Proton exchange membrane fuel cells: rationale, principle of operation and core materials

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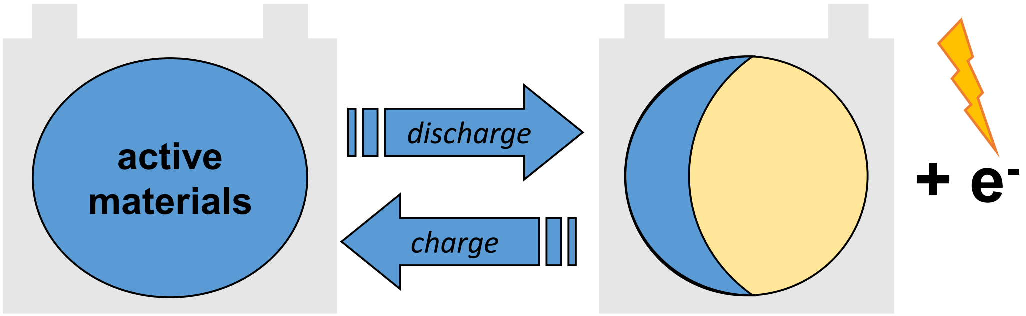
Overview:

- **Principle of operation of a PEMFC**
- **PEMFC core materials and their main properties**
- **Advantages and drawbacks of PEMFCs**

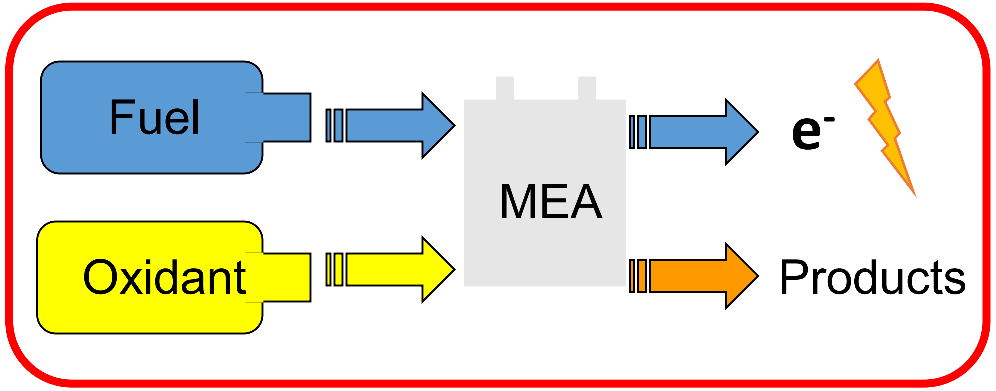
A few definitions

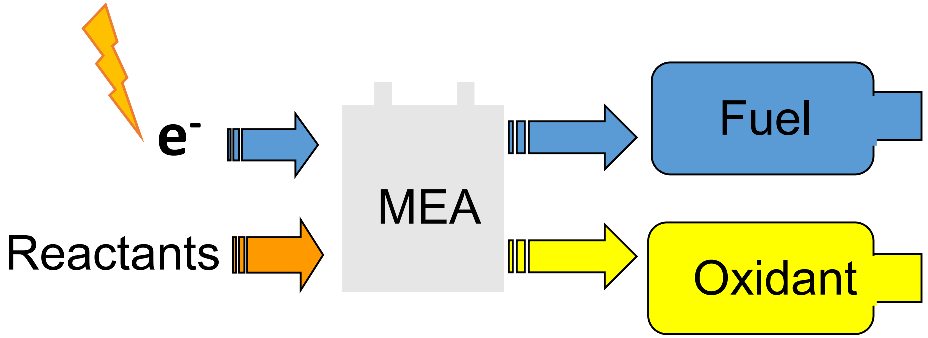
- **Electrochemical system:** **converter** of chemical energy into electrical energy *or reciprocally*

- **Closed systems:**
  - **Primary:** non rechargeable battery (generator)
  - **Secondary:** rechargeable battery

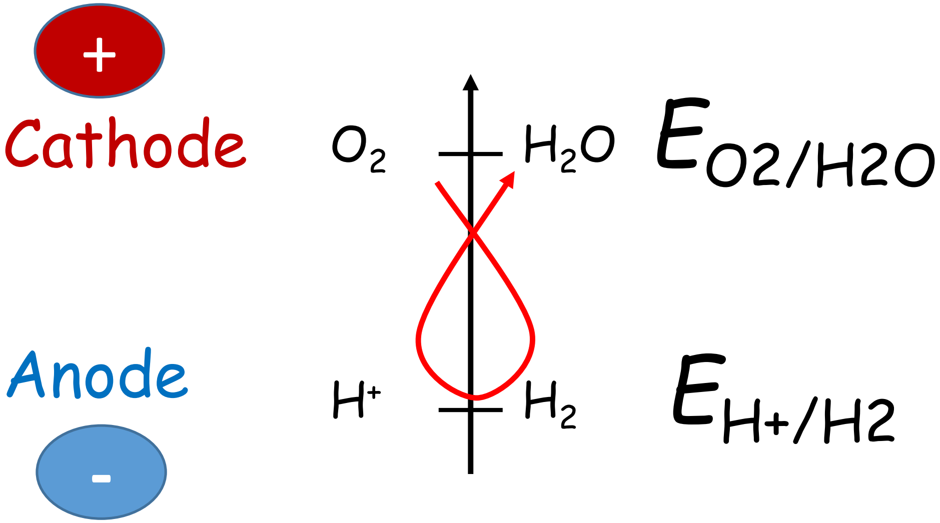


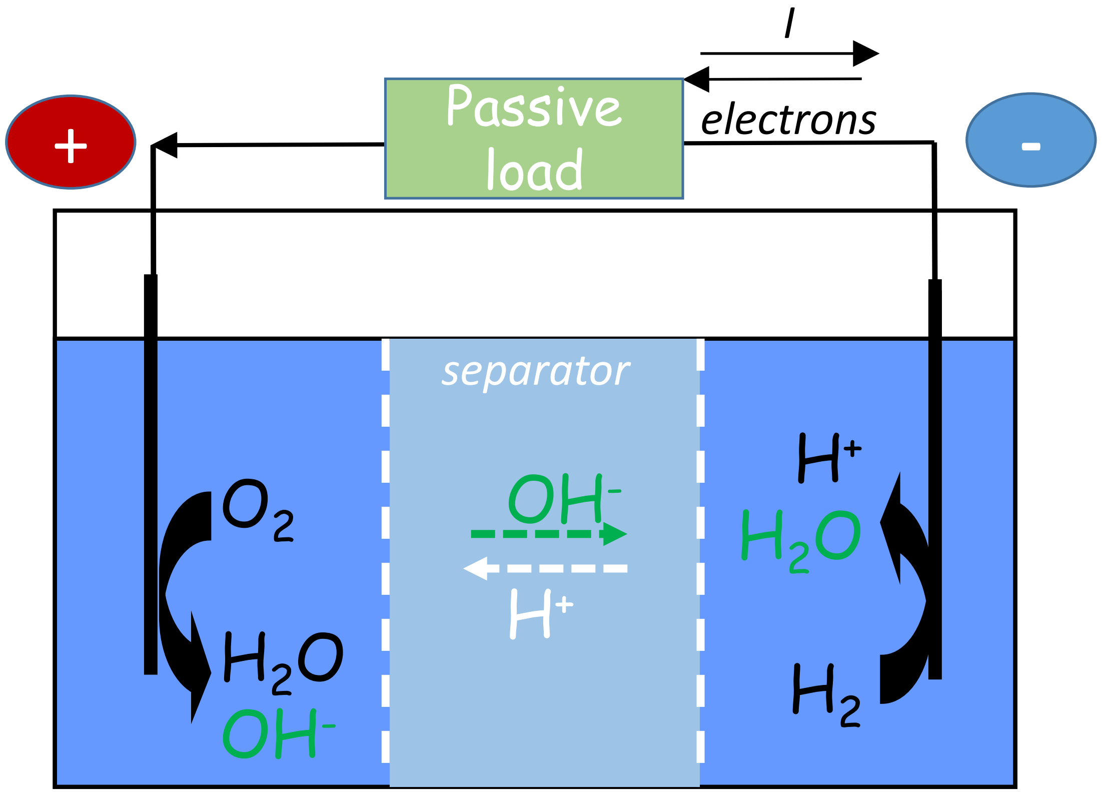
- **Open systems: fuel cells**, redox-flow cells, **electrolyzers**





Redox reactions: H_2-O_2 fuel cells





+ • **Positive electrode (O_2/H_2O couple)**

$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$ $E^0(O_2/H_2O) = 1.23$ V *vs.* SHE, acidic medium

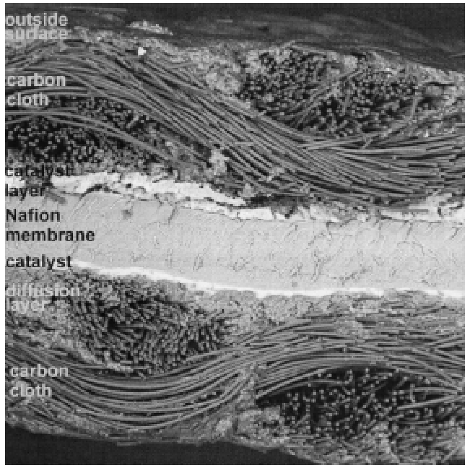
$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$ $E_b^0(O_2/H_2O) = 0.40$ V *vs.* SHE, alkaline medium

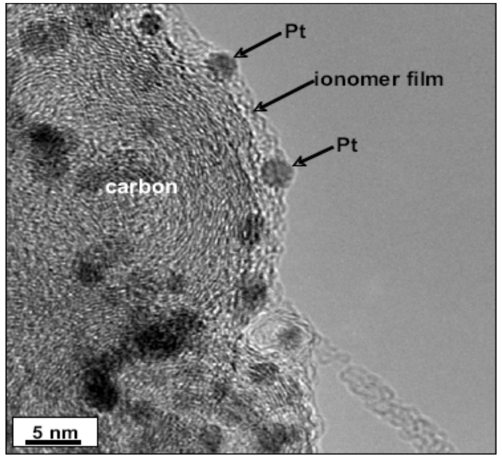
\- • **Negative electrode (H^+/H_2 couple)**

$2\,H_2 \rightarrow 4\,H^+ + 4\,e^-$ $E^0(H^+/H_2) = 0.00$ V *vs.* SHE, acidic medium

$2\,H_2 + 4\,OH^- \rightarrow 4\,H_2O + 4\,e^-$ $E_b^0(H^+/H_2) = -0.83$ V *vs.* SHE, alkaline medium

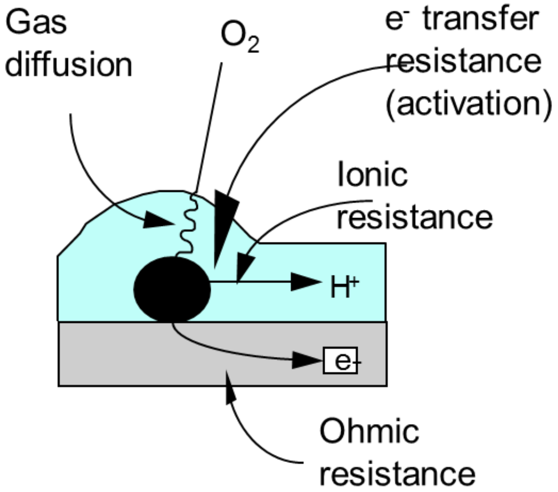
The core of the PEMFC: membrane electrode assembly (MEA)

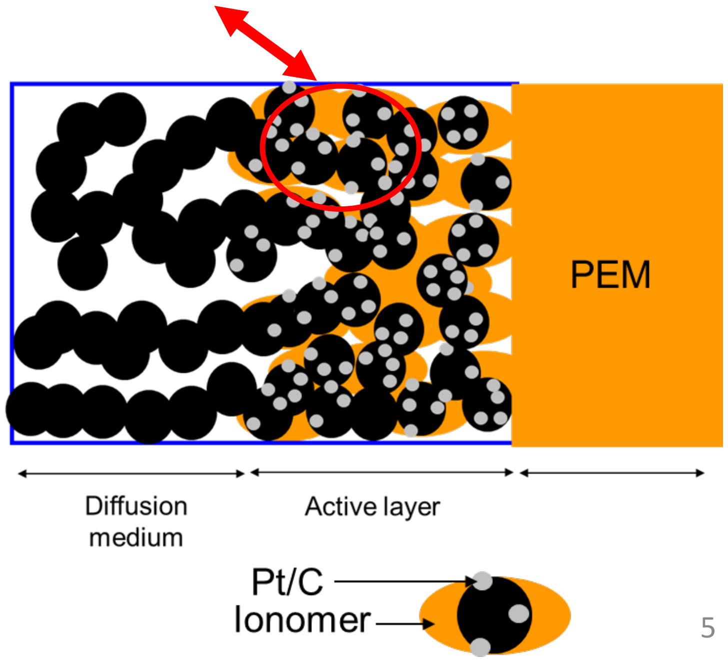




K.L. More et al. ECS Transaction ***3*** *(2006) 717*

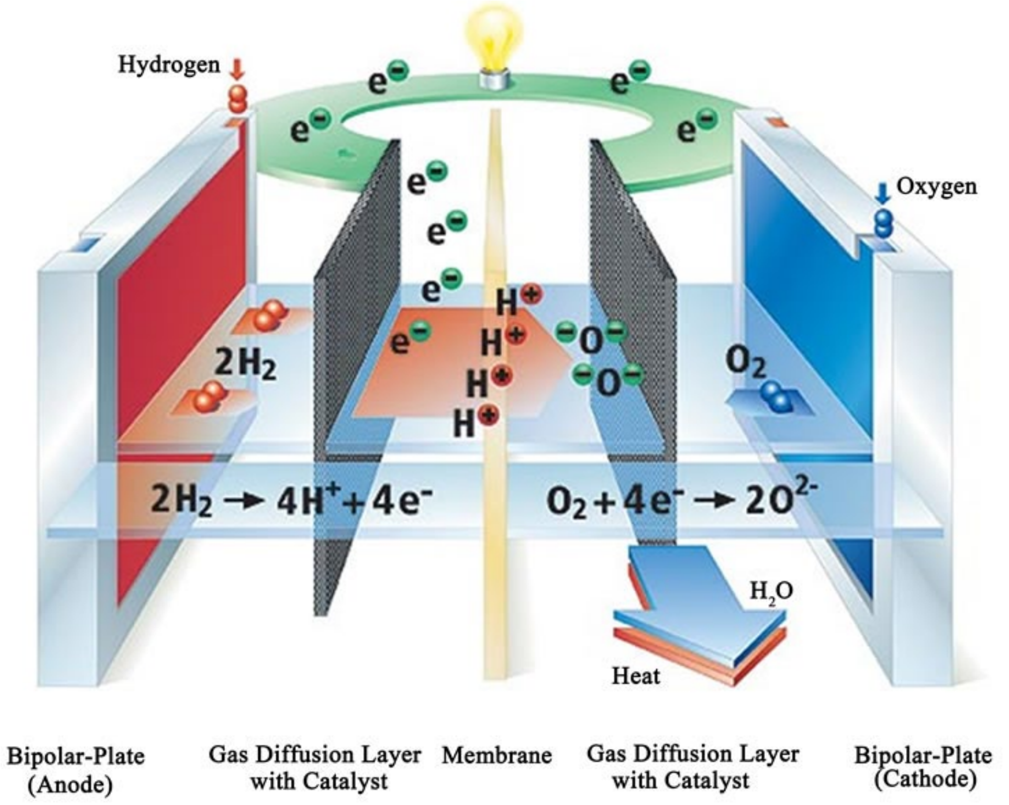
The triple contact

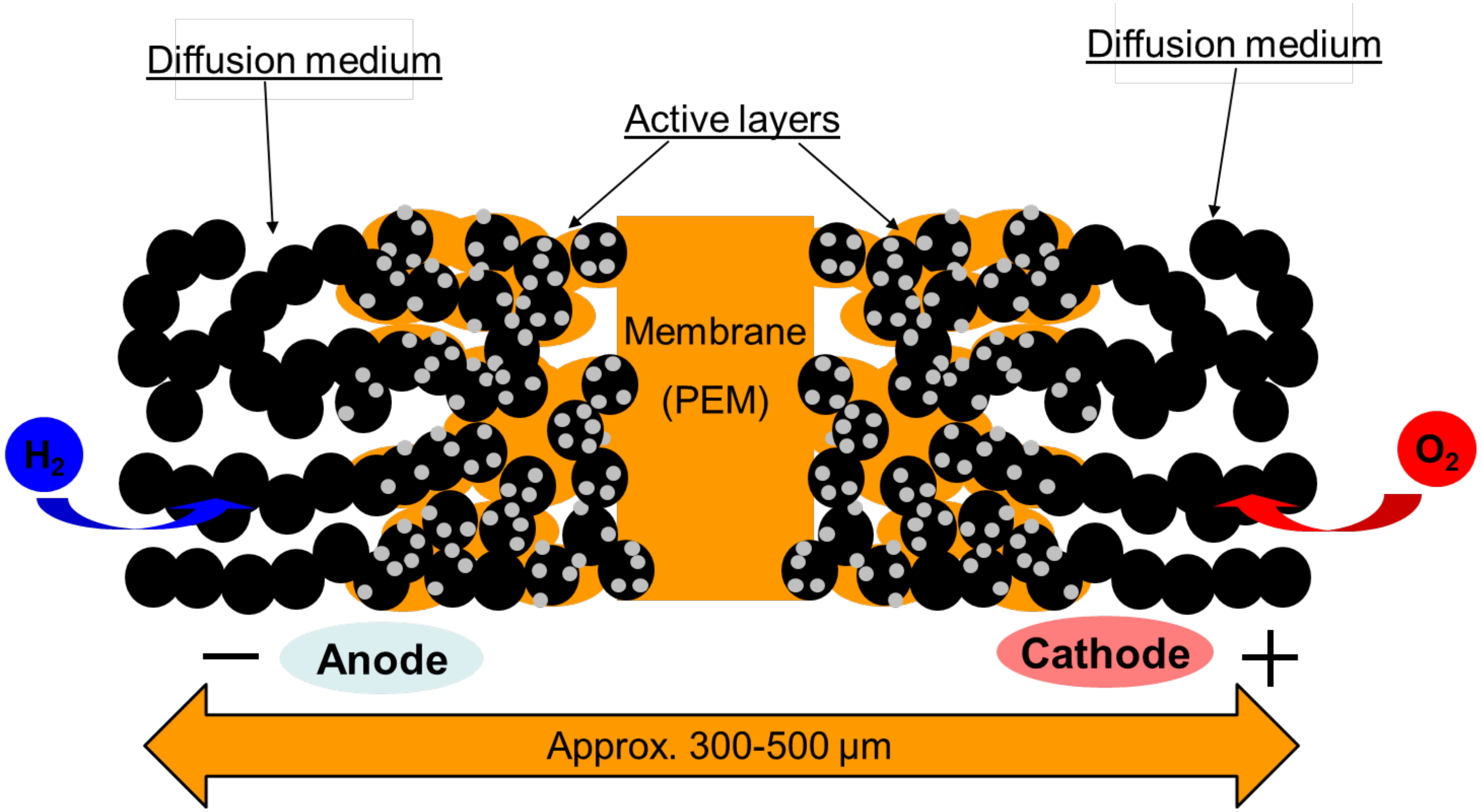




The triple phase boundary = interface reactant | ionomer | Pt/C should be distributed in the whole active layer thickness/surface

The core of the PEMFC: membrane electrode assembly (MEA)





The MEA structure/composition shall enable optimal (electro)catalytic reactions, whatever the operating conditions:

- **Electrocatalysis !**
- **Mass transport**
- **Heat transfer**

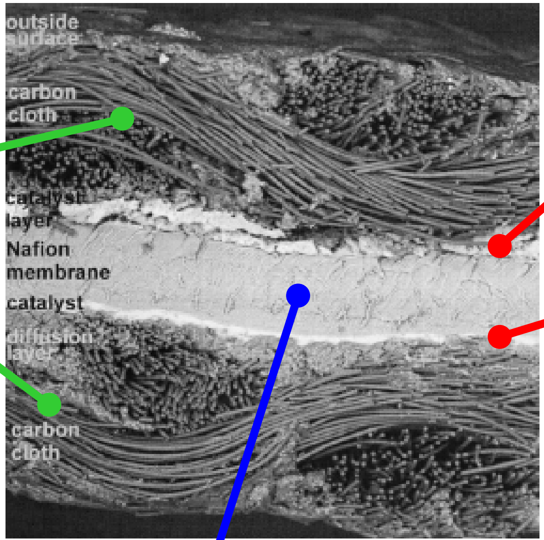
➔ Proper MEA core materials
➔ Proper MEA structure / cell design
➔ Proper balance of plant / system

Overview:

- Principle of operation of a PEMFC
- **PEMFC core materials and their main properties**
- Advantages and drawbacks of PEMFCs

The different materials and architecture of a PEMFC MEA

MEA



Gas Diffusion Layers (GDL)

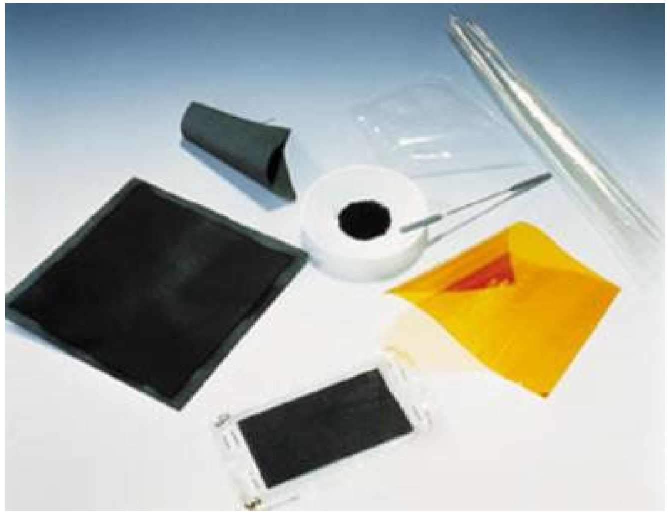
Reagent feeding
Products draining
(water & reagent excess)
Current collecting
Thermal management
Mechanical support

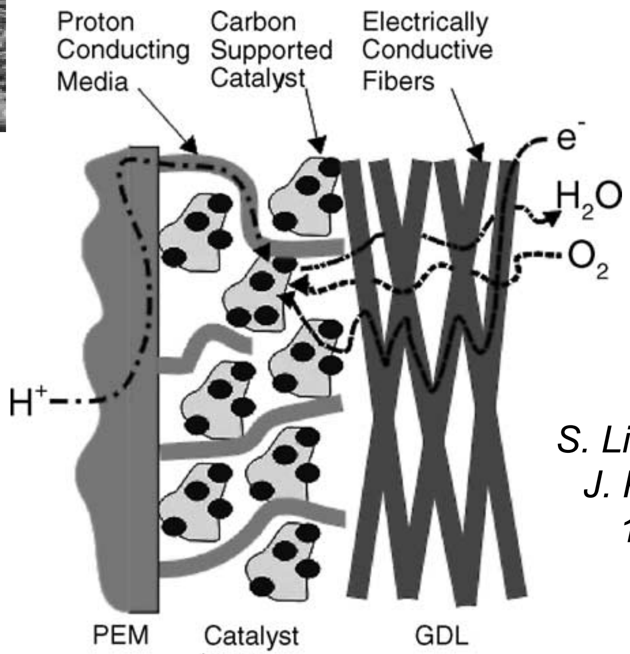
Active Layers (AL)

Electrochemical reactions
+ function of the GDL

Membrane

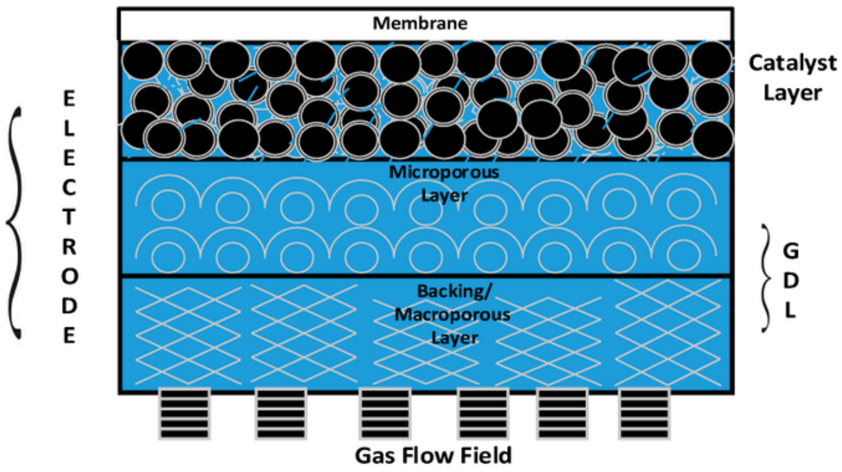
A & C reagent separation
Ionic transport
Electronic insulator
Mechanical support

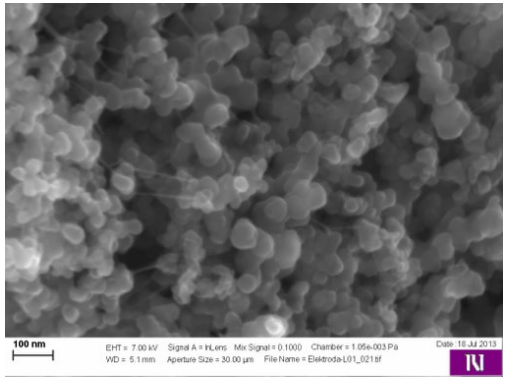




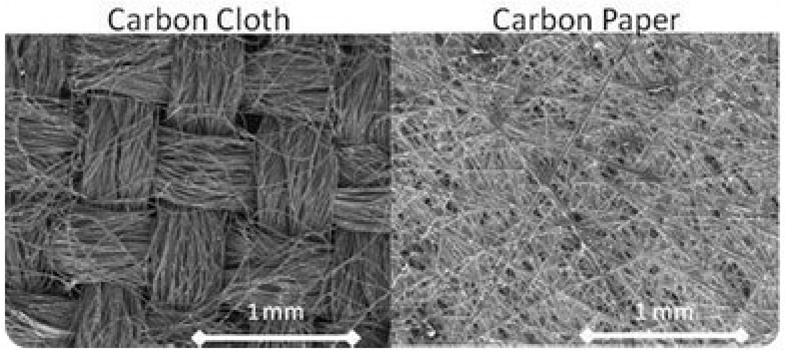
S. Litster, G. McLean, J. Power Sources, 130 (2004) 61

The gas diffusion layer





Microporous layer (carbon black + PTFE) = hydrophobicity + feeding/draining at nm scale



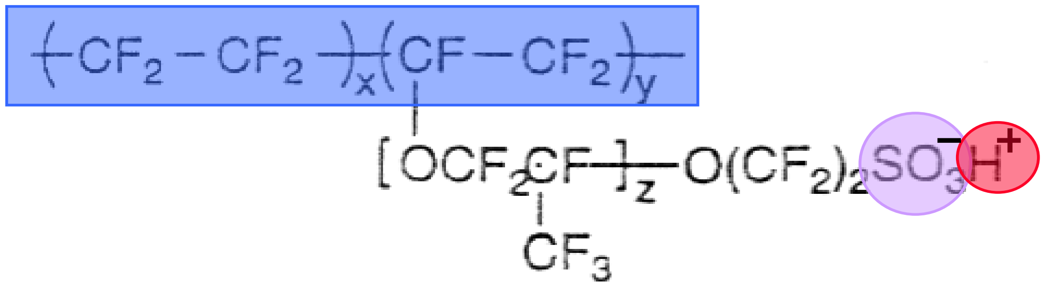
Macroporous layer (carbon fibers) = mechanical substrate

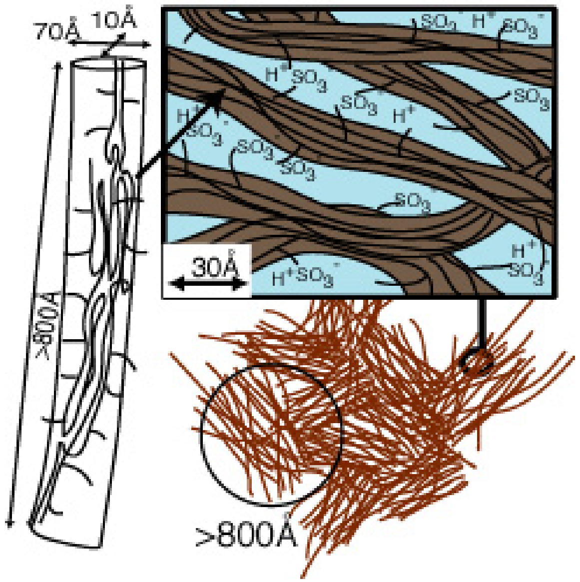
The gas diffusion layer ensures numerous properties

- Reagent feeding: from the bipolar plate – 100 µm “pores” to the active layer scale – 10-50 nm pores
- Products draining: hydrophobicity (water & reagent excess)
- Current collecting: electron percolation – small bulk resistivity small interfacial contact resistance
- Thermal management: high thermal conductivity
- Mechanical support

The ionomer and proton exchange membrane (Nafion®)

Proton-exchange perfluorosulfonated polymer





Nafion® structure at different scales

From G. Gebel et al. and D. Kreuer et al. (2000s)

PEM
- Separator (barrier)
- MEA mechanical support
- Polymer proton conductor
- e- insulator

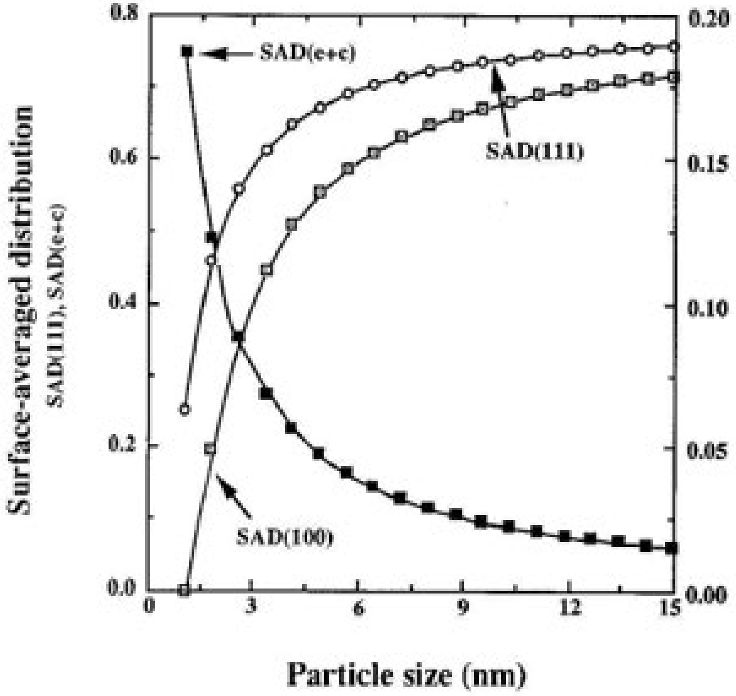
VS.

AL ionomer
- Permeable to reactants
- Binder
- Polymer proton conductor
  - ➔ H^+ percolation for Pt/C

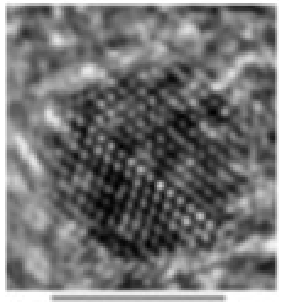
The Pt-based catalyst

Towards **large dispersion** (lower cost, higher surface area) ➔ nanoparticles of Pt(M)

Required **electronic conductivity** ➔ carbon support ➔ Pt(M)/C nanoparticles

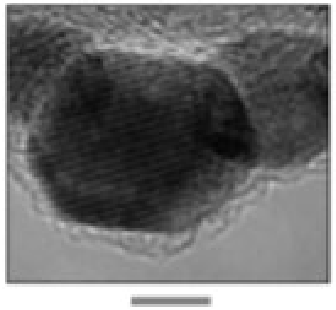


10 % Pt/Vulcan



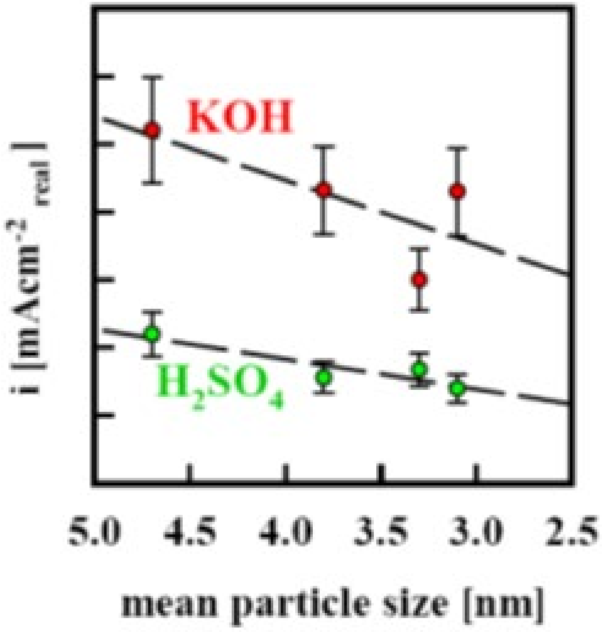
3 nm

40 % Pt/Vulcan



6 nm

- catalysts: 10, 20, 30, 40% Pt/C
- d=3.1 ± 1 nm, 3.3 ± 0.7 nm, 3.8 ± 1.7 nm, 4.7 ± 2.7 nm



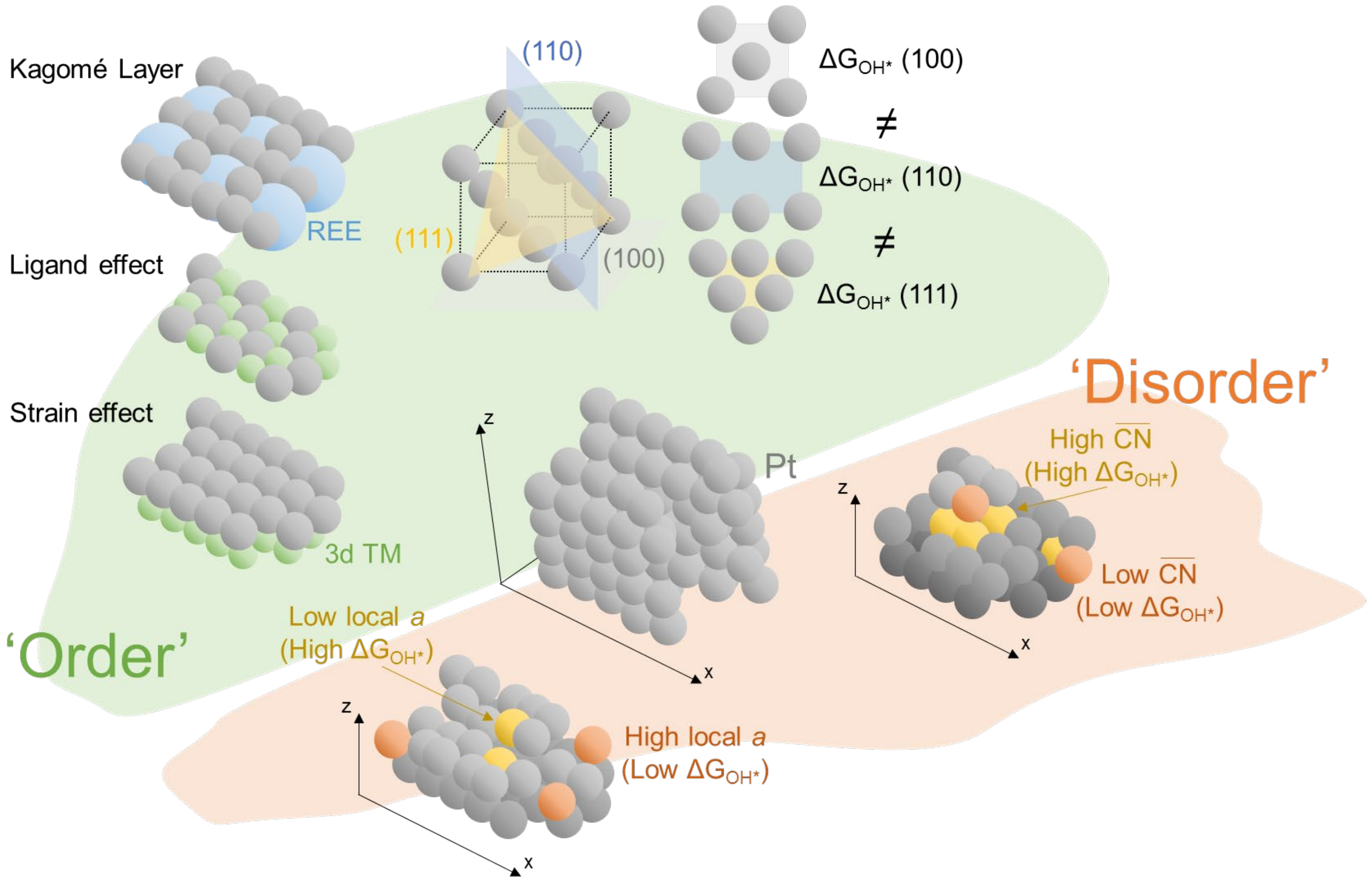
↳ SA increases with SAD(111)

↳ SA increases with SAD(100, e+c)

Smaller Pt(M) NPs are less intrinsically active than larger ones for the ORR

➔ Detrimental role of low-coordination number atoms (e + c)

Strategies towards "superactive" ORR electrocatalysts



Li, Asset, Atanassov, *J. Power Sources* **478** (2020) 228516.

Pt utilization in the catalyst layer

To be active, Pt(M) NPs need to satisfy the triple contact conditions

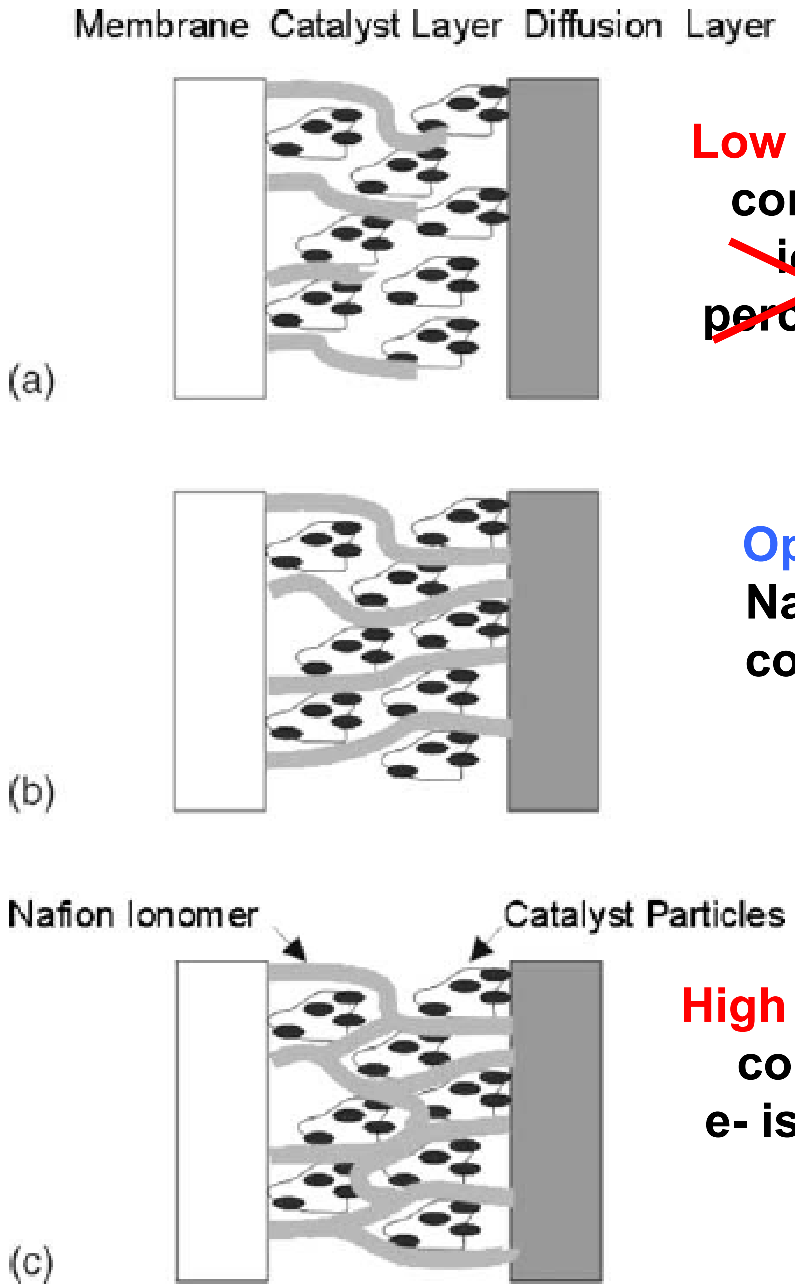
$$u = \frac{SA_{used}}{SA_{theoretical}}$$

SA_{used} → **Practical**

$SA_{theoretical}$ → **Theoretical**

u_{Pt} accounts for H⁺/e- percolation at Pt/C in PEMFC MEAs (static vision)…
➔ active area of electrocatalyst

…but not for mass-transport (dynamic operation)
➔ electrochemical performance



Low Nafion® content : ~~ionic percolation~~

Optimal Nafion® content

High Nafion® content: e- isolation

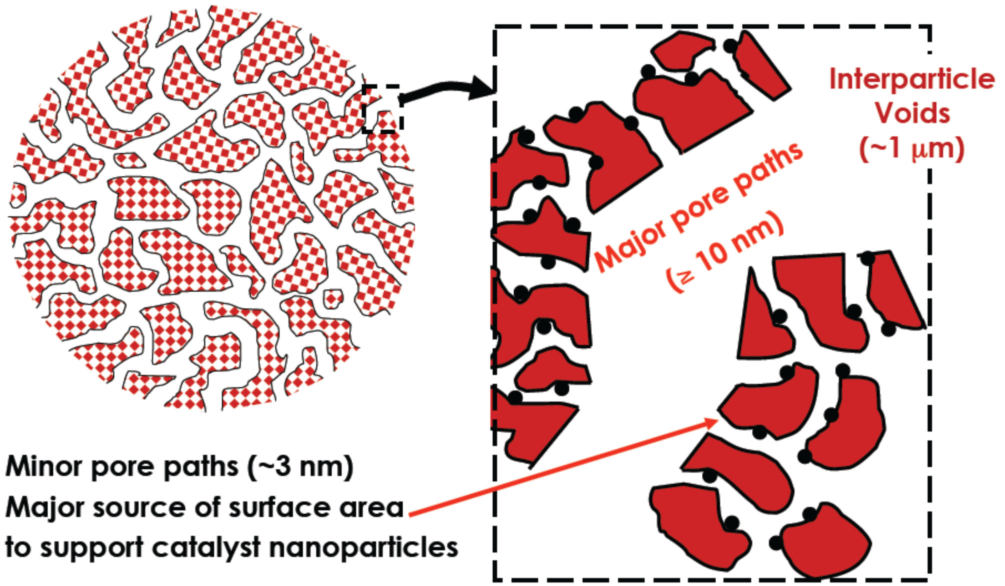
S. Litster, G. McLean, J. Power Sources, **130** (2004) 61

Pt effectiveness in the catalyst layer: diffusion to catalytic site!

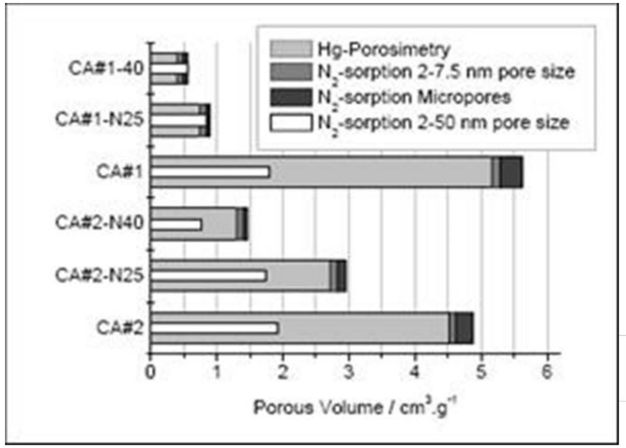
To provide current, utilized Pt(M) NPs need to be accessible to reactants

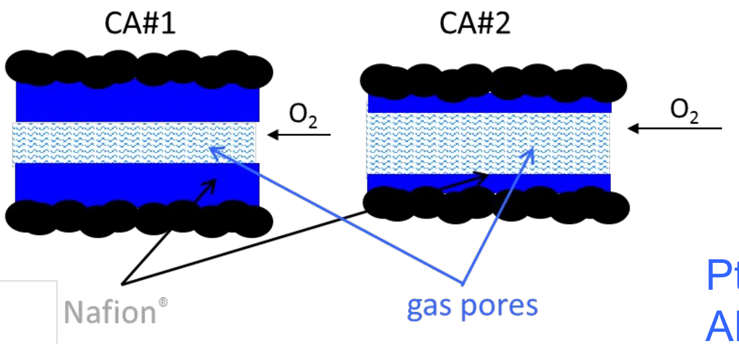
The MEA shall contain…

- **Small pores for active area (Pt dispersion)**
- **Large pores for mass-transport**



Courtesy of Plamen Atanassov – Univ. New Mexico, USA





Pt/carbon aerogel active layers: importance of the AL porosity on PEMFC performances

J. Marie, M. Chatenet et al. (2000s)

Pore diameter CA#1 > CA#2 (pristine CA)
Pore diameter CA#2 > CA#1 (active layer: Nafion® plugs CA#1 porosity)

PEMFC MEA → O_2 diffusion in gas pores → CA#2 favoured

The key parameter is NOT the C-substrate porosity but the **AL porosity**
➔ **Taylored porous materials** necessary
➔ **Taylored ink & electrode processing** mandatory

but also…

Y. Garsany et al. *J. Electrochem. Soc.* **165** (2018) F381
V. Yarlagadda et al. *ACS Energy Lett.* **3** (2018) 618

The MEA structure/composition drives the PEMFC initial performances

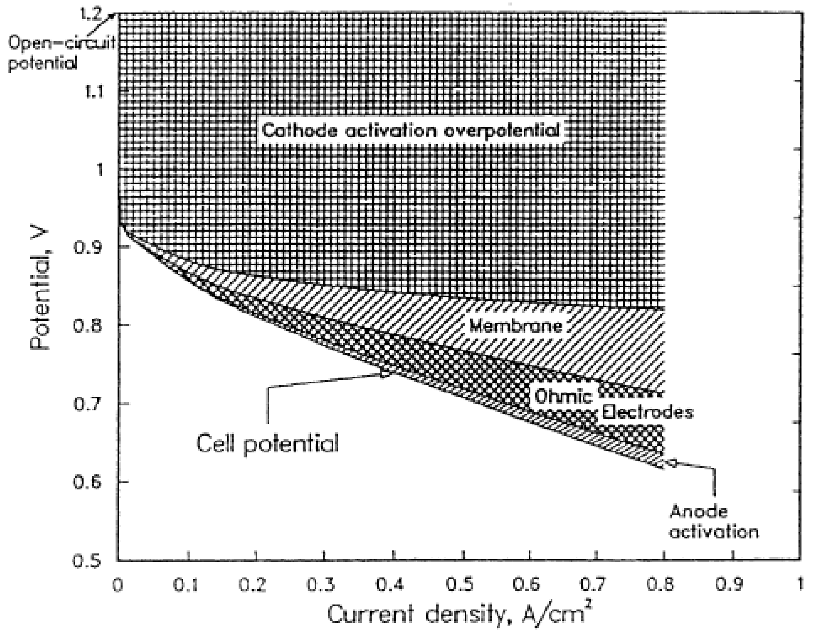
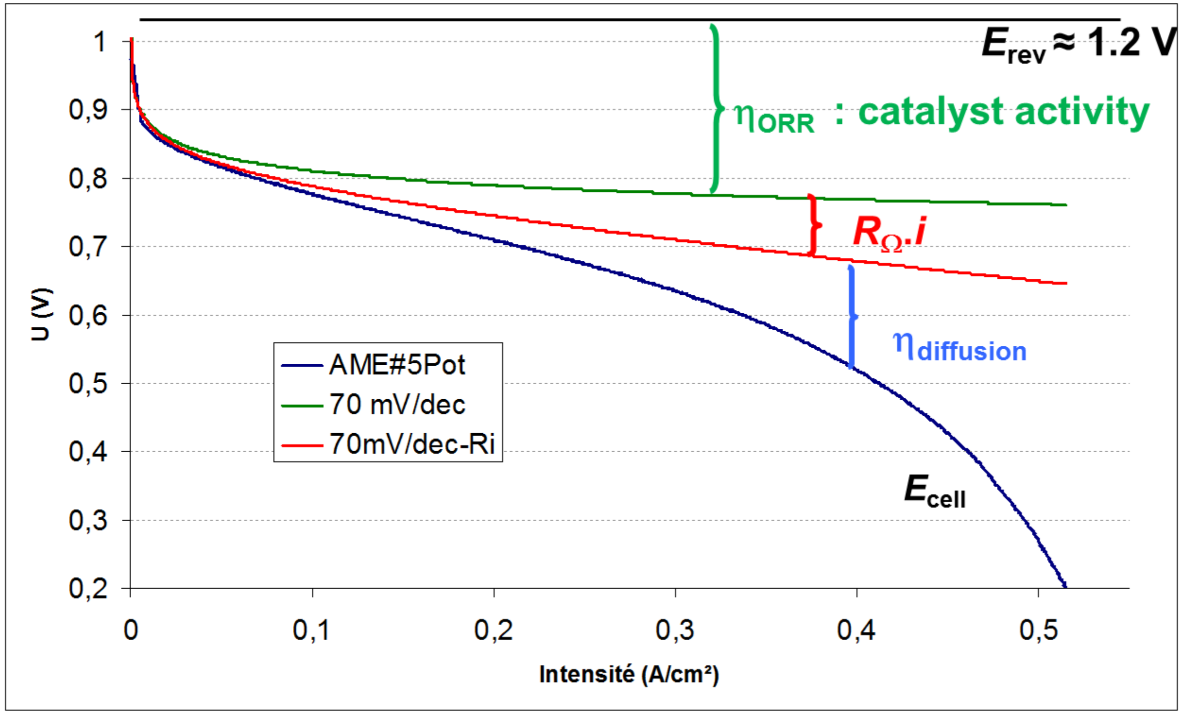


Fig. 9. Cell potential vs. current density characteristic curve of a typical PEM membrane–electrode assembly, with the nature and order of magnitude of the different overvoltages. From [26], with permission.

$$E_{cell} = E_{rev}(p_{H2}, p_{O2}, T) - \eta_{ORR} - i R_{\Omega} - \eta_{diffusion}$$



The MEA structure / composition shall enable optimal (electro)catalytic reactions, whatever the operating conditions

- **Electrocatalysis of ORR (and HOR)**
- **Electrical / proton conductivities**
- **Mass transport / water management**

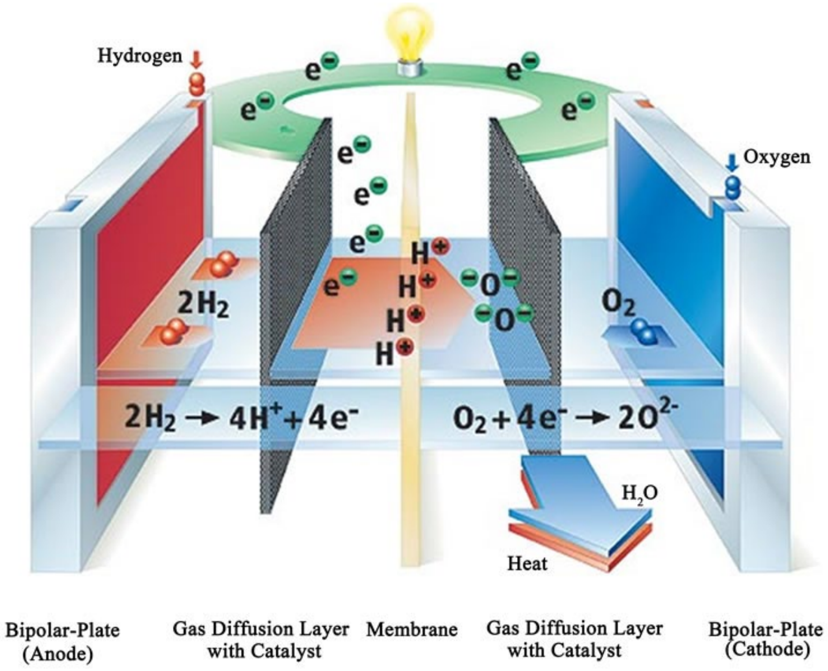
[1] *P. Costamagna, S. Srinivasan, J. Power Sources* ***102*** *(2001) 253*
[2] *H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, App. Cata. B* ***56*** *(2005) 9-35*

The unit cell voltage - thermodynamics

Anode

$H_2 \leftrightarrow 2\,H^+ + 2\,e^-$

(E^0 = 0 V *vs* SHE)



Cathode

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

(E^0 = 1.23 V *vs* SHE)

$$E^{eq-} = E^{0-} + \frac{RT}{2F}\ln\frac{a_{H^+}^2}{a_{H_2}} = 0 + \frac{0.059}{2}\log\frac{a_{H^+}^2}{a_{H_2}}$$

$$E^{eq+} = E^{0+} + \frac{RT}{2F}\ln\frac{a_{O_2}a_{H^+}^2}{a_{H_2O}} = 1{,}23 + \frac{0.059}{2}\log\frac{a_{O_2}a_{H^+}^2}{a_{H_2O}}$$

Nernst law
@ 298 K

Unit cell:

$U^{eq} = \Delta E^{eq} \approx 1.2$ V

- $E°$ = **standard potential**
- E^{eq} = **equilibrium potential**

The unit cell voltage - kinetics

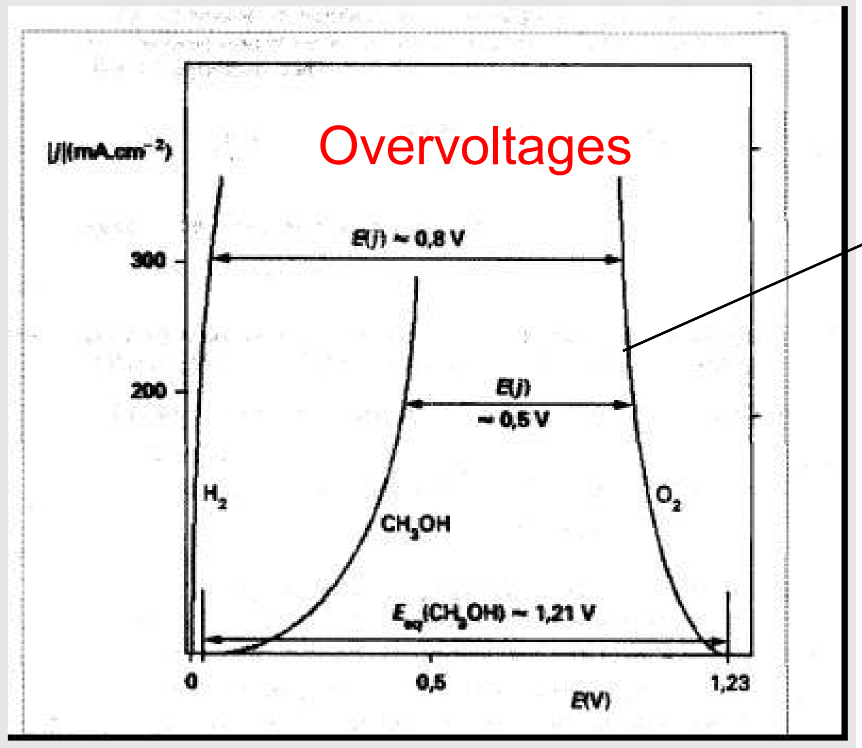
Out of equilibrium ($j \neq 0$) : $\boldsymbol{E(j) = E^{eq} - \eta_{act} - \eta_{ohm} - \eta_{conc,diff}} < E^{eq}$

$E^{eq} = E_{j=0}$ = f(thermodynamic)

$\boldsymbol{\eta}_{act}$ = f(S_{act}, electrocatalysis) ; $\boldsymbol{\eta}_{act} = \boldsymbol{\eta}_a + \boldsymbol{\eta}_c$ (anode & cathode activation)

$\boldsymbol{\eta}_{ohm}$ = f(R_{ions} & R_{e-}) in the membrane, the electrodes, at the contacts…

$\boldsymbol{\eta}_{conc,diff}$ = f([reactants]) = oxygen, hydrogen, protons + influence of liquid water

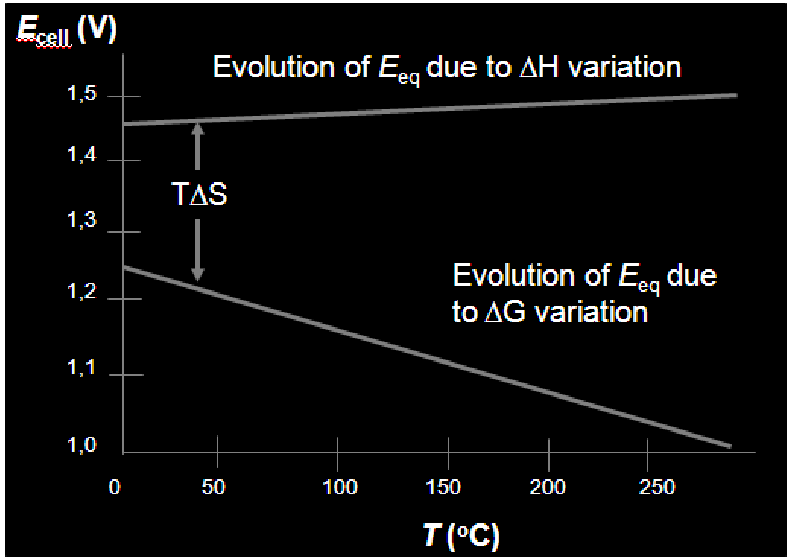


$O_2 + 4\ H^+ + 4\ e^- \leftrightarrow 2\ H_2O$

In pratice, a unit cell operates at a voltage below 1 V

$U^{pr} = \Delta E^{pr} \approx 0.6 - 1$ V

The efficiency of a PEMFC

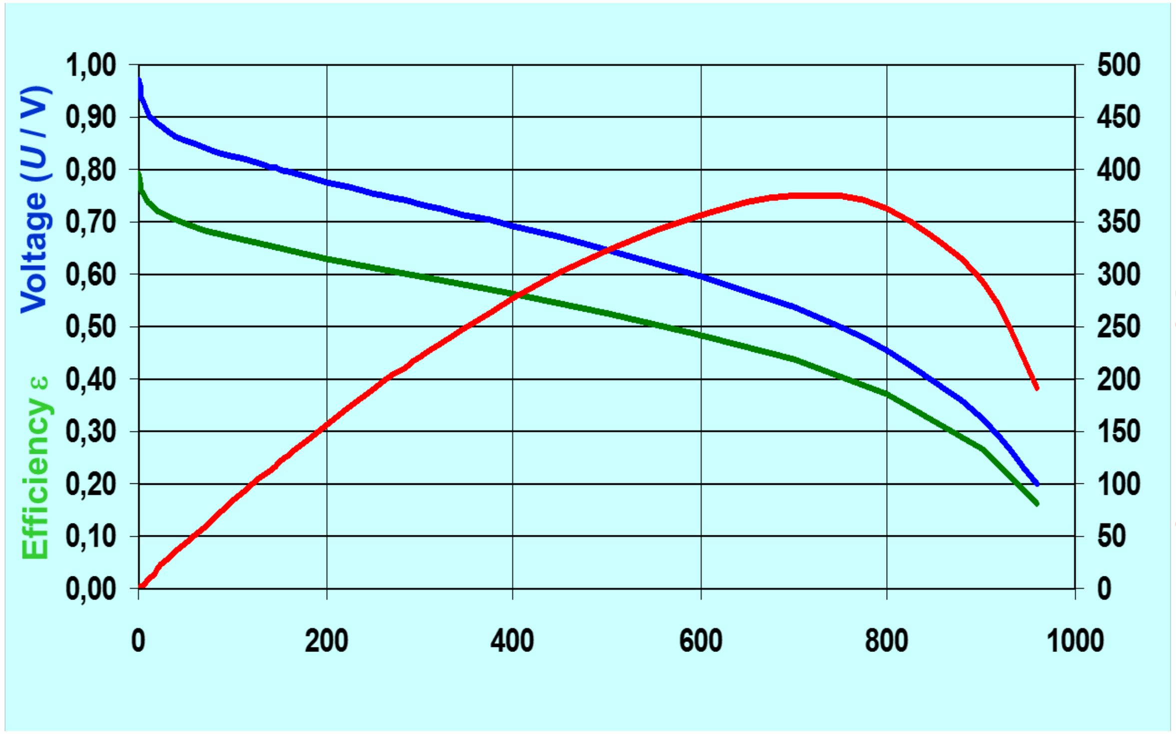


Evolution of E_{eq} with T – H_2 / O_2 fuel cell

- **Thermodynamics**: $\varepsilon_{rev} = \Delta G / \Delta H$ (= 83 % for H_2 @ 25°C)
- **Kinetics:**
  - **Potential** : $\varepsilon_E = E(j) / E^{eq}$ (40 - 60 %)
  - **Faradaic**: $\varepsilon_F = Q(j) / Q_{th}$ (≈ 100 % - all H_2 is used)

Efficiency of PEMFC module:

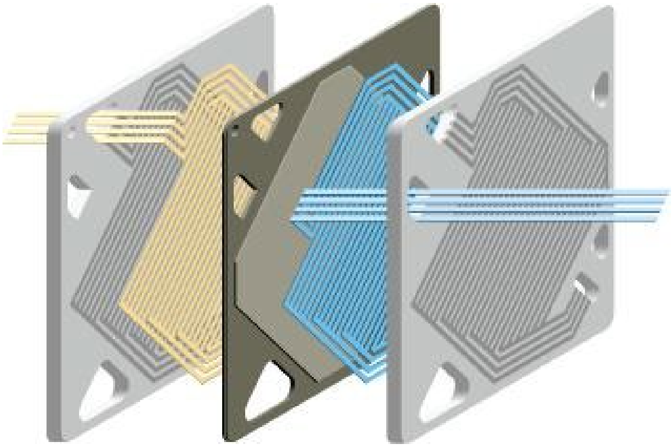
$\varepsilon_{PEMFC} = E(j) \times Q(j) / (-\Delta H) = \varepsilon_{rev}\, \varepsilon_E\, \varepsilon_F$ **≈ 50-55%**



Efficiency of PEMFC system:

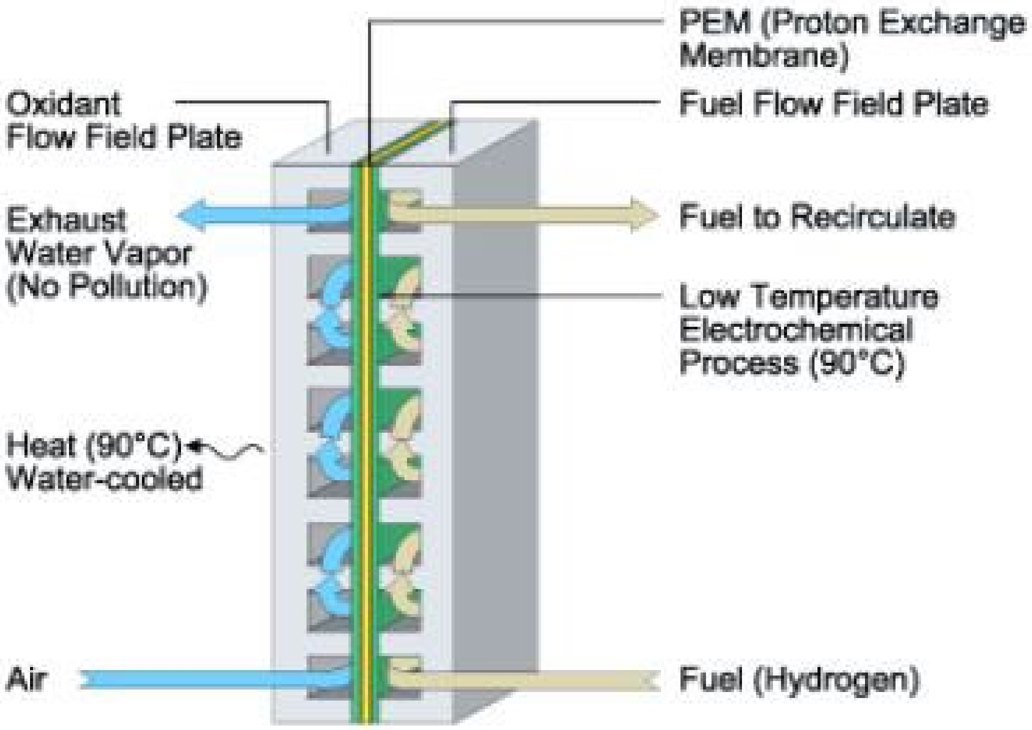
$\varepsilon_{system} = \varepsilon_{PEMFC} \times \varepsilon_{annexes}$ **≈ 45-50%**

Towards PEMFC stacks

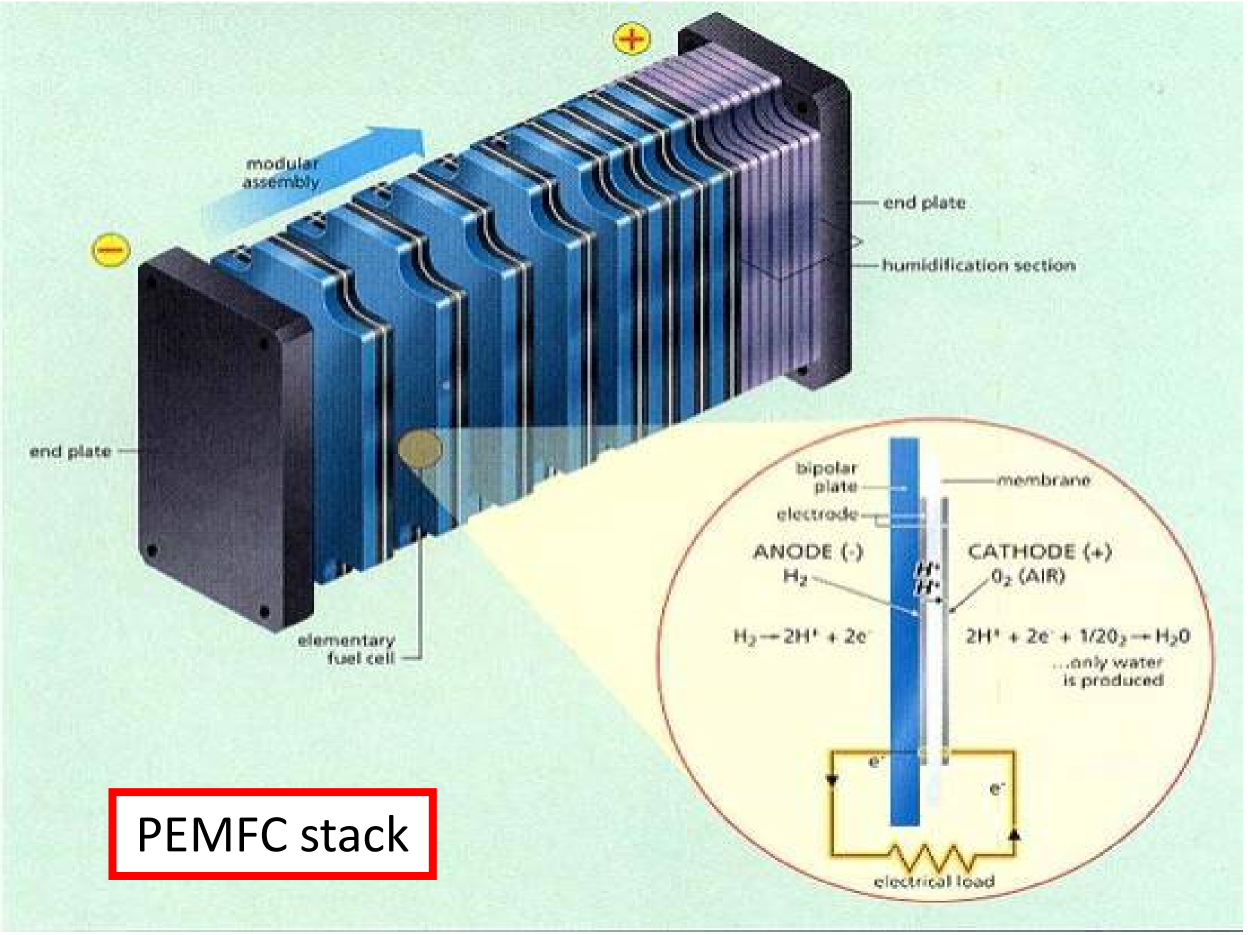


- ↗ voltage ⇒ series assembly (filter press)
- ↗ current ⇒ ↗ electrode surface area
- ↗ power ⇒ large area electrodes + cells in series

⇒ Bipolar plates (BP)



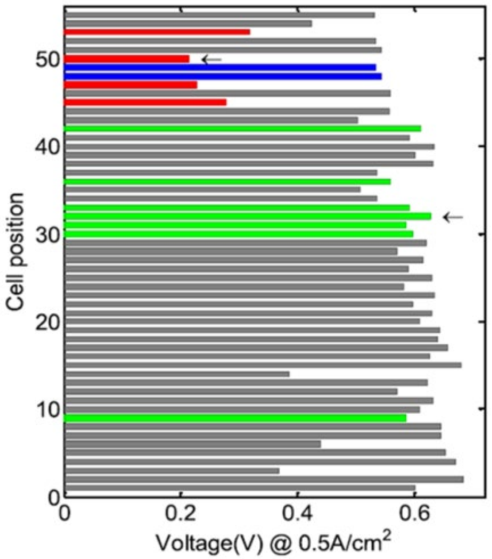
<u>BPs ensure inlet/outlet for each unit cell</u>

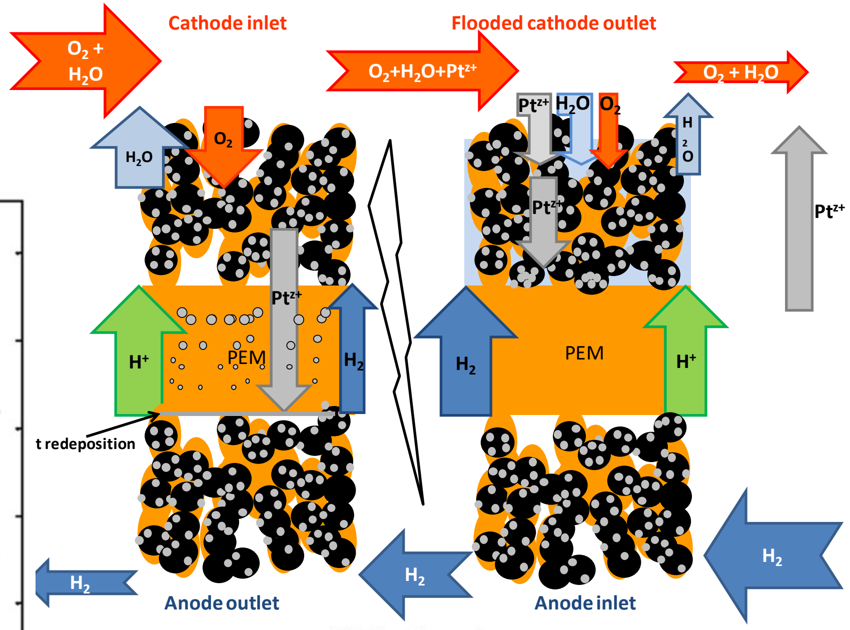


PEMFC stack

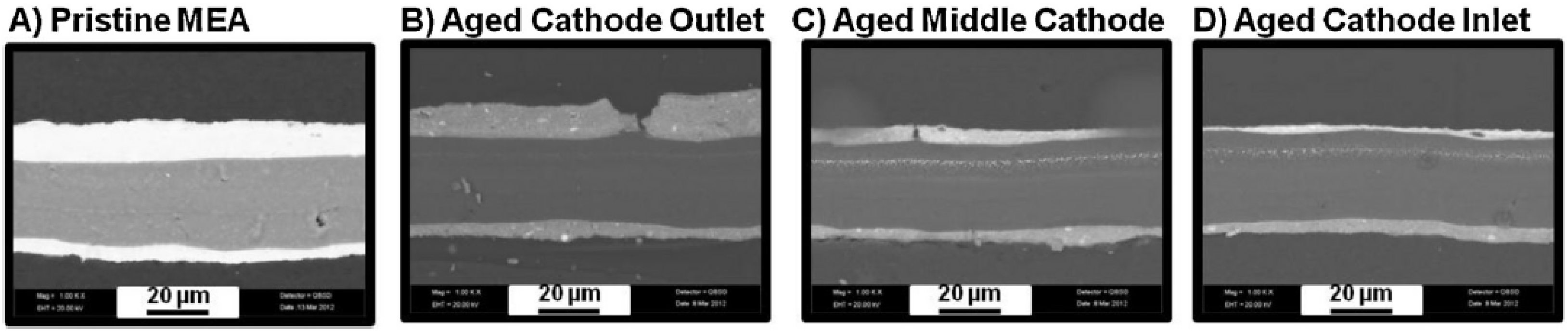
PEMFC should be durable (in theory) but do age…

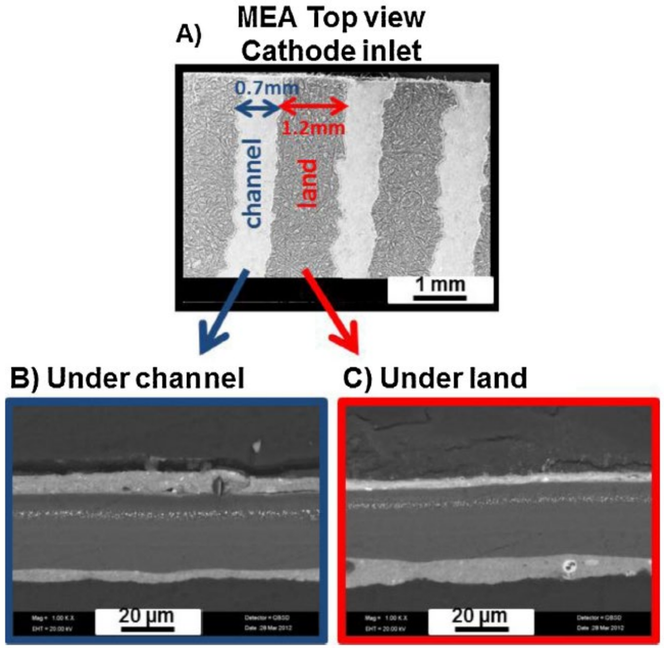
- The (local & global) PEMFC performances are linked to the **materials degradation** (PEM, GDL and AL all degrade)





- **PEMFC aging is localized** at multiple scales
  - At stack level: from one cell to the other
  - At cell level:
    - From the GDL to the PEM
    - Along the gas channels
    - In a region at the BP channel / land level





1. L. Dubau et al., *Fuel Cell*, **12** (2012) 188.
2. J. Durst et al., *Appl. Catal. B: Environmental* **138– 139** (2013) 416.
3. L. Dubau et al., *Int. J. Hydrogen Energ.*, **39** (2014) 21902.

Overview:

- Principle of operation of a PEMFC
- PEMFC core materials and their main properties
- **Advantages and drawbacks of PEMFCs**

Conclusion: advantages of PEMFC

- **Direct conversion of chemical energy into electricity**
  - Small emission of pollutant (zero if H_2 from renewable origin)
  - Larger efficiency

versus internal combustion engines

- **Fuel / Oxidant stored out of the conversion system**
  - Optimization of the cell / stack to the desired power
  - Autonomy tailored on demand (size of H_2 tank or frequency of refuelling)
  - Fast refuelling (stationary operation possible)
  - (Relative) safety of operation (even in case of thermal runaway)

- **Core materials (in principle) not consumed / altered in operation**

- **All solid cell**
  - No leak of corrosive liquid
  - Physical integrity / stability
  - Operation in all "positions"

versus batteries

Conclusion: drawbacks of PEMFC

- **Complex management of fluxes**
  - **Reactants**
  - **Products (liquid water at cathode / anode, accumulated N_2 at anode, etc.)**

- **Cost of core materials, assembly and processes of manufacturing**
  - **Pt-based catalysts**
  - **F-based ionomer / membrane**
  - **Gas-diffusion layers**
  - **(Sub)gaskets**
  - **Bipolar plates**

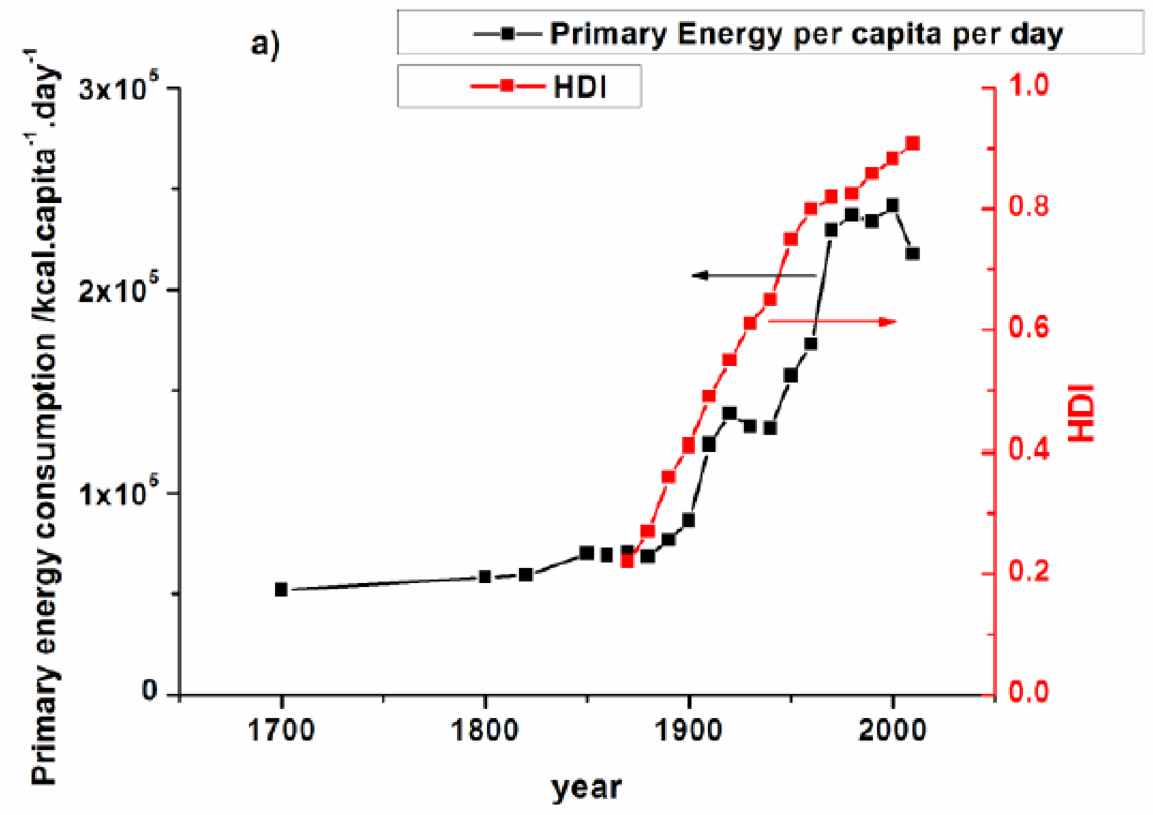
- **Complexity of the system design / production / implementation**

- **Practical durability in operation**

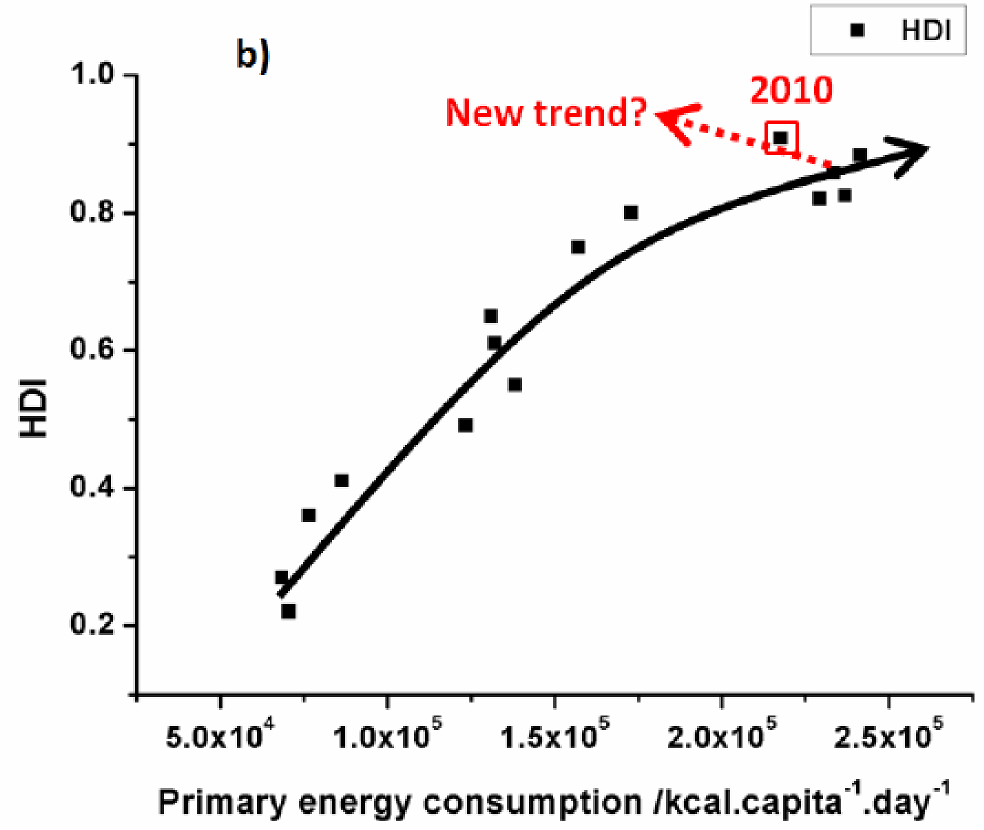
Extra:

- Principle of operation of a PEMFC
- PEMFC core materials and their main properties
- Advantages and drawbacks of PEMFCs
- **The global context and why PEMFC (and PEMWE) are useful**

The global context: link between growth and energy consumption



Evolution of the consumption of primary energy per capita & day [1, 2] and of the human development index (HDI)[3] in USA since 1700



HDI versus primary energy consumption

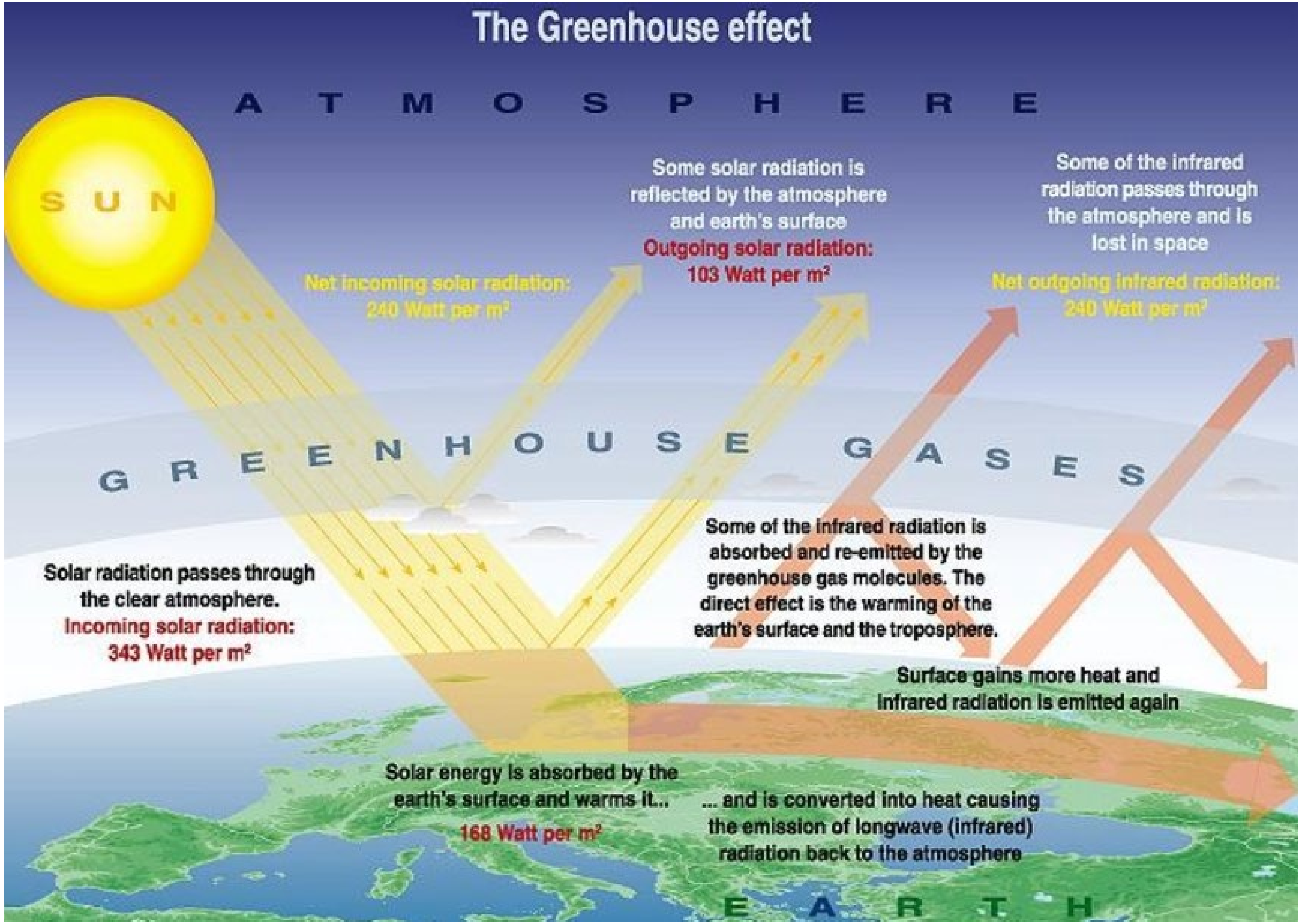
1850 - 1970 : **industrial development** and **growth of energy consumption**

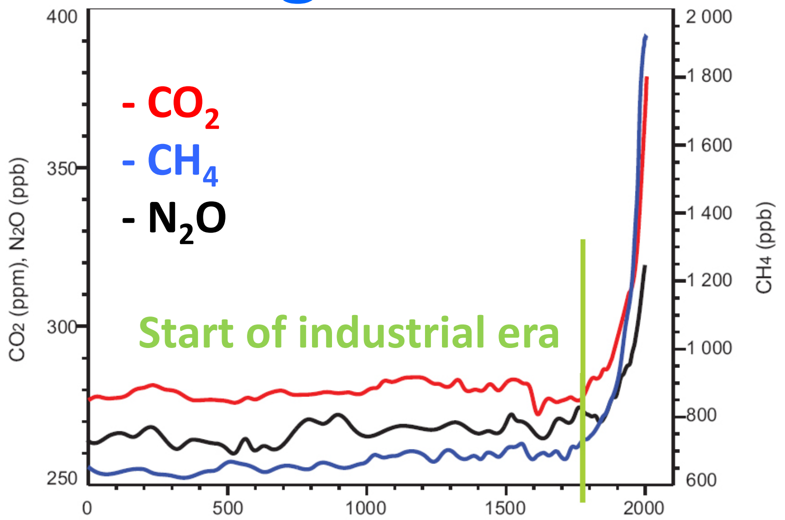
➔ **economic & social development**

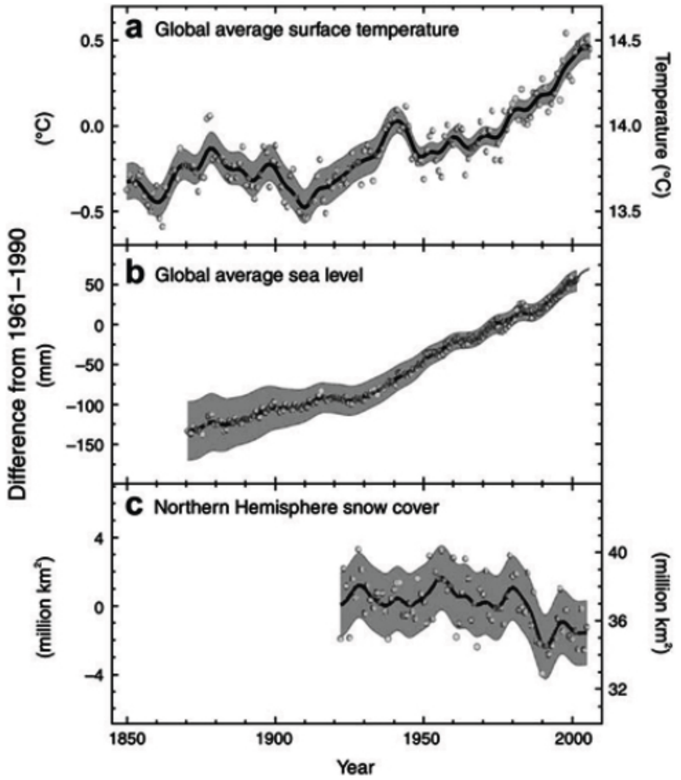
➔ **waste of natural resources, pollution, climate change, etc.**

1. White, L. A., *The Evolution of Culture: The Development of Civilization to the Fall of Rome*; McGraw-Hill, **1959**.
2. Kremer, M., *Quaterly Journal of Economics* **1993**, *108*, 681-716.
3. Goklany, I. M., *The Improving State of the World: Why We're Living Longer, Healthier, More Comfortable Lives on a Cleaner Planet* Cato Institute, **2007**.

The global context: origin of the climate change



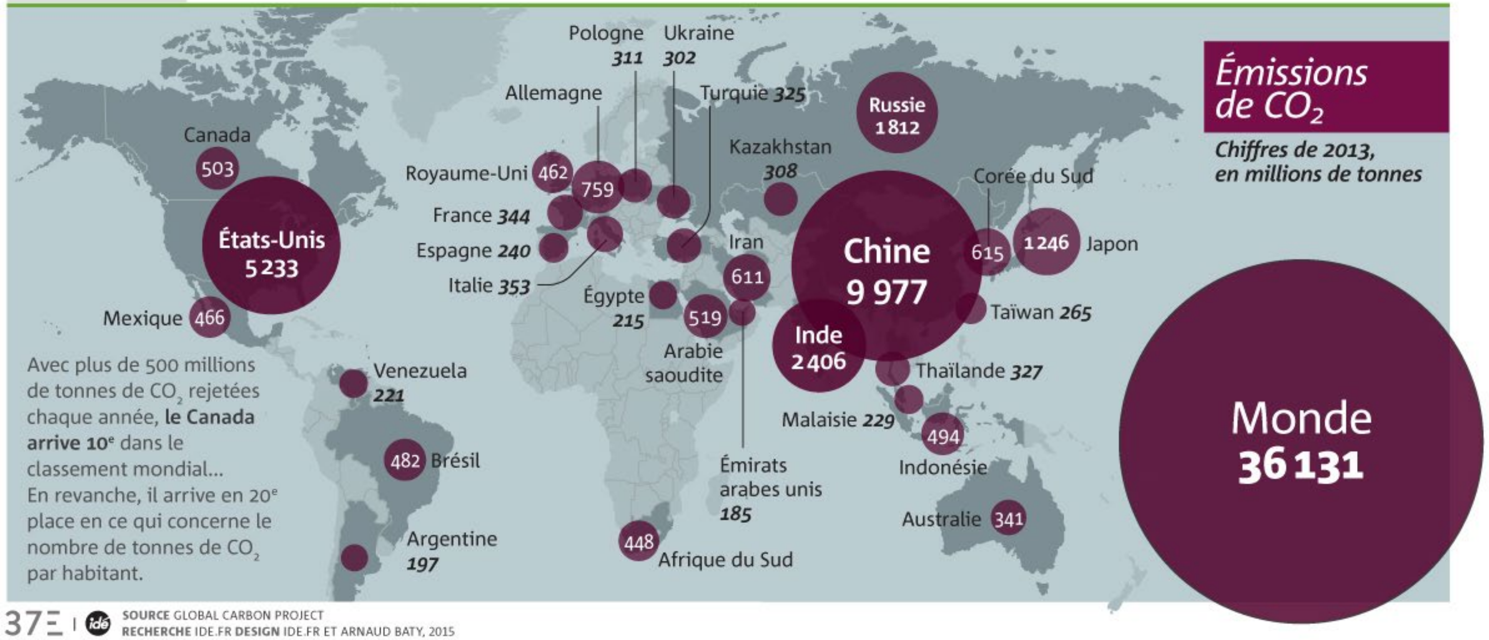


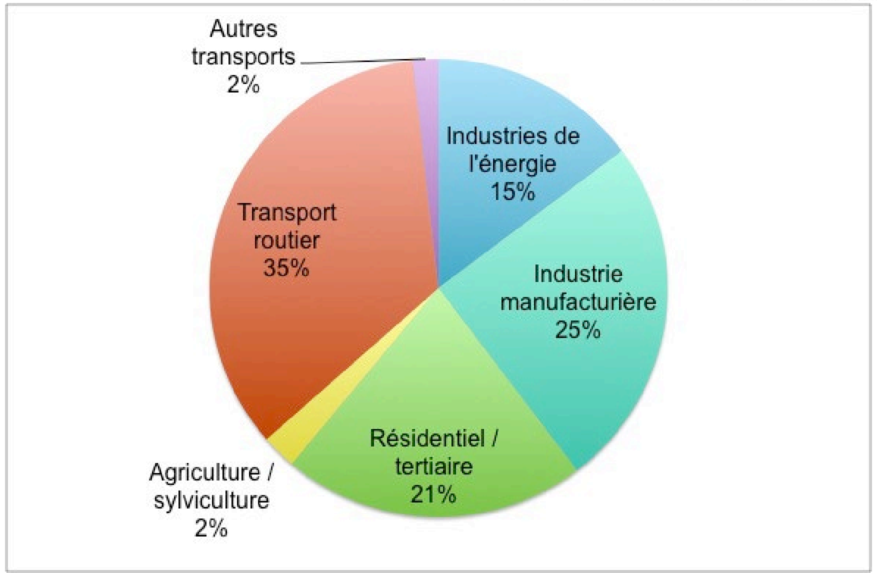


Human activities increase greenhouse gas emission ➔ **climate change!!**

The global context: origin of the climate change

The 30 largest CO_2-emiter countries





Electricity production + transport > 50% CO_2 emissions

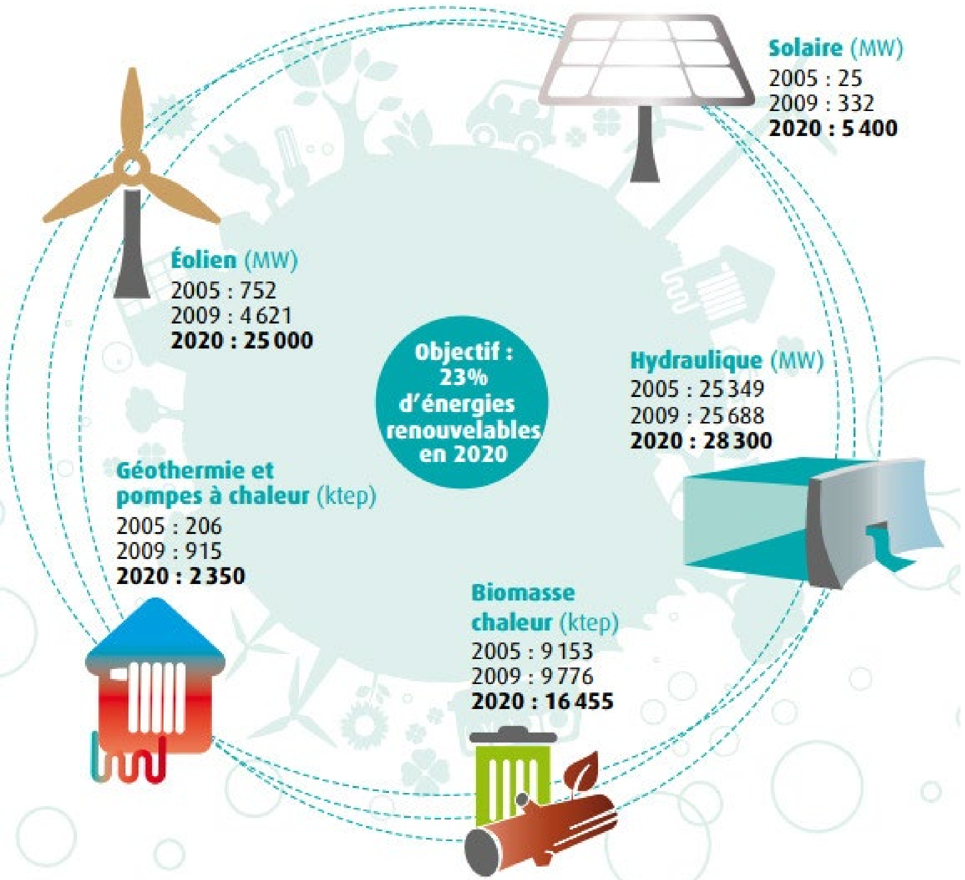
↓↓↓

Our energy policy must be changed !!!

↓↓↓

Renewable energies

Renewable energies and the need for their storage



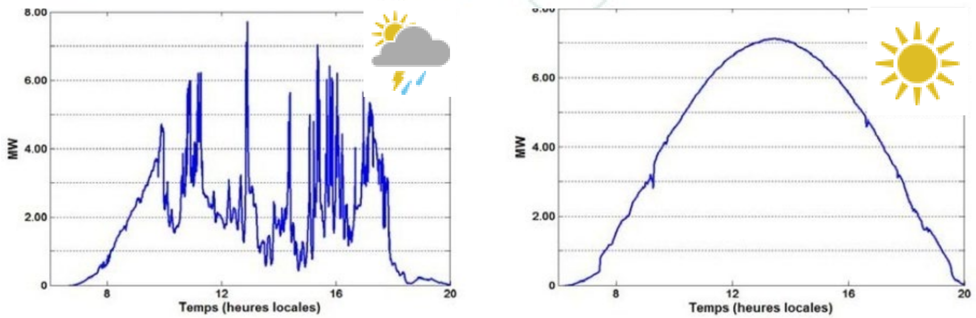
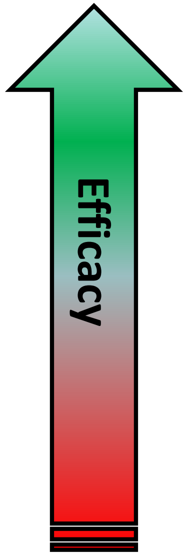


Illustration of the intermittency of photovoltaic production (Myrthe site, Corsica, France)

Renewable electricity is intermittent…

… storing it (large amounts & long term) is mandatory !

- **Pumped hydroelectricity (dams + reversible turbines) – saturated…**
- **Batteries – too costly and not durable**
- **Water electrolyzers + Fuel cells**



Water electrolyzers & fuel cells coupled to renewable energies

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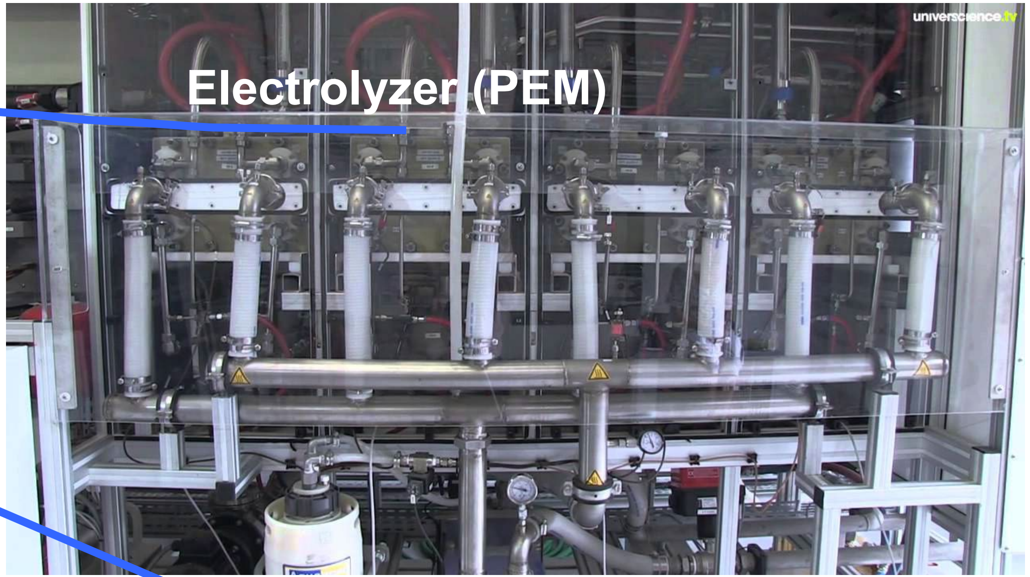
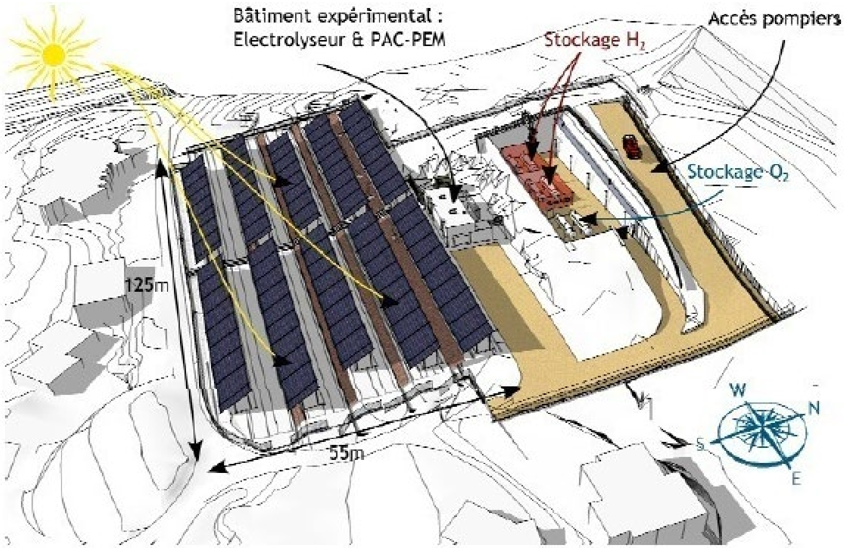
PLATEFORME MYRTE

Mission hYdrogène Renouvelable pour l'inTégration au réseau Electrique



Water electrolyzers & fuel cells coupled to renewable energies



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PLATEFORME MYRTE

Mission h**Y**drogène **R**enouvelable pour l'in**T**égration au réseau **E**lectrique

O_2 + 2 H_2

Key figures of MYRTHE

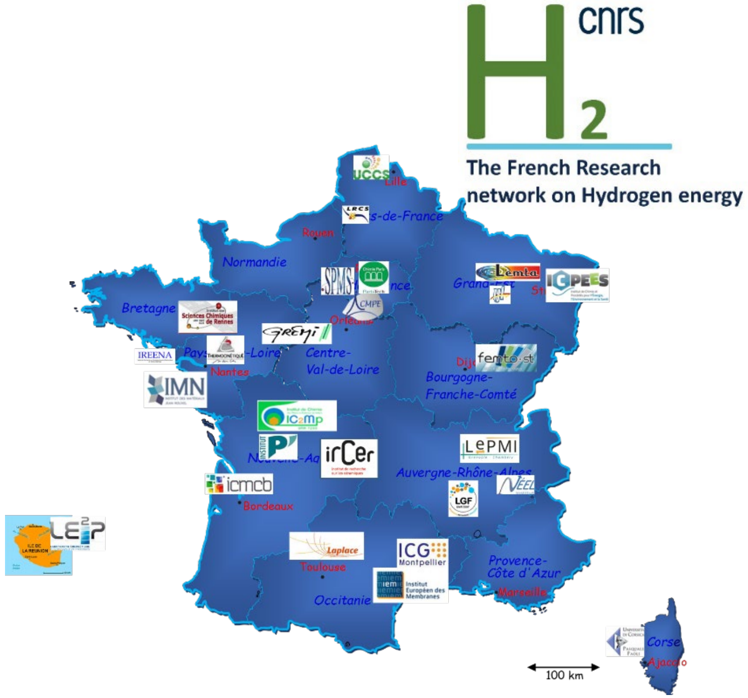
- **9000 m² solar panels**
  - 560 kW production (peak)
  - Instantaneous consumption + **excess**???
- **Electrolyzer** + **storage** (40 bar 2 H_2 + O_2)
  - **Storage** 2 H_2 + O_2 ⇔ 22 h autonomy of PEMFC
- **Fuel cell** (PEMFC) 200 kW
  - **Enables** electrical production peaks (when necessary)

P-t-G + PEMFC enables to adapt the production of electricity to the demand without oversizing the solar panels…

The small world of PEMFCs: mobility and stationary power

Worldwide, before 2019
Courtesy of Plamen Atanassov – UCI, USA

In France, since 2019



Air Liquide
cea
ALSTOM · mobility by nature ·
PSA GROUPE
Helion HYDROGEN POWER AREVA
GROUPE RENAULT
SYMBIO A FAURECIA MICHELIN HYDROGEN COMPANY
MICHELIN A BETTER WAY FORWARD
faurecia inspiring mobility
SAFRAN