PART C:

HYDROGEN CONVERSION TO ELECTRICITY

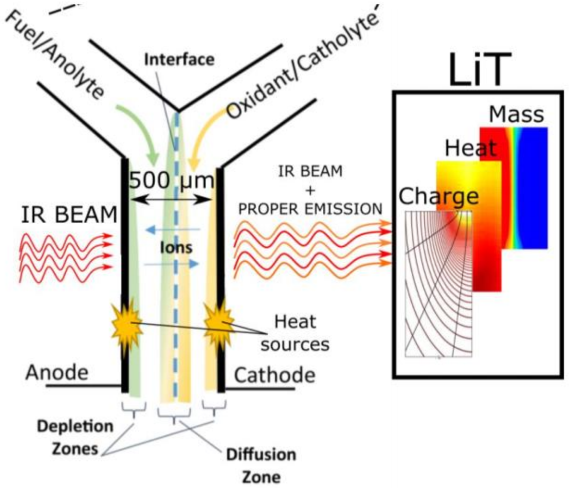
Stéphane Chevalier

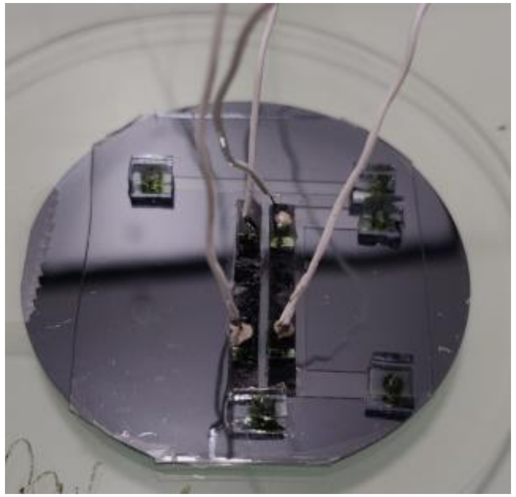
Few word about me

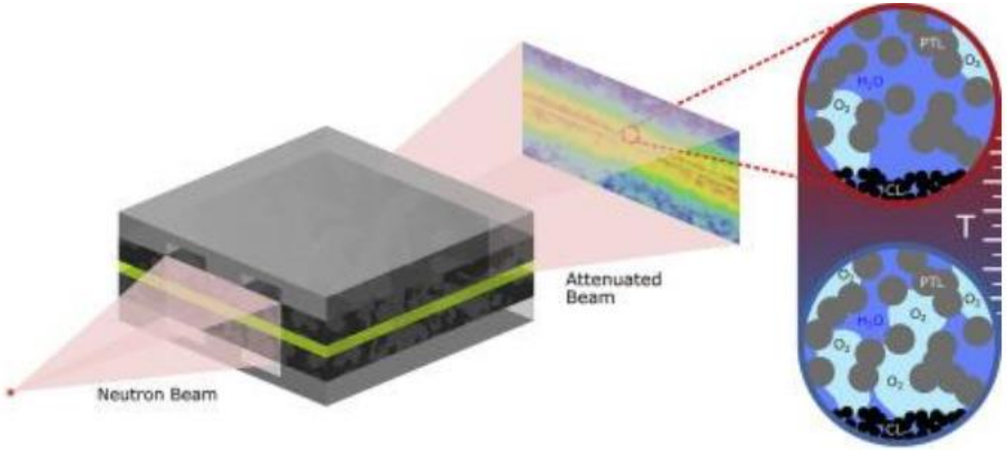
Stéphane Chevalier
Associate Professor since 2018
PhD from Nantes University in Heat transfer and Energetics

Resume
Graduate from Polytech Nantes Engineering school
Post doctoral fellow from Nantes and Toronto University

Current research :
Characterization and modelling of energy transfer in microfluidic fuel cells using multiphysic imaging techniques







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OUTLINES

1. Fuel cell technologies

    - main parts : from materials to system

    - PEM fuel cells

    - Membraneless fuel cells

    - Tripple point

2. Fuel cell physics

    - polarization curve

    - power output & efficiency

    - energy balance during the hydrogen conversion

    - main equations

3. Fuel cell sizing

    - first tools to estimate the fuel cell power output

    - examples and calculation of fuel cell power.

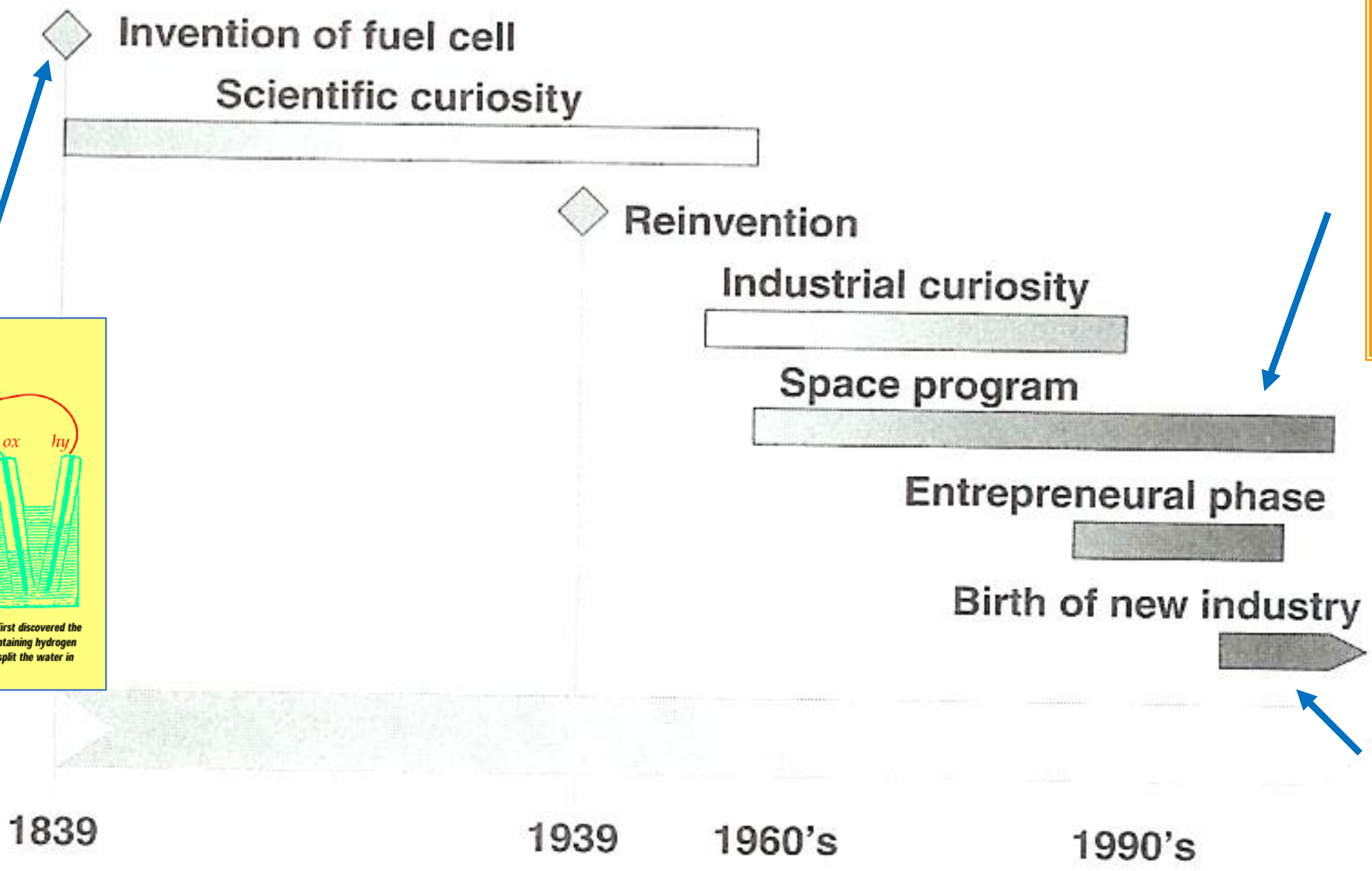
Learning Outcomes

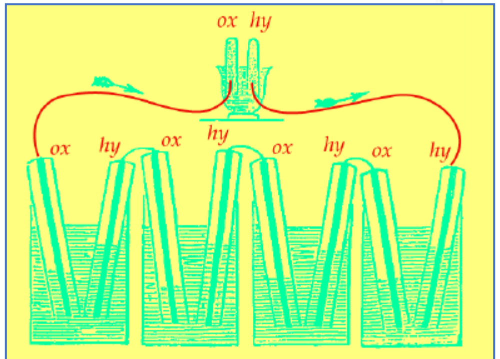
By the end of the course, the student must be able to:

1. Classify the different fuel cell technologies
2. Understand the main physical phenomena occurring during the energy conversion
3. Do a basic modelling of the fuel cell polarization curve
4. Design an electrical chain powered by a fuel cell

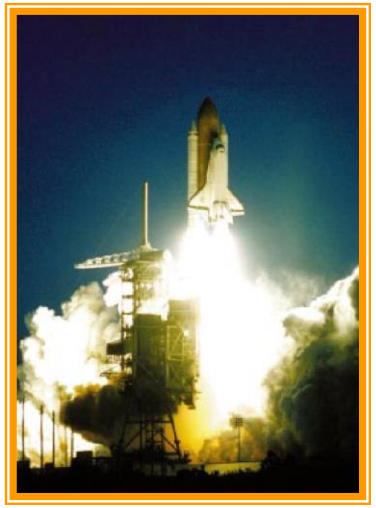
FUEL CELL TECHNOLOGIES

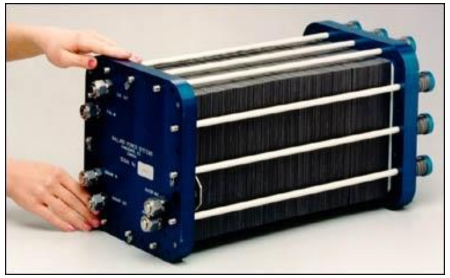
Brief History





In 1839, William Grove, a British jurist and amateur physicist, first discovered the principle of the fuel cell. Grove utilized four large cells, each containing hydrogen and oxygen, to produce electric power which was then used to split the water in the smaller upper cell into hydrogen and oxygen.





HYDROGEN ENERGY OF THE FUTURE?

Octobre 2002

Octobre 2002

HYDROGEN ENERGY OF THE FUTURE?

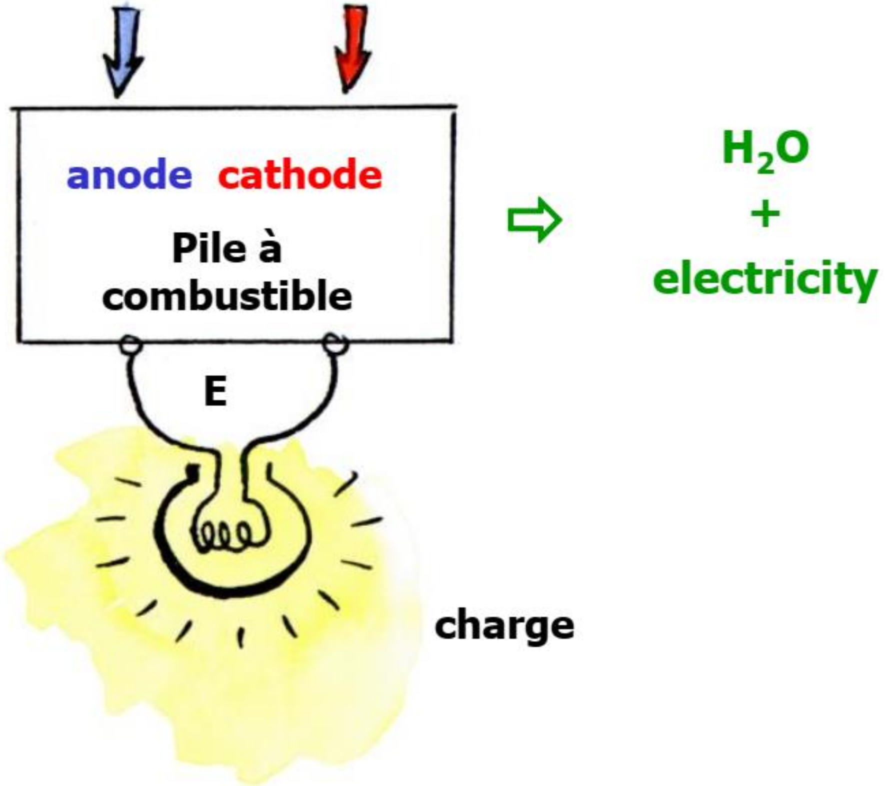
- It is possible to produce H_2 by methods that do not induce greenhouse gases.
- Its use does not cause emission of greenhouse gas.
- It is virtually inexhaustible…

HYDROGEN ENERGY OF THE FUTURE?

Electricity can be used (V > 1.23 V) to break water molecules H_2O and to produce hydrogen and oxygen gases at room temperature

→ **Water electrolysis** Michael Faraday (1791-1867)

$$H_2O(l) \rightarrow H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \quad : \Delta H = \text{enthalpy}$$



ΔG : free enthalpy

$\Delta G = \Delta H - T\Delta S$ (S:entropy)

242.000 - 44,4 T J

Quantitatively :

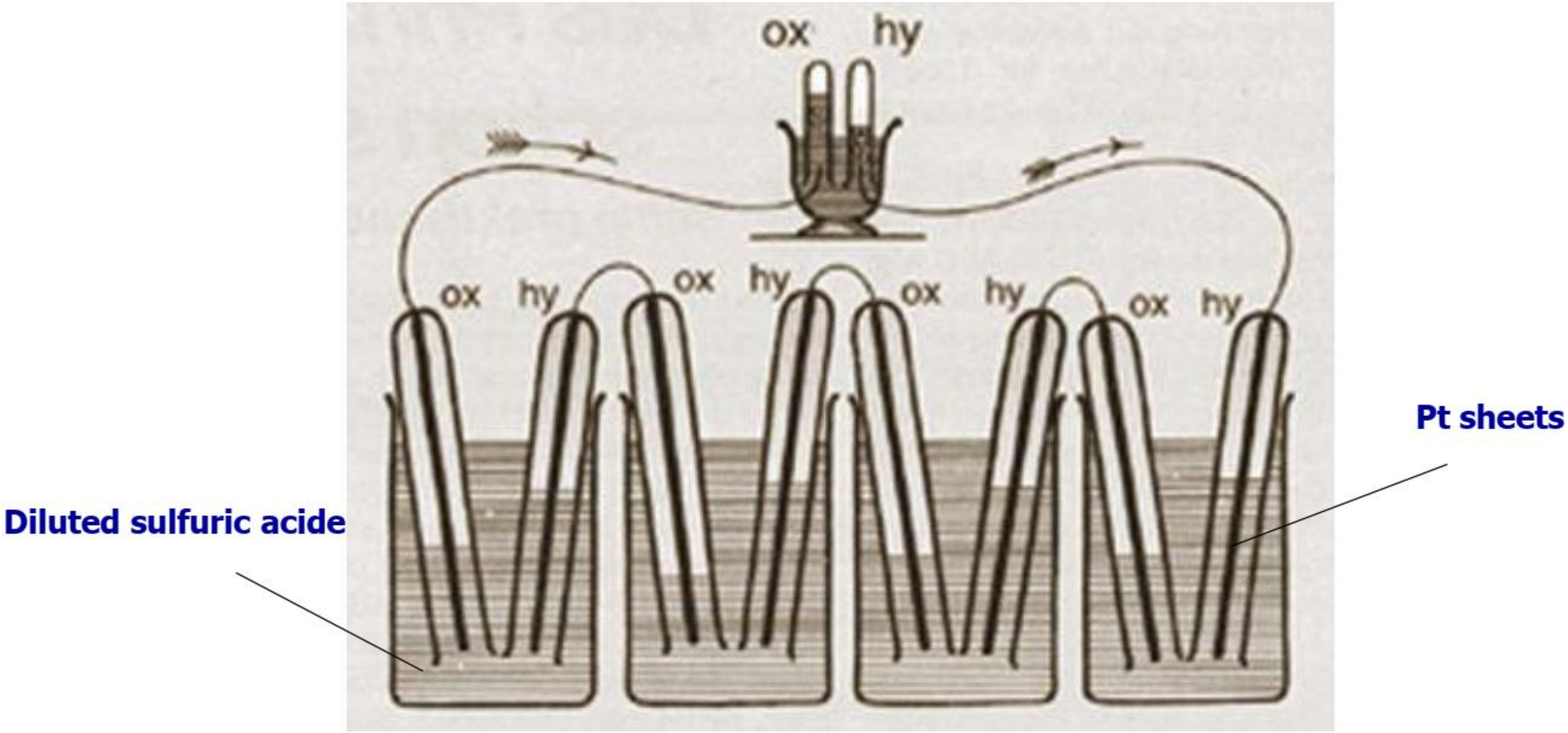
$\Delta G = -nF\,E$ (Walter Nernst 1864-1941)

First fuel cell

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) = H_2O(g)$$

Phil. Mag. Ser.314-127 (1839) : « On voltaïc series and the combination of gases with platinum »

First fuel cell



Phil. Mag. Ser.314-127 (1839) : « On voltaïc series and the combination of gases with platinum »

THE GROVE EXPERIENCE…

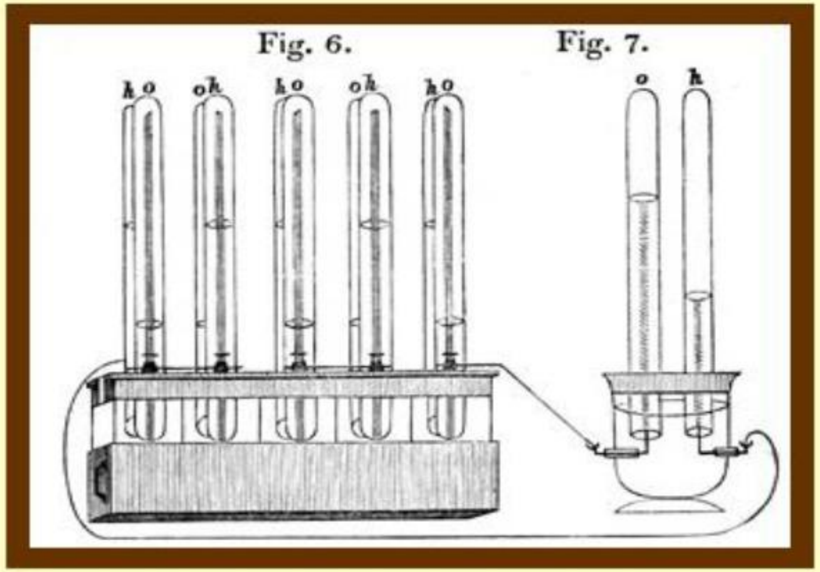
I cannot but regard the experiment as an important one.*

William Grove writing

to Michael Faraday, October 1842

W. R. Grove,
Philos S3, **(14) 86,**
127 (1839).

Fuel Cell Origins



William Grove's drawing of an experimental "gas battery" from an 1843 letter

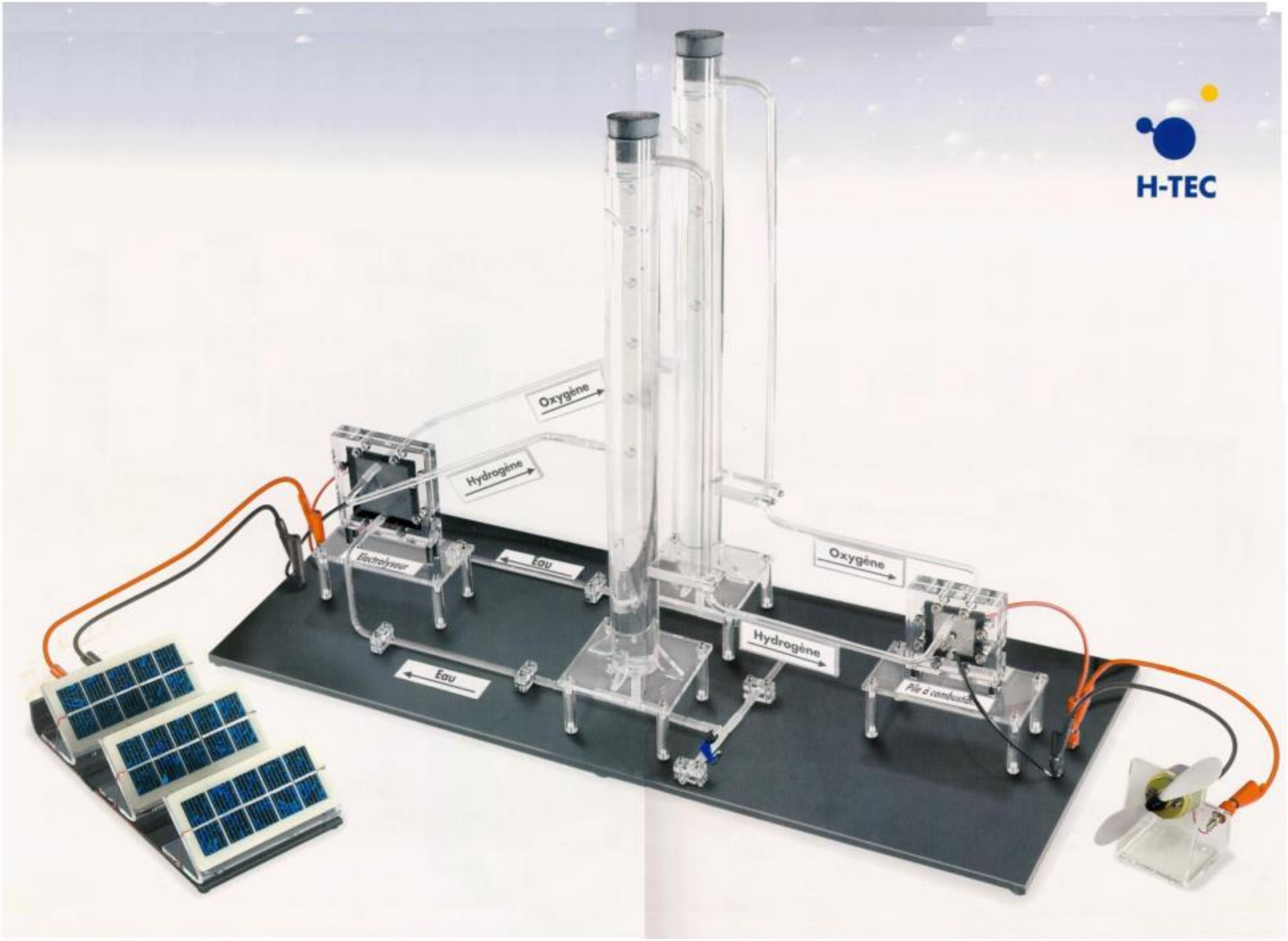
Image from *Proceedings of the Royal Society*

The two figures above appear on page 272 of the *Philosophical Magazine and Journal of Science*, 1843, with William Grove's letter "On the Gas Voltaic Battery."

* Je ne peux pas ne pas considérer l'expérience comme importante.

… AND THE SAME ONE IN THE XXI CENTURY

Today, the present demonstration set-up, is very close to the Grove experience (the water electrolysis is suppling the fuel cell).



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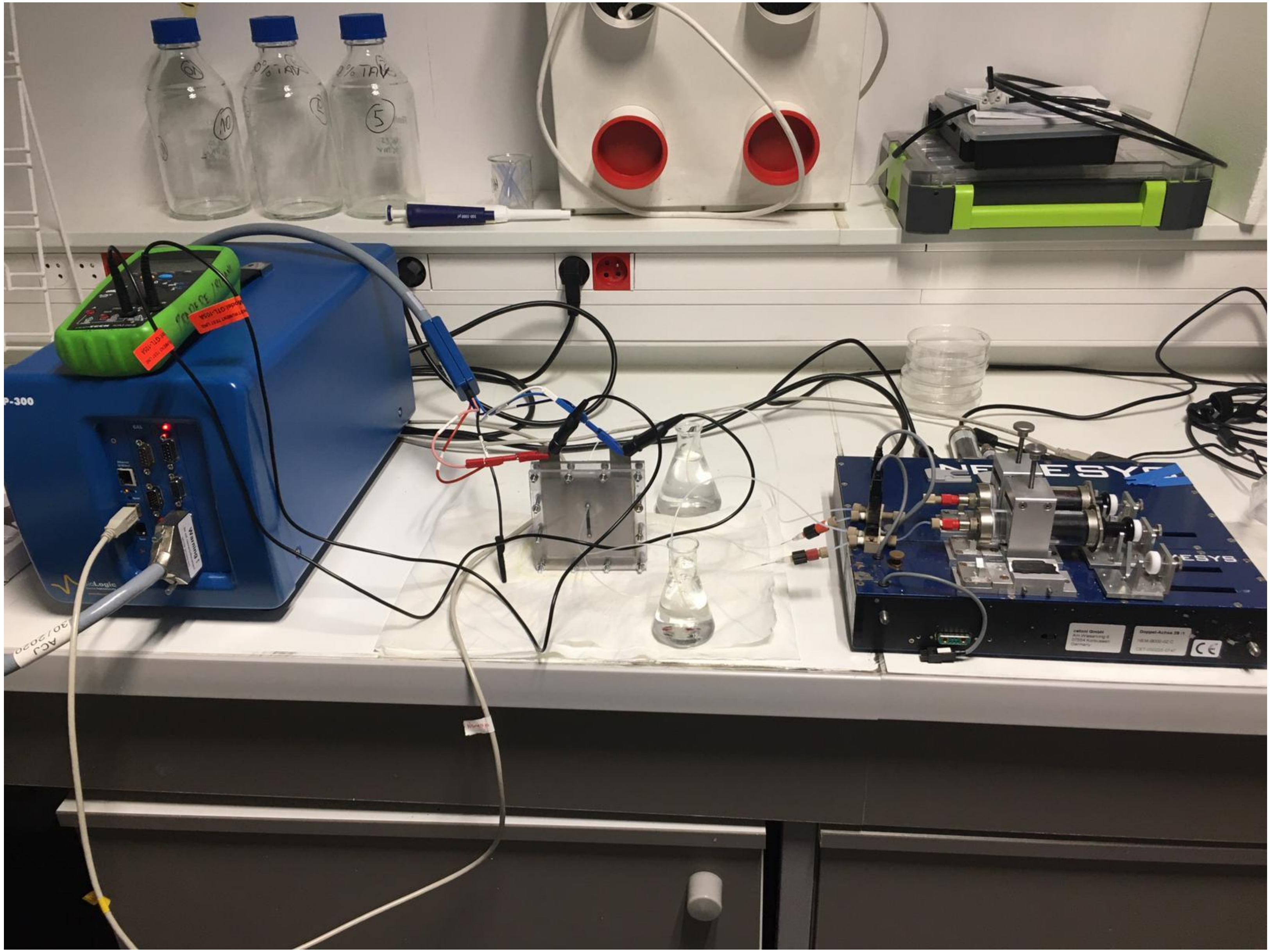
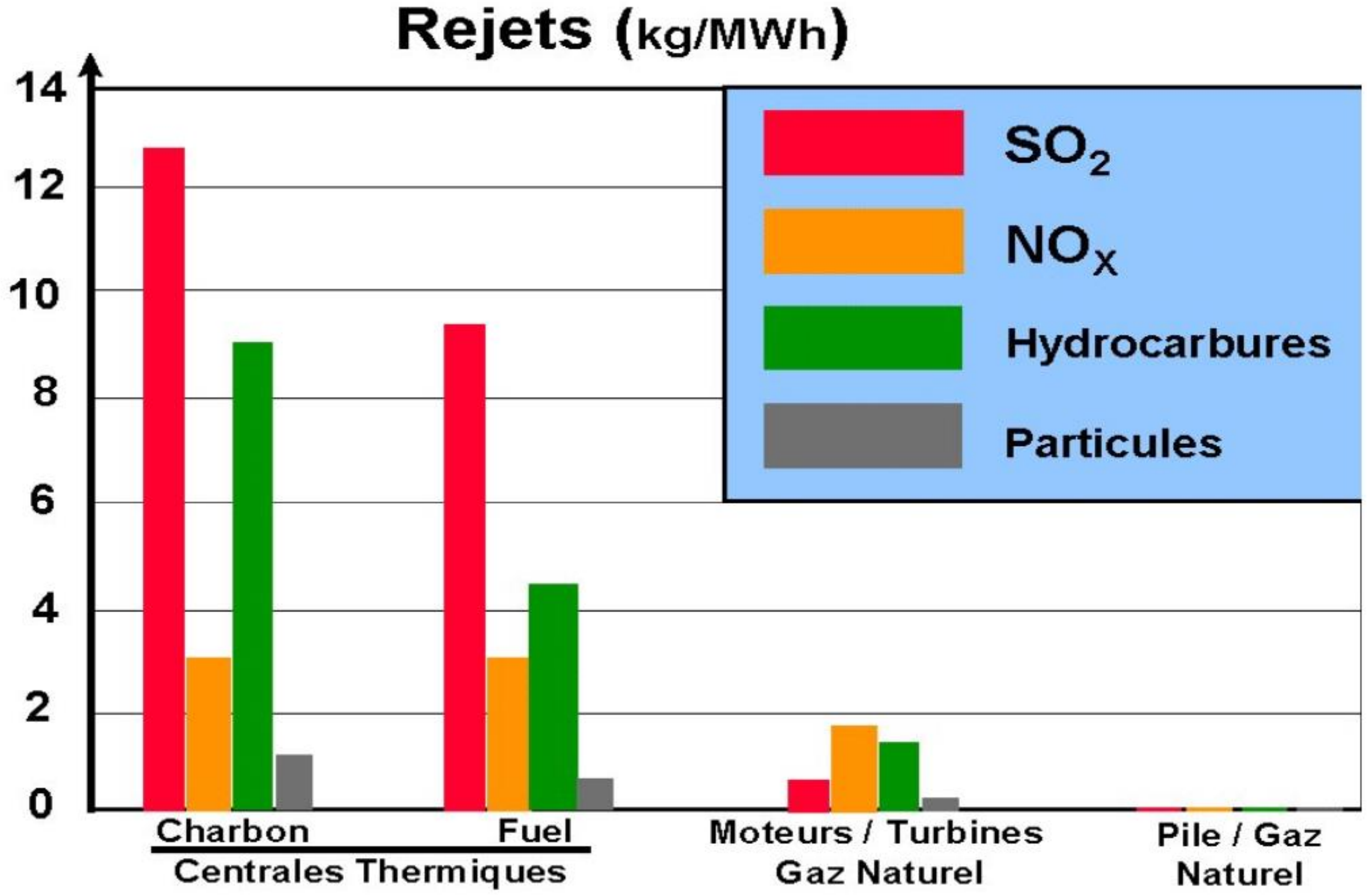


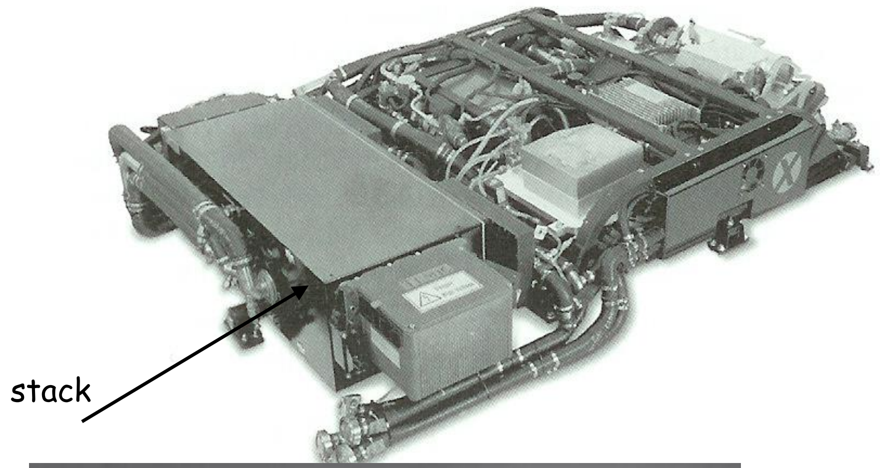
SOME ADVANTAGES OF FUEL CELLS

No noise pollution (except for the auxilary pumps).

Very low level of chemical pollution (NO_x, SO_x) and water as effluent.

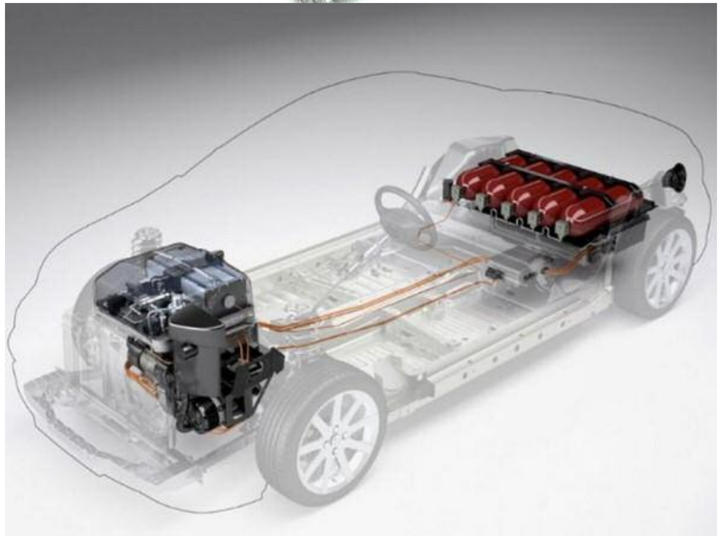


FUEL CELL SYSTEMS



Fuel cell engine75 kW PEMFC
(Ballard Power System)

Made of PEMFC stack, humidification, pump, AC/DC convertor, compressor



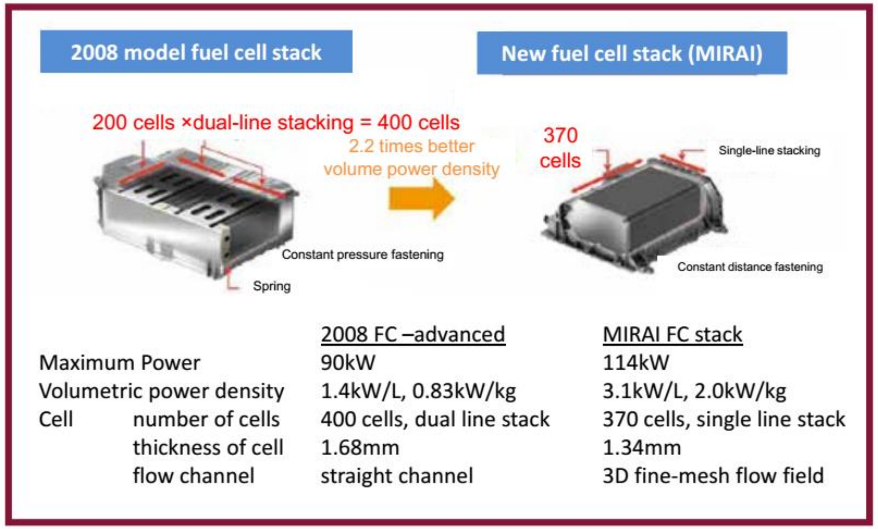
GENEPAC project: collaboration CEA/ Peugeot Citröen (France)

FC vehicle available:

- Honda FCV
- Hyundai ix35
- Toyota Mirai

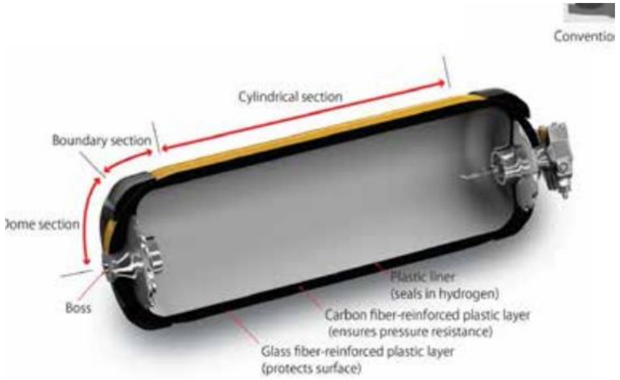
Currently 1000 vehicles sold in US

FUEL CELL SYSTEMS



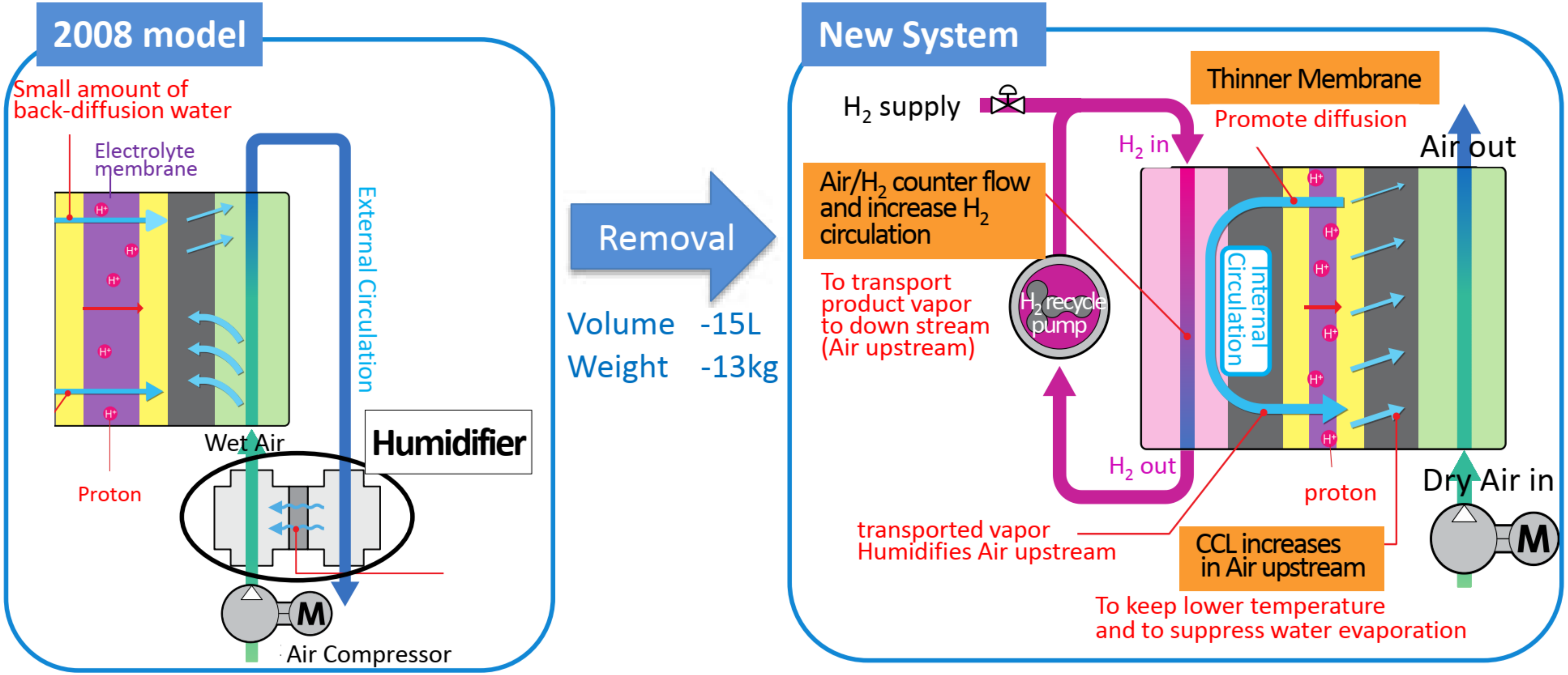
Vehicule being sold by Toyota (2016)
Engine Output = 114 kW (150 hp)
H2 storage = 2 tanks at 700 bars
Mileage = about 500 kms.

FC cost in 2016: €45/kw



FUEL CELL SYSTEMS

Progresses and performance increase made by Toyota for its fuel cell car (between 2008 and 2016):



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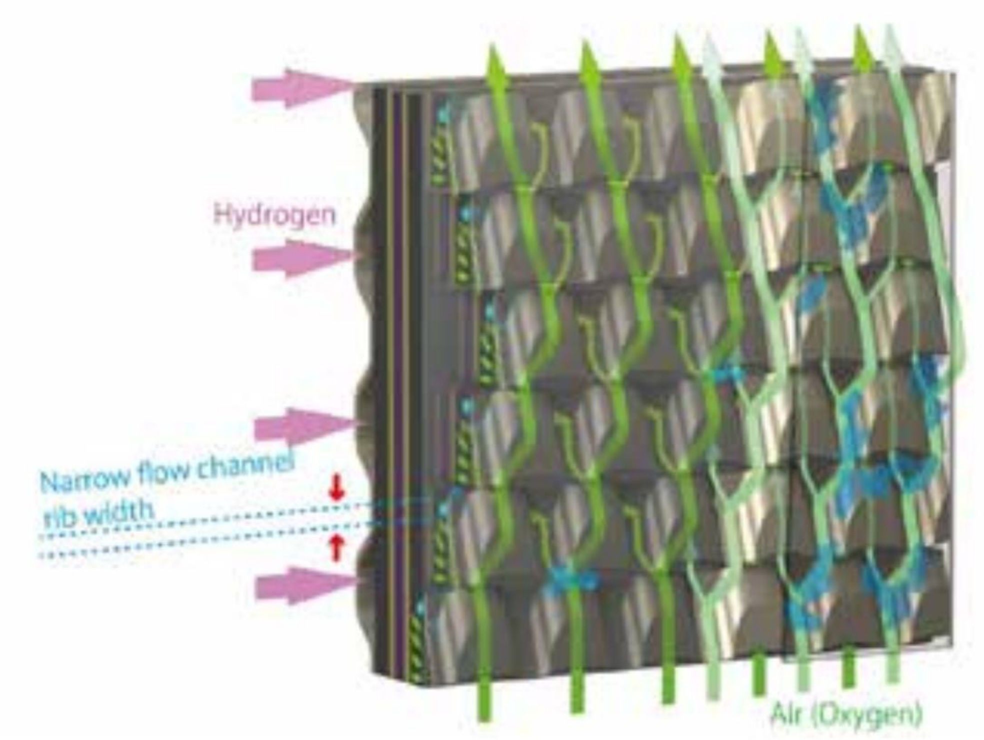

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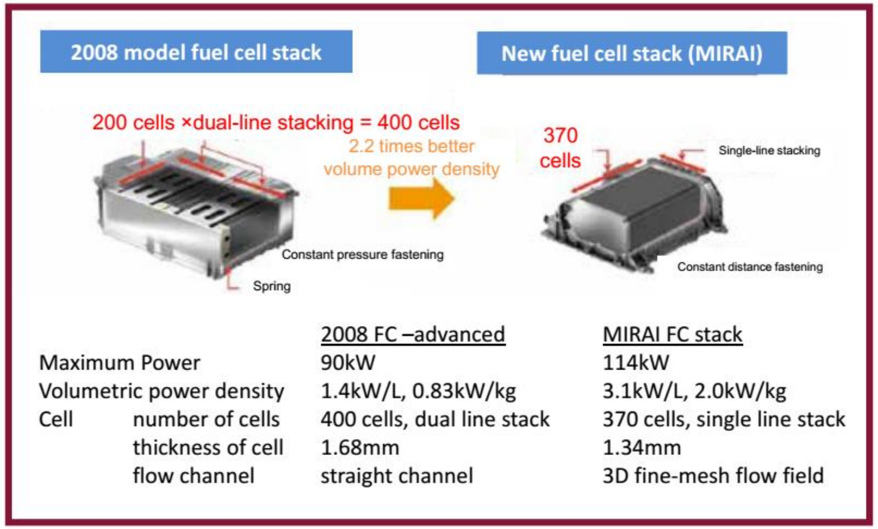
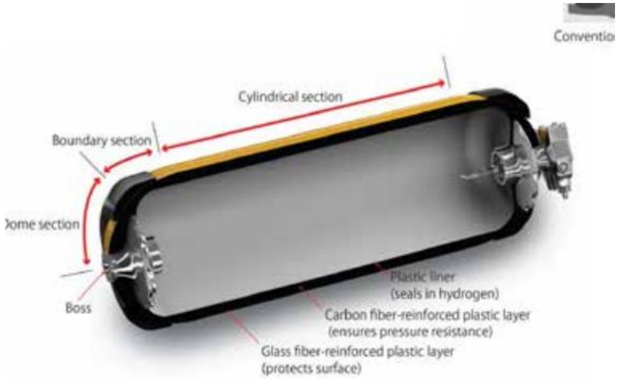
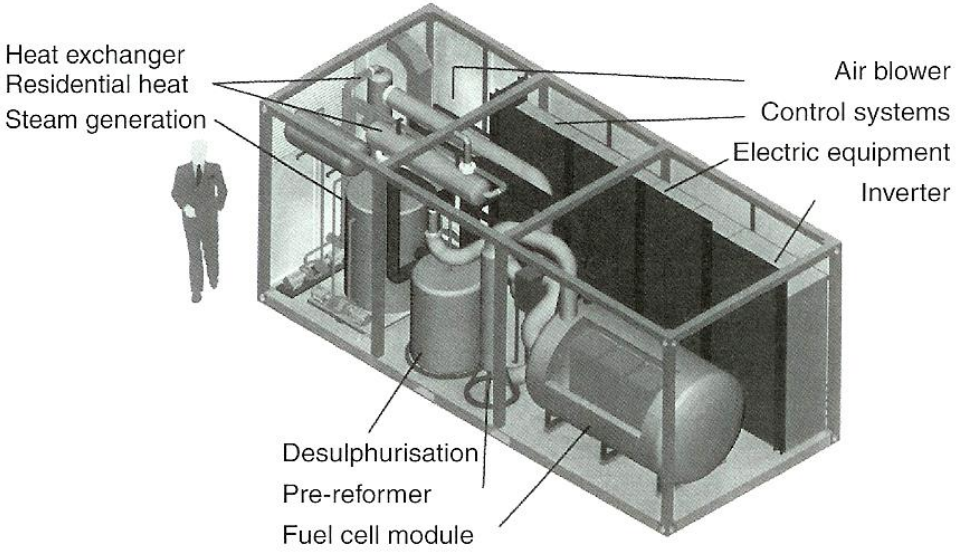


		2008 FC –advanced	MIRAI FC stack
Maximum Power		90kW	114kW
Volumetric power density		1.4kW/L, 0.83kW/kg	3.1kW/L, 2.0kW/kg
Cell	number of cells	400 cells, dual line stack	370 cells, single line stack
	thickness of cell	1.68mm	1.34mm
	flow channel	straight channel	3D fine-mesh flow field



FUEL CELL SYSTEMS



Cogeneration plant 250 kW
With low temperature fuel cell PEMFC
(Ballard Power Systems)

Installed in Berlin in 2000.

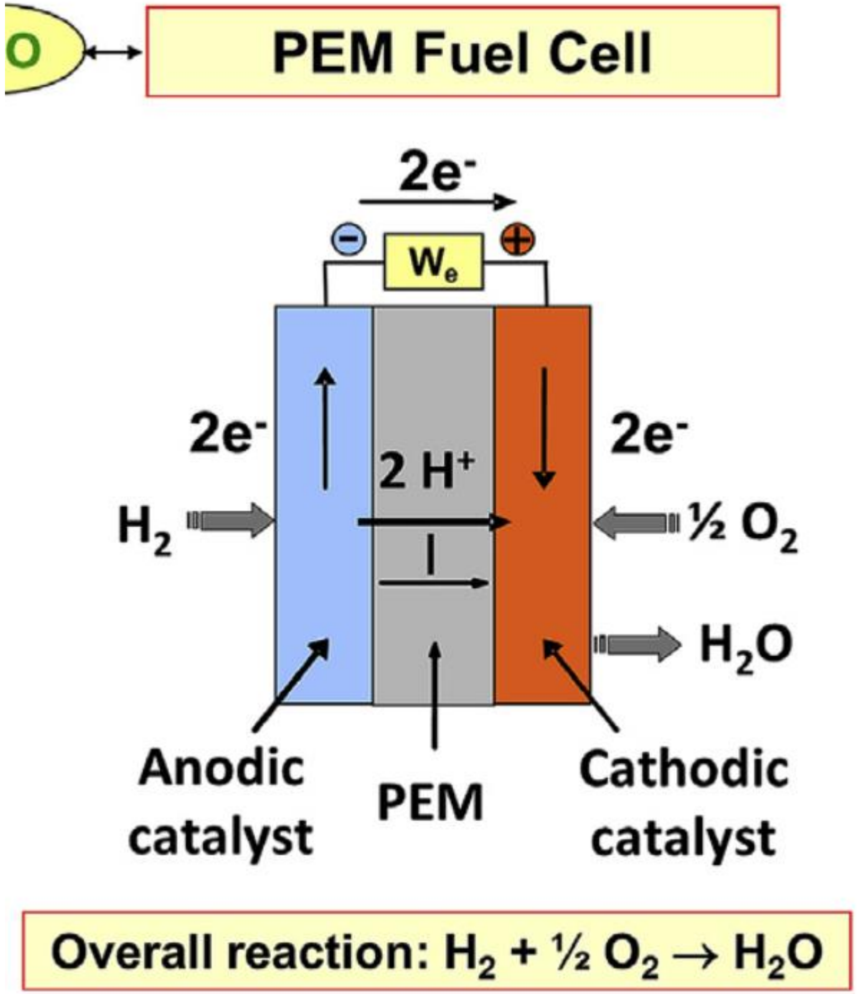
Cogeneration plant 100 kW
With high temperature fuel cell SOFC
(Siemens Power Generation)

MATERIALS FOR PEMFCs

Type de pile	Anode (catalyseur)	Électrolyte	Cathode (catalyseur)	Température	Applications
Proton Exchange Membrane Fuel Cell (PEMFC)	$H_2 \rightarrow 2H^+ + 2e^-$ (Pt)	Perfluored polymer (H^+, SO_3^-) H^+ ➡	½ $O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (Pt)	60-90°C	Portable Transport Stationnary
Direct Methanol fuel cell (DMFC)	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (Pt)	Perfluored polymer (H^+, SO_3^-) H^+ ➡	½ $O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (Pt)	60-90°C	Portable Transport
Phosphoric Acid Fuel Cell (PAFC)	$H_2 \rightarrow 2H^+ + 2e^-$ (Pt)	H_3PO_4 (58-100%) H^+ ➡	½ $O_2 + 2H^+ + 2e^- \rightarrow H_2O$ (Pt)	160-220°C	Transport Stationnry
Alcaline Fuel Cell (AFC)	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ (Pt,Ni)	KOH (8-12N) OH^- ⬅	½ $O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (Pt-Au, Ag)	50-250°C	Spatial Transport
Molten Carbonate Fuel Cell (MCFC)	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ (Ni+10%Cr)	$Li_2CO_3/Na_2CO_3/K_2CO_3$ ⬅ CO_3^{2-}	½ $O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ (NiO_x+Li)	650°C	Stationnary
Solid Oxide Fuel Cell (SOFC)	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$ (cermet Ni-ZrO_2)	ZrO_2 -Y_2O_3 ⬅ O^{2-}	½ $O_2 + 2e^- \rightarrow O^{2-}$ Perovskites ($La_xSr_{1-x}MnO_3$)	750-1050°C	Stationnary

FUEL CELL PHYSICS

MAIN PHYSICAL PHENOMENA



Half reaction at the anode (oxidation):

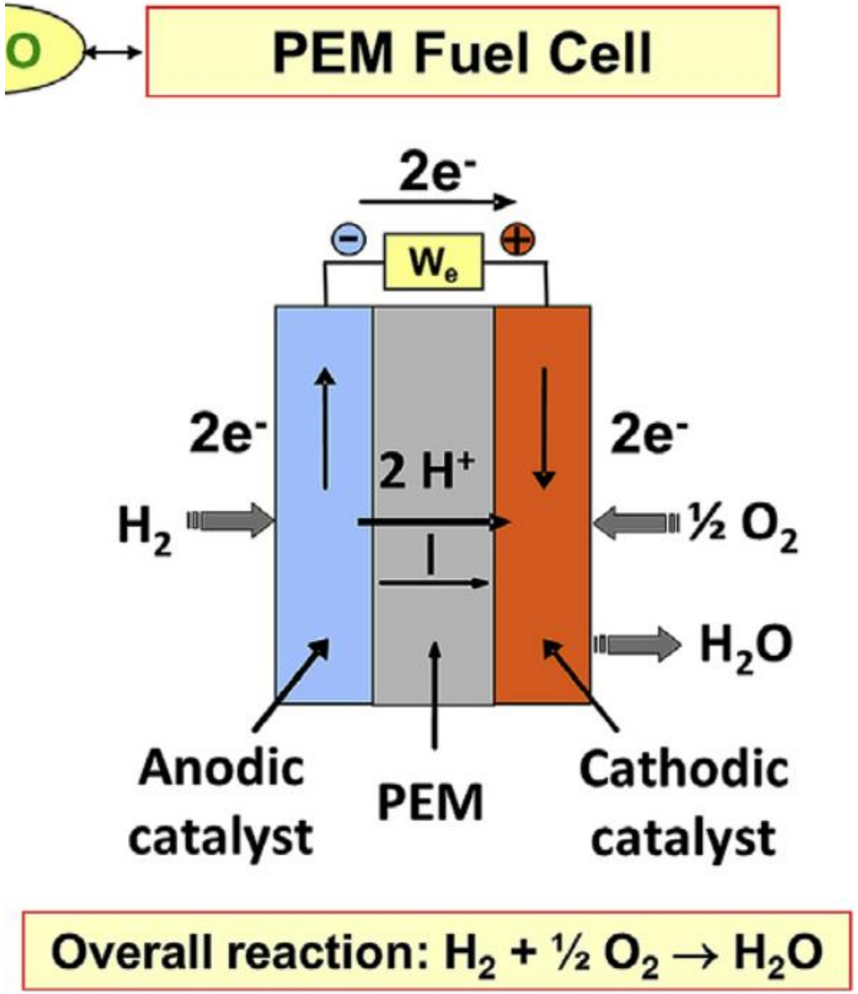
$$H_2 \rightarrow 2H^+ + 2e^-$$

Half reaction at the cathode (reduction):

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

[1] C. Lamy, From hydrogen production by water electrolysis to its utilization in a PEM fuel cell or in a SO fuel cell: Some considerations on the energy efficiencies, Int. J. Hydrogen Energy. 41 (2016) 15415–15425. https://doi.org/10.1016/j.ijhydene.2016.04.173.

MAIN PHYSICAL PHENOMENA



The anode is the electrode where the oxydation reaction takes place (*electrons doner*)

The cathode is the electrode where the reduction reaction takes place (*electrons acceptor*)

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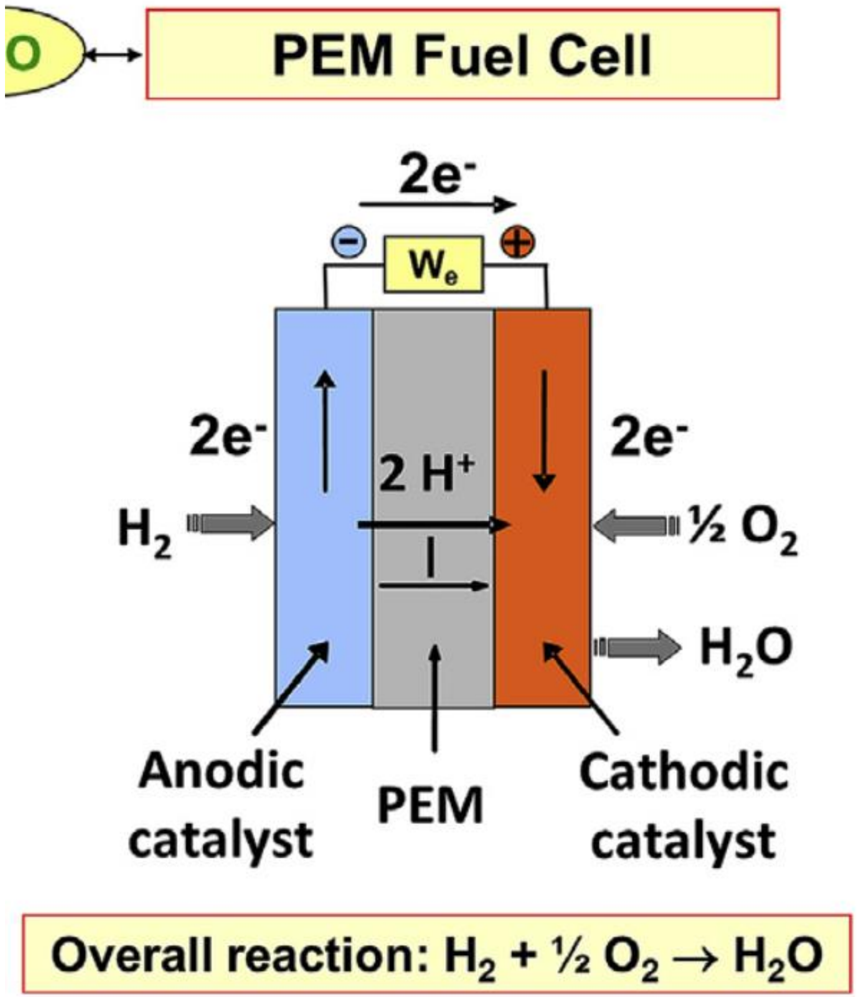


The reference potential (measured at OCV) is given by the Nernst law:

$$E_{rev} = E^{ref}(T) + \frac{R.T}{n.F}.\ln\left(\frac{[H_2].[O_2]^{0,5}}{[H_2O]}\right)$$

where E^{ref} is the reference potential of the reaction:

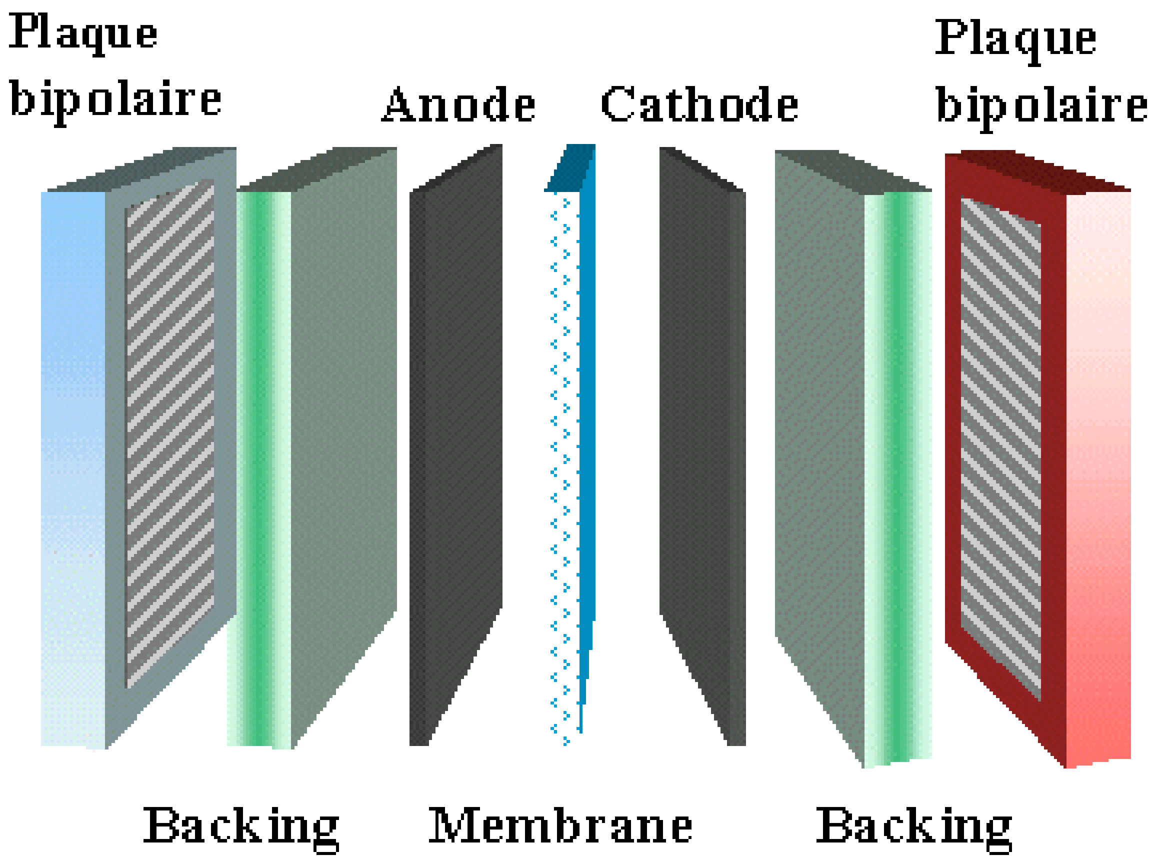
$$E^{ref} = \frac{\Delta H - T.\Delta S}{n.F} = \frac{\Delta G}{n.F} = 1,23V$$

➔ $[H_2]$ and $[O_2]$ can be taken equal their respective partial pressure

➔ $[H_2O]$ is the solvent, so taken to 1

[1] C. Lamy, From hydrogen production by water electrolysis to its utilization in a PEM fuel cell or in a SO fuel cell: Some considerations on the energy efficiencies, Int. J. Hydrogen Energy. 41 (2016) 15415–15425. https://doi.org/10.1016/j.ijhydene.2016.04.173.

MAIN COMPONENTS IN PEMFC



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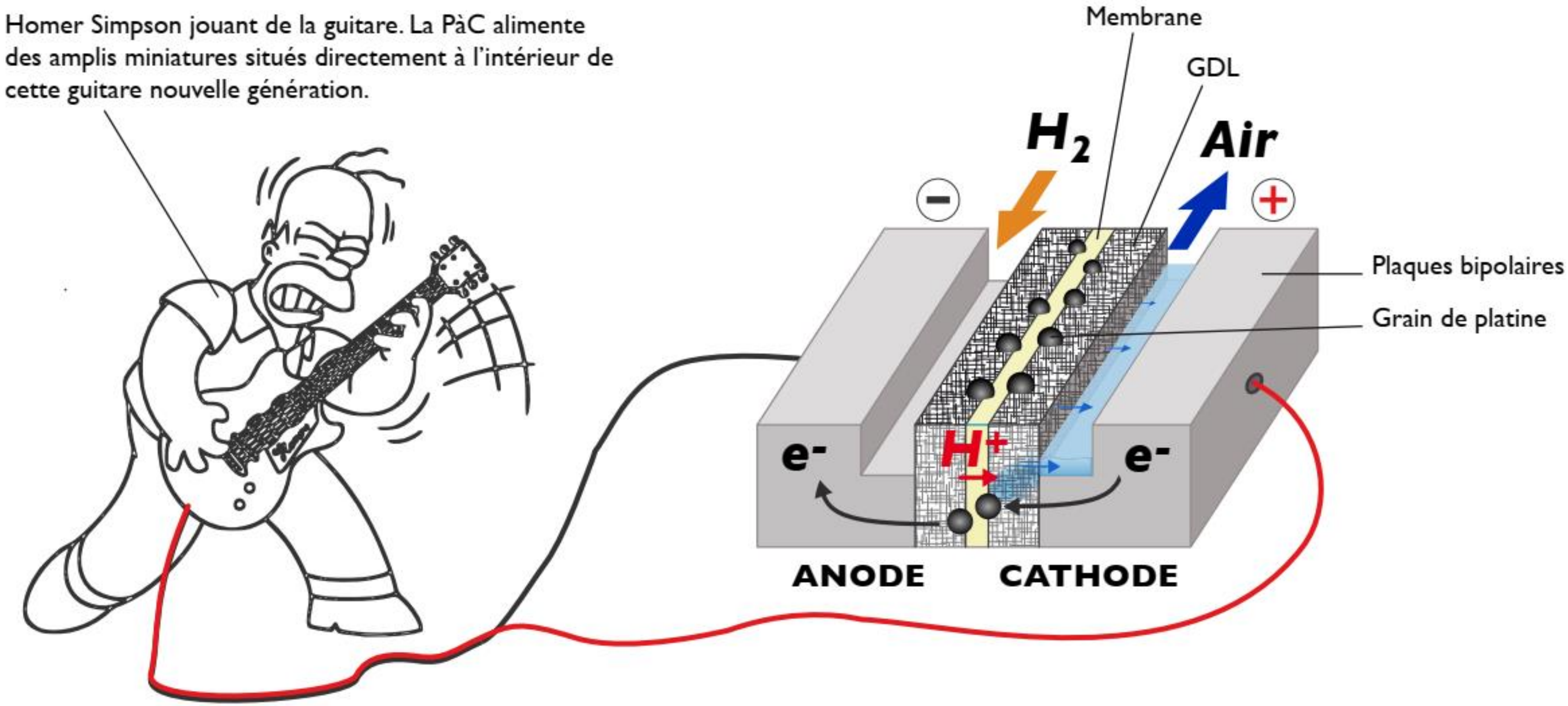
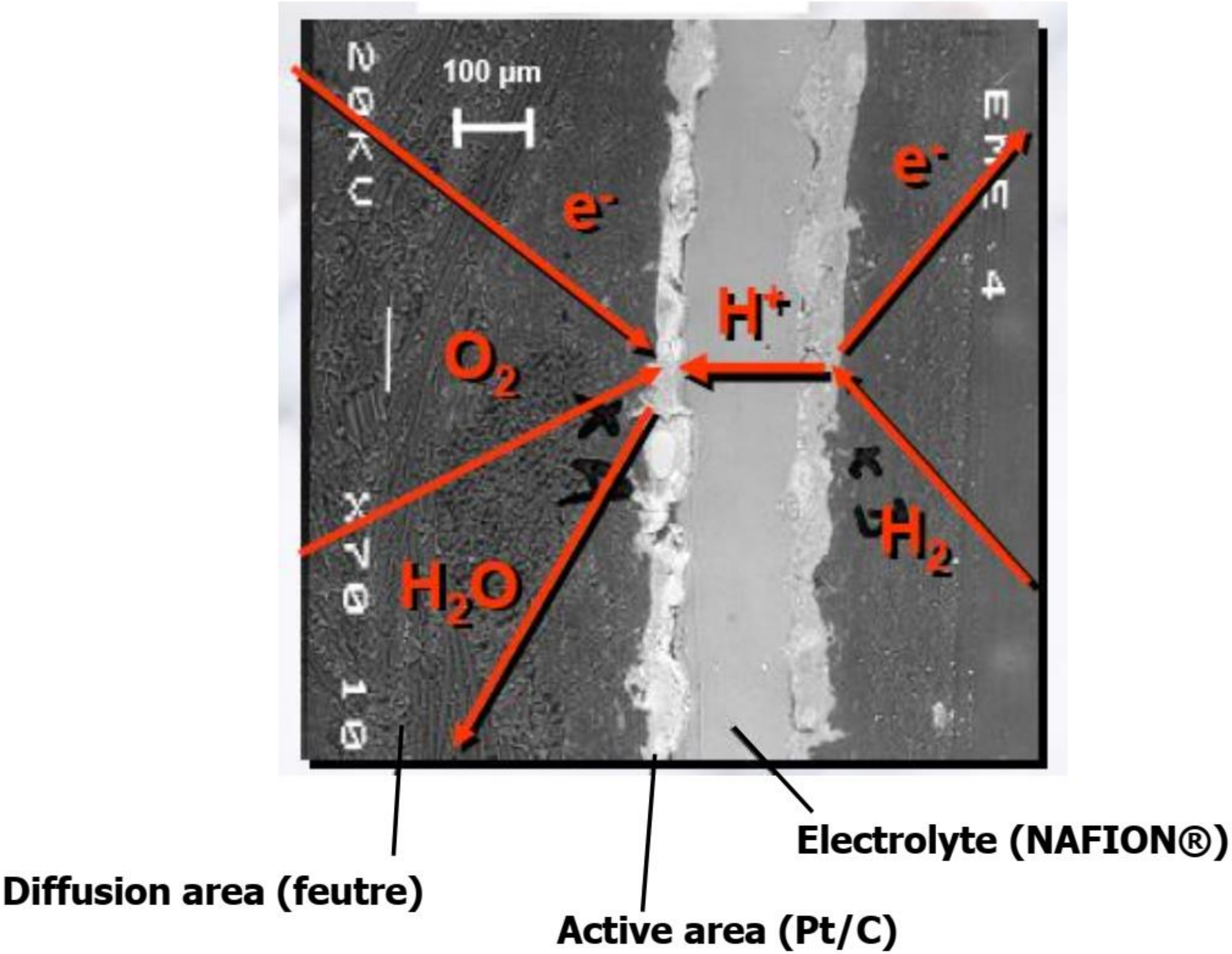


MATERIALS FOR PEMFCS



Triple phase Boundary

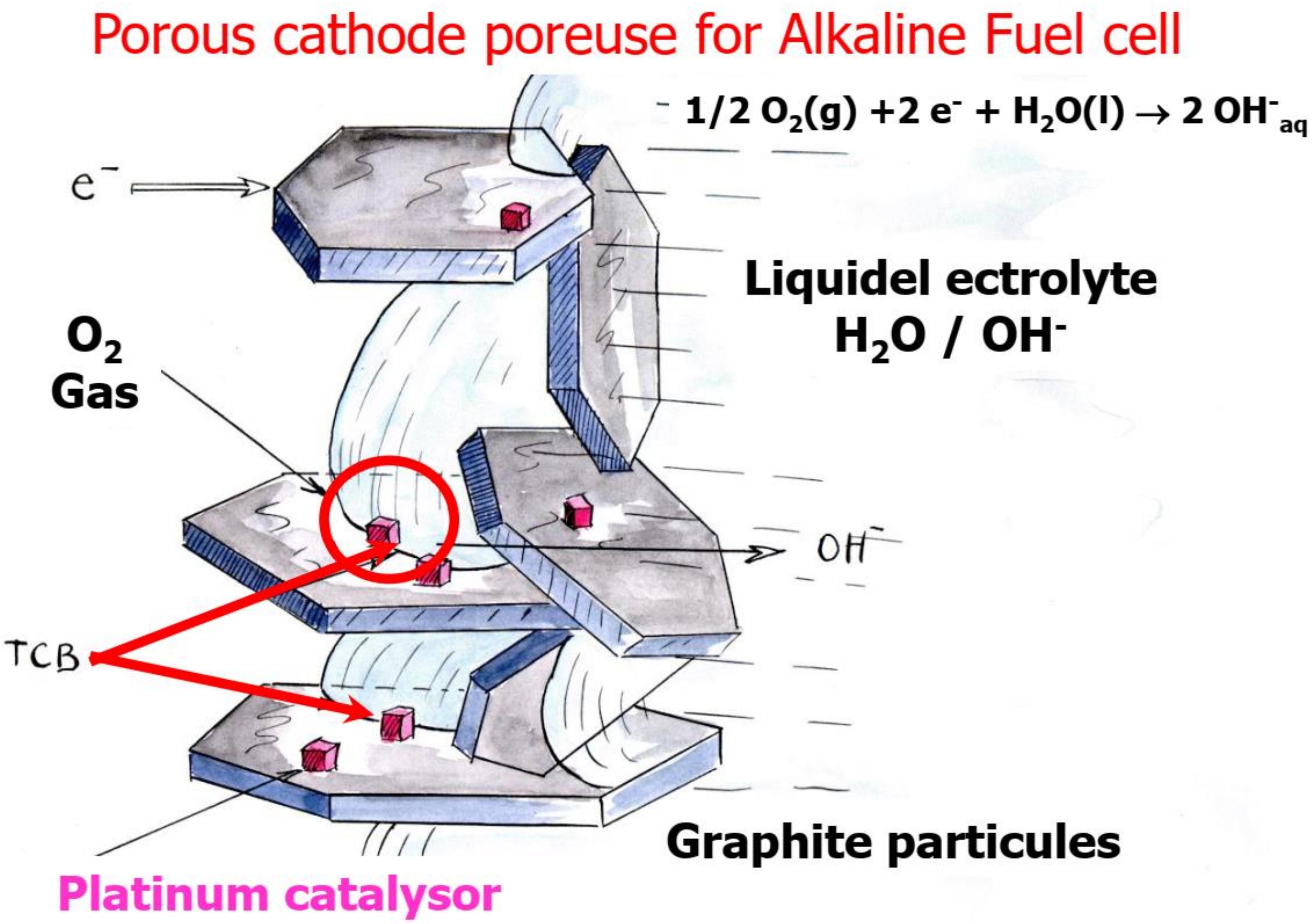
The percolation of three different phases is required to produce the reaction

1. Gas phase → porous electrodes

2. Electrons → graphite or carbon particles

3. Ionic conductor → membrane (solid or liquid)

TRIPLE PHASE BOUNDARY



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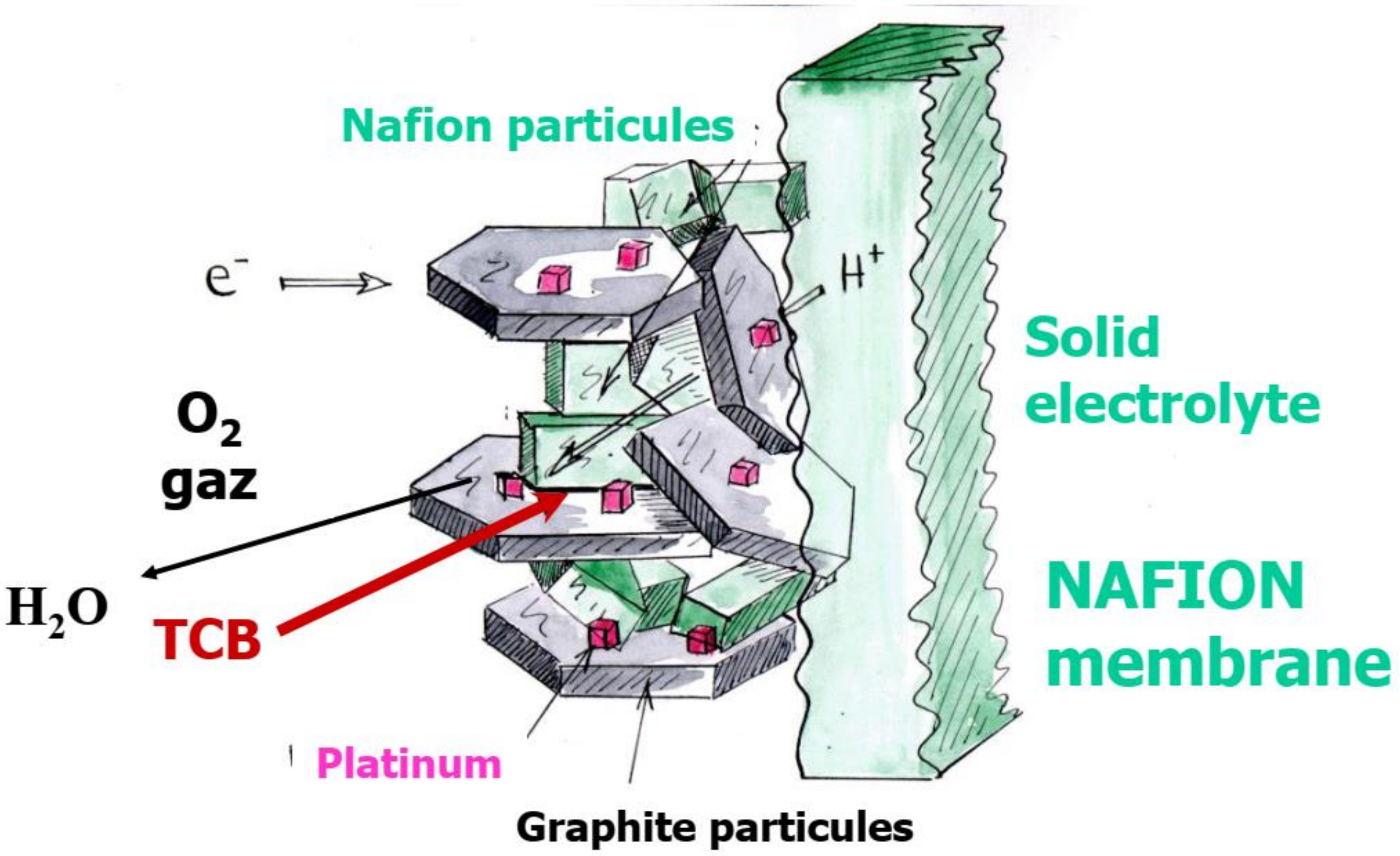


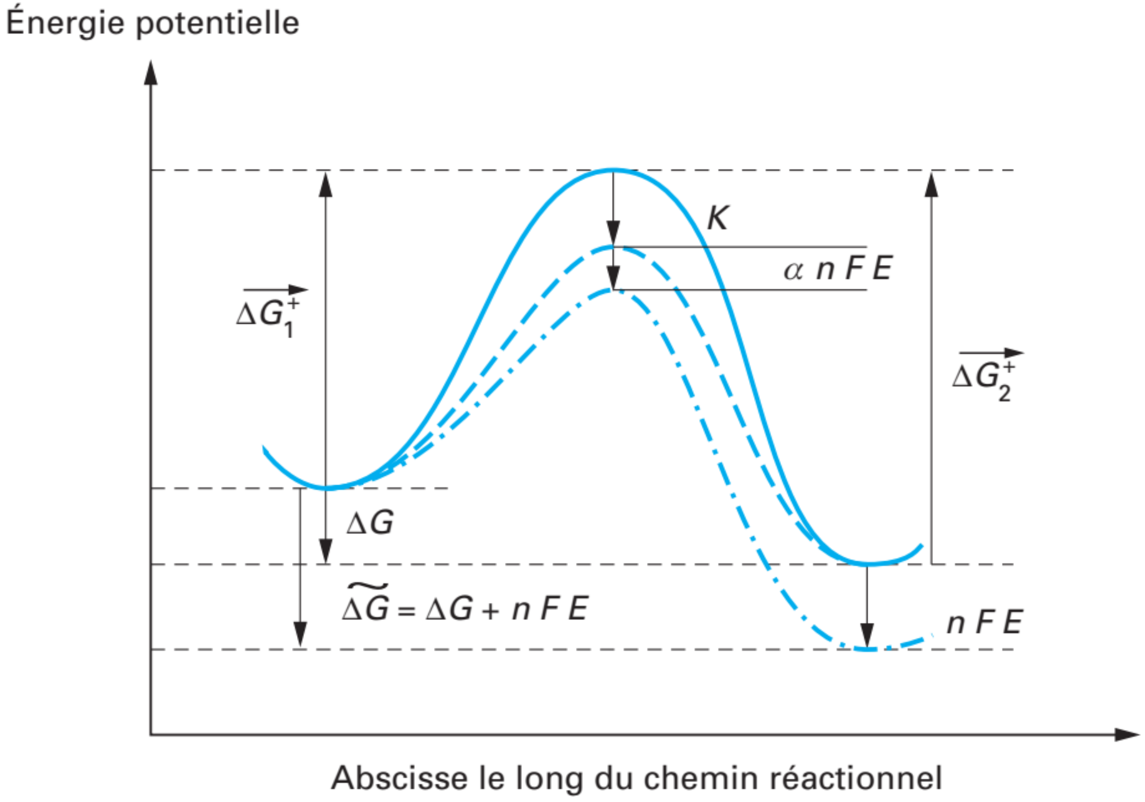
Porous cathode for PEMFC

ACTIVATION LOSSES

In any chemical reaction, the change of the chemical potential is sources of entropy generation, and energy losses.

➔ Modeled by an overpotential, η

➔ The bultler-Volmer law link the overpotential to the current



$$\eta = E - E^{rev}$$

$$j = i_0 . \left[\frac{c_{\text{red}}}{c_{\text{red}}^{ref}} \exp\left(\frac{\alpha.n.F}{R.T} . \eta \right) - \frac{c_{\text{ox}}}{c_{\text{ox}}^{ref}} \exp\left(- \frac{(1-\alpha).n.F}{R.T} . \eta \right) \right]$$

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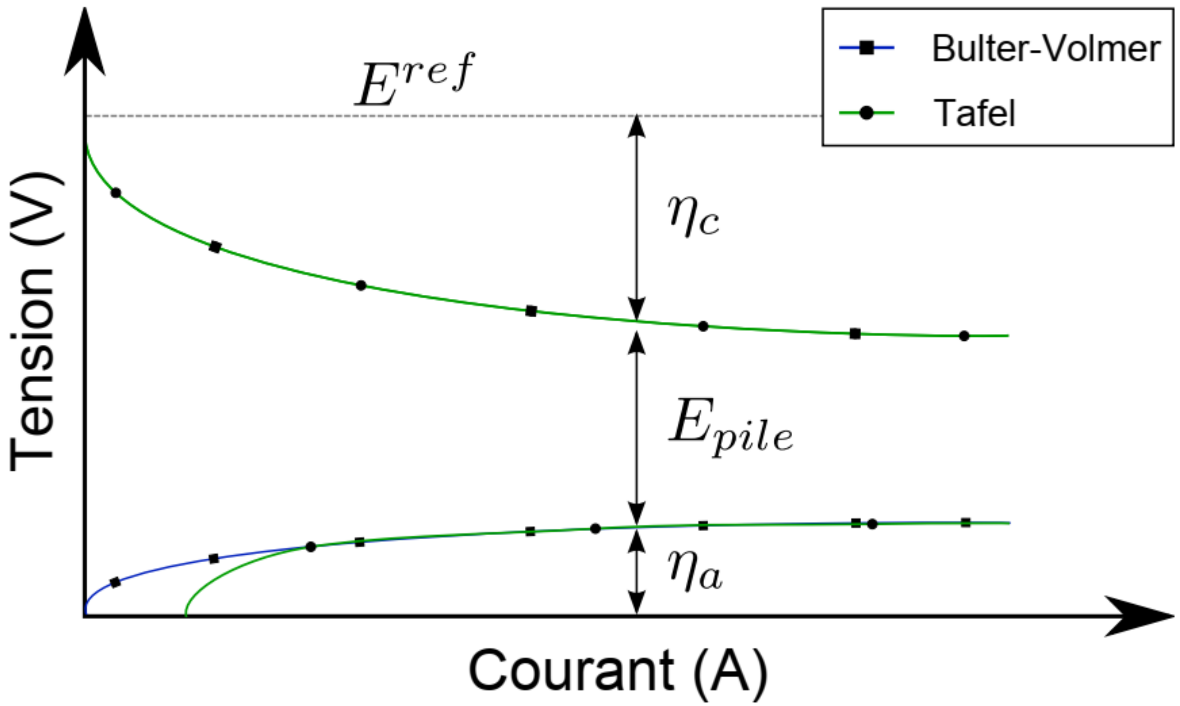

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OHMIC LOSSES

The transport of charges in a resistor make an ohmic losses in in it.

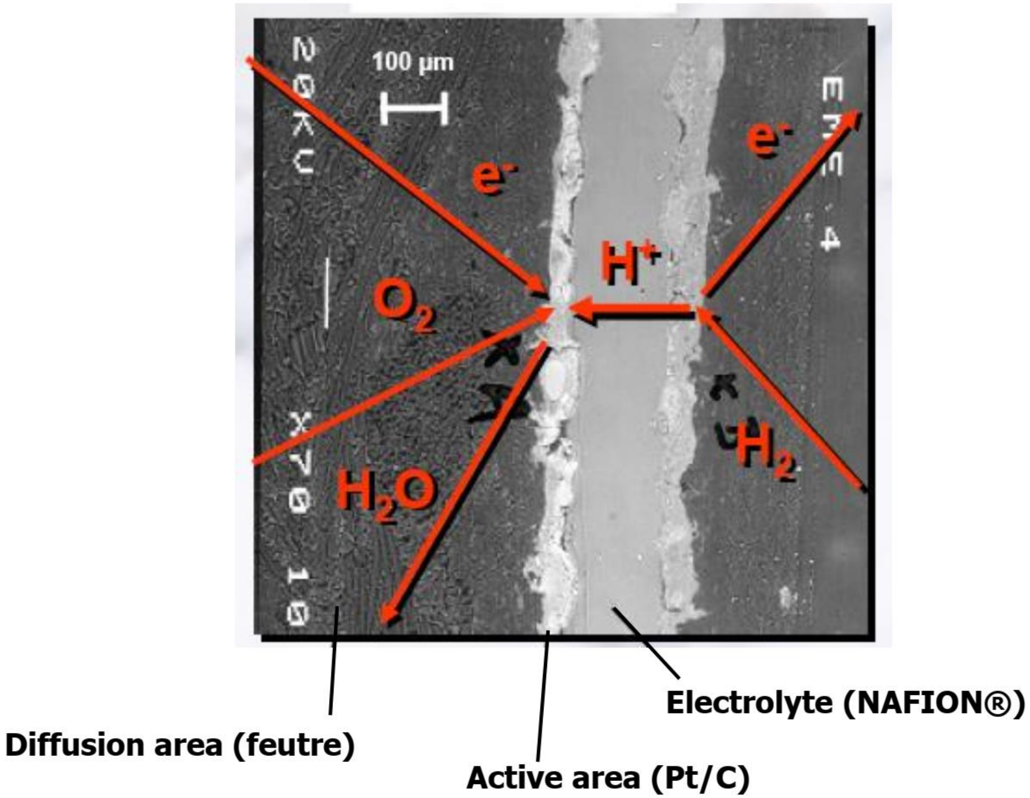
➔ It is governed by the Ohm's Law

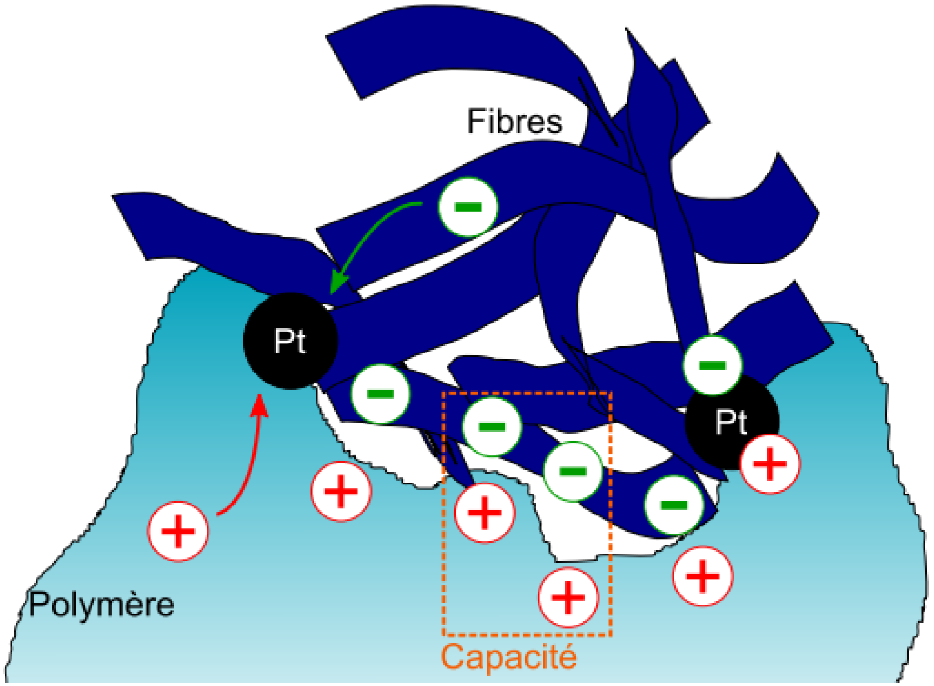
➔ A capacity is also present at the interface between the electrolyte and the fiber

$$\vec{j} = -\sigma.\vec{\nabla}\eta$$

$$\sigma_m = (0,005139.\lambda - 0,00326).\exp\left(1268.\left(\frac{1}{303} - \frac{1}{T}\right)\right)$$

$$C.\frac{\partial \eta}{\partial t} + \mathrm{div}(\vec{j}) = \dot{S}$$

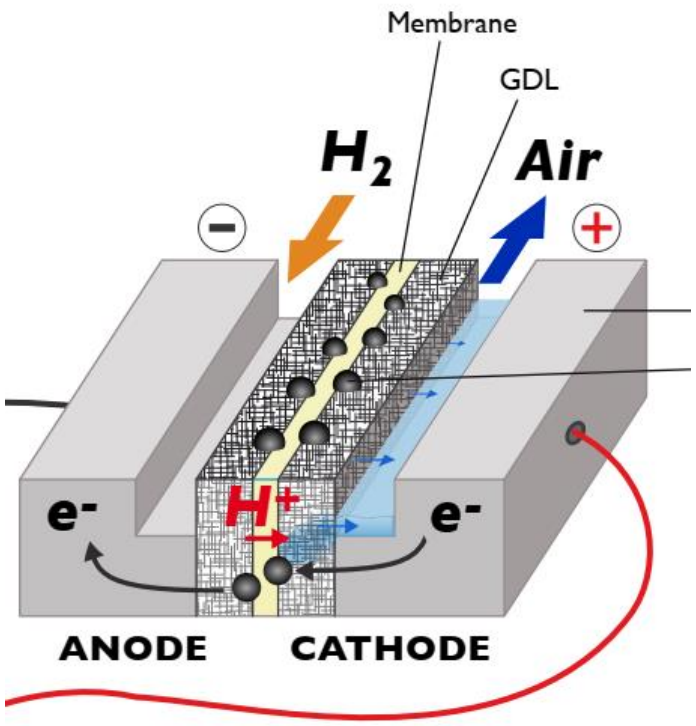




MASS TRANSPORT LOSSES

The mass transport is governed by two phenomena:

1. By diffusion in the fibrous media (Fick's Law)
2. By pressure in the channel (Navier-Stokes equations)

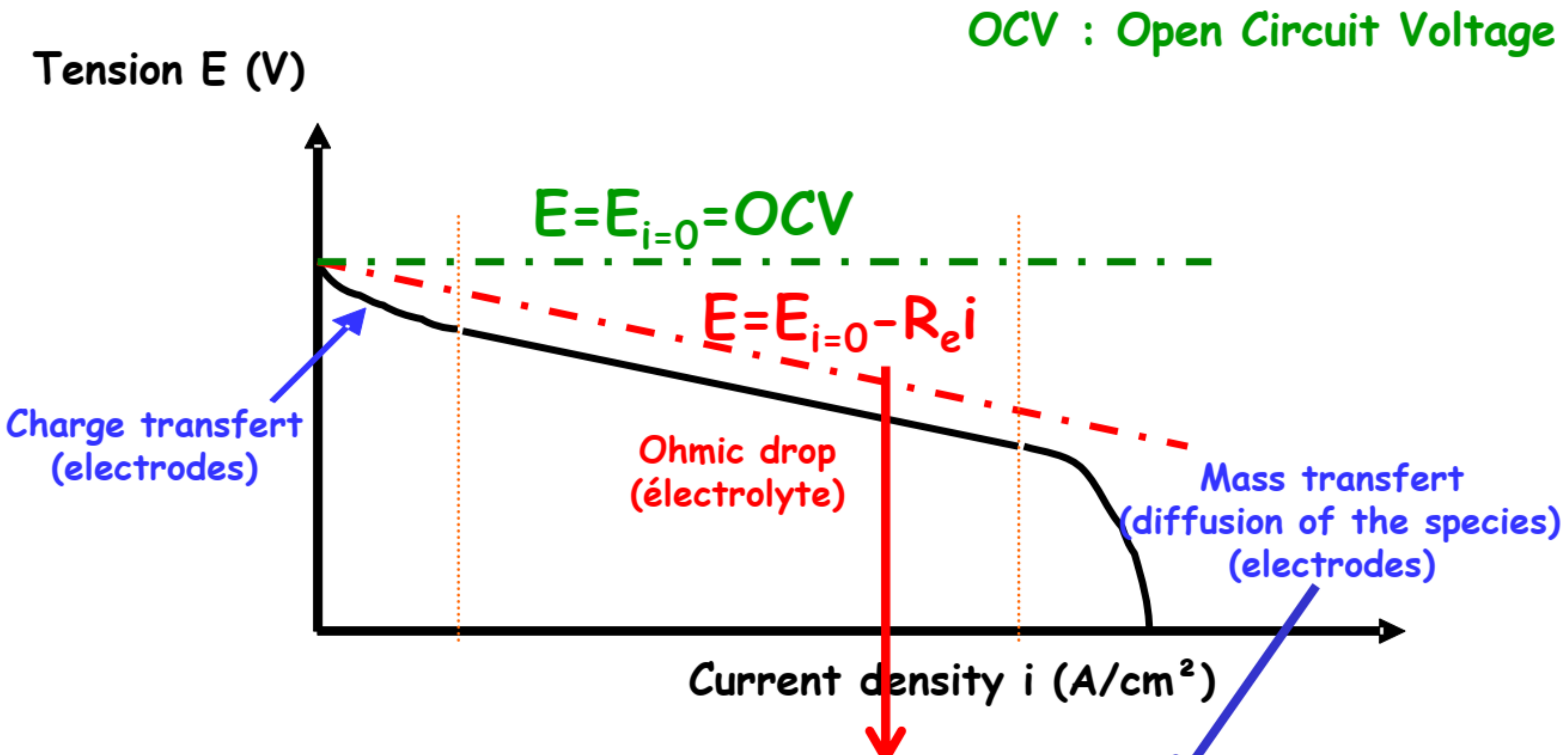


$$\frac{\partial c}{\partial t} - D\nabla^2 c = 0$$

$$\frac{\partial \vec{\mathbf{u}}}{\partial t} + \vec{\mathbf{u}}.\vec{\nabla}\vec{\mathbf{u}} = \vec{f} + \vec{\nabla}p + \mathrm{div}(\nu_m.\vec{\nabla}\vec{\mathbf{u}})$$

$$\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho_m.\vec{\mathbf{u}}) = 0$$

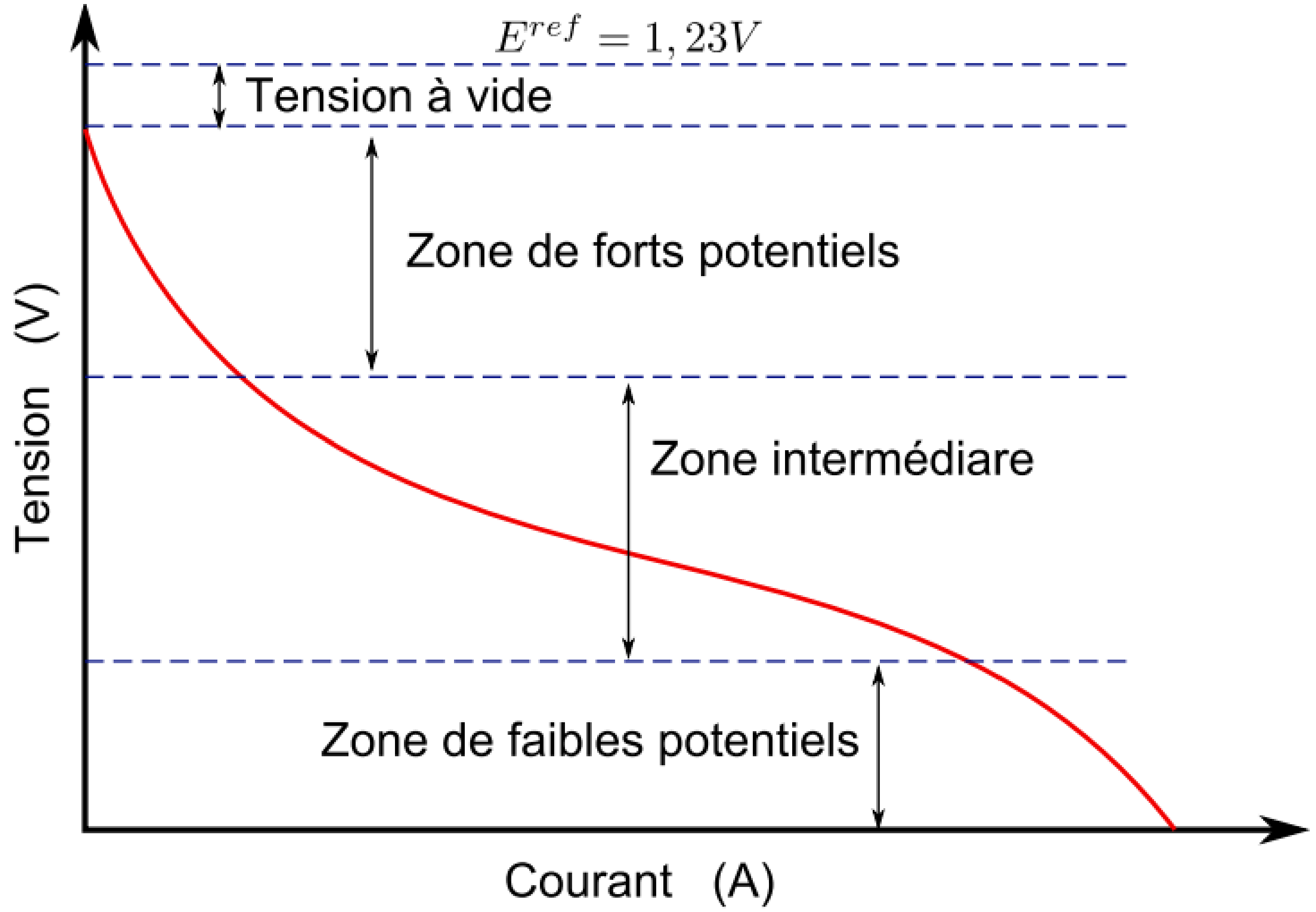
POLARIZATION CURVE



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

The fuel cell produces not only electricity but **also heat**

POLARIZATION CURVE



The fuel cell produces not only electricity but **also heat**

FUEL CELL EFFICIENCY

Exercice : calcul du rendement théorique

PàC : $$\Theta_{\mathrm{PaC}} = \frac{\Delta G(T)}{\Delta H(T)}$$

Moteur Thermique : $$\Theta_{\mathrm{MT}} = 1 - \frac{T_F}{T}$$ (Carnot)

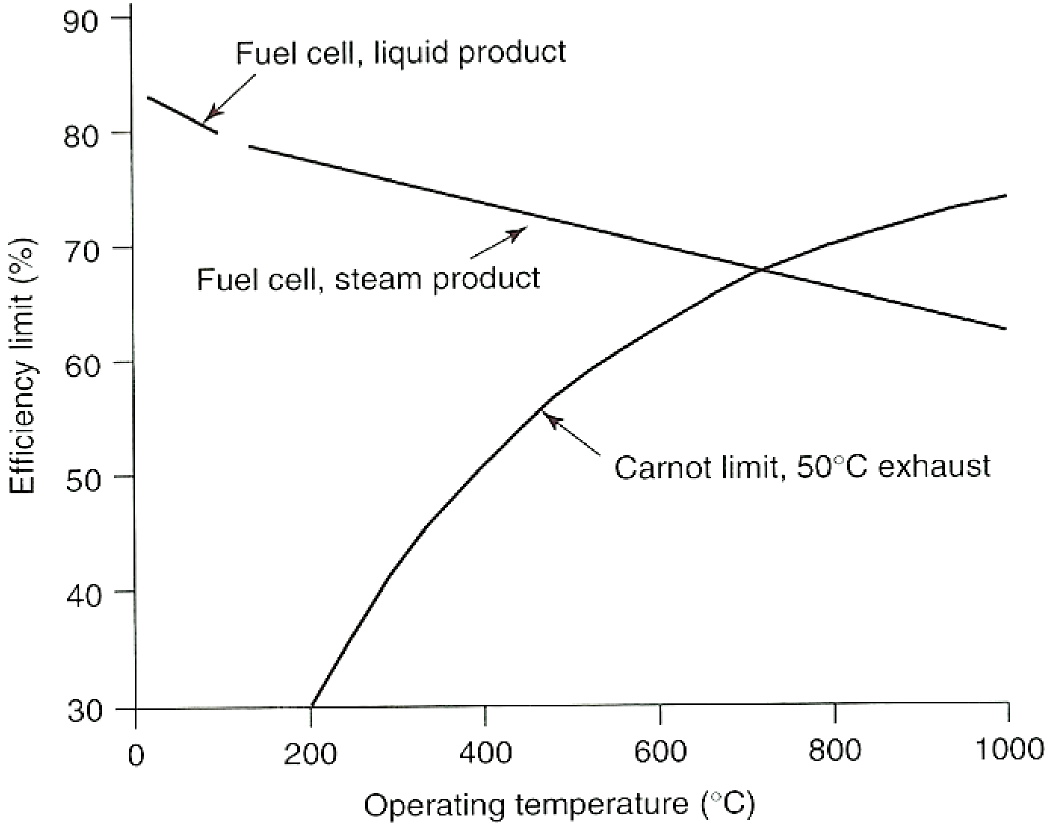
Thermodynamic value for the oxygen/hydrogen reaction	**Value**
ΔH (333 K)	285 kJ
ΔH (1073 K)	251 kJ
ΔG (333 K)	237 kJ
ΔG (1073 K)	169 kJ
T_F	295 K

1. Calculer les rendements à 60 °C puis à 800 °C.
2. Quel est le système le plus performant ?

Fuel cell efficiency

Temp (K)	**333**	**1073**
Pac	83%	67%
MT	11%	73%

FUEL CELL EFFICIENCY



FC thermodynamic efficiency:

$$\Theta = \frac{\Delta G}{\Delta H} = \frac{237(\text{kJ})}{285(\text{kJ})} = 0,83$$

For the temperature lower then 700°C the FC have a better efficiency compared to the classical thermal engine

FUEL CELL EFFICIENCY

The fuel cell efficiency can also be calculated from the potentials as

$$\varepsilon_E = \frac{E(j)}{E_{eq}} = 1 - \frac{(|\eta_a(j)| + |\eta_c(j)| + R_e j)}{E_{eq}} \leqslant 1$$

η_a and η_c are the anode and cathode overpotential
R_e is the electrolyte resistance

➔ The fuel cell voltage is the image of the efficiency, i.e. it keeps decreasing as long as the cell produce more current

➔ The grail of the fuel cells is to produce a lot of current at high voltage !

Mass conservation

Rien ne se perd, rien ne se crée, tout se transforme

The creation of current has to be linked to an equivalent consumption of hydrogen and oxygen : it is the charge and mass conservation.

In electrochemistry, it is given by the so-called Faraday law as

$$N = \frac{I}{nF}$$

N is the molar rate (mol/s)
I is the current (A)
n is the number of electron involved in the half reaction
F is the Faraday constant (C/mol)

➔ To convert it in volumetric flow rate, we use the molar volume, i.e. $q_v = N/V_m$.
➔ $V_m = RT/p \approx$ 22,4 l/mol in standard pressure and temperature.

ENERGY CONSERVATION

Rien ne se perd, rien ne se crée, tout se transforme

From the energy point of view also, there is also a conservation. It is more convenient to expressed it in terms of electrical power as

$$P^0 = P_{heat} + P_{out}$$

$$P_{heat} = (E^0 - E)I$$

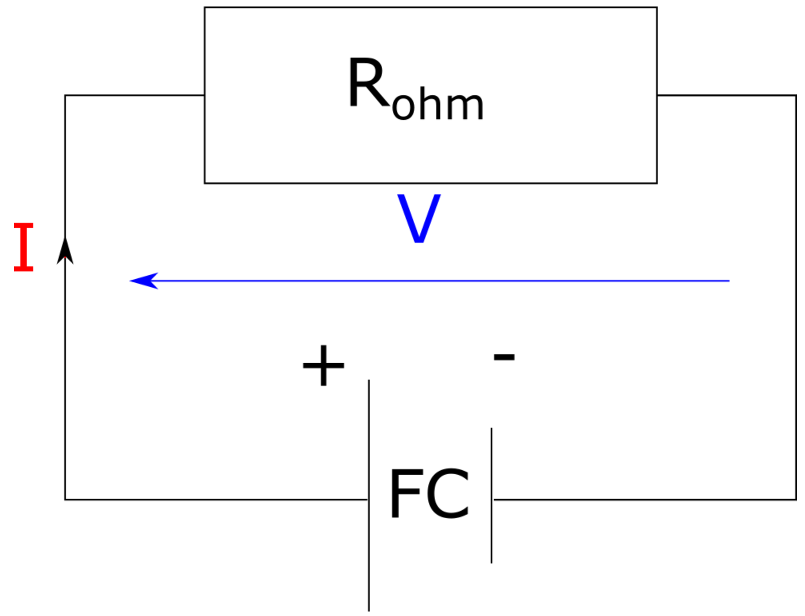
P_{heat} is the heat release power (W)
$E^0$is the reference potential (V)
E is the cell potential (V)
I is the cell current (A)

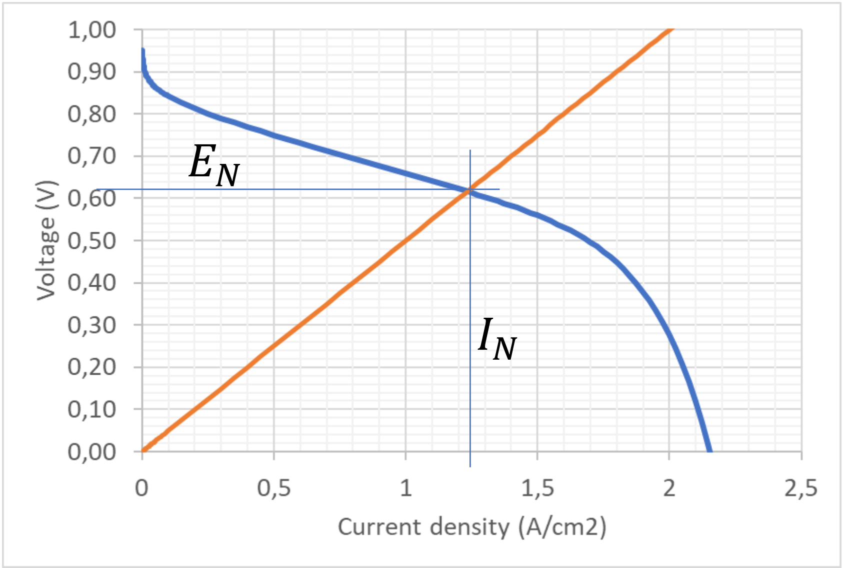
OPERATING POINT

What happen when a fuel cell is connected to a load ?

➔ The operating point is determined when the load curve meet the fuel cell polarization curve

➔ Example of load curve, i.e. $E_{load} = R_{\Omega} I$



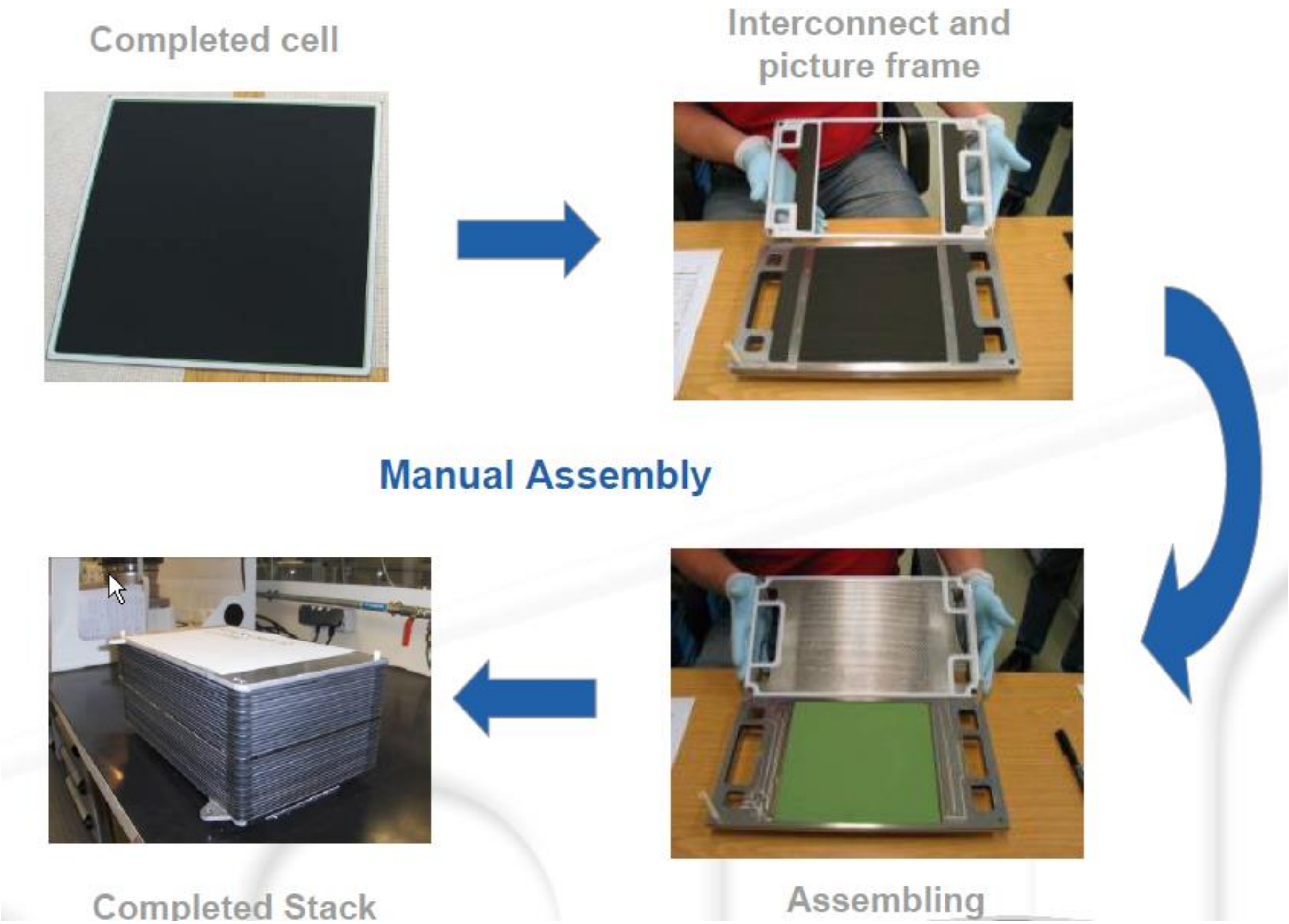


➔ E_N and I_N are both the operating potential and current

FUEL CELL SIZING

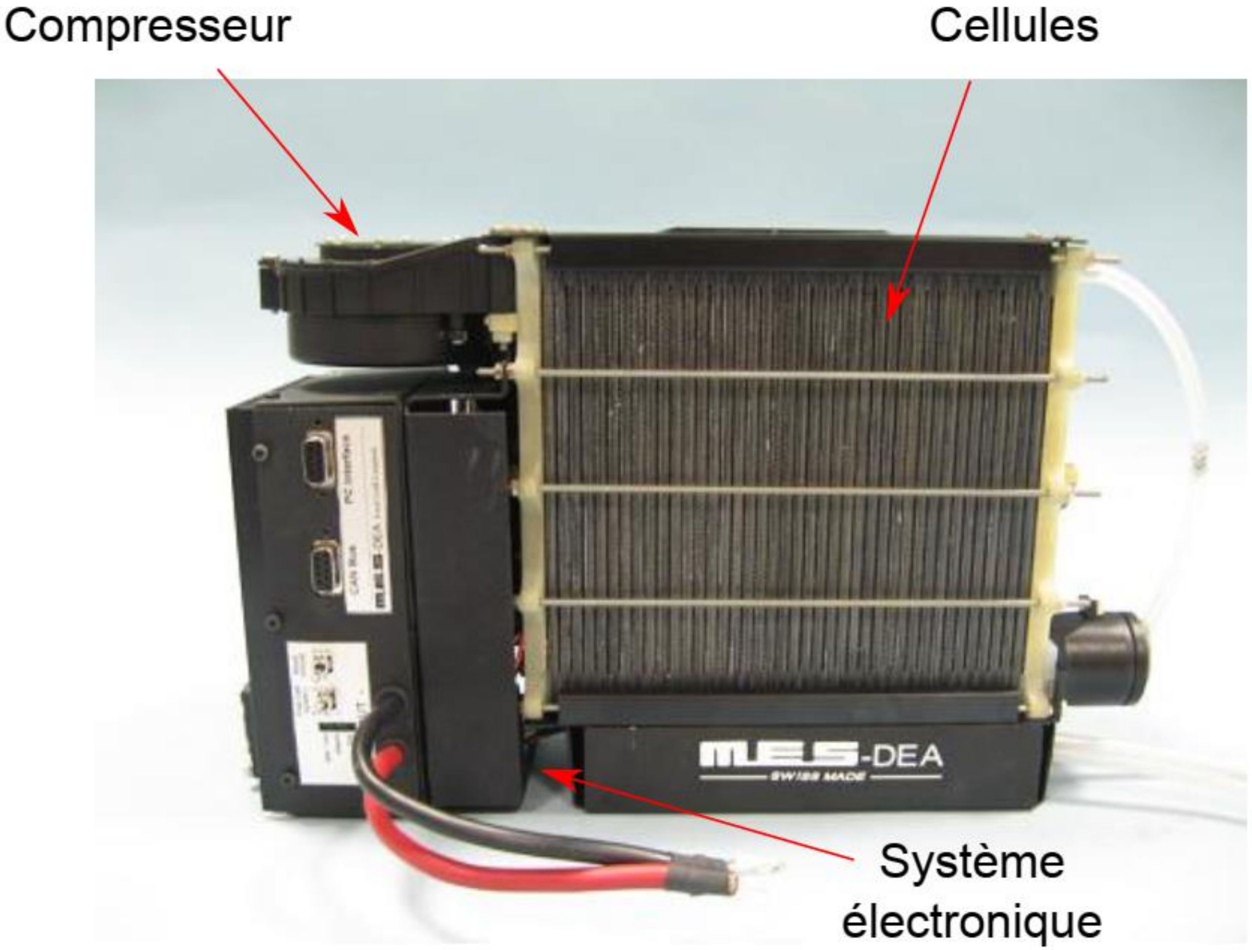
POWER OUTPUT OF A STACK

A fuel cell stack is composed of several single cells (from a dozen to a hundred)



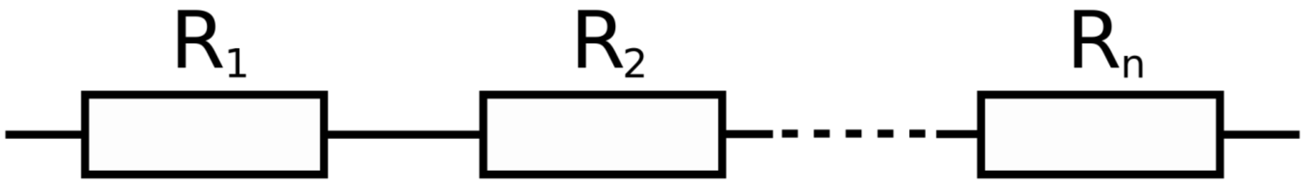
POWER OUTPUT OF A STACK

A fuel cell stack is composed of several single cells (from a dozen to a hundred)



POWER OUTPUT OF A STACK

The cell are connected in series :



Current produced by a fuel cell stack : $I_{stack} = I_{cell}$

Voltage obtained by a fuel cell stack : $V_{stack} = N \times V_{cell}$

In contrast, the hydrogen and air are connected in parallel in each cells, so

$$q_{v,stack} = N \times q_{v,cell}$$

$$\Delta p_{stack} = \Delta p_{cell}$$

POWER OUTPUT OF A STACK

The power of the stack is simply the sum of the individual power of each cell in the stack

$$P_{stack} = I_{cell} \sum_{i=1}^{N} E_i = I_{cell} E_{stack}$$

➔ If all the cells have roughly the same power, it is just the multiplication of an average single cell power to the number of cells

➔ Increasing the number of cells increase the stack power

Air stoichiometry

Since the oxygen from air is considered as free reactant, it is usually sent in excess in the fuel cell to:

- ➔ Remove the water generated by the reaction
- ➔ Cool the cell
- ➔ Limit the mass transport losses at the cathod

From the fluidic point of view, the cell are connected in parallel, so the total flow rate is :

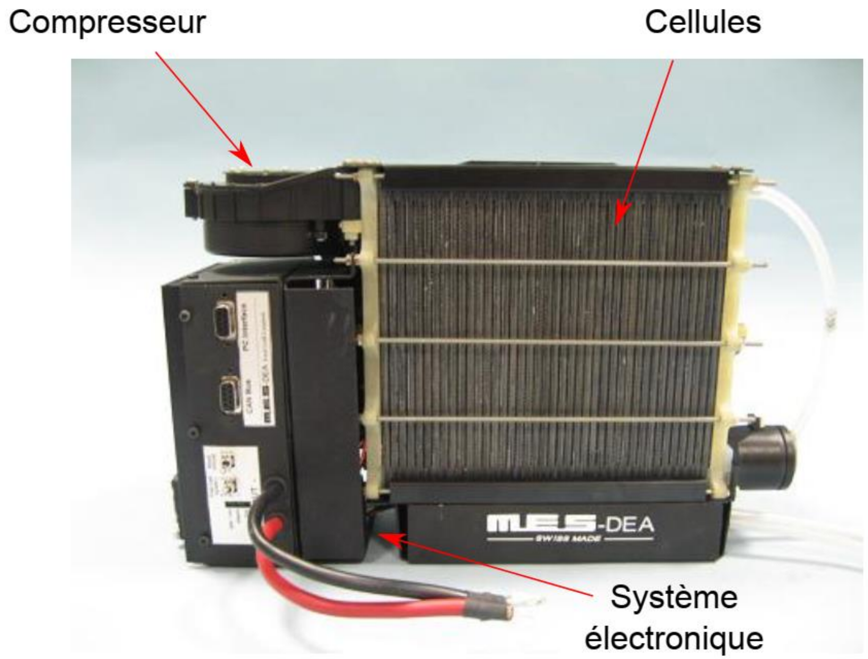
$$q_{v,tot} = \lambda \sum_{n=1}^{N_{cell}} q_{v,n} \approx \lambda N_{cell} q_{v,cell}$$

➔ Usually a stoichiometry, λ, between 3 and 5 is used

➔ Increasing the air stoichiometry also increase the power consumption of the compressor

NET EFFICIENCY

The net efficiency is given by the fuel cell power minus the consumption of the auxiliaries, divided by the theoretical power of the system



$$\eta_{stack} = \frac{net\ power}{reference\ power}$$

$$\eta_{stack} = \frac{E_{stack}I - P_{aux}}{N \times E^0 \times I}$$

CONCLUSIONS

MAIN OUTPUTS

Fuel cells main physical phenomena governing the performances :

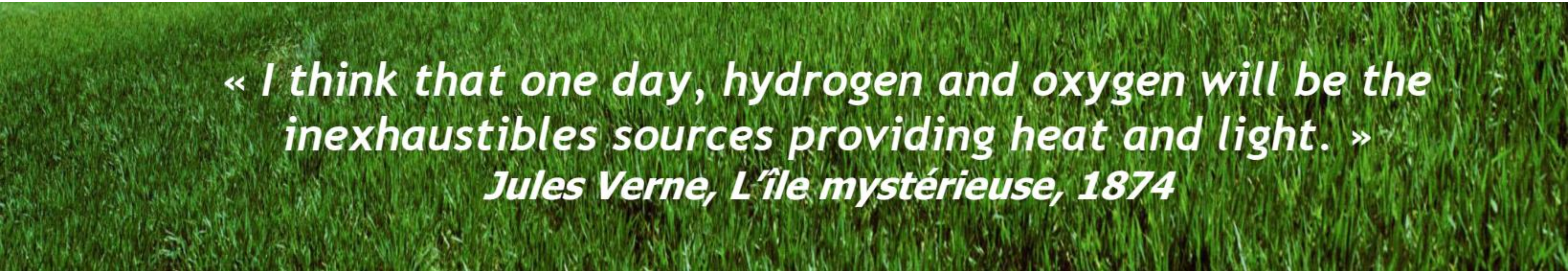
- Activation
- Charge transport
- Mass transport

- Fuel cell consumption and efficiency

- Fuel cell material needed to make it work

- Fuel cell operating point when plugged on a circuit

- Fuel cell sizing and design tools to answer a specific need


« I think that one day, hydrogen and oxygen will be the inexhaustibles sources providing heat and light. »
Jules Verne, L'île mystérieuse, 1874