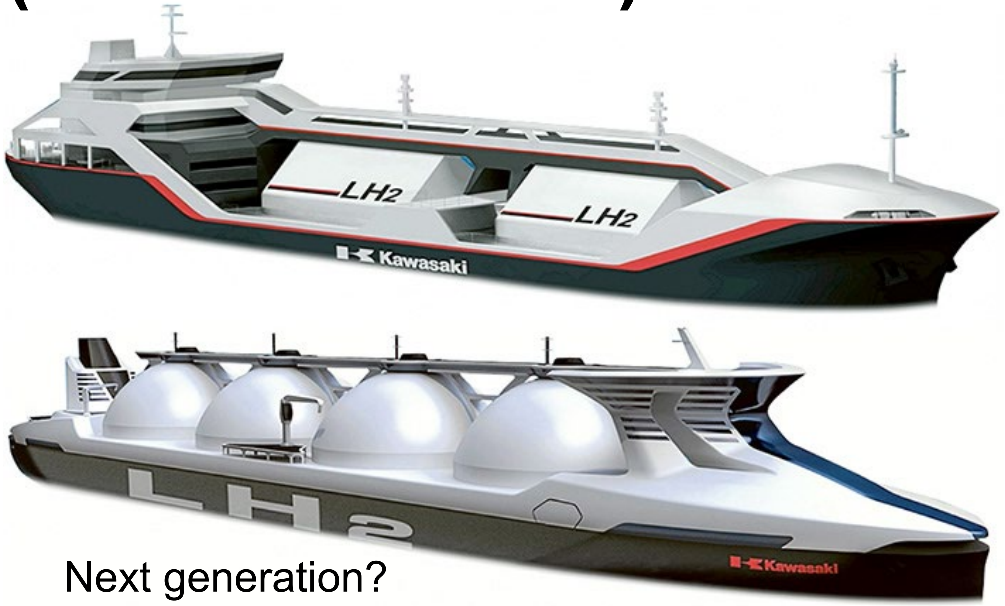
Energy cost of shipping of hydrogen



Notes: LH2 = liquefied hydrogen; NH3 = ammonia; LOHC = liquid organic hydrogen carrier. Numbers show the remaining energy content of hydrogen along the supply chain relative to a starting value of 100, assuming that all energy needs of the steps would be covered by the hydrogen or hydrogen-derived fuel. The Haber-Bosch synthesis process includes energy consumption in the air separation unit. Boil-off losses from shipping are based on a distance of 8 000 km. For LH2, dashed areas represent energy being recovered by using the boil-off gases as shipping fuel, corresponding to the upper range numbers. For NH3 and LOHC, the dashed area represents the energy requirements for one-way shipping, which are included in the lower range numbers.

Global Hydrogen Review 2022

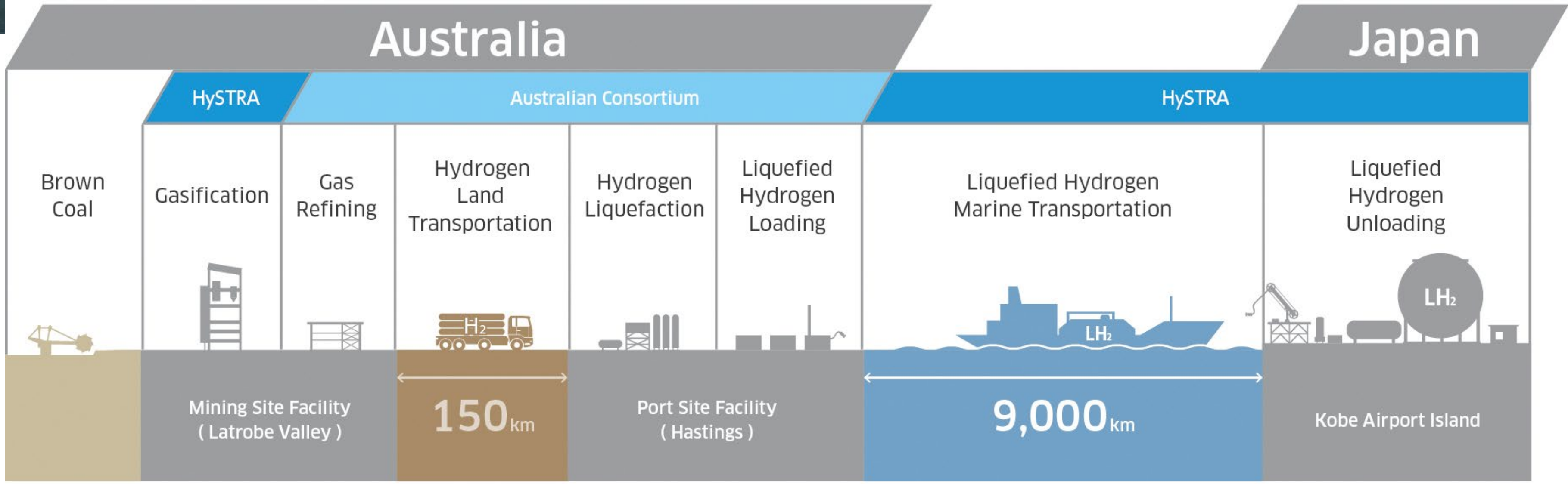
First liquid hydrogen carrier (December 2019)



Next generation?

Kawasaki Heavy Industries
Tank cargo capacity:
1,250 m^3

For transport of energy from Australia to Japan



All for now, but I'll be back