From Hydrogen production to Electrochemical conversion

Olivier JOUBERT,

Prof. Univ-Nantes and director of CNRS- FRH2 research network

ELaboration of NANOmaterials for the recovery, conversion, transport and storage of energy

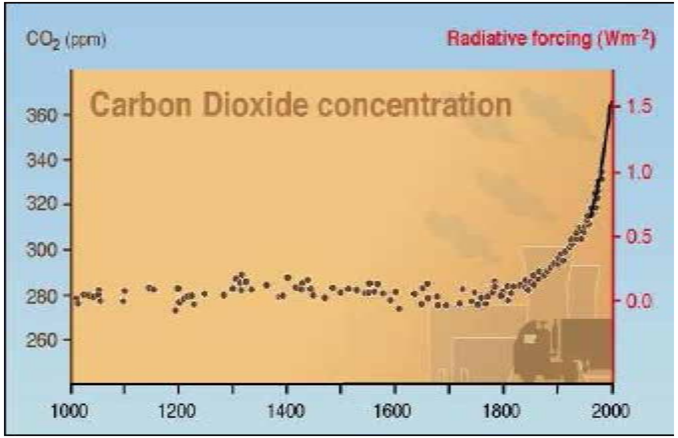
11-16 June 2023 Aussois (73500) (France)

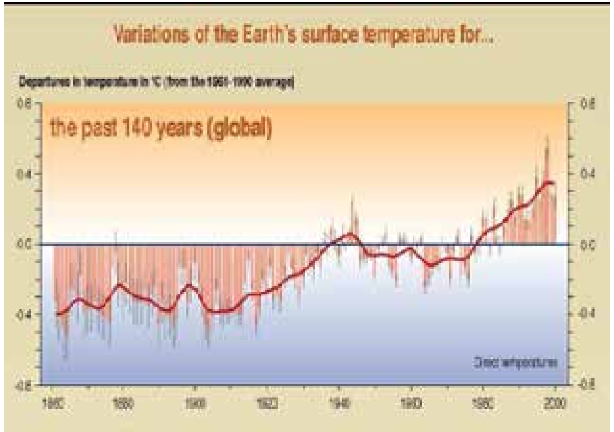
https://frh2.cnrs.fr

Plan

I Context: energy transition

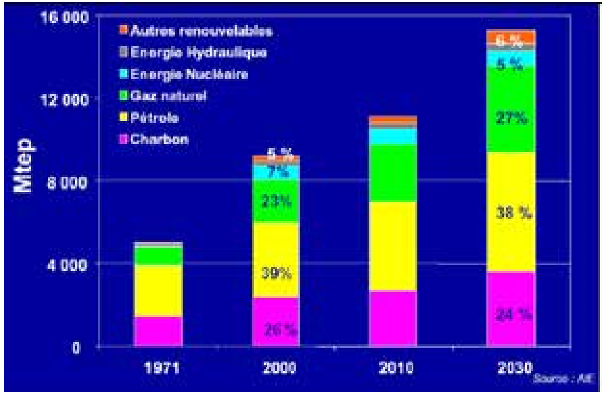
greenhouse gas emission





global warming

fossil energy resources



increase of energy demand

Targets of french energy policies

Decreasing Energy consumption -17%

↓

Reduction of produced energy

Decreasing the dependancy to Fossil fuels -40%

↓

Increasing the part of Renewable energies

Reducing the depency to nuclear power plant (target = 50%)

Carbon neutrality

↓

Low carbon emission Capture & Storage

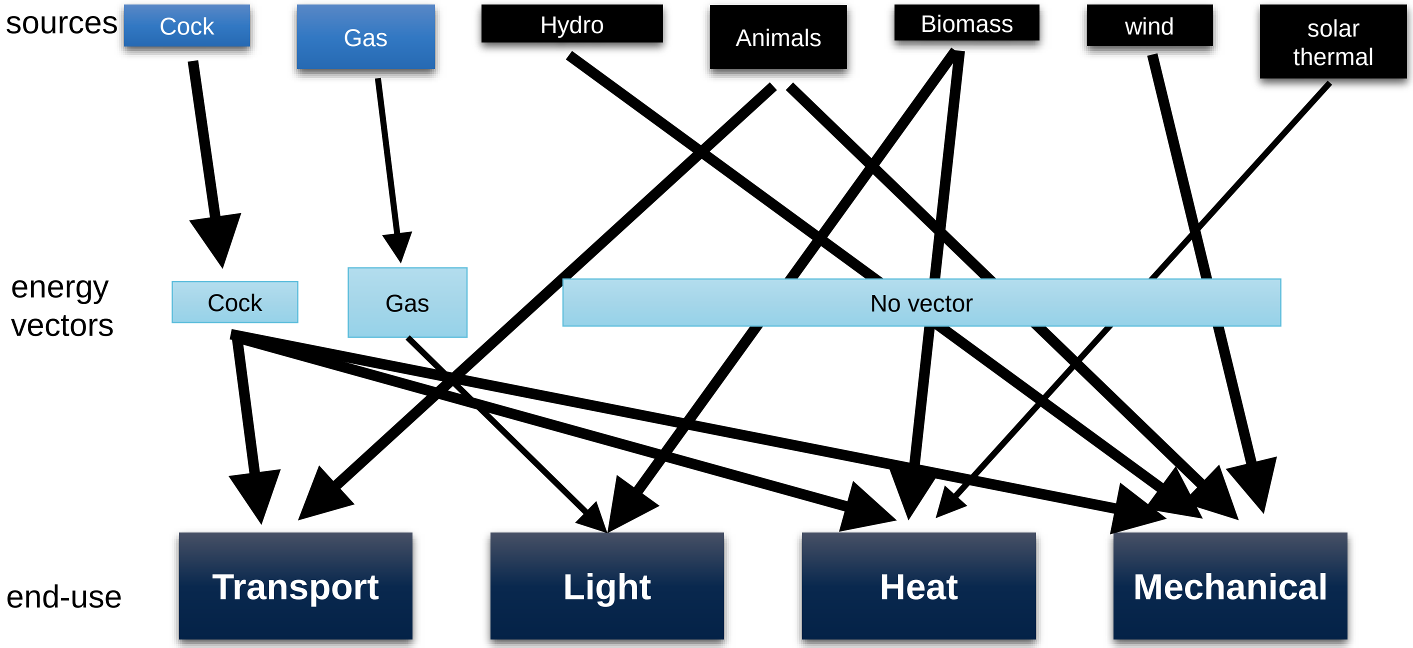
Solution?

increasing renewable energy production

& diversifying the energy mix

The French Research network on Hydrogen energy

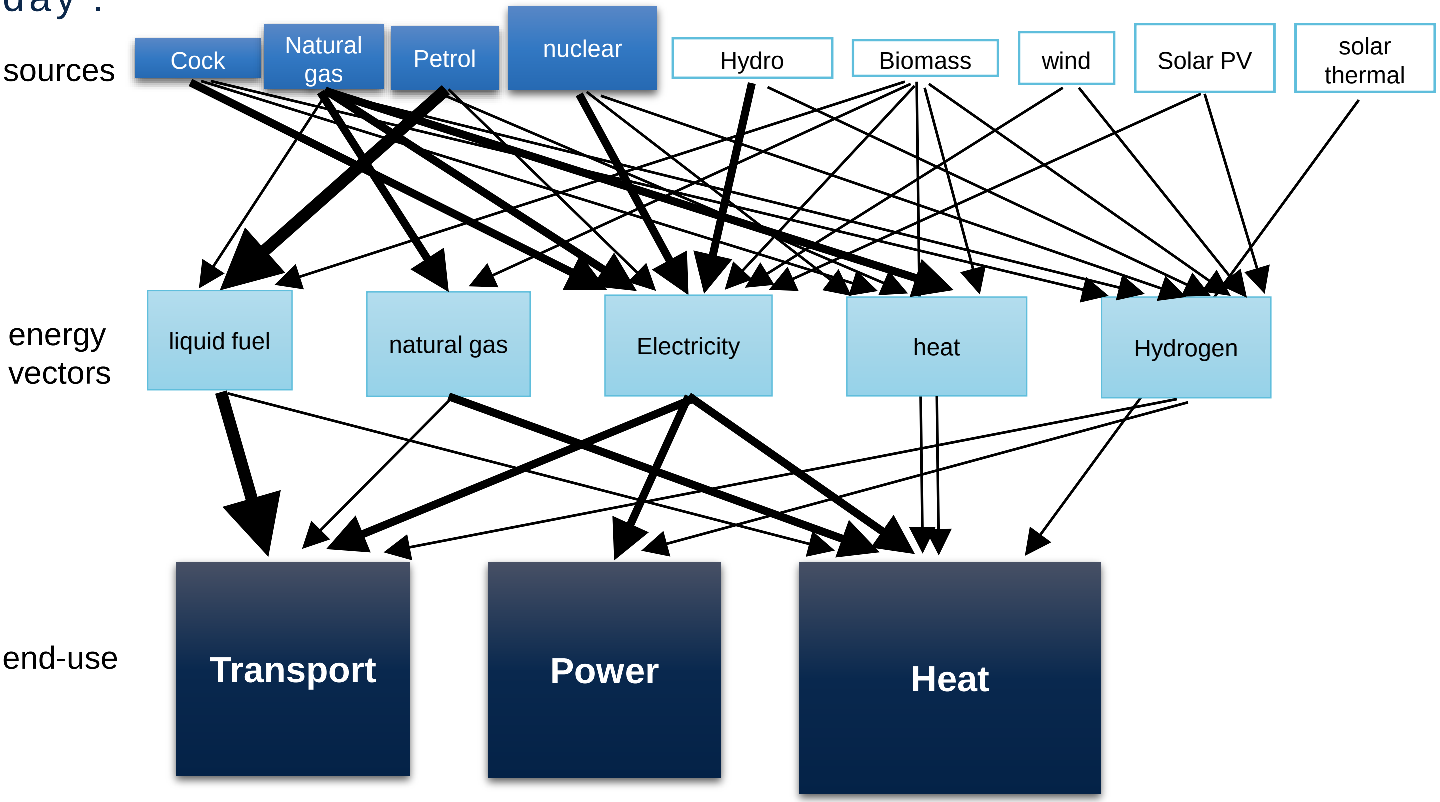
Back to XIXth century: renewable and fossil energy sources



no energy vector for renewable energy

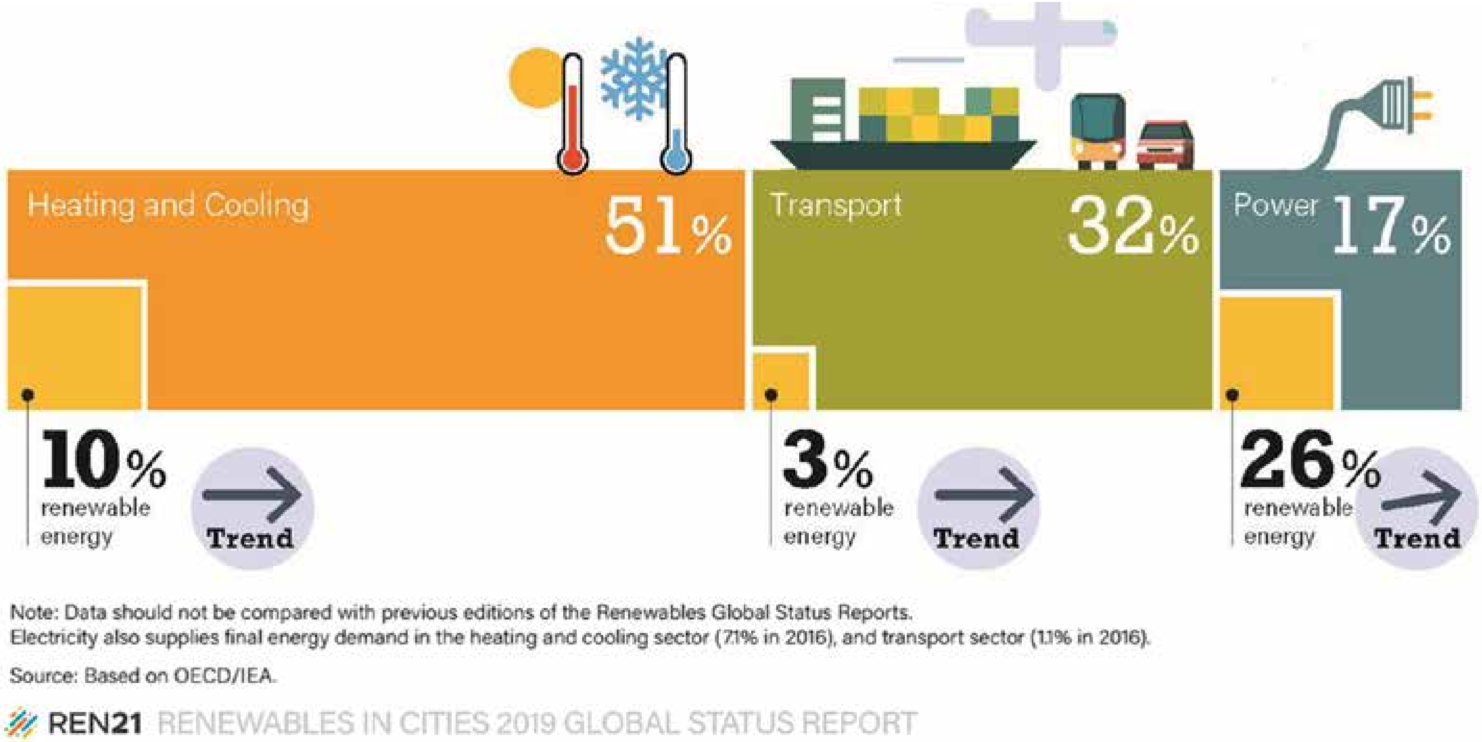
- only 2 vectors: cock (eg for train) and gas for cooking and light
- energy sources close to the end-user

Today :



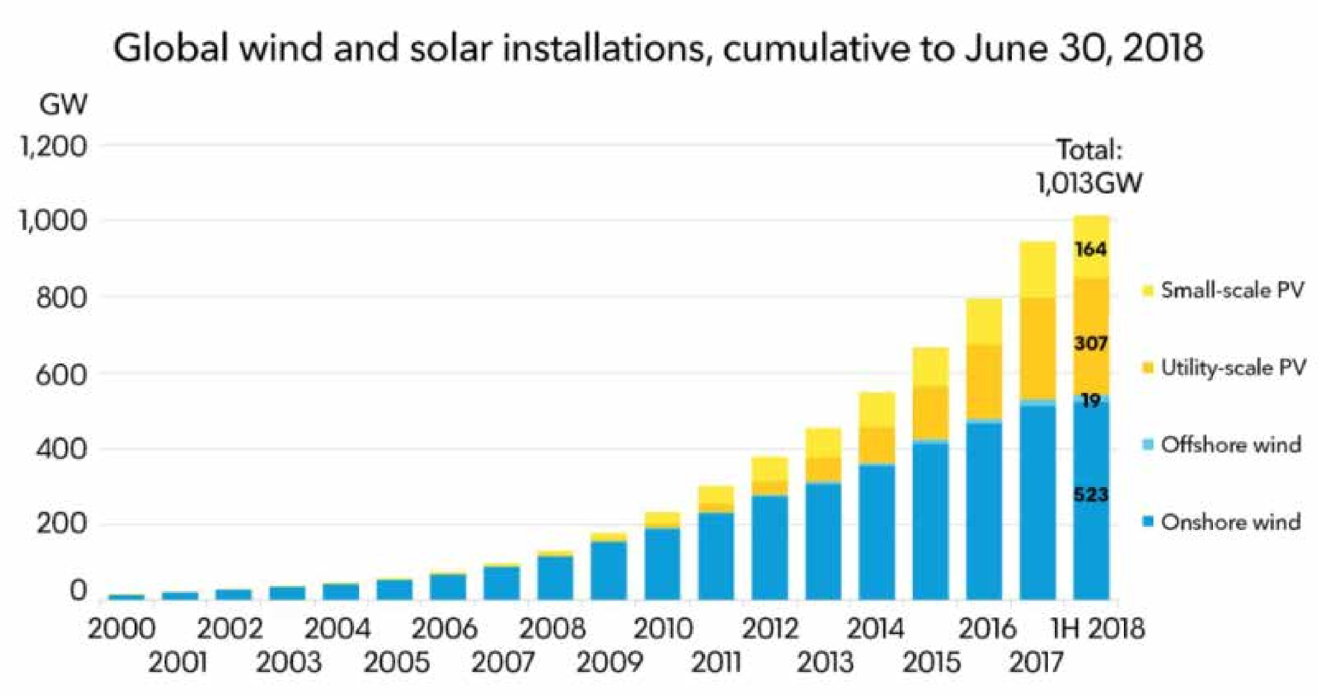
Cock is no more an energy vector. "New" vectors: e-, H_2…

Today: fossil fuel is the major energy source

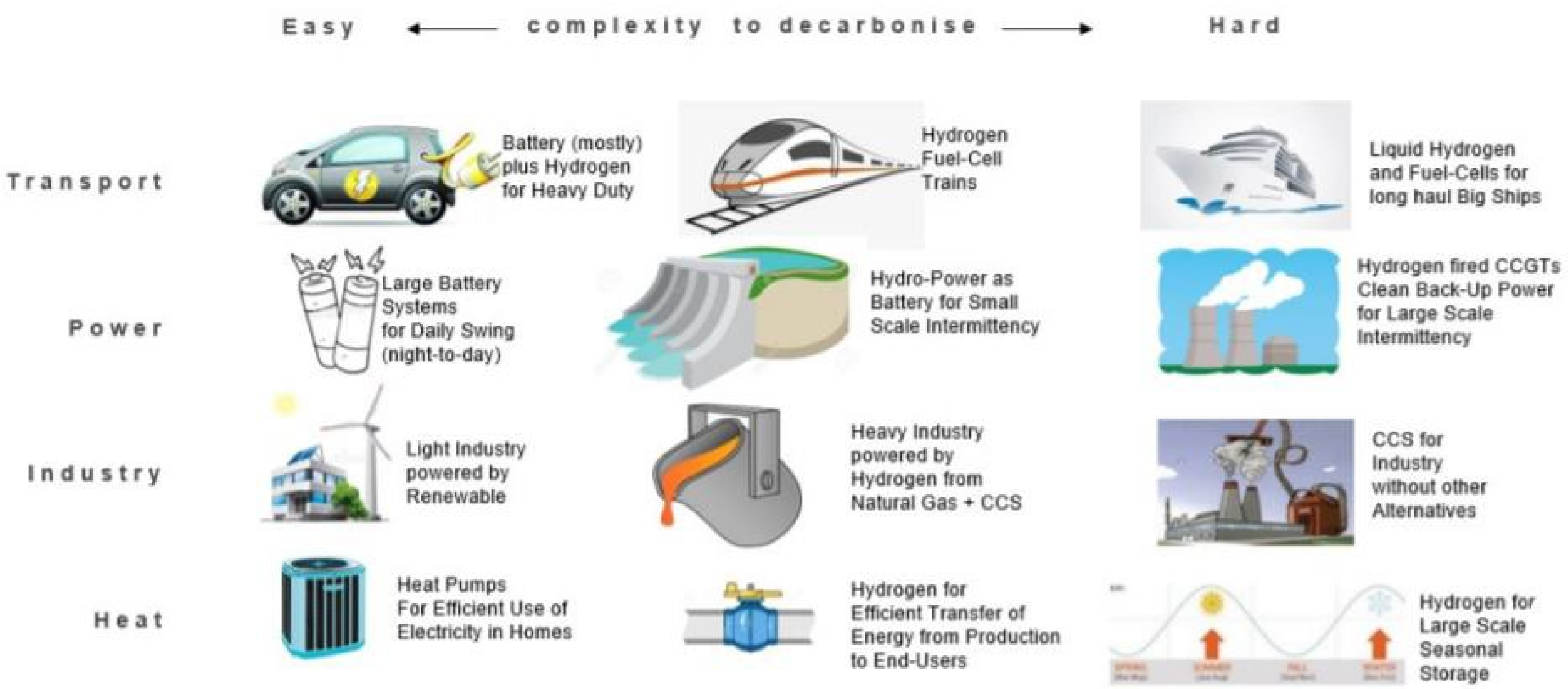


The way to increase the part of renewable energies?

Decarbonization of electricity: rapid growth of solar and wind power



Decarbonising energy systems: Multiple technologies to address the challenge

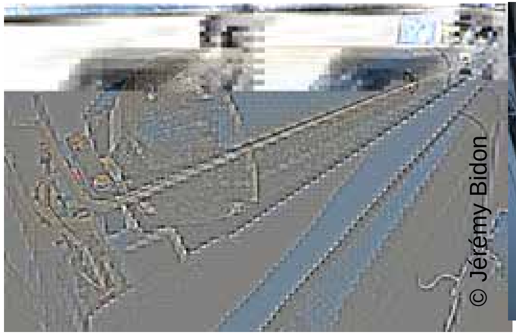


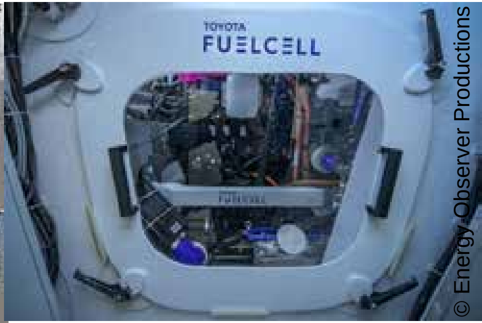
Hydrogen can (will) play a major role in the energy transition

Batteries vs hydrogen Storage In "Energy Observer" boat

© Jérémy Bidon

Li batteries: 1400kg (>700L) for 112 kWh



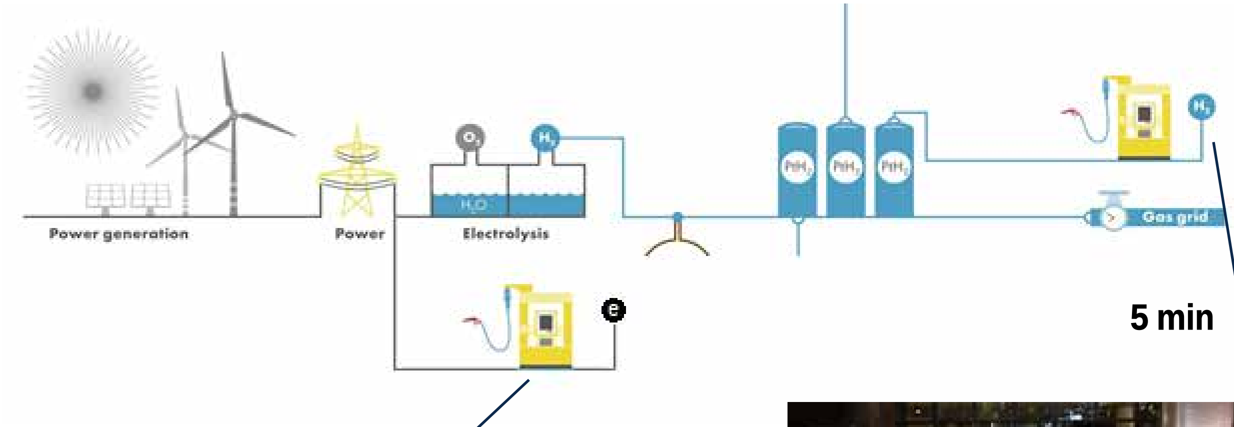


Hydrogen storage:
8 pressurized tanks of 332L allow a total of 63 kg of hydrogen (the energy equivalent of 230 liters of petrol). This volume represents a clear global energy stored of 1 MWh.

Hydrogen storage + Fuel cell: 1700kg for 1000 kWh

Weight of 1kWh: 12.5kg of batteries or 1.7kg of H_2 (including FC)
But both are needed!! (complementary)

A solution for mobility



5 min

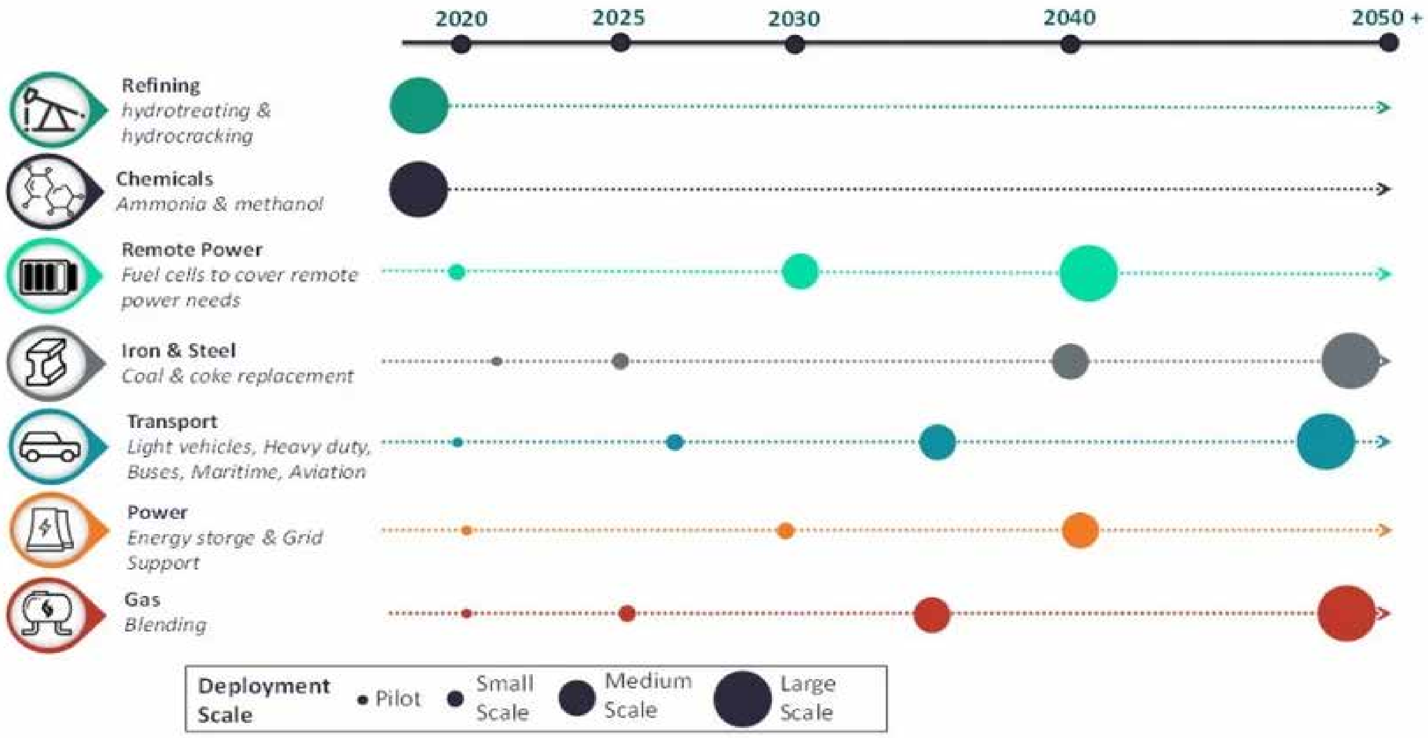
21 h

Renault **Zoe** batteries: energy 41 kWh, weight 300 kg, 57kW electrical engine, 400km autonomy

Hyundai IX 35: H_2 5.6 kg (185kWh) + fuel cell (300kg in all), 100 kW electrical engine, 650 km autonomy

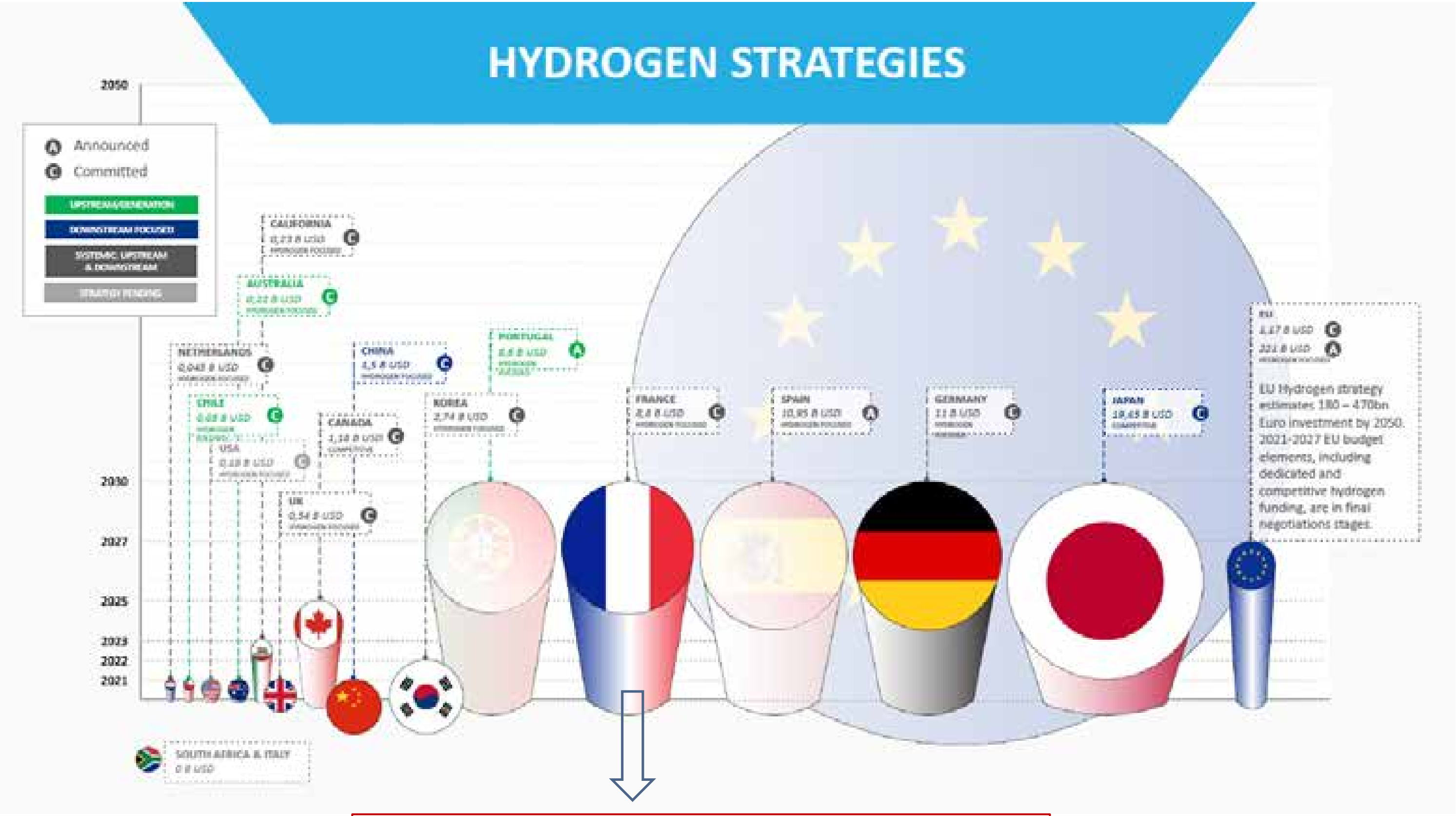
The French Research network on Hydrogen energy

Carbon free Hydrogen to decarbonize the industry and transport



Source: GlobalData Thematic Research

Hydrogen Initiatives over the world



The French Green Hydrogen Plan 2020-2030

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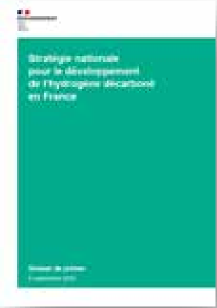
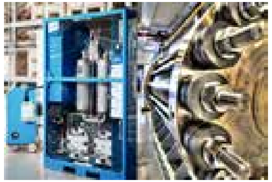


A MASSIVE PLAN TO BECOME A LEADING PLAYER IN THE GREEN H2 FIELD WITH 3 MAIN OBJECTIVES :

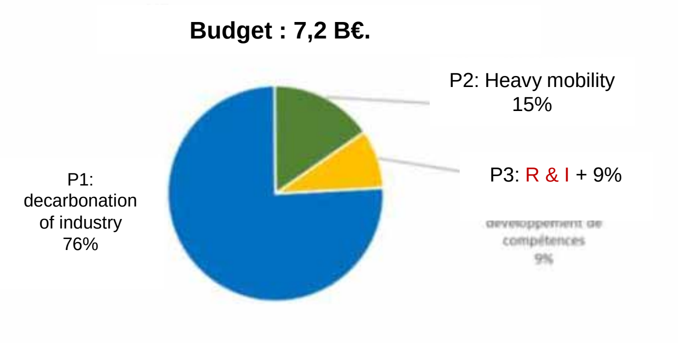
BY 2030



TO ACHIEVE MASS-PRODUCTION OF H2 BY ELECTROLYSIS (CAPACITY OF **6.5 GW**) AND SAVE **6MT** CO2 BY 2030

TO PROMOTE CARBON-FREE H2 FUELED HEAVY MOBILITY

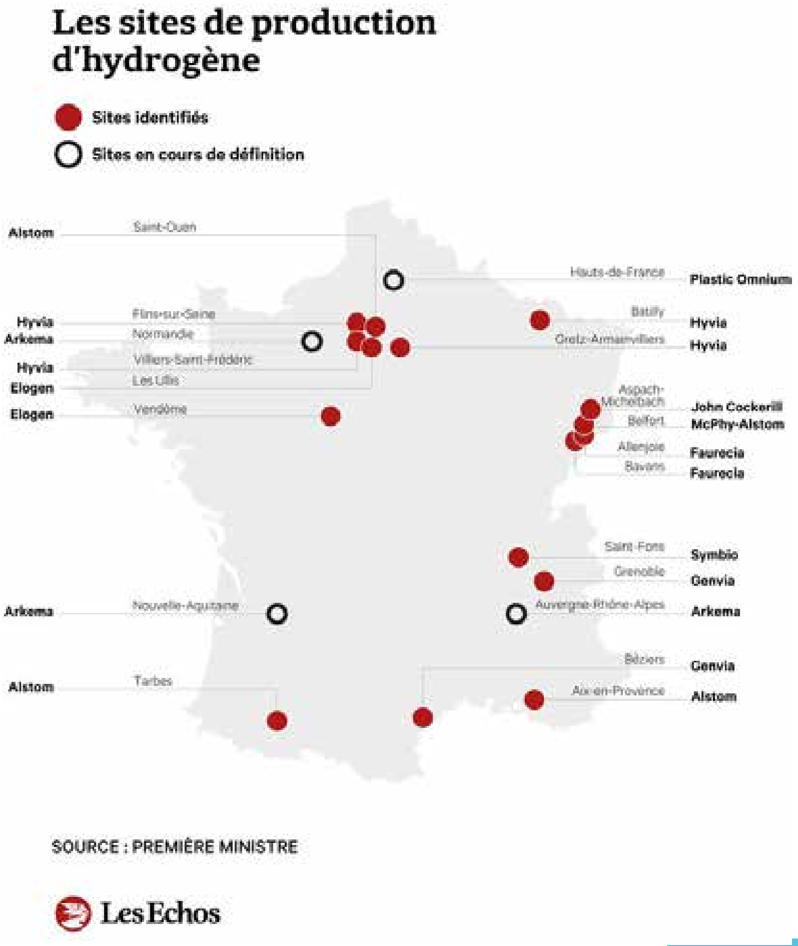
TO DEVELOP A FULLY INTEGRATED AND COMPETITIVE SECTOR WITH **50 TO 150K** JOBS



https://www.tresor.economie.gouv.fr/Articles/4a1ac560-a021-4358-a466-f5430928a1db/files/7d2fd0e2-8a3d-4ce8-bbb3-94cbd5b9c3d1

Recent announcements of the Fr

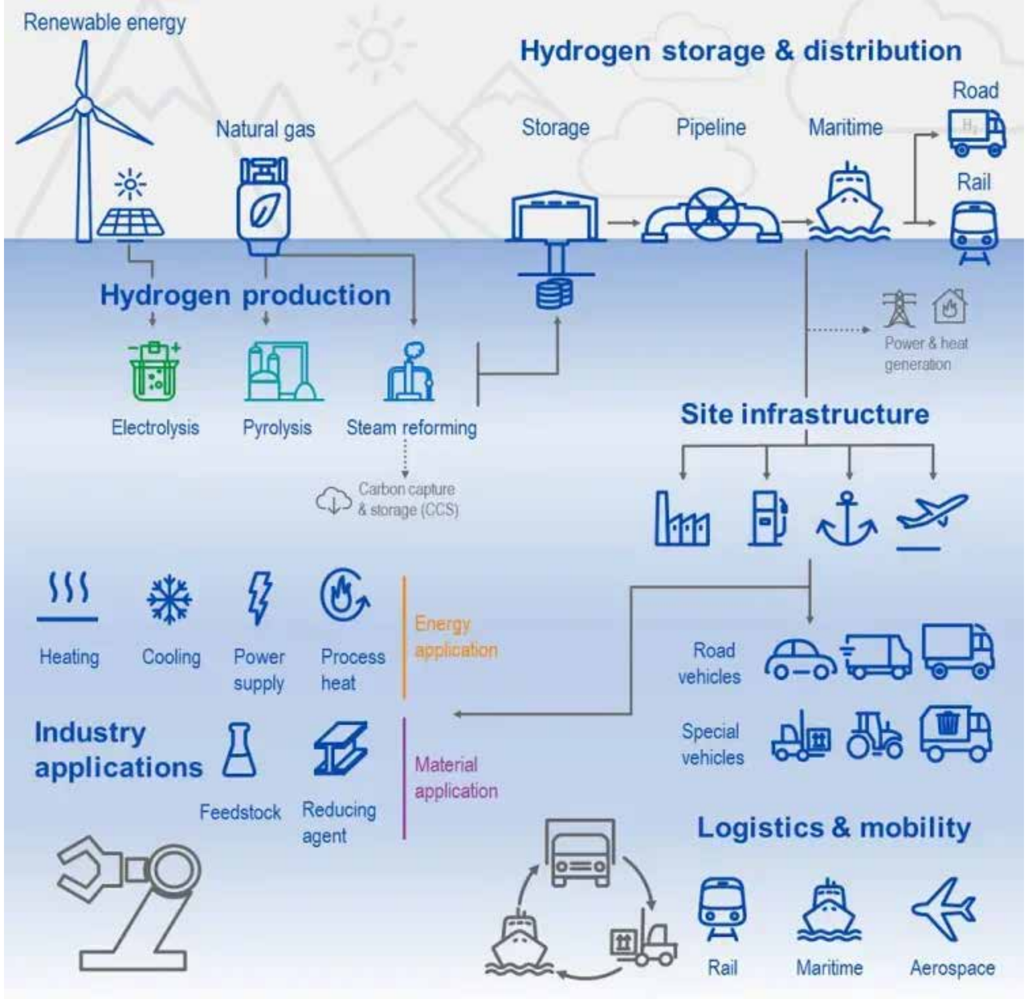
September 28, 2022:
The French State announces to invest 2.1 billion euros in 10 "gigafactories" which will be located all over the territory, and should make it possible to create nearly 5,200 direct jobs



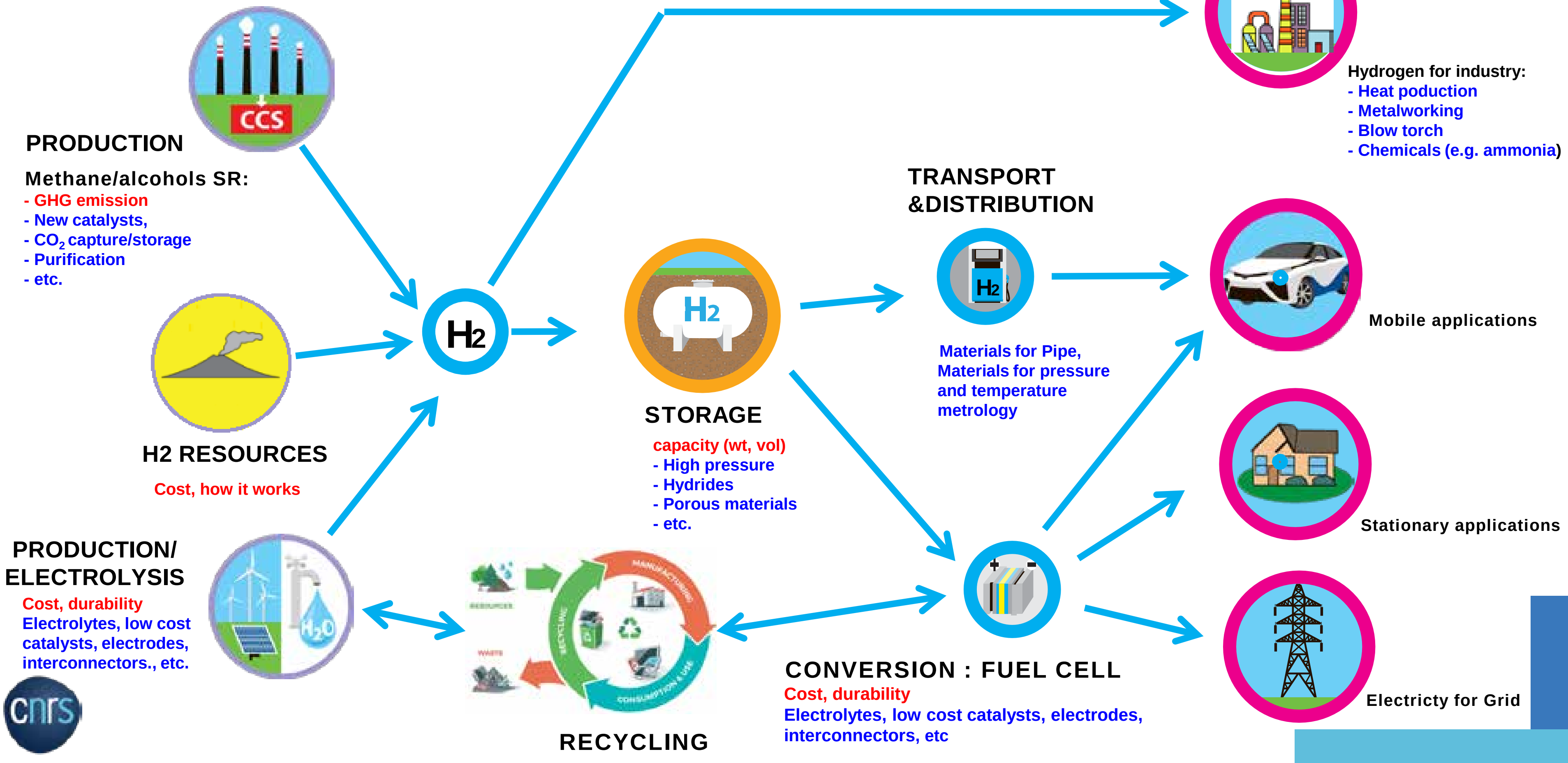
the Hydrogen Value Chain

The usual Hydrogen value chain is divided in three areas: **production**, **storage / distribution**, **and use / application**.

To produce huge amount of hydrogen and to develop new applications (mobility) à **need to accelerate the development of each part of the value chain.**



Hydrogen Value Chain: technology still needs improvements and R&D



FRH2 : French Research network on Hydrogen Energy

30 laboratories,
300 full time researchers
4000 papers (2014-2019)
4 start-up

Activities:
electrolyzer/storage/fuelcell

Aims :
- to strengthen collaborations between CNRS labs and to favor project development
- to present innovations and technological progresses

cnrs

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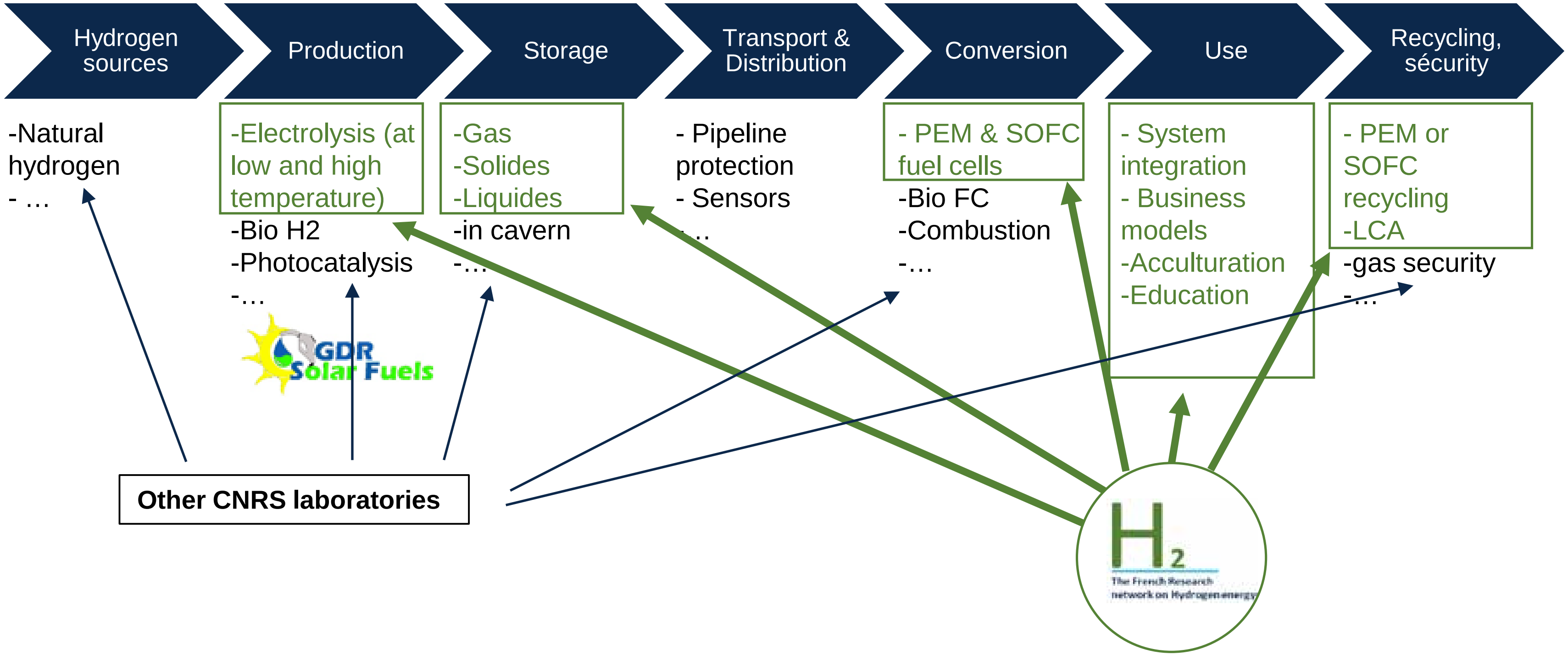
H_2 activities at the CNRS. The place of FRH2 in the Hydrogen Value Chain



II "Hydrogen"

- "H", the most abundant element in the universe (75% by weight and 92% in number of atoms)

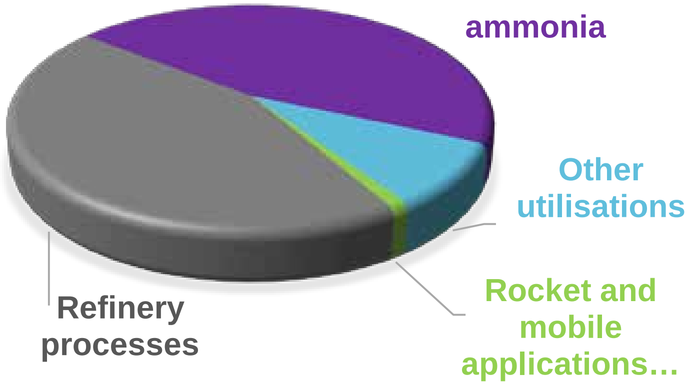
- The molecule "H_2": very large weight energy density ...

33 kWh / kg ... > 3x Gazoline

- A powerful energy vector (rocket, electricity and heat production with a hydrogen fuel cell) but little used as such currently

World annual production: 75 million tons

99% are used for industrial applications.



Some key facts of Hydrogen: mobile (e- and thermal) + stationary applications (e- and thermal) to decarbonize these utilizations

3.7 L

2.75 kg

6€

petrol

=

33 kWh

25 L

(700 bars)

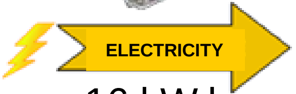
1kg

7€

H₂

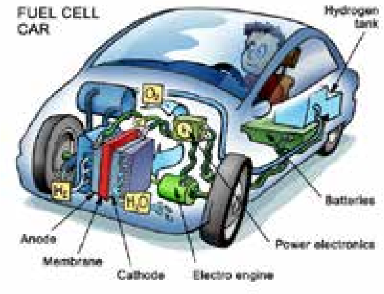
Heat

Fuel cell



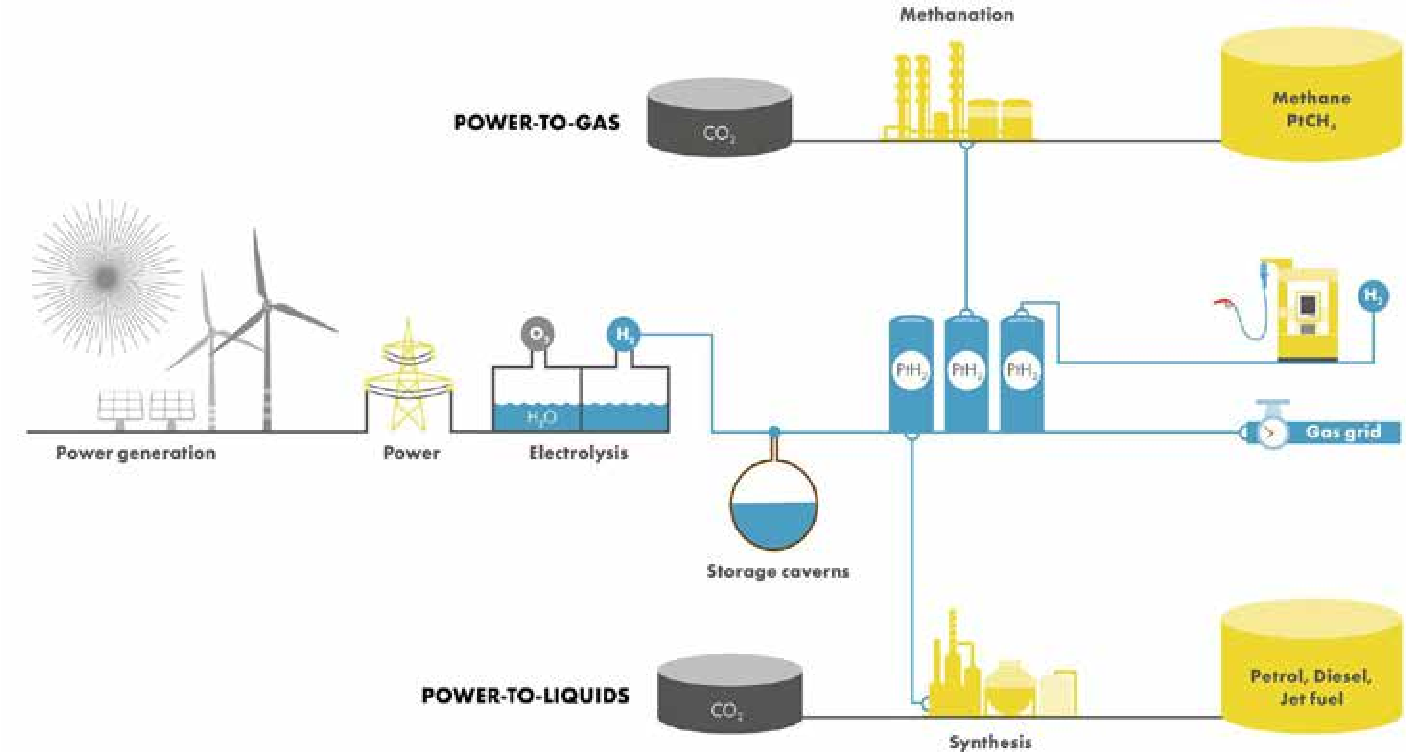
16 kW.h

Energy for 1-2 days



100 km range

Some key facts of Hydrogen: production of other molecule using CO_2. To decarbonize industry



III Hydrogen production

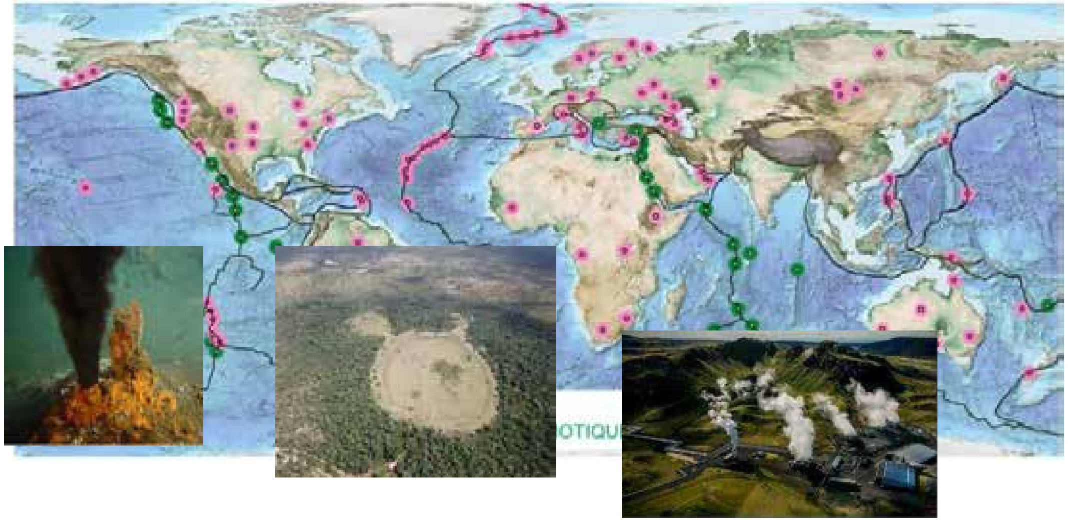
On earth, the atmosphere is generally oxidizing (N_2 neutral). The H_2 molecule is a reducing agent (it reacts easily with oxygen).

à There is no Hydrogen molecule in our atmosphere

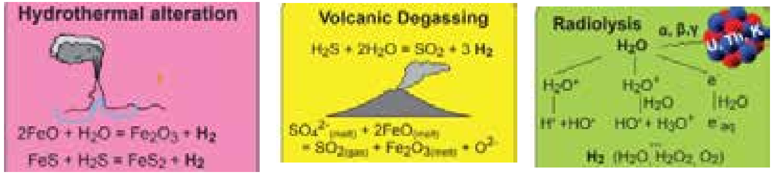
à We need to produce H_2 using "H" containing molecules

Natural H_2 (also called white Hydrogen)

A long list of known emanations



Origin of native H_2?



Modified from Klein et al., 2020 Elements, Vol. 16, pp. 19–24

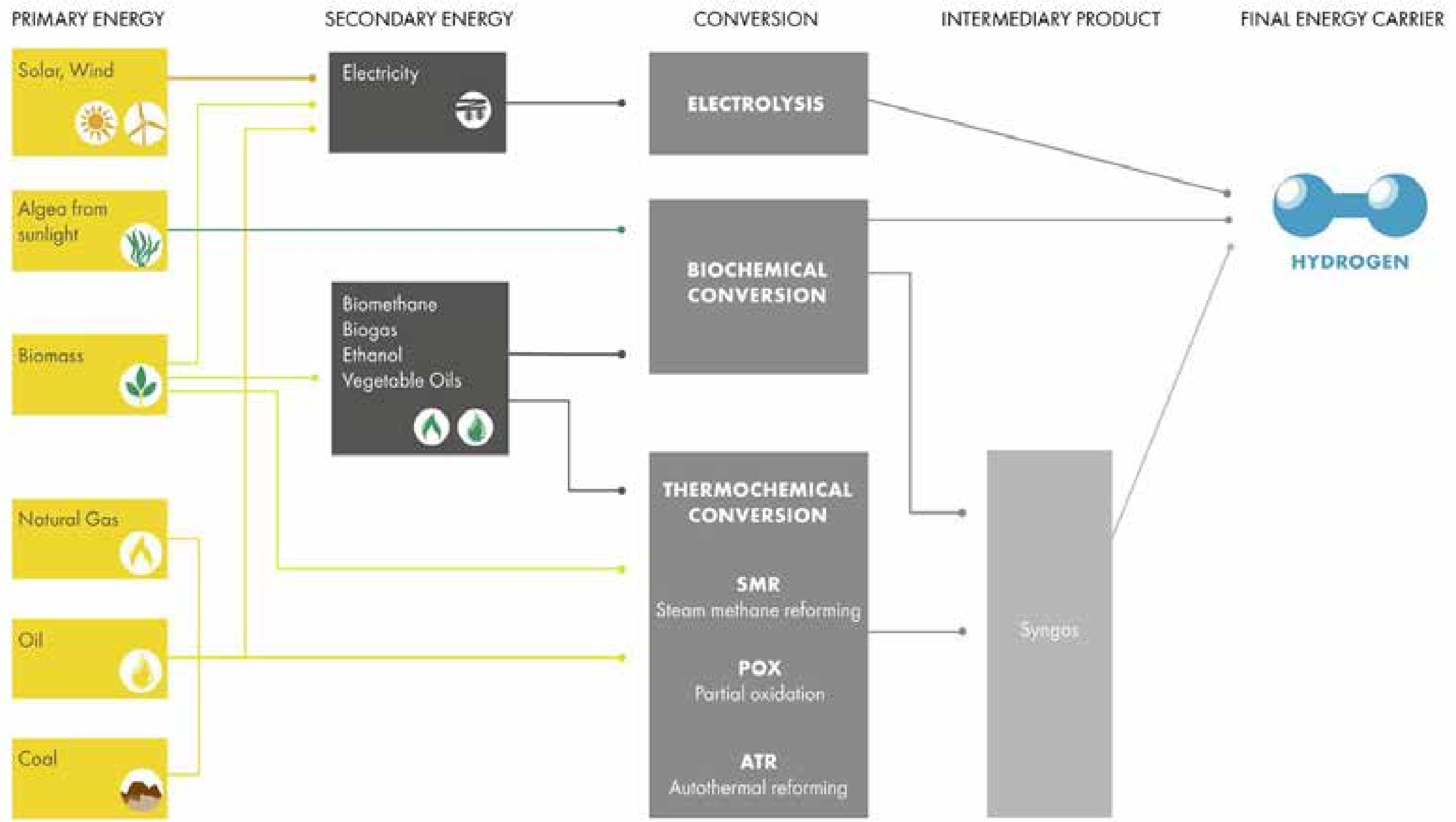
- What are the volumes of H_2 in these reservoirs?
- What are the results of the production test of the wells?
- Is long-term exploitation feasible?
- Is this resource renewable?
- Can we artificially enhance the production? Is there a local market or an export market for this energy source?

Fairy circles have been identified in Mali, Brazil, Ukraine, Russia, and US. Natural hydrogen (98% pure) is produced from a field in Mali for 7 years.

Conclusion: Known for long time but not easy to produce (great depth, more than 2,000 meters)

The company "la française de l'énergie" announced a few days ago the discovery of important natural hydrogen reserves in the Lorraine mining basin around the Folschviller well (Moselle). The first estimates report 46 billion tonnes!! (vs World annual production: 75 million tons)

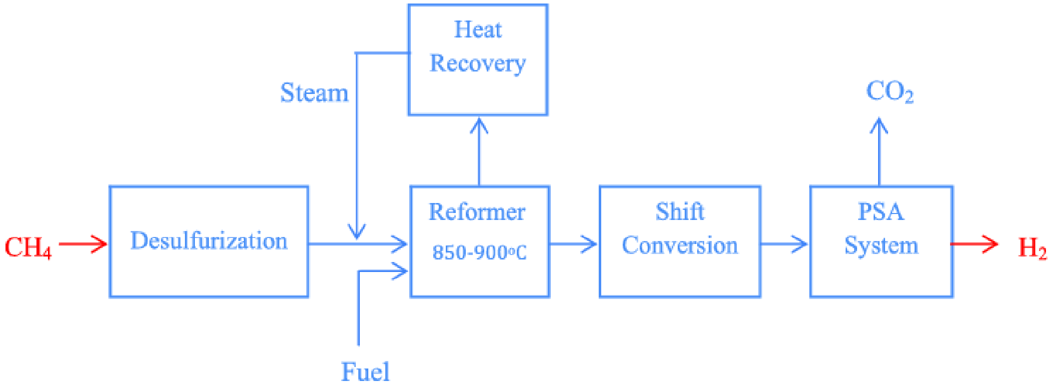
III Hydrogen production

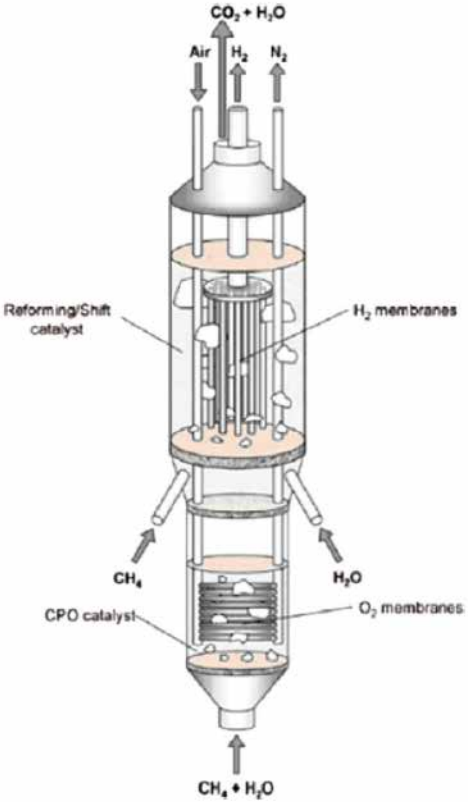


Hydrogen production

Hydrogen production Method	Advantages	Disadvantages	Efficiency	Cost [$/kg]
Steam Reforming	Developed technology & Existing infrastructure	Produced CO, CO_2 Unstable supply	74–85	2.27
Partial Oxidation	Established technology	Along with H_2 Production, produced heavy oils and petroleum coke	60–75	1.48
Auto thermal Reforming	Well established technology & Existing infrastructure	Produced CO_2 as a byproduct, use of fossil fuels.	60–75	1.48
Bio photolysis	Consumed CO_2, Produced O_2 as a byproduct, working under mild conditions.	Low yields of H_2, sunlight needed, large reactor required, O_2 sensitivity, high cost of material.	10–11	2.13
Dark Fermentation	Simple method, H_2 produced without light, no limitation O_2, CO_2-neutral, involves to waste recycling	Fatty acids elimination, low yields of H_2, low efficiency, necessity of huge volume of reactor	60–80	2.57
Photo Fermentation	Involves to waste water recycling, used different organic waste waters, CO_2-neutral.	low efficiency, Low H_2 production rate, sunlight required, necessity of huge volume of reactor, O_2-sensitivity	0.1	2.83
Gasification	Abundant, cheap feedstock and neutral CO_2.	Fluctuating H_2 yields because of feedstock impurities, seasonal availability and formation of tar.	30–40	1.77–2.05
Pyrolysis	Abundant, cheap feedstock and CO_2-neutral.	Tar formation, fluctuating H_2 amount because of feedstock impurities and seasonal availability	35–50	1.59–1.70
Thermolysis	Clean and sustainable, O_2-byproduct, copious feedstock	High capital costs, Elements toxicity, corrosion problems.	20–45	7.98–8.40
Photolysis	O_2 as byproduct, abundant feedstock, No emissions.	Low efficiency, non-effective photocatalytic material, Requires sunlight.	0.06	8–10
Electrolysis	Established technology Zero emission Existing infrastructure O_2 as byproduct	Storage and Transportation problem.	60–80	10.30

Steam reforming of methane





De Falco Marcello, Marrelli Luigi, Iaquaniello Gaetano. Membrane reactors for hydrogen production processes,264.London,England:Springer;2011.

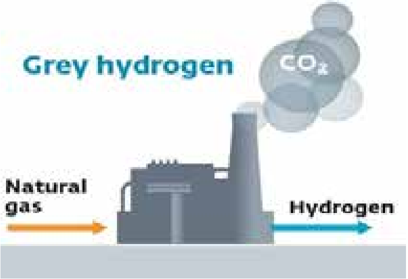
Reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	$\Delta H_{295} = -206$ kJ/mol
Water gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$	$\Delta H_{298} = -41$ kJ/mol
	$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	$\Delta H_{298} = 165$ kJ/mol

CO_2 emission: 16 to 20%vol (10 kg / kg of H_2)
Efficiency : 70%
Cost : 1.5 to 5 €/kgH_2

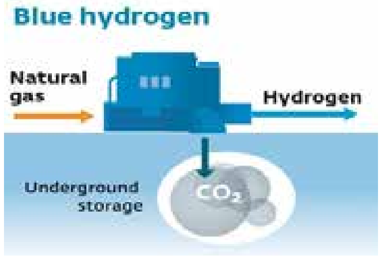
H2: Almost never in the natural molecular state on earth ... it must be produced

"carbonized" H2
96%

From fossil resources (gas, oil, coal) ("gray")



Cost : 1.5 to 5 €/kgH_2



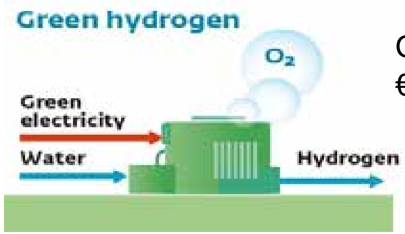
Over-Cost : +1€/kgH_2

"Decarbonized" H_2
(<3kg CO_2/kg H_2)
4%

From fossil resources but with CO_2 sequestration ("blue")

From water electrolysis using electricity from nuclear plant ("yellow")

From water electrolysis (using renewable electricity) and / or renewable resources ("green")



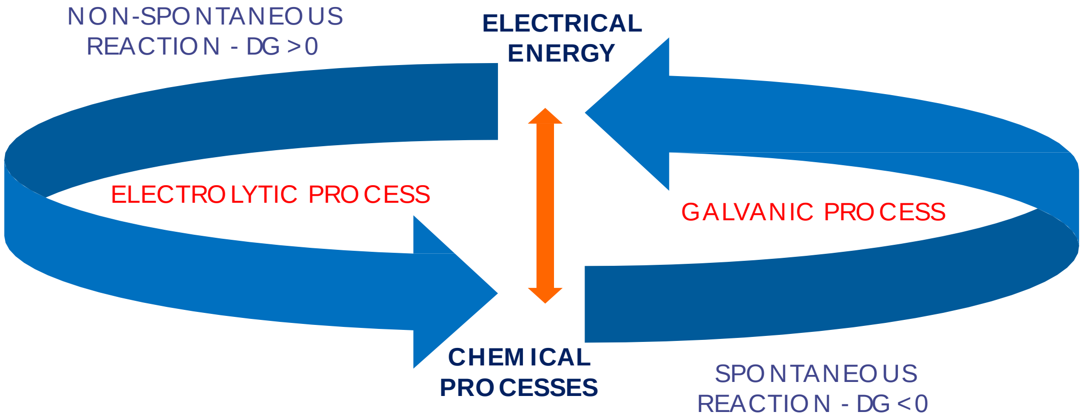
Cost : 5-10 €/kgH_2

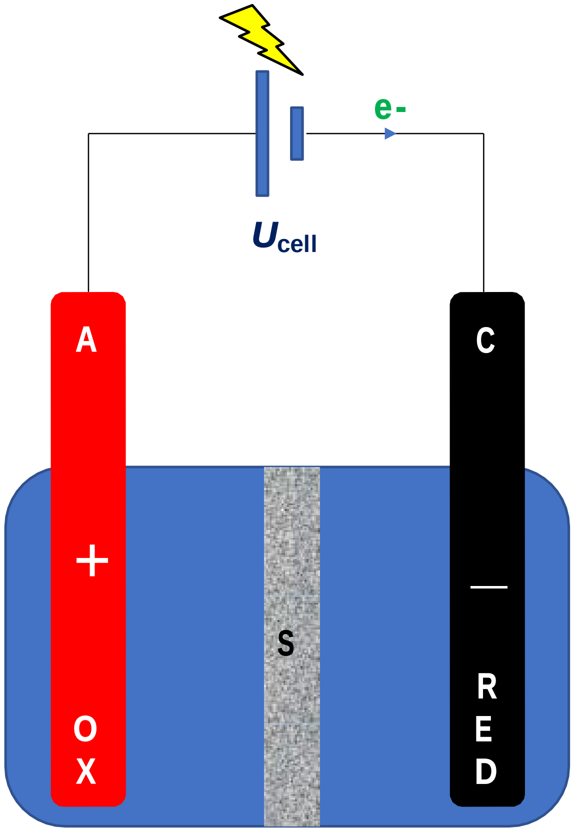
Electrochemical device

TWO types of electrochemical reactions:

1. If a cell voltage is created by a chemical reaction à **GALVANIC REACTIONS** (e.g. batteries, fuel cells etc)

2. If a chemical reaction is driven by an external applied cell voltage à **ELECTROLYTIC REACTIONS** (e.g. water electrolysis)





ELECTROLYTIC CELL

Water Electrolyser

Definition: A typical water electrolyser comprises three (main) components: an **electrolyte (E)**, a **cathode (C)**, and an **anode (A)**.

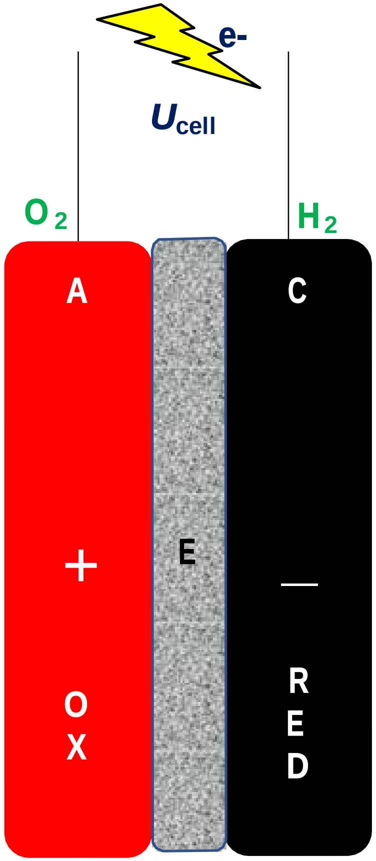
Energy supplied with an externally generated voltage that must exceed the equilibrium voltage of water splitting, decomposes water molecules into

hydrogen gas in the Hydrogen Evolution Reaction (HER) at the cathode, and **oxygen gas in the Oxygen Evolution Reaction (OER) at the anode**.

Water electrolysers are electrochemical devices used to split water molecules into hydrogen and oxygen by passage of an electrical current.

@Anode: Oxygen Evolution Reaction - OER

@Cathode: Hydrogen Evolution Reaction - HER



Water Electrolysis

Electrochemical reaction

WATER à GREEN HYDROGEN + GREEN OXYGEN

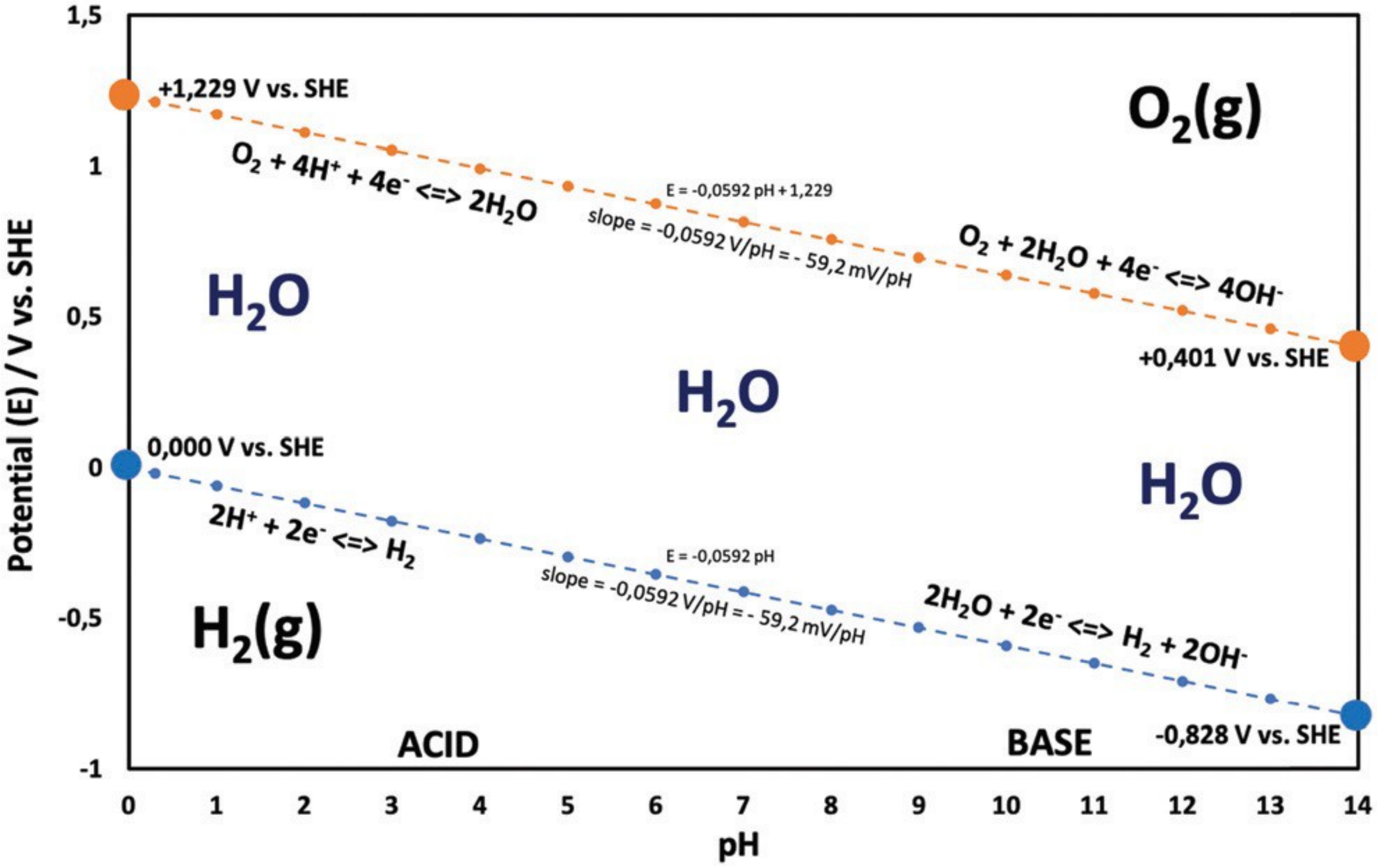
«GREEN» ELECTRONS (RENEWABLES)

$2H_2O$ à $2H_2 + O_2$ $DG^o = +237$ kJ / mol_{H2}

9 kg of water produces 1 kg of H_2 (*) and 8 kg of O_2

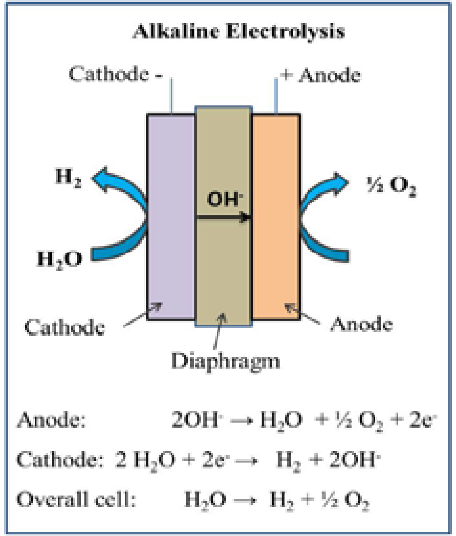
* 1kg = 100km with an usual car

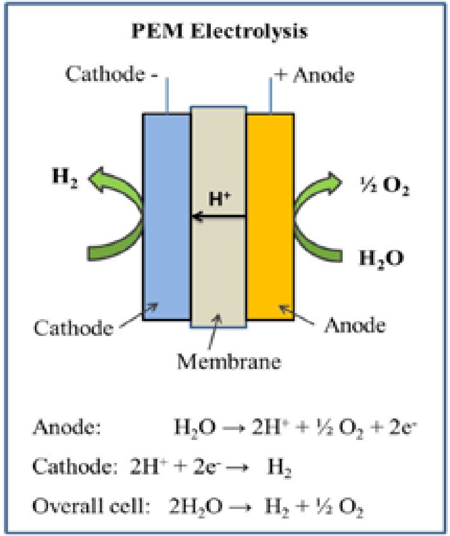
Pourbaix Diagram for Water

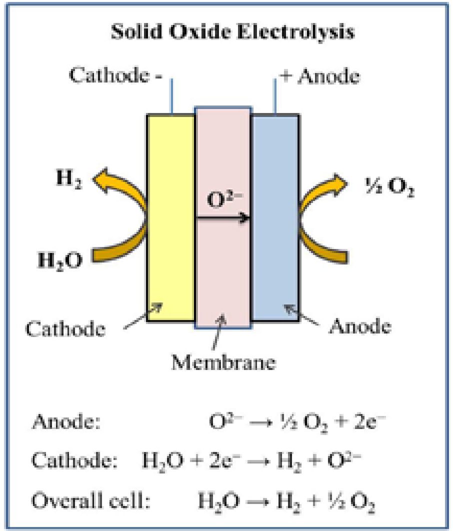


U^o = D G^o/nF = 237000/(2 x 96485) = 1,23 V

Water ELECTROLYSERS







Electrolysis process	**Alkaline**	**Proton Exchange Membrane**	**Solid Oxide**
Temperature, efficiency	50-80°C, <65%	50-80°C, <70%	500-900°C, >90%
Advantages	Well established technology. Non-noble electro catalysts. Low cost technology. The energy efficiency is (70–80%). Commercialized	High current densities. Compact system design and Quick Response. Greater hydrogen production rate with High purity of gases (99.99%). Higher energy efficiency (80–90%). High dynamic operation	Higher efficiency (90–100%). Non-noble electro catalysts. High working Pressure
Disadvantages	Low current densities. Formation of carbonates on the electrode decreases the performance of the electrolyser. Low purity of gases. Low operational pressure (3–30 bar). Low dynamic operation	New and partially established High cost of components. Acidic environment. Low durability. Commercialization is in near term	Laboratory stage. Large system design. Low durability

S. Shiva Kumar, V. Himabindu /Materials Science for Energy Technologies 2 (2019) 442–454

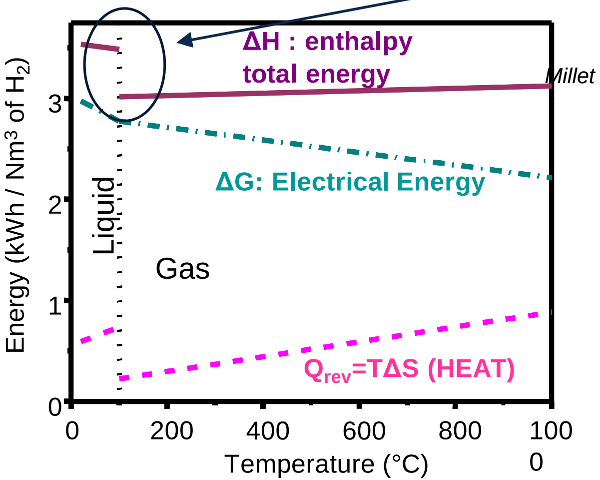
thermodynamic point of view: Low temperature vs High temperature Electrolysis

Decomposition of water
by electrolysis (liquid or gas state)

$H_2O_{(l\ or\ g)}$ à $H_{2\,(g)} + ½\ O_{2\,(g)}$

DH (H_2O_l) = + 285.8 kJ mol^{-1}
DH (H_2O_g) = + 250 kJ mol^{-1}

very endothermic reaction! But **ΔH** is lower at high temperature



Source: Chase *NIST-JANAF Thermochemical Tables* (1998) Monograph 9, 1325

when the temperature increases, part of the electrical energy (**ΔG)** can be replaced by HEAT (which can very low cost).

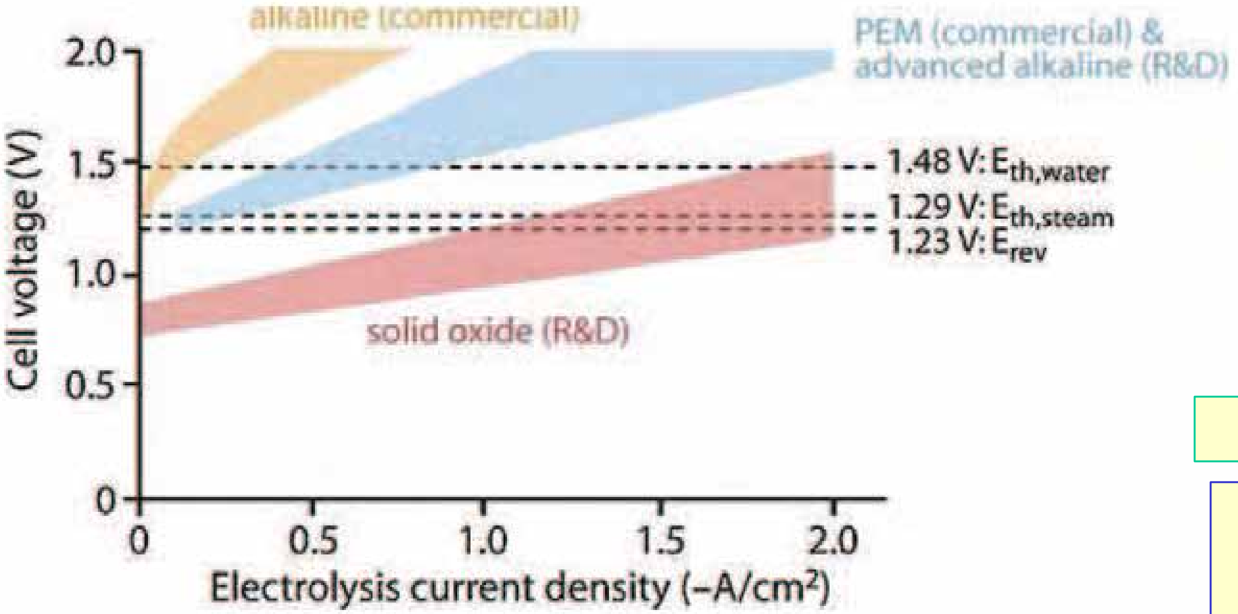
Low temperature electrolysis :
Electricity/Heat = 85/15
High temperature electrolysis (700-850°C): Electricity/Heat = 70/30

P. Millet, Fundamentals of water electrolysis, in Hydrogen Production by Electrolysis, A. Godula-Jopek (ed.), Wiley-VCH, 2015

Thermoneutral potential

Eficiency

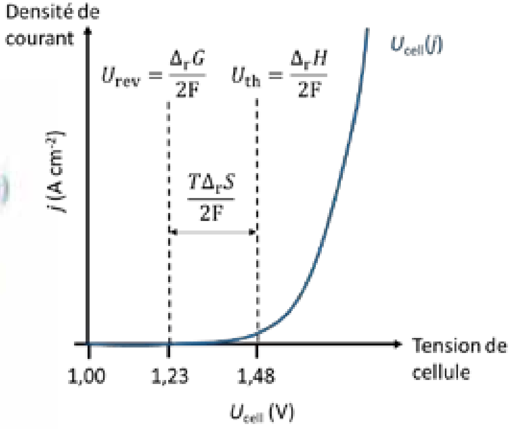
Electrical Consumption



Hydrogen production

Low Temp. Electrolysis: 60 kWh/kg H_2

High Temp. Electrolysis: < 40 kWh/kg H_2



Millet P., Électrolyseurs de l'eau à membrane acide, Techniques de l'ingénieur, (2007).

$V_{tn,T} = - DH_T/nF$

Liquid water

$V_{tn,25°C} = 1.481$ V

Gaseous water

$V_{tn,800°C} = 1.286$ V

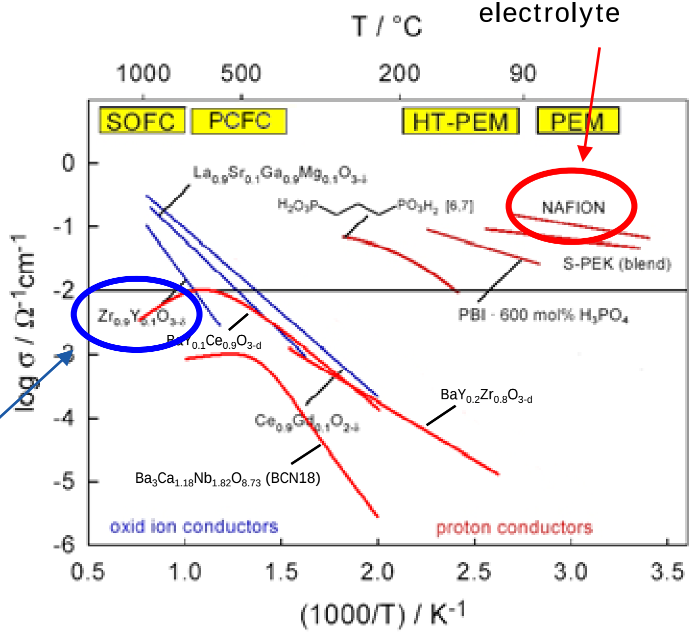
Why the operating temperature is low or high:

The electrolyte!!!

The operating temperature is conditioned by an ionic conductivity > 10 ms/cm

HT electrolyte

Low temperature electrolyte

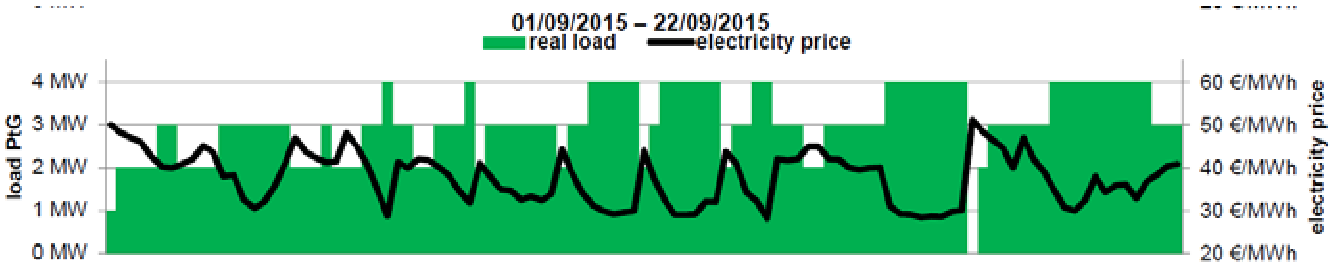


from K.D.Kreuer SSPC- 2004

Example of real activities:
The Energiepark in Mainz (Germany)

- §Connected to a wind-farm (8 MW)
- §6.3 MW peak electrolyzer :
- - 3 stacks,
- - each: 2.1 MW, 2M€, 225Nm^3/h, 35bars, 17t, 6.3m length)
- §1000 kg storage (33 MWh)

high-dynamic PEM pressure electrolyser (SIEMENS, SILIZER 200) with an input current of up to 6 MW: the largest in the world (in 2015)



production d'H_2 lorsque le tarif de l'électricité est bas...

But also in France (in Bouin in Vendée close Noimoutier Island at 100 km from Nantes)

Lhyfe

wind farm à Lhyfe company: 300 to 1000 kilos per day à Hydrogen station in La Roche-sur-Yon (Hydrogen electrical mobility trucks)

cnrs Nantes Université IMN INSTITUT DES MATÉRIAUX DE NANTES JEAN ROUXEL

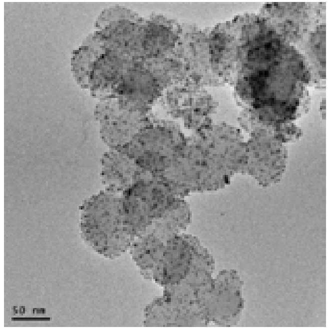
Recent announcement (April 2023)

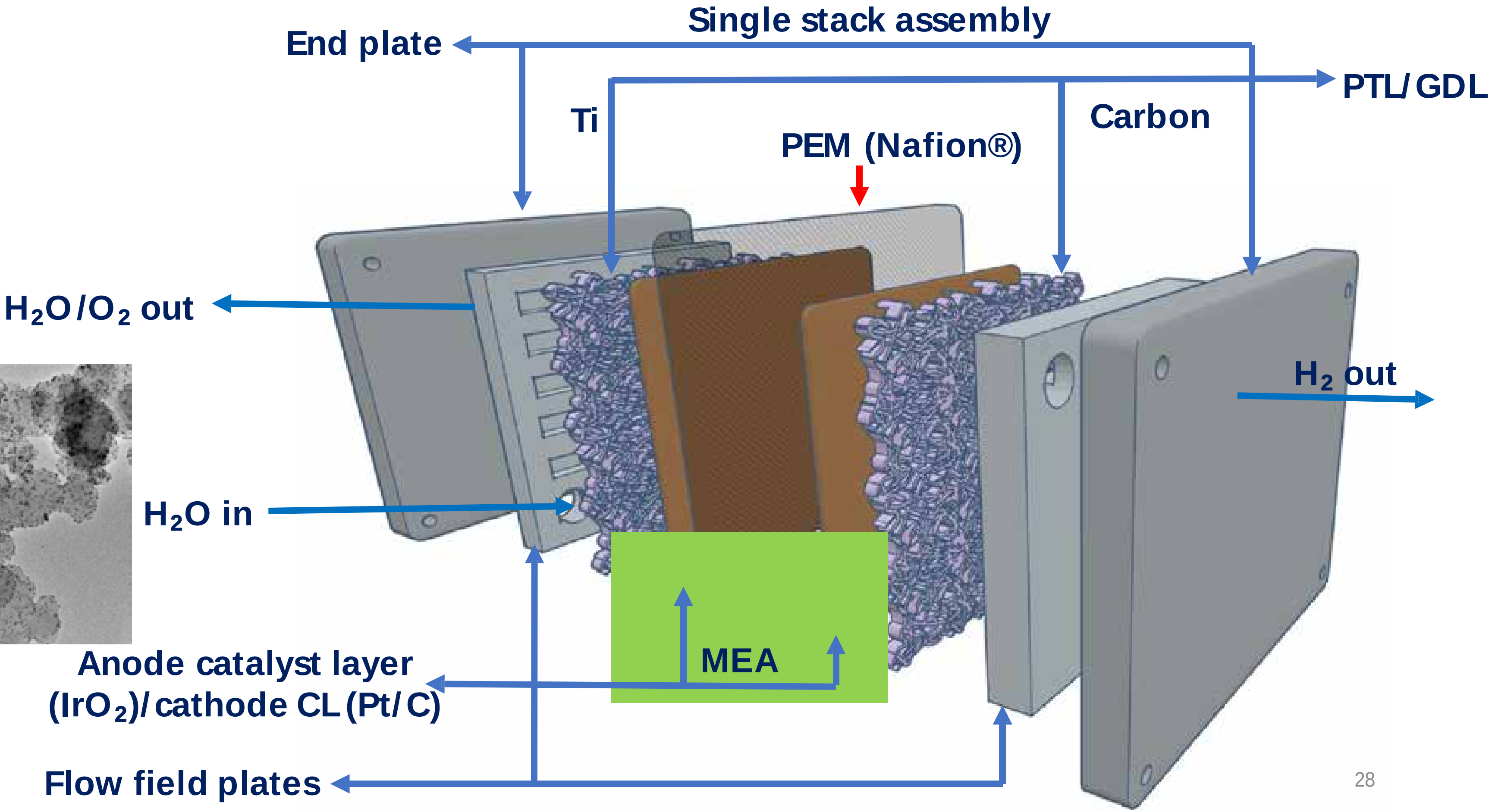
The installation of the largest solid oxide electrolyser on the planet has just been successfully carried out in the Neste biofuels refinery in Rotterdam, in the Netherlands. The 2.6 MW device was manufactured by the German company Sunfire.

With an operation at 850 ° C, its yield turns out to be at least 20 % higher than that of equivalent to low temperature devices….

https://www.h2-mobile.fr/actus/hydrogene-plus-grand-electrolyseur-oxyde-solide-monde-entre-service/

A PEM water electrolyser in details:





PEMWE

Catalytic materials and support (collector) materials?

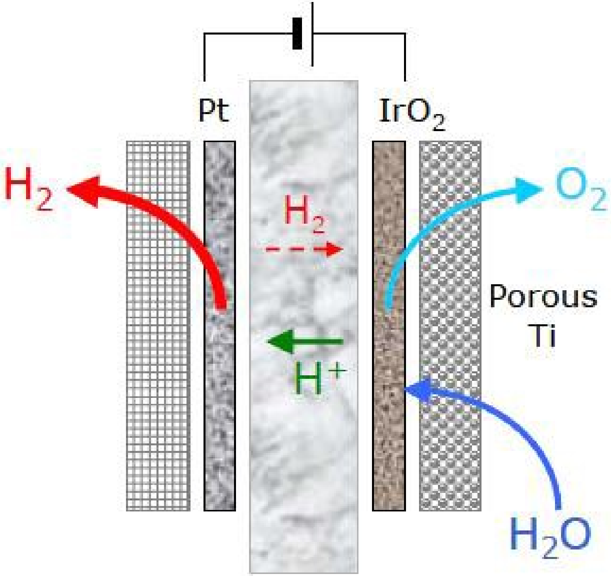
Cathode

Pt black (ca. 1 mg_{Pt} cm^{-2})

Pt/C (0.5 mg_{Pt} cm^{-2})

Þ Problematic close to that of PEMFC

Structured carbon support for favoring bubble release



Anode

IrO_2, RuO_2 (doped with SnO_2, TaO_2, SbO_2, etc.), 2 – 4 mg cm^{-2}

Doped or undoped porous TiO_x as catalysts support

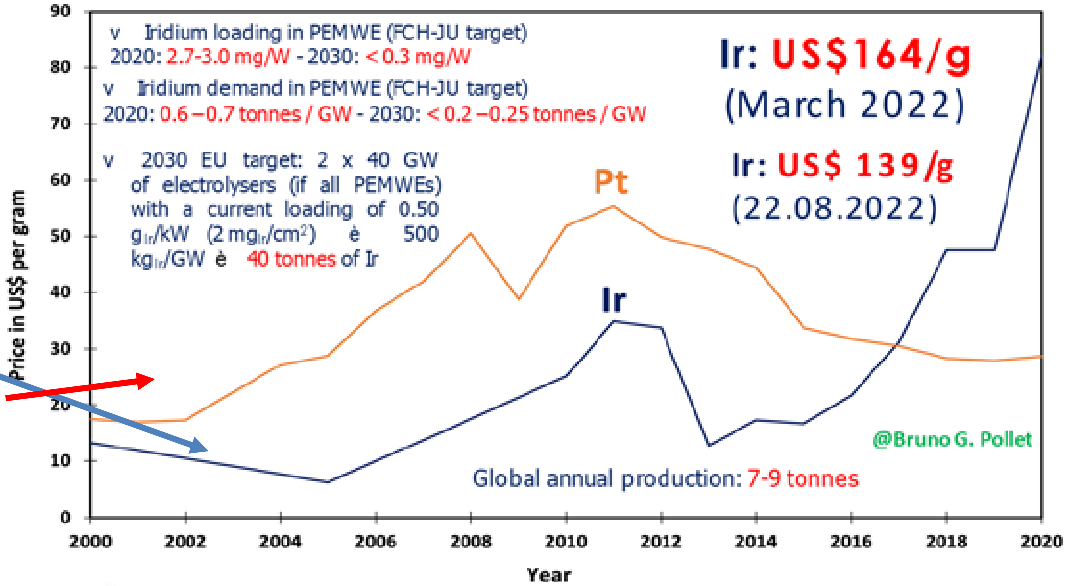
Porous Ti as current collector

Membrane

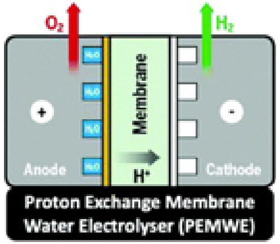
PTFE Reinforced PFSA membrane (pressure up to 30 bars)

PEMWE: the cost of the catalyst

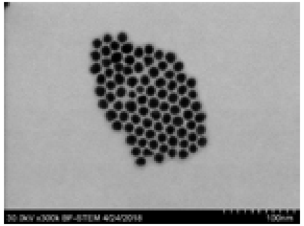
Operating temperature	50–80 °C
Operating pressure	<70 bar
Electrolyte	PFSA membranes
Separator	Solid electrolyte (above)
Electrode/catalyst (oxygen side)	Iridium oxide
Electrode/catalyst (hydrogen side)	Platinum nanoparticles on carbon black
Porous transport layer anode	Platinum coated sintered porous titanium
Porous transport layer cathode	Sintered porous titanium or carbon cloth
Bipolar plate anode	Platinum-coated titanium
Bipolar plate cathode	Gold-coated titanium
Frames and sealing	PTFE, PSU, ETFE

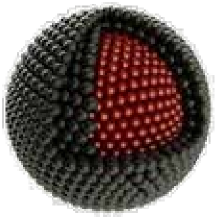


Parameter	2020 status	2020 target	2035 target	Future
Ir (mg cm^{-2})	2–5	1	0.2–0.40	0.05–0.2
Ir (g kW^{-1})	<2.5 (0.33/0.5/0.67)	0.40	0.05–0.4	0.01–0.4
Pt (mg cm^{-2})	1–2	1	0.5	0.05
Pt (g kW^{-1})	0.5–1	0.5	0.25	0.1
Current density (A cm^{-2})	2	2	3	5
Power density (W cm^{-2})	3	3	8	10
Electrode area (m^2)	0.12	—	—	0.50



R&D Focus





Catalyst

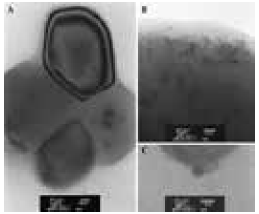
- **Removing the supply and price bottlenecks of precious metal (Pt, Ir, Ru, etc.) usage by replacing them with earthly abundant materials and robust, low-cost syntheses.**
- **To develop platinum group metal-free (PGM-free) HER/OER catalysts as viable replacement for Ir in PEMWE.**

Membrane

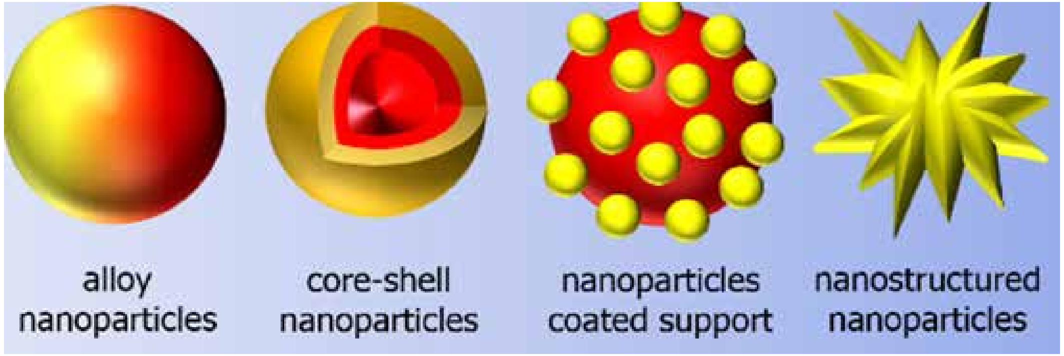
- Use ultra-thin, low EW (equivalent weight), reinforced membranes with good mechanical and H_2 cross-over resistance.

PTL

- Use coatings on PTL to reduce contact resistance and passivation. Also, PTL's morphology/pore-structure should be designed to improve catalyst utilization and provide a smooth support for the ultra-thin membranes.



OER/ HER Catalyst Development for LT-WE



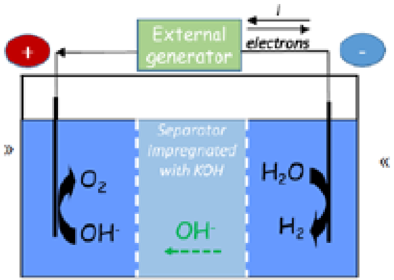
- Generally, one of the most critical barriers for electrochemical water splitting is to use **high-performance** and **durable electrocatalytic material** that allow both **fast HER** and **OER reaction kinetics** and **low overpotentials**.

- The choice of HER and OER catalysts in **acidic**, **neutral** and **alkaline electrolytes** is important as the HER and OER reaction kinetics and overpotential will differ.

Some examples of research activities

Ex : alcaline electrolysis

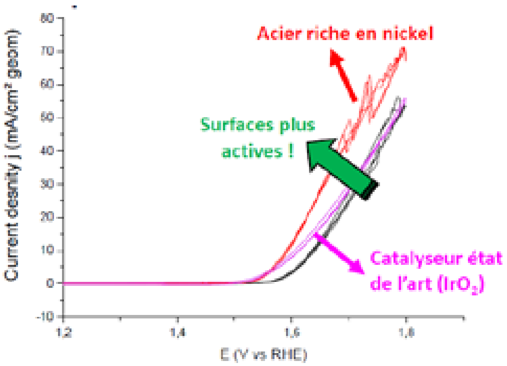
Catalyseur « état de l'art » = IrO_2



Catalyseur « état de l'art » = Pt/C

Contact : Marian Chatenet (LEPMI)

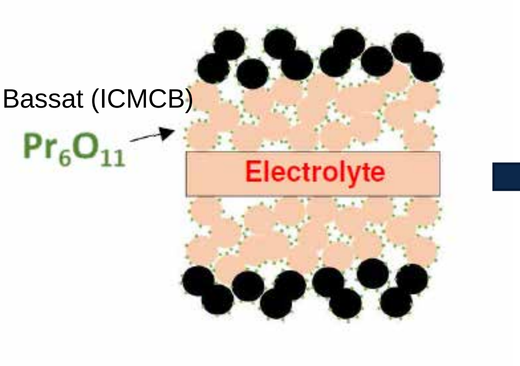
Noble metals do not always make active and durable catalysts !!
Some steels and oxides are more active and durable than noble catalysts (SOA)

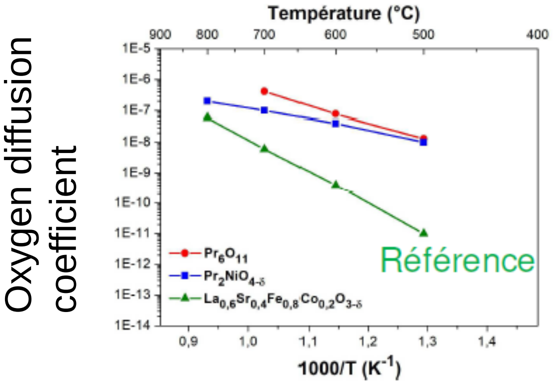


Dégagement de O_2 sur acier et IrO_2 en 1 M KOH, T = 25°C

Ex : Solid oxide electrolyser cell

Contact : Jean-marc Bassat (ICMCB)





Performance improvement with a "simple" oxide compared to SOA materials

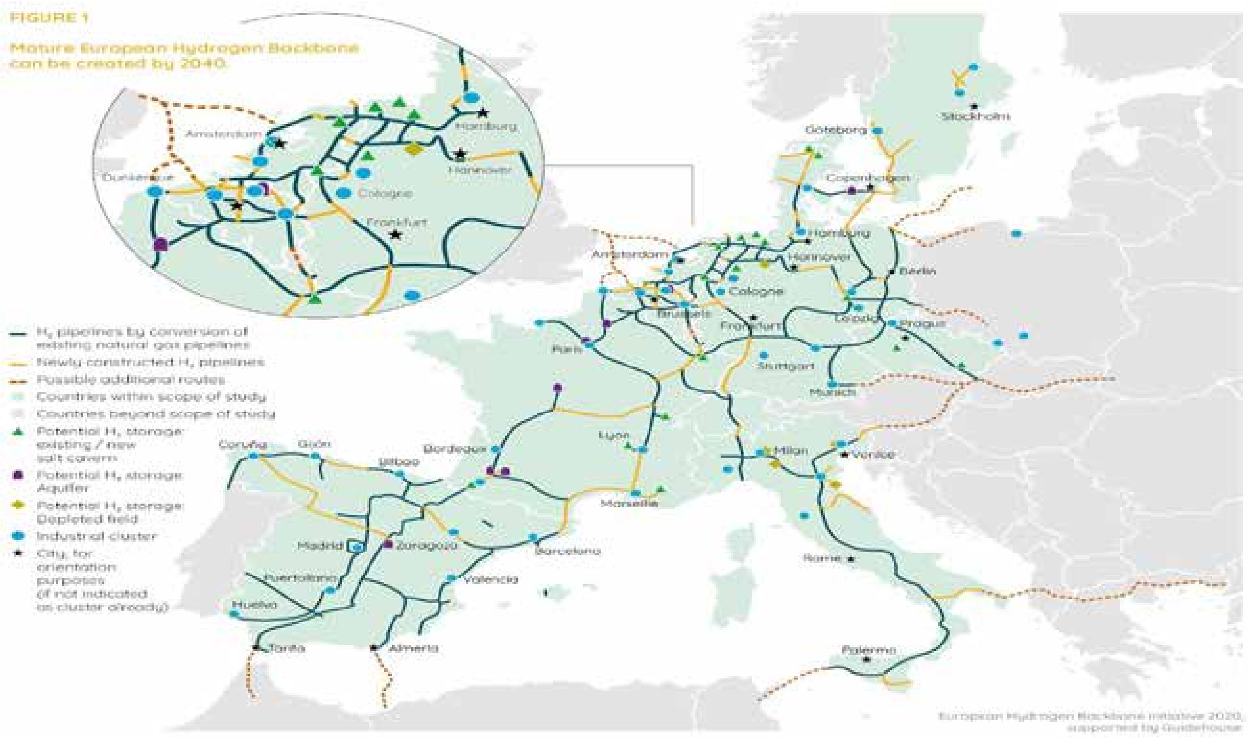
R&I challenges and opportunities

issues: Increasing outlet pressure, reversibility, co-electrolysis, decreasing PGM for PEMEC (1 mg of IrO_2 / cm^2), lifetime for SOEC

solutions :

- New shaping methods
- New materials (eg reduction of nickel content via nano particle integration)
- New architectures: design, barrier layers, Proton ceramic conducting cells
- Purification, compression (electrochemical)
- Recycling
- Multiphysical tests on long durations or accelerated tests

The European Hydrogen Backbone ("EHB")



- **6 800** km in 2030; **23,000 km by 2040**,
- Estimated transport cost: **0.09-0.17 €/kg per 1000 km**,

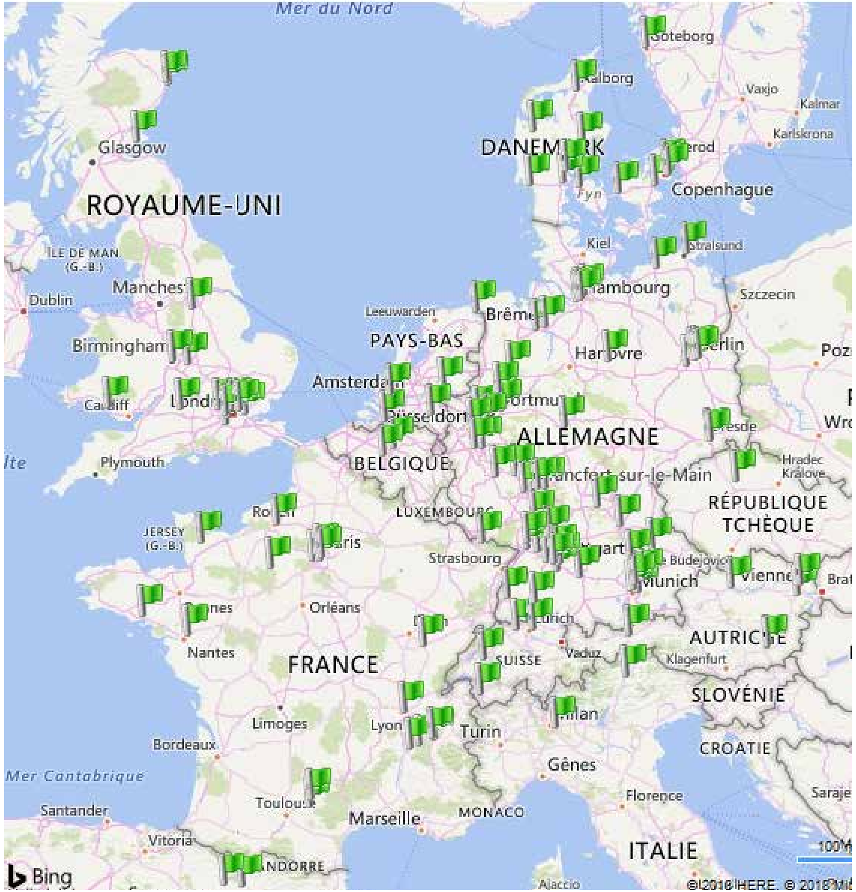
Hydrogen Refueling Station (HRS)

TOTAL HRS in
Karlsruhe (Germany)

Mobile HRS in Nantes
(McPhy)

The French Research
network on Hydrogen energy

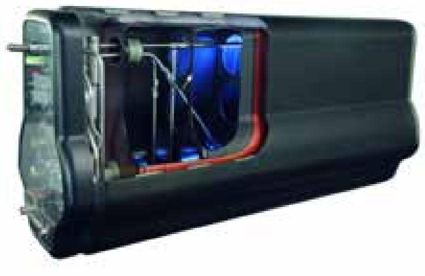
Europe (2017): 138 HRS. The German public hydrogen refuelling infrastructure is the second largest globally with 45 public stations (56 total), ahead of the USA (40 stations) and only surpassed by Japan with 91 public stations.



The French Research network on Hydrogen energy

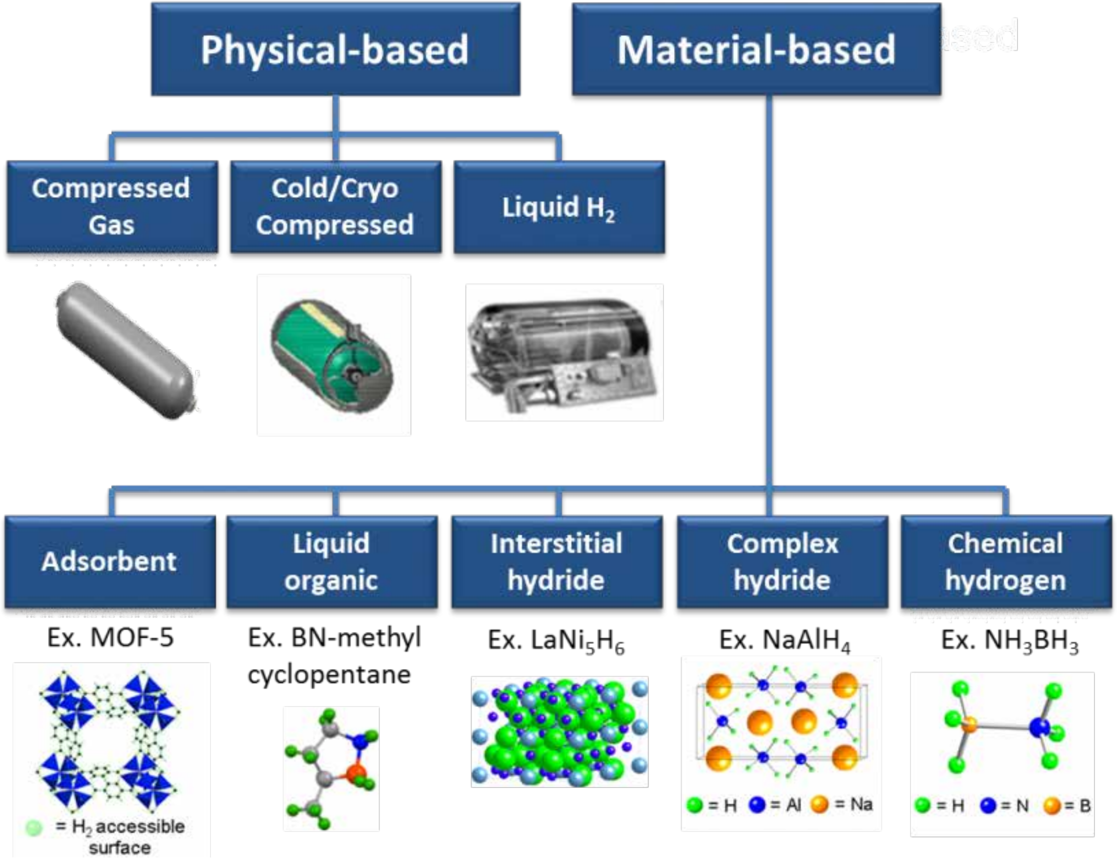
The Hydrogen storage (a joke !!!)

Liquid H_2
(BMW)



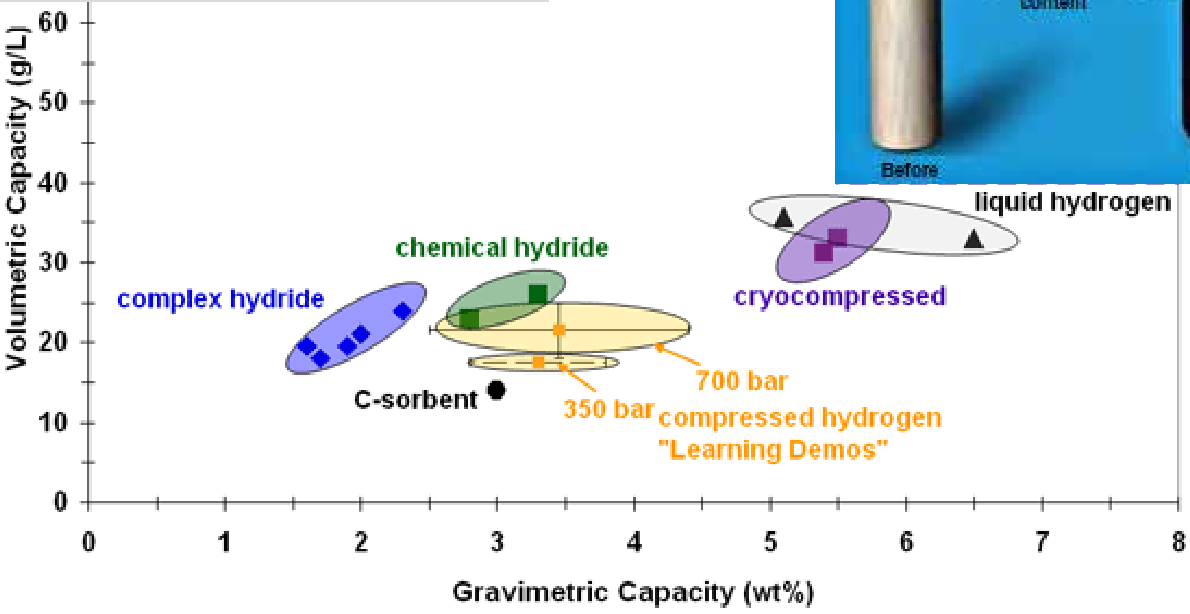
Compressed H_2
(PSA)

- gas in high-pressure tanks (350–700 bar).
- liquid requires cryogenic temperatures because the boiling point of hydrogen at 1 atm is −252.8°C.
- Hydrogen can also be stored on the surfaces of solids (by adsorption) or within solids (by absorption).



Storage

Specific targets:
- •1.5 kWh/kg system (4.5 wt.% hydrogen)
- •1.0 kWh/L system (0.030 kg hydrogen/L)
- •$10/kWh ($333/kg stored hydrogen capacity).



R&I challenges and opportunities

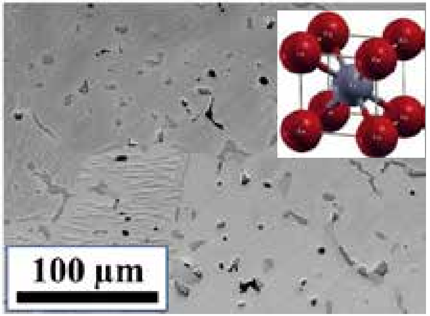
Issues: Improve compressed H_2 storage and develop solid storage with good weight capacities (> 3-4wt% ambient) with a competitive price!

solutions :

- Coupling calculations / new compositions for reversible solid storage at room temperature in ultra-light materials
- Metal nanoparticles inserted into porous materials to reduce the operating temperature and improve storage reversibility
- Decrease the content of critical raw materials and carbon, develop recycling processes
- Optimize energy efficiency in storage / electrolyser or fuel cell coupling,
- Improvement of the (thermo-) mechanical resistance of compressed H_2 tanks,
- Increased safety of high pressure storage

Ex : H_2 storage in solids

Titanium-type alloys having a reversible capacity greater than 1.5 Wt.% at room temperature and pressure less than 25 bar, charge / discharge speed (<2 minutes) and lifetime higher than 250 cycles. Up-scaling to 4 tonnes (GKN Powder Metallurgy)



Eurpoean project HyCARE (Hydrogen CArrier for Renewable Energy Storage)

Contact : Fermin Cuevas (ICMPE)

Ex: Magnesium Hydrolysis

Reacts @ room temperature

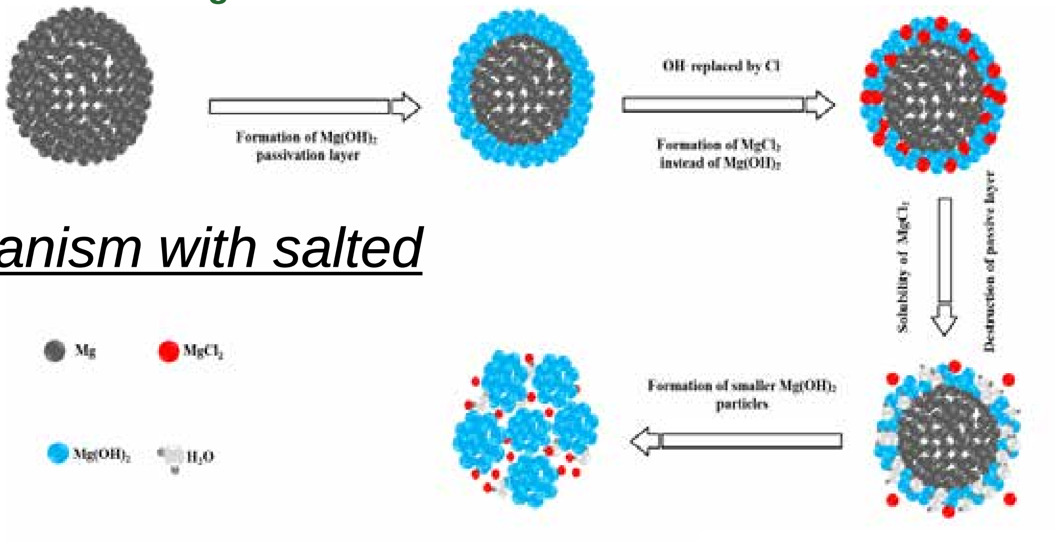
Ø *$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$* *$\Delta_r H = -354$ kJ.mol^{-1}*

J

- ü **3.3 wt. % of released hydrogen**
- ü **produced $Mg(OH)_2$ – not harmful**
- ü **Abundance and low cost of Mg**

L

Reaction quickly stopped by a passive layer of $Mg(OH)_2$ on the material surface !



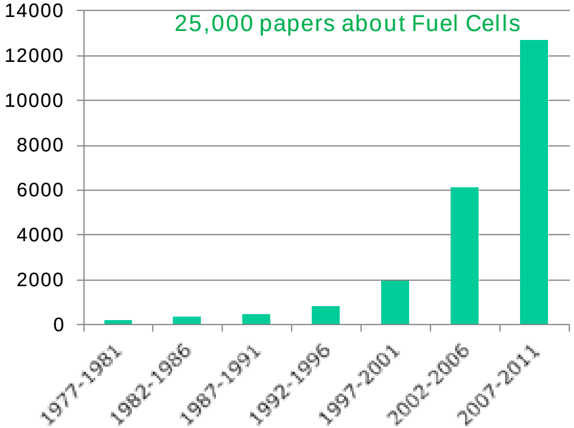
<u>New! Mechanism with salted water</u>

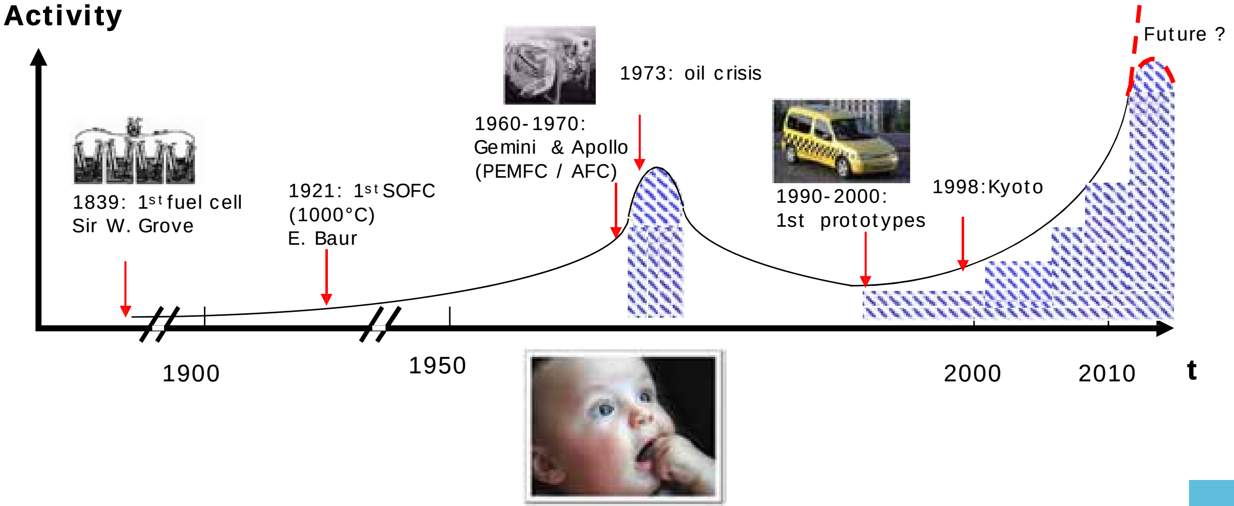
Patent: FR 15 59518 / EP2016/073905

V Fuel cell

History…

- XVIIIst century: fuel cell discovery
- Years 60: first steps
- Years 70: intensive researches
- Years 80: stand-by
- Years 90-2000: revival !

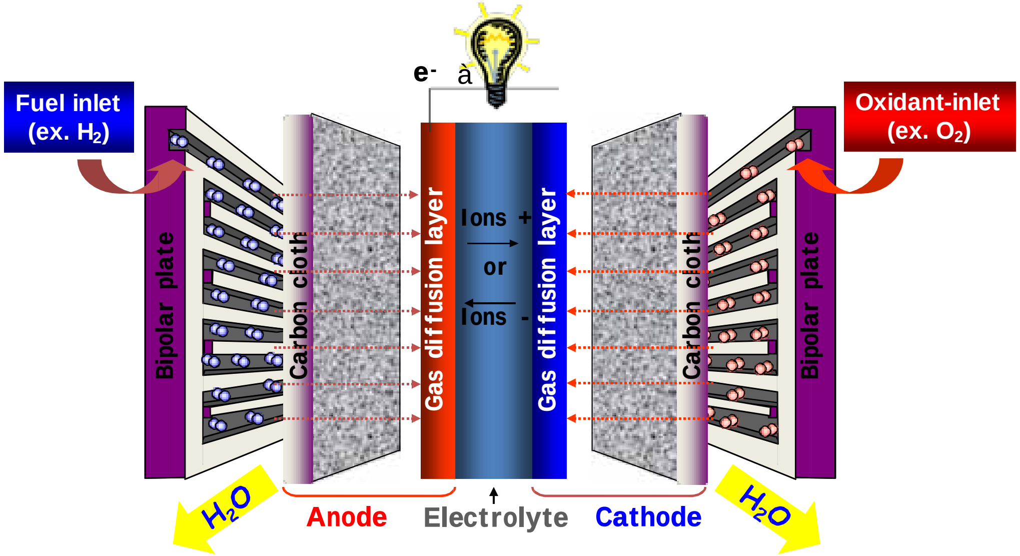




How it works

A fuel cell is a power supply device based on the **conversion of chemical energy into electrical energy** by the following reaction:

Fuel (H_2, CH_3OH,…) + ½ O_2 ® H_2O + e- + DH + (CO_2)



Oxydation :

H_2 à 2 H^+ + 2 e^-

or

H_2 + O^{2-} à H_2O + 2 e^-

Réduction :

½ O_2 + 2 H^+ + 2 e^- à H_2O

or

½ O_2 + 2 e^- à O^{2-}

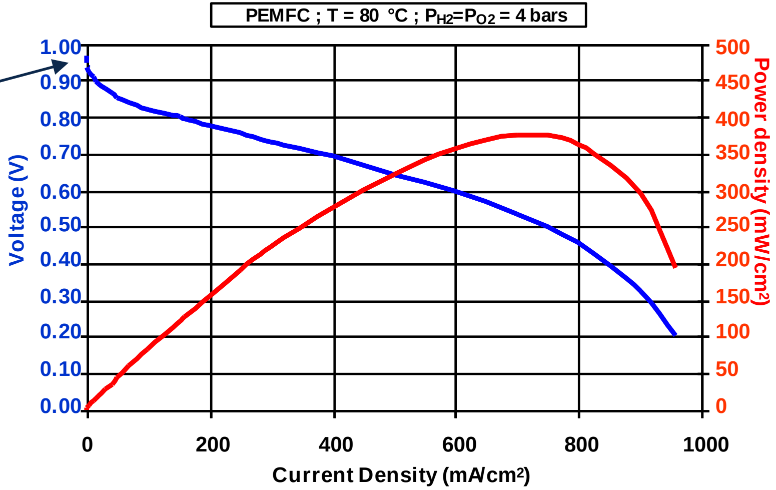
$$E_{i=0} = \frac{-\Delta G}{2F} \cdot \sim 1V$$

Fuel cell performance

Fuel cell performance can be assessed by current-voltage curves.
i-V curves show the voltage output of a fuel cell for a given current load.
Ideal fuel cell performance is dictated by thermodynamics (Nernst)

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln\left(\frac{1}{p_{H_2} p_{O_2}^{1/2}}\right)$$

Partial Pressure of H_2 (atm)	Partial Pressure of O_2 (atm)	Open Circuit Voltage (V)
1	1	1.229
1	2	1.233
1	3	1.236
1	4	1.238
1	5	1.239

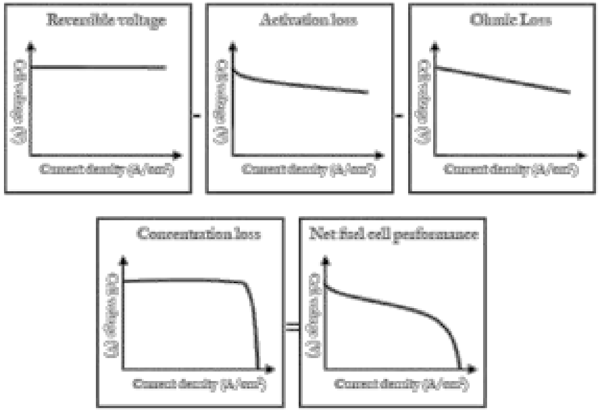


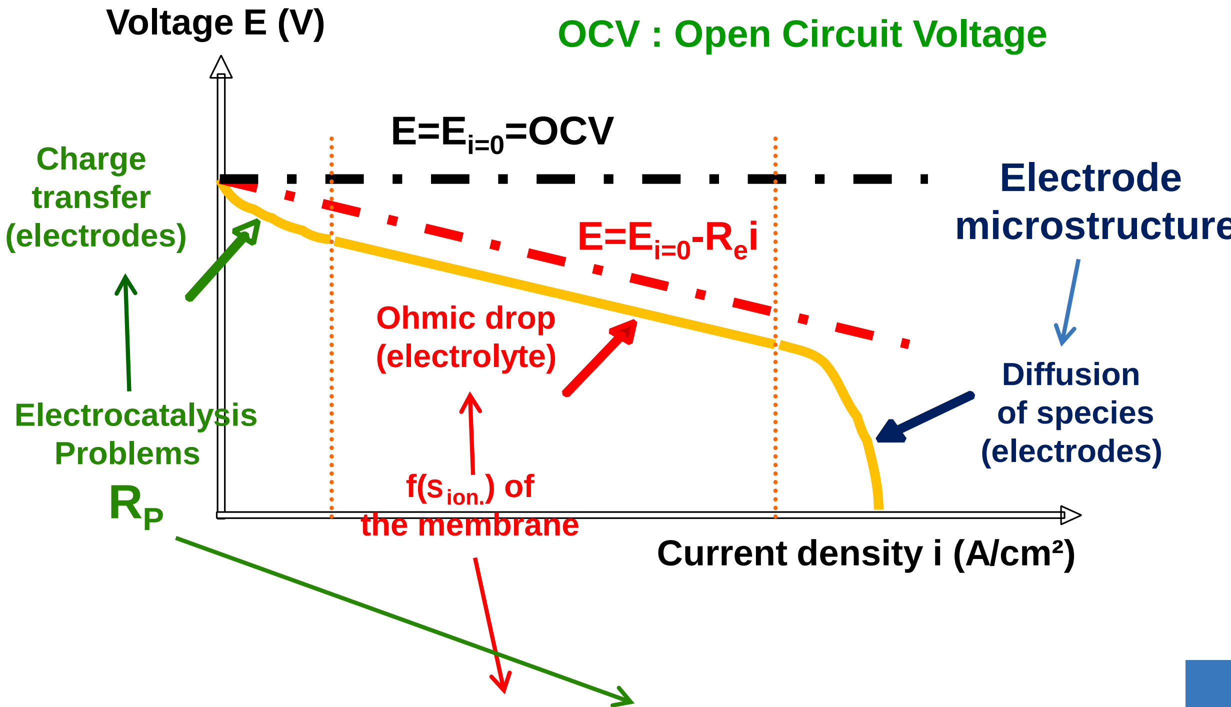
Performance = Voltage vs current
under current: $E(i) < E_{i=0}$

Fuel cell performance

Real fuel cell performance is always less than ideal fuel cell performance due to losses.
The major types of loss are :

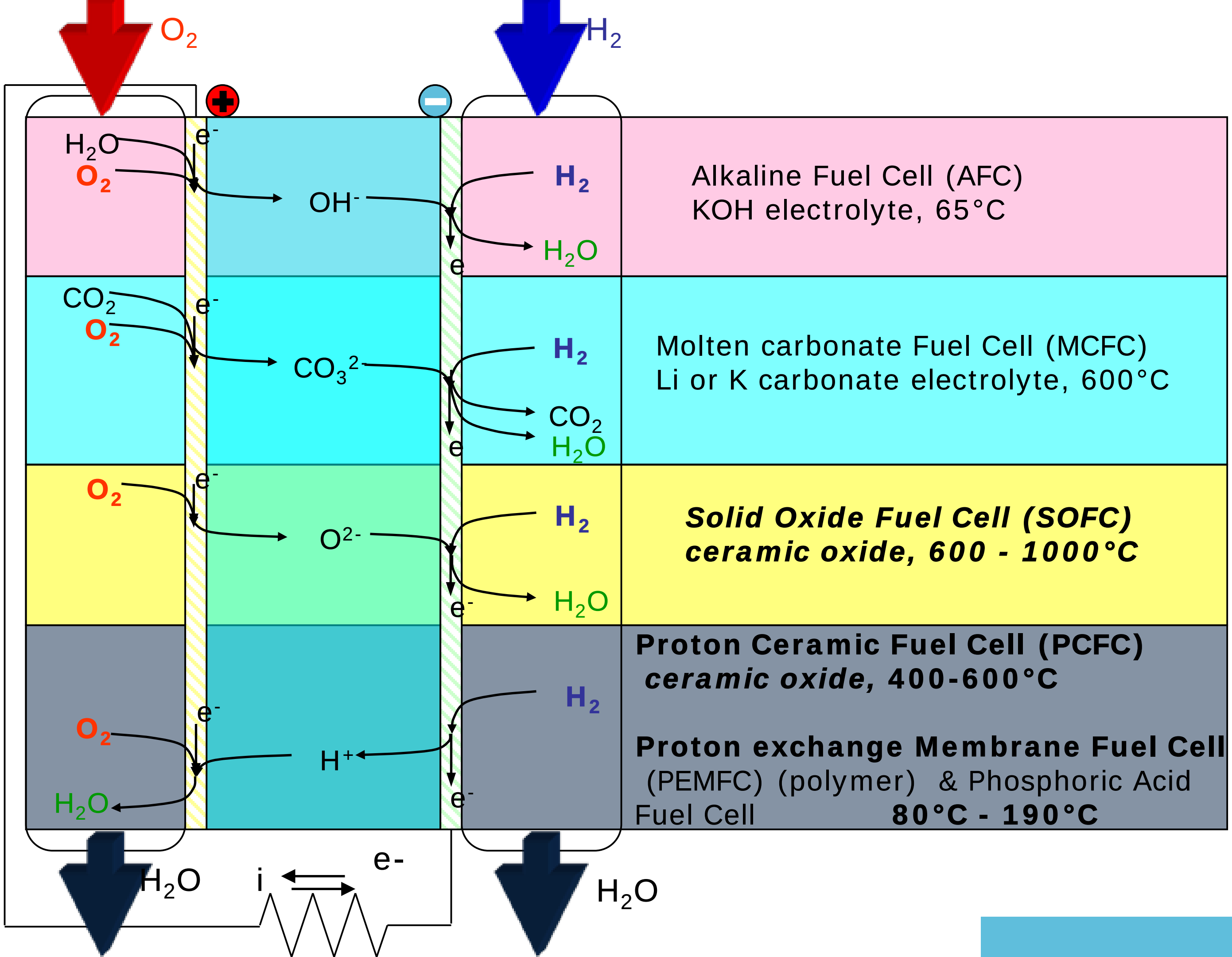
- **Activation loss** (losses due to electrochemical reaction)
- **Ohmic loss** (losses due to ionic and electronic conduction)
- **Concentration loss** (losses due to mass transport)





$$E(i) = E_{i=0} - R_e i - S|\eta|$$

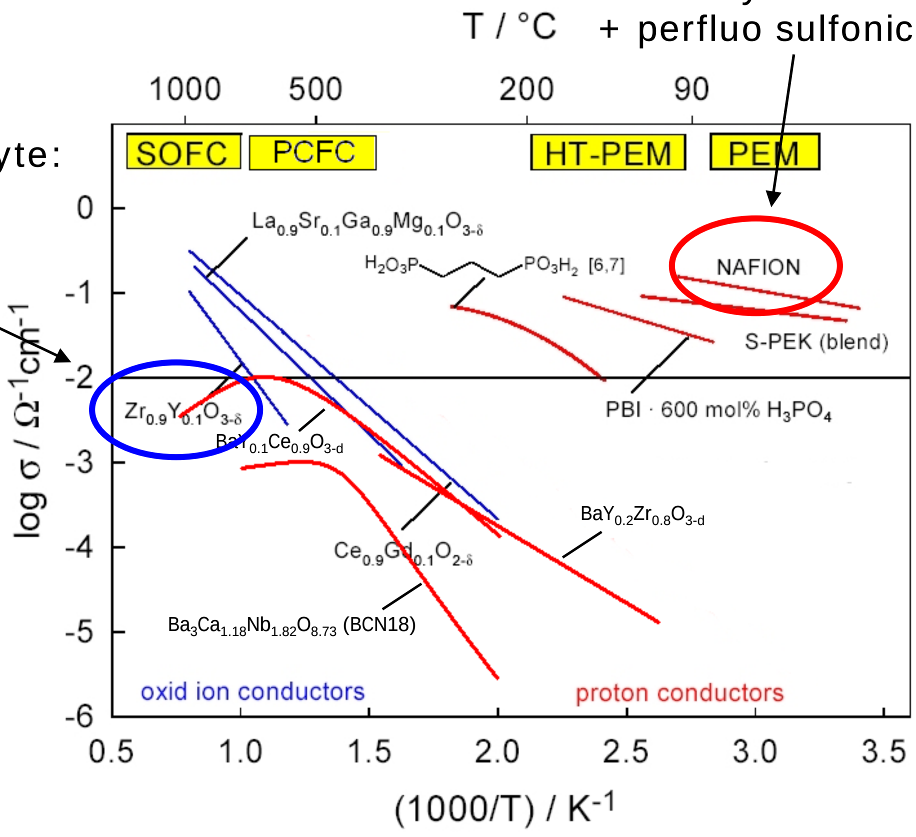
Fuel cell types



operating temperature ?

usual PEMFC
electrolyte: TEFLON
+ perfluo sulfonic acid

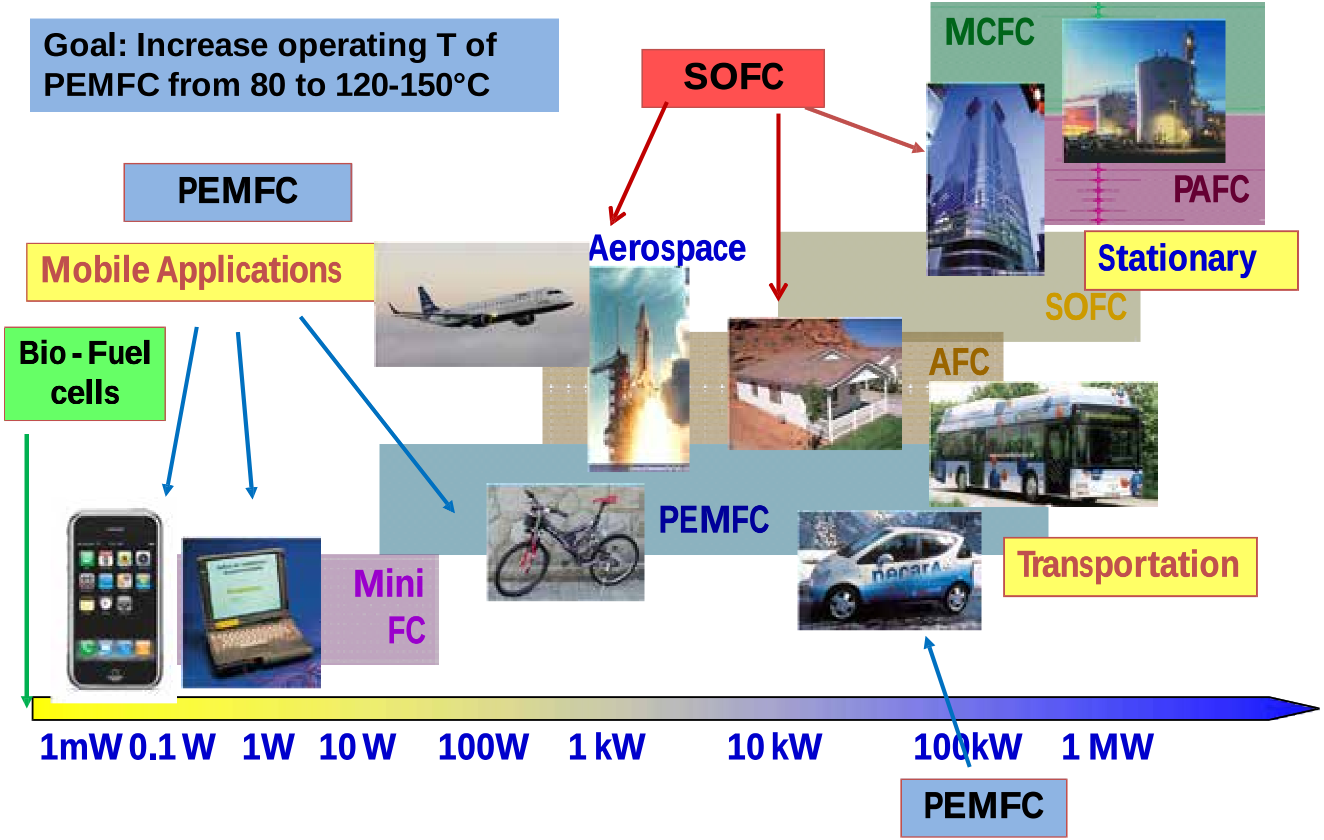
usual SOFC electrolyte:
stabilized zirconia



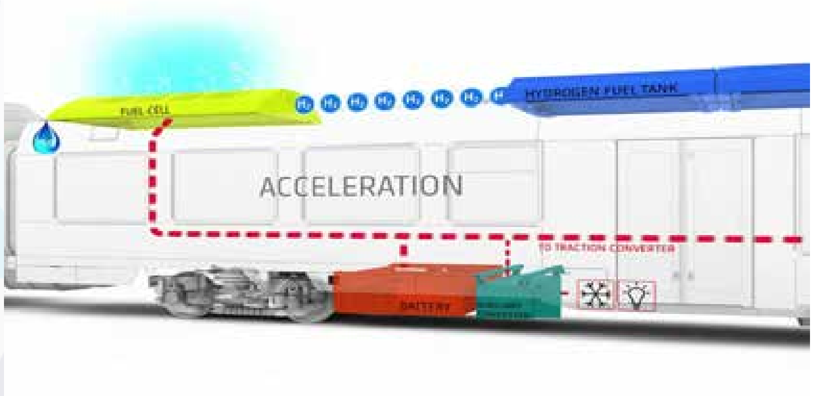
electrolyte conductivity vs temperature:
usual target 10mS/cm at operating temperature
(Arrhenius Law)

from K.D.Kreuer SSPC- 2004

Applications



For train…



ALSTOM CORADIA ILINT

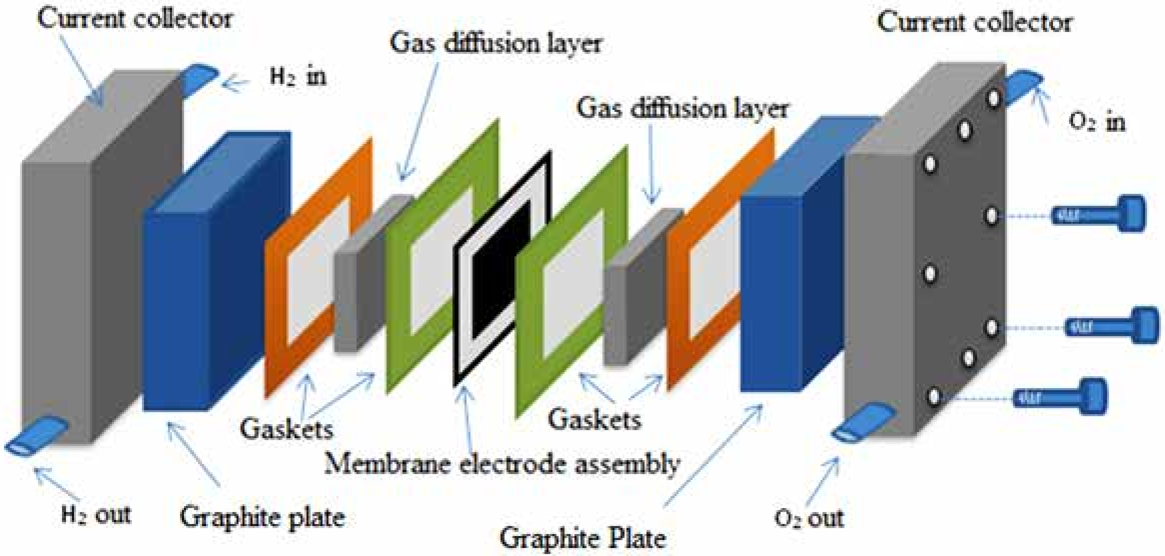
Autonomy: up to 600 kilometers, carrying 220 passengers at 160 km/h.

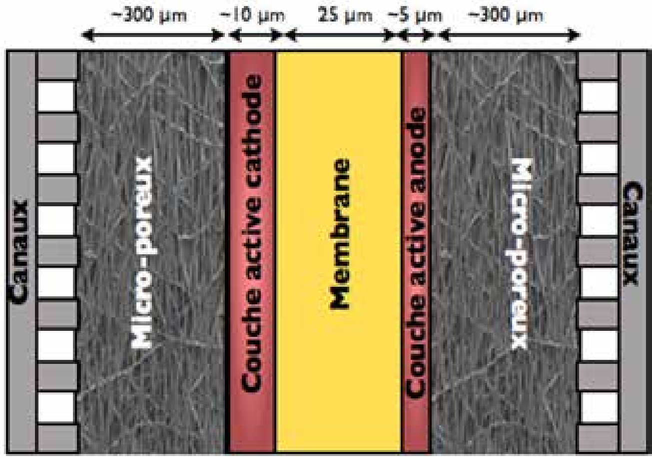
- Since September 17, 2018, two of these trains have been in commercial service in Germany
- February 1-3, 2023: First circulation on French network on the Tours-Loches line.

For buses: Hydrogen bus of Pau (south France)

Since 2020: 8 articulated buses (van Hool) 18 m
Electric motor (2,200 kw @ 1500 rpm)
FC from BALLARD 100KW
Consumption H_2: 10-12 kg/100km
Autonomy: 240 km
Tanks 38.7 kg at 350bar
145 passengers

PEMFC

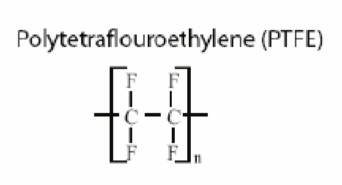




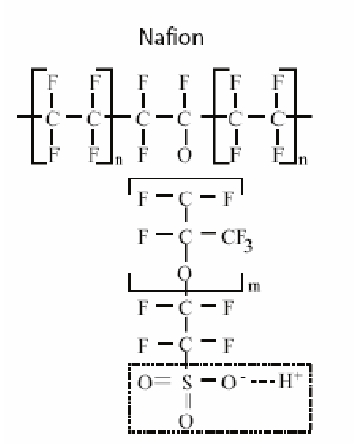
La PEMFC et ses composants

Polymer Electrolyte Membrane: the NAFION

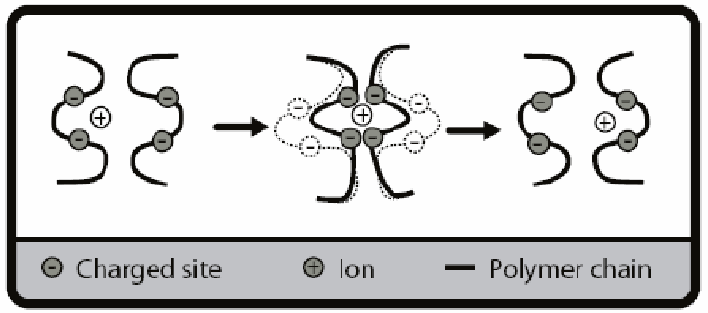
Persulfonated polytetrafluoroethylene (PTFE) – known as **Nafion** – exhibits extremely high proton conductivity based on the vehicle mechanism.



Nafion has a PTFE backbone for mechanical stability with sulfonic groups to promote proton conduction.



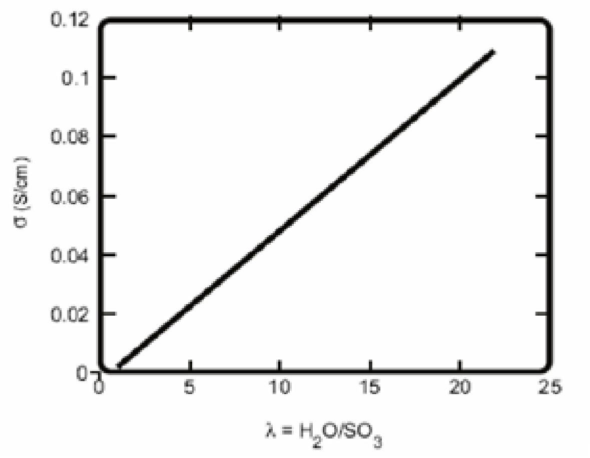
Vehicle mechanism:
Ions are transported through free-volume spaces by hitching a ride on certain free species as these vehicles pass by.



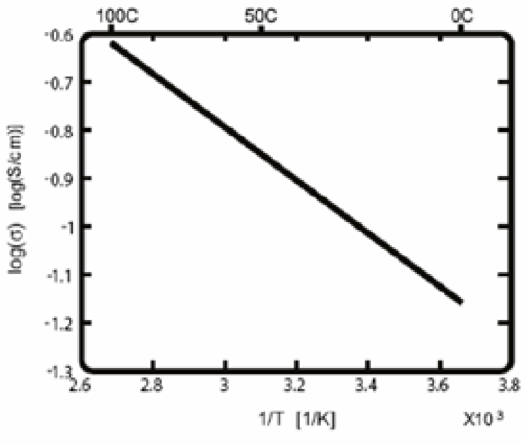
Schematic of ion transport between polymer chains. Polymer segments can move or vibrate in the free volume, thus inducing physical transfer of ions from one charged site to another.

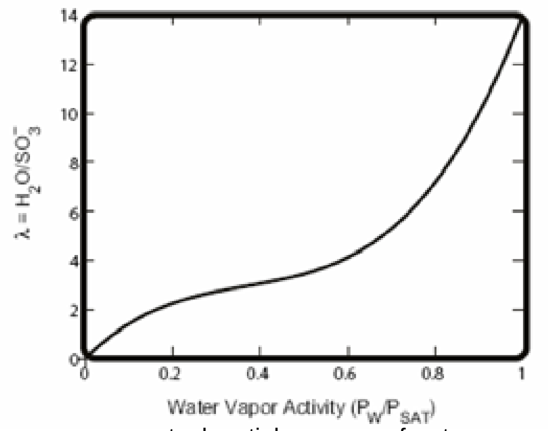
Ionic conductivity

Ionic conductivity of Nafion versus water content λ at 303 K.



Ionic conductivity of Nafion versus temperature when λ=22.





p_W: actual partial pressure of water vapor

p_{SAT}: saturation water vapor pressure

$$\sigma(T,\lambda) = \sigma_{303K}(\lambda)\exp[1268(\frac{1}{303} - \frac{1}{T})]$$

where $\sigma_{303K}(\lambda) = 0.005193\lambda - 0.00326$

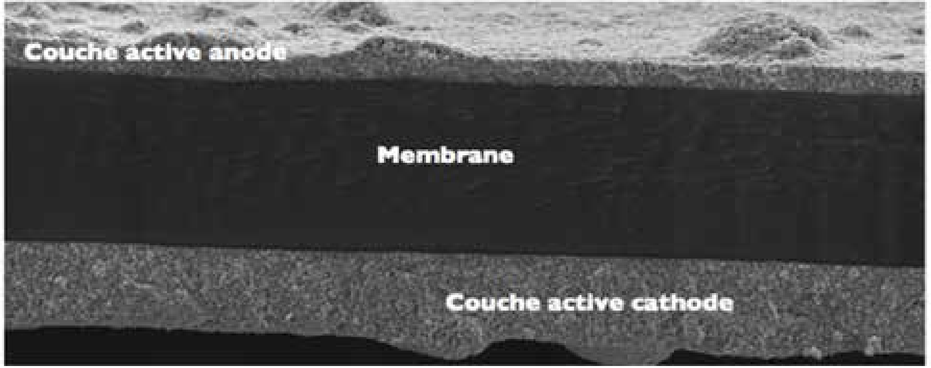
σ: conductivity (S/cm) of the membrane

T (K): temperature

à Hydration of the membrane is necessary!

The water is essential for the protonic conductivity of the Nafion . Therefore, the fuel cell made up of Nafion can not work at high temperatures. Thus the general operating temperature of the PEMFC is around 80° C.

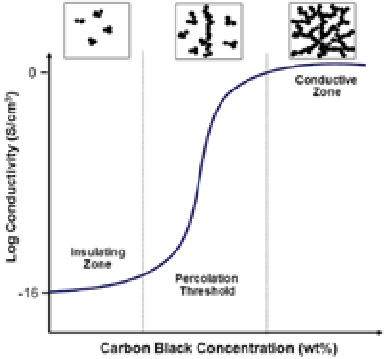
ELECTRODE materials

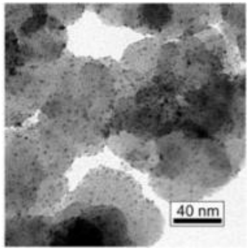


Difference in thickness of active layers: the Pt loading rate of the cathode is 2 to 4 times higher than that of the anode

Due to the low operating temperature, the electro-catalysts have a central part in the PEM fuel cell (and electrolyser as well).
Carbon supported platinum or platinum alloys are commonly used as catalyst on both the anode and the cathode of PEMFC.
The **oxygen reduction reaction (ORR)** taking place on the cathode has sluggish kinetics, which give a major contribution to the efficiency loss of the fuel cell à **High amount of catalyst** is required on the cathode to reach sufficient activity compared to the fast hydrogen oxidation reaction on the anode.
Platinum is used as an active catalyst for not only hydrogen electrooxidation at anode but also used for oxygen electroreduction at cathode of PEMFC à The major bottleneck of the commercialization of the PEMFC **is the high cost** of Membrane Electrode Assembly (MEA).

Platinum is generally dispersed on carbon support (Pt/C) to obtain high surface area as well as to promote internal mass transfer of reactants in an electrode.





*Carbon Ink loaded with **Pt** + ionomer + PTFE*

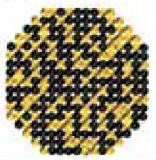
Example :
Pt = 30 000€/kg,
25g in the TOYOTA FCHEV Mirai

Christophe Coutanceau (IC2MP)

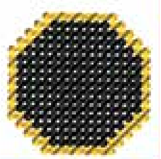
New Catalysts for low temp. PEM FC

Development of synthesis methods for active, selective and stable catalysts for the ORR and the oxidation of small molecules with energetic interest

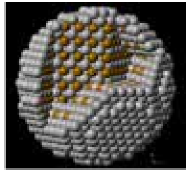
PGM-based Catalysts



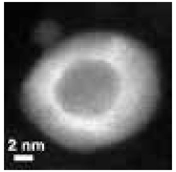
alloys



Core-shell

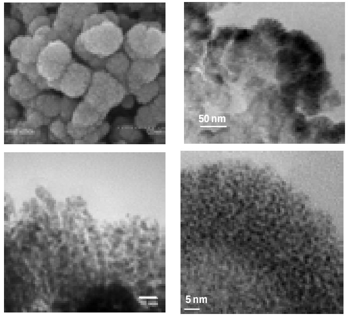


intermetallic

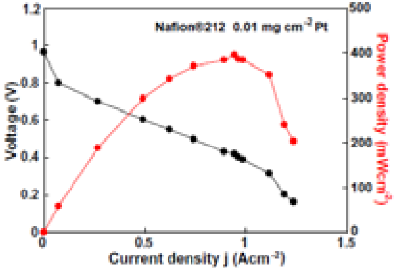


"Hollow" Pt NPs

New electrode architecture

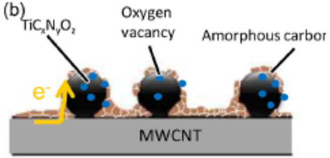


M. Cavarroc, et al. Electrochem. Comm. 11 (2009) 859–861 ;
P. Brault et al. ChemSusChem 6 (2013) 1168-1171.

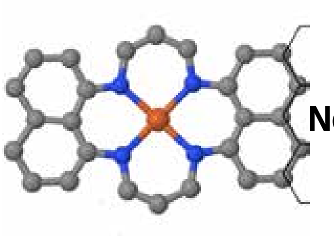


0.02 mg_{Pt} cm^{-2}; 0.4 W cm^{-2} => 20 kW_e / g_{Pt}

Titanium carbonitride ($TiCN_xO_y$)



T Hayashi et al., Electrochim.Acta 209 (2016) 1–6



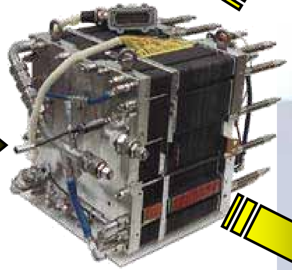
No-PGM based catalysts

F. Jaouen et al., GDR HySPàC, Poitiers, 2014 ; A. Serov et al., Nano Energy (2015) 16, 293–300.

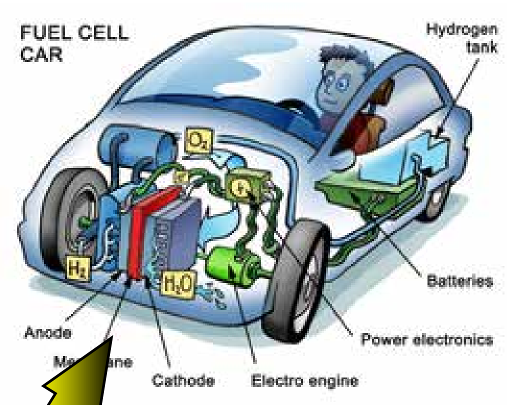
From single cell to systems:

Unit cell Anode/electrolyte/cathode

Stacking with interconnect plates



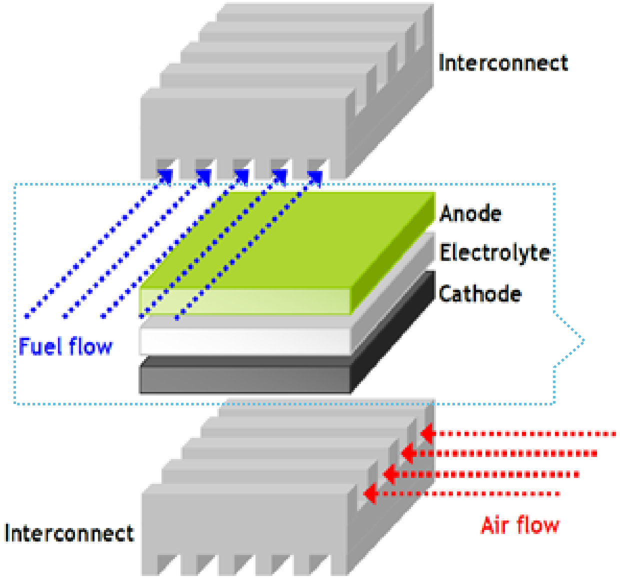
a stack

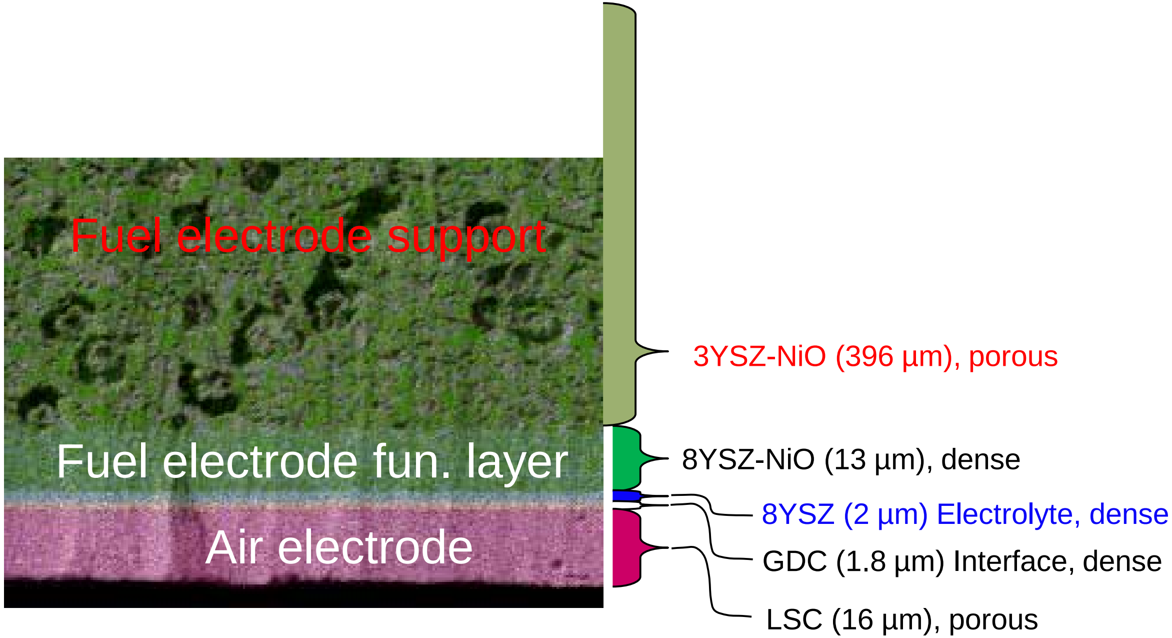


FC system integration

Electrolyser integration

Solid oxide Fuel cells: ceramic high operating temperature (700-900°C) fuel cells





Requirements / State Of the Art Materials

	Cathode	Electrolyte	Anode
Ionic Conductivity @700 °C ($S.cm^{-1}$)	≥ 10^{-2}	≥ 10^{-2}	≥ 10^{-2}
Electronic Conductivity @ 700 °C ($S.cm^{-1}$)	≥ 100	$<10^{-4}$	≥ 100
Stability (atm)	0.21	$10^{-21} \leq pO_2 \leq 0.21$	10^{-21}
Microstructure	Porous	dense	Porous
Thickness	15 - 40 µm	≤ 10 µm	≈ 300 µm
SOA Materials	LSM, LSCF, …	YSZ	YSZ/Ni

LSM : $La_{1-x}Sr_xMnO_{3-\delta}$
LSCF : $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$

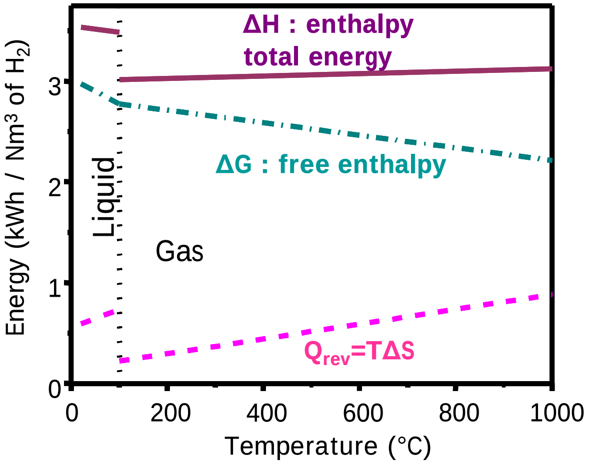
YSZ : $Zr_{1-x}Y_xO_{2-x/2}$
(ZrO_2 + x %mol Y_2O_3)

Ceria doped compound: barrier layer in order to prevent diffusion between cathode and electrolyte

thermodynamic point of view

- A fuel cell converts **directly and continuously chemical energy** in **electricity**

- FCs use the free enthalpy part of the total energy of the reaction **H_2 + ½ O_2 → H_2O (**very exothermic) to produce electricity.

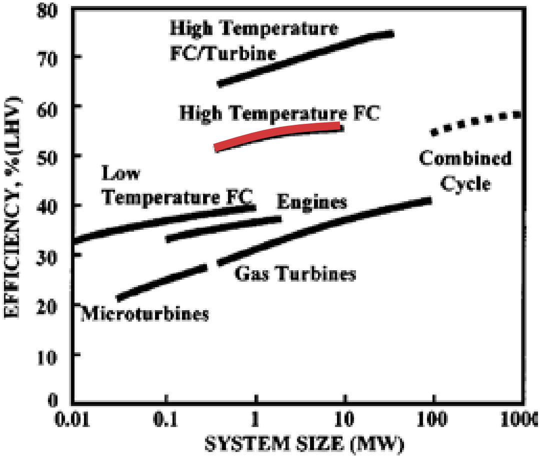


$\Delta H = \Delta G + T\Delta S$ ~ -250 kJ/mol

Æ Low operating FCs (high ΔG) are better compared to high temperature FCs but convenient cogeneration (H&P) is possible for SOFC

Source: Chase *NIST-JANAF Thermochemical Tables* (1998) Monograph 9, 1325

SOFC = High Electrical Efficiency



M. FAROOQUE, H. C. MARU,
Proceed. IEEE, VOL. 89, NO. 12, (2001)

electrical efficiency of fuel cells:

- better than other electric power plants
- running under NG : SOFC more convenient

Table 1 | Theoretical electrical efficiency of fuel cells operated on various fuels with commonly reported system values.

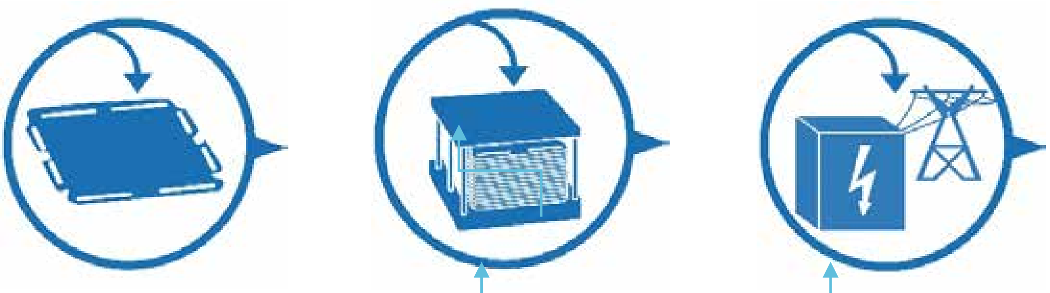
Fuel cell type	Fuel	Overall reaction	Operating temperature (°C)	Theoretical efficiency (%)	Actual system efficiency (%)	
				Electric	Electric	CHP
PEMFC	H_2	$H_{2(g)} + {}^1/_2O_{2(g)} = H_2O_{(l)}$	60–80	83	45–50	80–90
PEMFC	NG	$CH_{4(g)} + 2O_{2(g)} = CO_{2(g)} + 2H_2O_{(l)}$	60–80	–	35–40	80–90
DMFC	CH_3OH	$CH_3OH_{(l)} + 1{}^1/_2O_{2(g)} = CO_{2(g)} + 2H_2O_{(l)}$	20–60	97	20–25	n/a
AFC	H_2	$H_{2(g)} + {}^1/_2O_{2(g)} = H_2O_{(l)}$	70	83	45–60	n/a
PAFC	NG	$CH_{4(g)} + 2O_{2(g)} = CO_{2(g)} + 2H_2O_{(g)}$	200	–	40	90
SOFC	NG	$CH_{4(g)} + 2O_{2(g)} = CO_{2(g)} + 2H_2O_{(g)}$	600–1000	92	45–60	90
MCFC	NG	$CH_{4(g)} + 2O_{2(g)} = CO_{2(g)} + 2H_2O_{(g)}$	650	92	45–55	90
DCFC	Carbon	$C_{(s)} + O_{2(g)} = CO_{2(g)}$	500–1000	100	70–80	90

PEMFC, Polymer Electrolyte Membrane Fuel Cell; DMFC, Direct Methanol Fuel Cell; AFC, Alkaline Fuel Cell; PAFC, Phosphoric Acid Fuel Cell; SOFC, Solid Oxide Fuel Cell; MCFC, Molten Carbonate Fuel Cell; DCFC, Direct Carbon Fuel Cell.

S. Badwal et al, Frontiers in Chemistry · (2014)

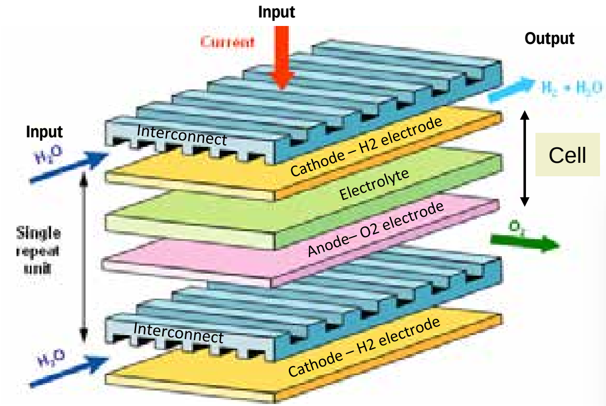
SOFC (and SOEC) other components

- **single cells (electrodes-electrolyte assembly) are connected to each other by metallic interconnectors (chromium based) and sealed to form stacks**



- **single cells Stacking**

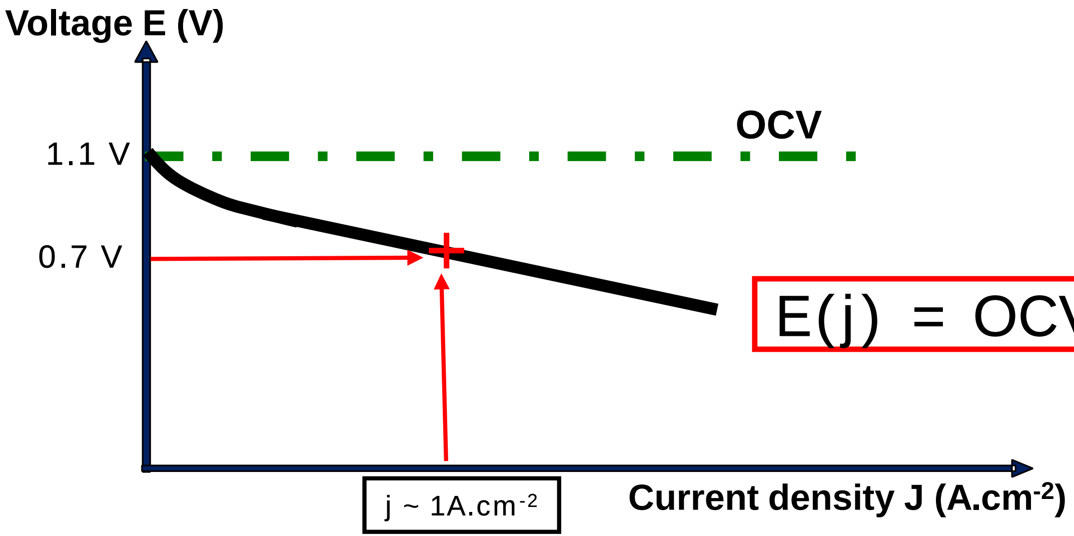
- **system Integration: stack + Balance of Plant components**



SOFC shipments

SOFC shipments grew by about 50% year on year
mainly : Ene-farm CHPs program in Japan (about 40% SOFC) and Bloom Energy (Power only) for onsite power generation in the US .

SOFC usual targets:



$E(j) = OCV - R_e i - S|h|$

usual target: At E = 0.7 V, j > 1A.cm^{-2} à P > 700 mW/cm^2

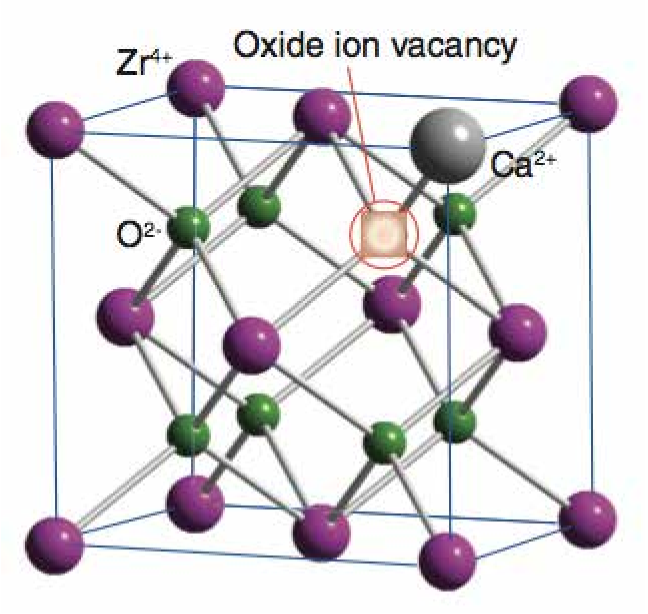
ASR_{cell} < ≈ 0.45 W.cm^2

$R_{elect.}$ < 0.15 W.cm^2 $R_{P\ an.}$ <0.10 W.cm^2 $R_{P\ cath.}$ <0.20 W.cm^2

s = 10^{-2} S/cm , 15mm

SOA ELECTROLYTE

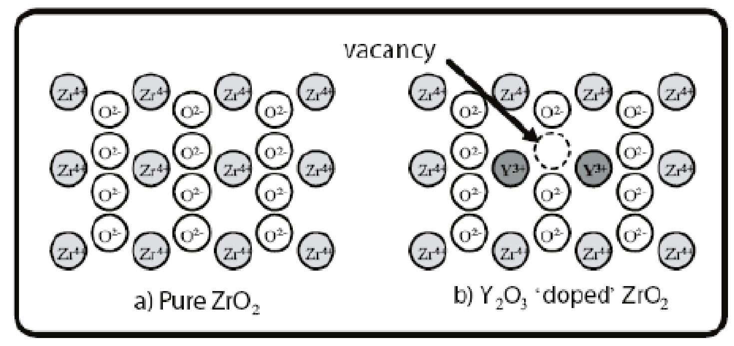
Zirconium oxide (ZrO_2) substituted compound:
Y_2O_3 : $Zr_{1-x}Y_xO_{2-x/2}$
Called "YSZ" (Yttria Stabilized Zirconia)
- The substitution stabilizes the cubic phase of zirconia; a fully (cubic) stabilized zirconia is obtained with a **Y_2O_3**-content of >7 mol%
- Y^{3+} has lower valency than zirconium ion (Zr^{4+}), induces the generation of oxygen vacancies for charge compensation.



Fluorite type structure

Ionic conduction in ceramic electrolytes: ion transport in SOFC

YSZ: yttria stabilized zirconia
Adding yttria to zirconia introduces oxygen vacancies due to charge compensation effects

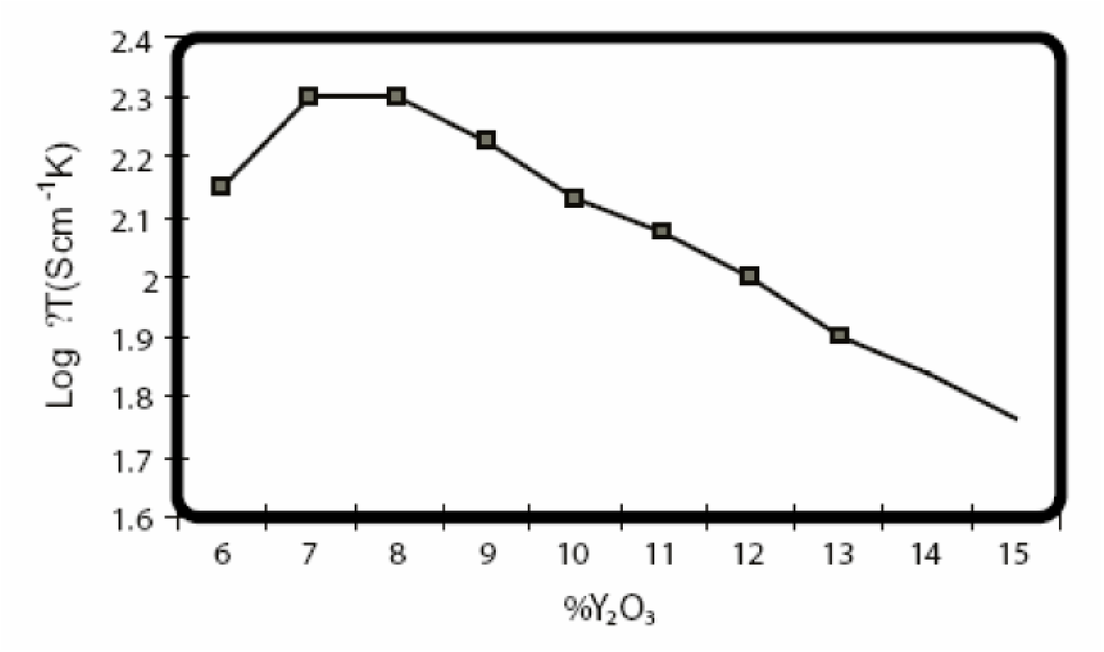


View of the (110) plane in a) pure ZrO_2 and b) YSZ. Charge compensation effects in YSZ lead to creation of oxygen vacancies. One oxygen vacancy is created for every two yttria atoms doped into the lattice.

Conductivity is determined by the combination of carrier concentration c and carrier mobility u:

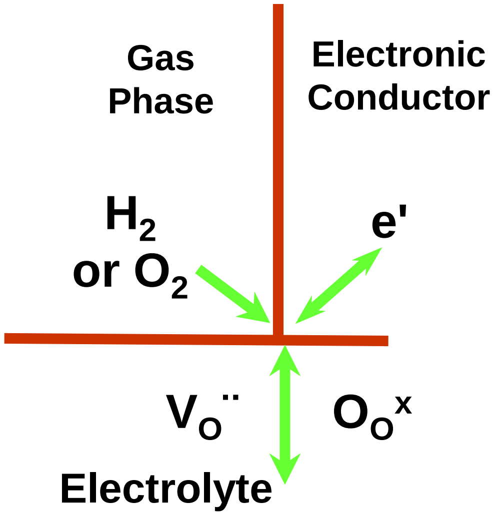
$$\sigma = (|z|F)cu$$

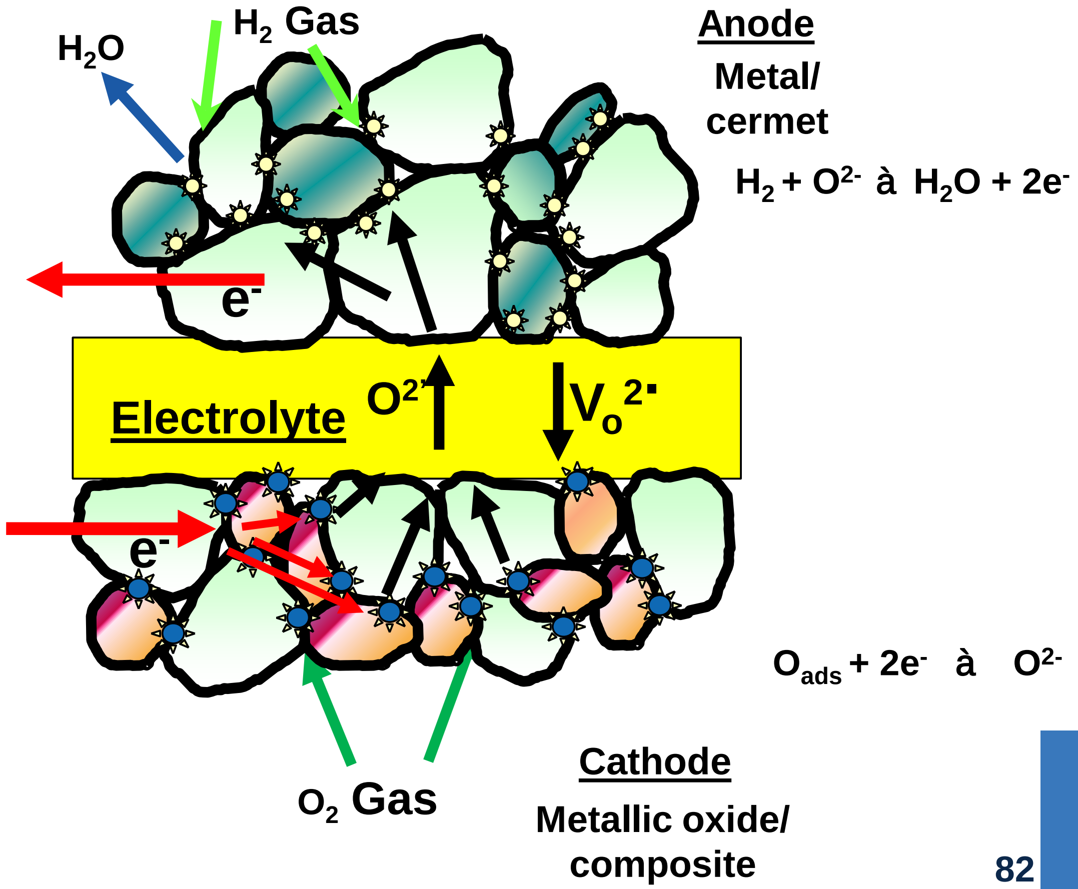
In YSZ, carrier concentration is determined by the strength of the yttria doping.
Increasing yttria content => increased oxygen vacancy concentration, improving conductivity
* There is an upper limit to doping



The French Research network on Hydrogen energy

Electrodes: Triple Phase Boundary





Oxygen reduction reaction (ORR) at the cathode of SOFC

$O_2 + 4e^-$ è $2\ O^{2-}$

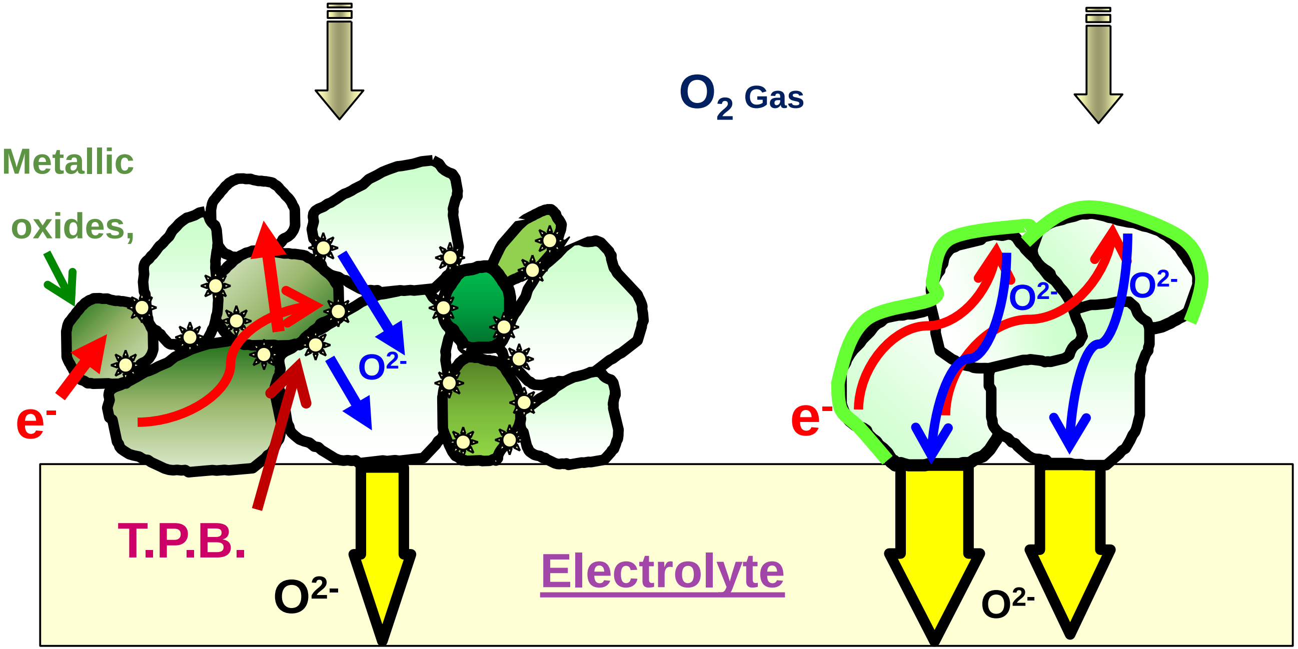
For metallic oxides, *i.e.* Composite electrodes

O.R.R. at the Triple Phase Boundary

M.I.E.C. oxides

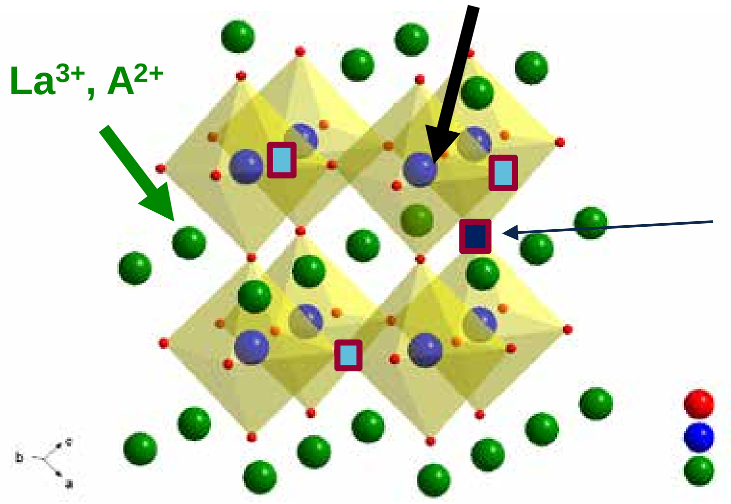
Mixed Conducting Oxides (e^-, O^{2-})

Double Interface Boundary



Cathode materials

AMO_3 perovskites A : La^{3+} è Sr^{2+} or Ca, Ba; $M^{n+,(n+1)+}$: Mn, Fe, Co, Ni



Early material: $(La_{1-x}Sr_x)_{1-d}MnO_3$ LSM

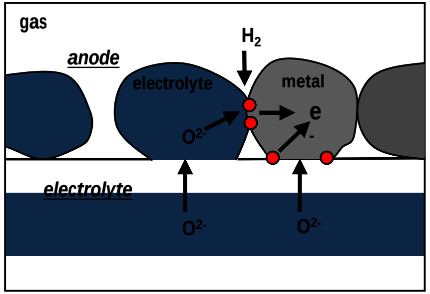
$(La,Sr)CoO_{3-d}$ (LSC)
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-d}$ (LSFC)
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ (BSCF)

$0.05 < d < 0.20$

Oxygen non-stoichiometry f(T)

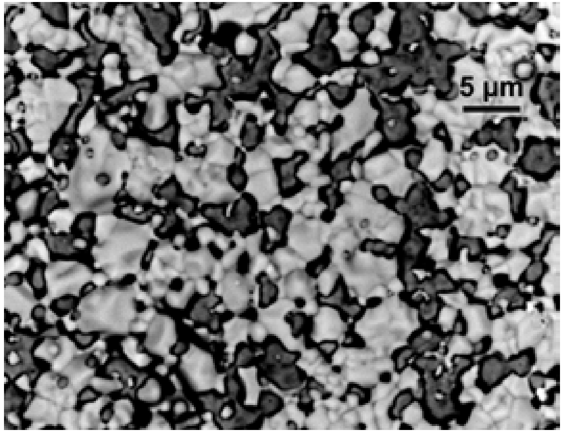
Disordered vacancies at high temperature

The usual anode : cermet



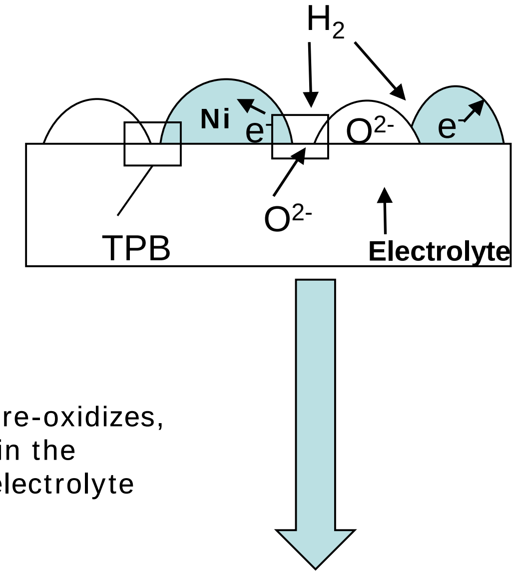
● **Triple phase boundary**

Specs	anode
porosity	**30-40% vol**
composition	**Ni: 40% w, YSZ: 60% w**
conductivity	**electronic (Ni) & ionic (YSZ)**



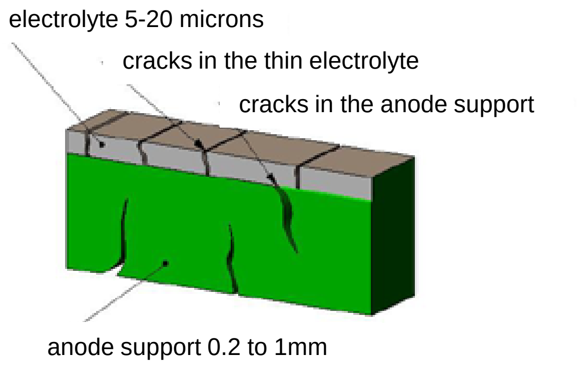
anode at different scales

The usual anode : cermet



usually a cermet :
Ni + ionic conductor (e.g. YSZ)

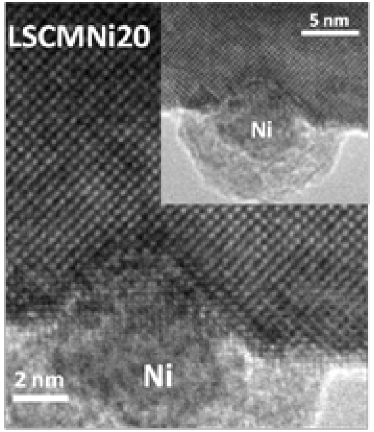
redox cycles : When the nickel re-oxidizes, it expanses and cracks appear in the anode support and in the thin electrolyte

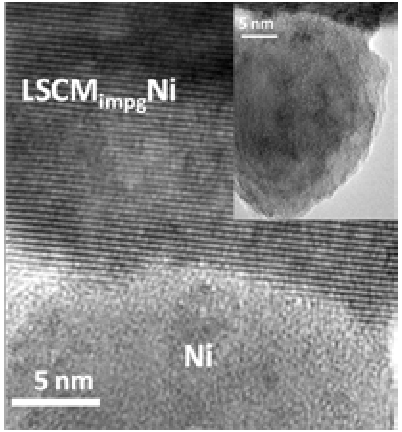


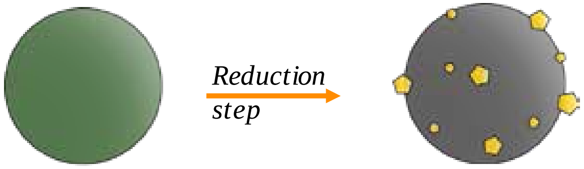
Solution : using Mixed Ionic and Electronic Conductor but **no** material good conductor and good catalyst!

Improving the Fuel electrode material properties: **exsolution** of Ni nanoparticles as catalyst!

$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.3}Ni_{0.2}O_{3-d}$







Single phaseoxide

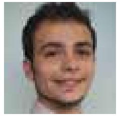
Nano-Particles dispersion on electrode material

Anode Material	Rp (W.cm^2)	f_1 (Hz)	Rp_1 (W.cm^2)	f_2 (Hz)	Rp_2 (W.cm^2)
LSCM	**0.20(1)**	3000	0.072(7)	447	0.127(7)
$LSCM_{0.3}Ni_{0.2}$	**0.20(1)**	3862	0.105(5)	1348	0.098(5)
LSCMimpNi	**0.139(6)**	1334	0.072(3)	492	0.067(3)

- Exsolution or impregnation of metallic nanoparticles facilitates H_2 dissociation (better Rp_2 / LSCM)
- Better Rp of Ni-impregnated LSCM vs exsoluted $LSCM_{0.3}Ni_{0.2}$ due to higher surface concentration of Ni in H_2
- Exsolution produces nanoparticles firmly anchored to grain surface avoiding agglomeration (better for long term operation)

Impregnation versus exsolution: Using metal catalysts to improve electrocatalytic properties of LSCM-based anodes operating at 600 °C
<u>Léonard Thommy</u>, Olivier Joubert, Jonathan Hamon, Maria-Teresa Caldes
International Journal of Hydrogen Energy, 41-32, 14207–14216 (2016)

PhD Léonard Thommy (2016)

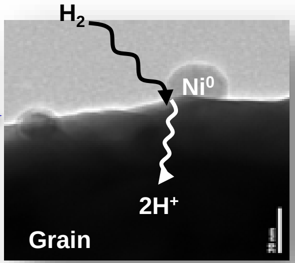


Exsolution can also improve the ionic conductivity

Metallic nanoparticles (Ni, Ru) catalyze the hydrogen dissociation

Promote proton incorporation reactions : metal nanoparticles (Ni)

$BaCe_{0.9-x}Y_{0.1}Ni_xO_{3-\delta} + H_2$ → exsolution of Ni

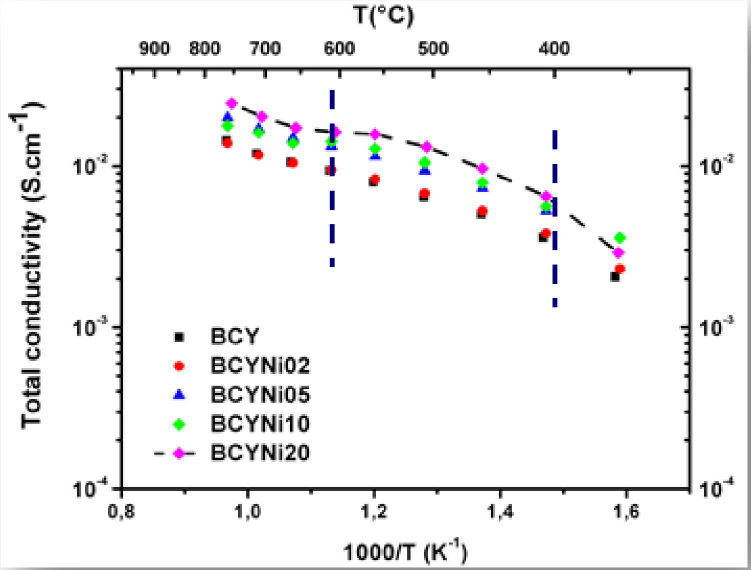


→ Electrical and catalytic properties

Increasing charge carrier concentration of the Electrolyte

Caldes et al, Chem. Mater. (2012) 24, 4641−4646

Electrical conductivity: EIS under 5 % H2 / Ar



below 600°C :

- total conductivity increases with Ni content

VI Conclusion

Nanomaterials have a crucial role in hydrogen devices (Fuel cells or electrolysers). See the number of publications!

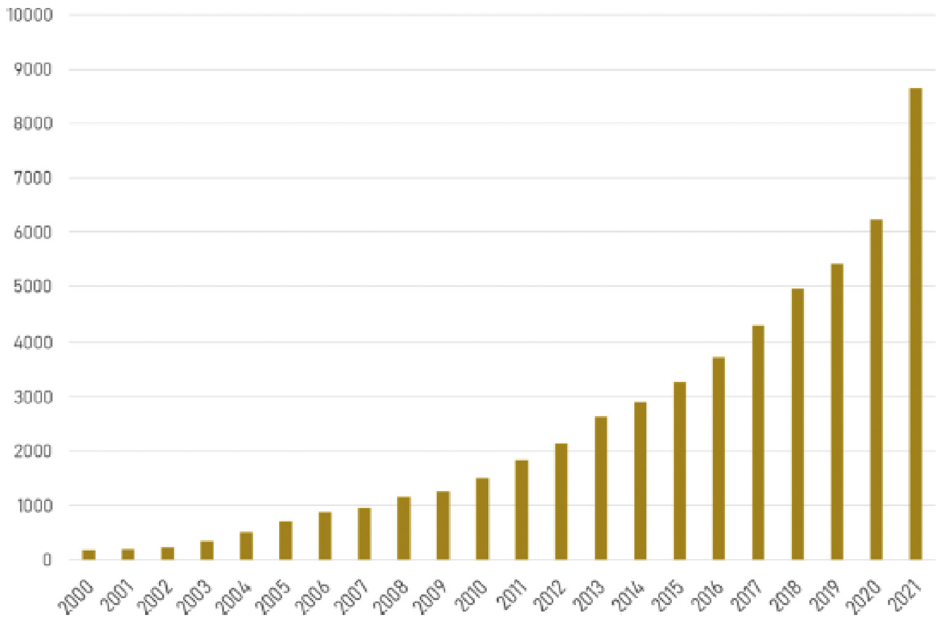


Fig. 5 – Increasing number of journal publications on the research and the development of nanomaterials in fuel cell (Keyword search "Nano AND Fuel cell" in http://www.sciencedirect.com, Dec 2021).

The French Research network on Hydrogen energy

There are several ways to improve properties and performance of these systems for example through
the implementation of 1D, 2D and 3D nanostructures

Table 5 – Multi-dimensional nanocomposite materials.

System	Applications	Remarks	Synthesis methods	Ref
1D on 1D				
Pt nanorods - nitrogen doped carbon nanotubes (CNT)s	PEMFC	Improved durability, better stability of nanorods gained from the N-CNT support.	[a]PECVD	[135]
CoO nanorods/C	DBFC	High catalytic activity and good durability	Hydrothermal	[35]
Ni/NiO nanorods -coated nanofoams	DAFC	Increase surface area, high porosity, and abundance of nanorods active sites lead to excellent activity and long stability	Hydrothermal	[125]
Hetero- structured simple perovskite nanorod-decorated A site-deficient double perovskite $PrBa_{0.94}Co_2O_{5+\delta}$ cathode	SOFC	Rapid oxygen reduction reaction (ORR) kinetics and outstanding durability in air with CO_2	In-situ ex-solving process	[136]
Nanorod-like $CoFe_2O_4$	MFC	Excellent kinetic activity of electron transfer and low resistance through four-electron reaction pathway	Hydrothermal	[137]
Lanthanum titanate ($LaTiO_{3-\delta}$) nanorods	SOFC	Better electrical conduction process in the material owing to the thermally activated process.	Hydrothermal	[138]
Pt nanorods with a highly distorted configuration	PEMFC (ORR)	Superior ORR performance and high stability	Hydrothermal	[139]
MoO_3 nanorods/$Fe_2(MoO_4)_3$	SOFC	Excellent long-term stability at high temperature	Hydrothermal combined with an in situ diffusion growth	[140]
3D				
Pt nanoflowers -porous silicon	DMFC	Exhibit excellent catalytic activity	Chemical reduction	[128]
Fe_3O_4 nanoparticles - 3D N-doped graphene aerogels (N-GAs)	ORR	High current density, better durability	Hydrothermal, freeze drying and thermal treatment	[130]

[a] Plasma-enhanced chemical vapor deposition.

i n t e r n a t i o n a l journal o f hydrogen energy 4 7 (2 0 2 2) 1 8 4 6 8 e1 8 4 9 5

The French Research network on Hydrogen energy

Other challenges

Scientific and technical locks

- Increase **energy efficiency**: From 45-55% to around 65%
- **Sustainability** of the fuel cell system

for PEMFC systems:

- 5000 hours expected for light vehicles (3000-3500 hours today)
- 30,000 hours expected for trucks
- Up to 100,000 hours for stationary and rail

- **Cost** (during the life cycle)

Link with the deployment of an industrial sector

- **Socio-technical transition**

  - Socio-economic aspects: H2-energy is not known
  - Important link with public policies