1MG11: FUEL CELL VEHICLES Part 1: Fuel Cell Technology

> Pierre Duysinx LTAS-Automotive Engineering University of Liege Academic year 2021-2022

# References

- C.C. Chan & K.T. Chau. Modern Electric Vehicle Technology. Oxford Sciences publications. 2001.
- M. Ehsani, Y. Gao, S. Gay & A. Emadi. Modern Electric, Hybrid Electric, and Fuel Cell Vehicles. Fundamentals, Theory, and Design. 2<sup>nd</sup> edition. CRC Press, 2010
- L. Guzzella & A. Sciaretta. Vehicle Propulsion Systems. Introduction to Modeling and Optimization. 3<sup>rd</sup> edition. Springer Verlag 2013.
- J. Larminie & A. Dicks. Fuel Cell Systems Explained. J. Wilez & sons. 2001.
- J. Pukrushpan, A. Stephanopoulou & H. Peng. Control of Fuel Cell Systems. Springer. 2004.
- Les Piles à Combustibles <u>http://www.annso.freesurf.fr/index.html#plan</u>
- Fuel cell org: <u>www.fuelcell.org</u>

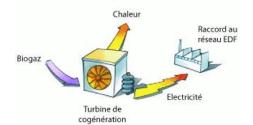
# Introduction

# Energy: A sustainable approach

- Reduction of the energy consumption
  - Reduction of the energy needs: modification of the way of life and energy consumption usage



- Combination of several energy usages
  - Integrating the processes
  - E.g. combined heat and electricity production
- Reduction of the energy losses
  - Insulation of buildings
  - Reducing the friction losses



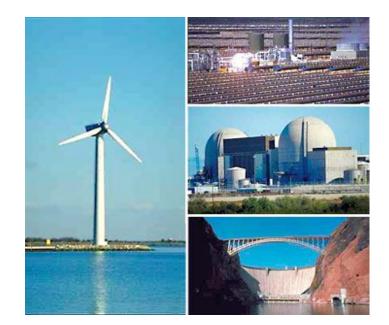


# Energy: A sustainable approach

- Exploitation of alternative energy sources
- Alternative energy sources
  - Biomass



- Waste (energy valorization of wastes : burning wastes, heat valorization of exhaust by burning gases)
- Solar energy
  - Photovoltaic conversion
  - Thermal conversion
  - Wind energy
  - Hydro-electric production
- Nuclear:
  - A new start?



#### Improving the energy conversion efficiency

- Steam engine (1850): 3%
- Gas turbine (1945): 10%
- Internal combustion engine (1950): 20%
- Electric power plant (1960): 41%
- Turbine gas steam (1990): 51%
- Fuel cell (2000): 50%
- Solid Oxide FC + gas turbine (2005): >75%
- Fuel cell + cogeneration (2019) > 90%





# Improving the energy conversion efficiency

- Question:
  - How to convert the chemical energy of the fuel into electricity?
- Classical (thermodynamic) approach :
  - Combustion
  - Thermal engine
  - Generator
- Efficiency limited by Carnot
  - Carnot principle

$$W = \eta \, \Delta H$$
$$\eta_{max} = 1 - T_c / T_h$$

### Improving the energy conversion efficiency

- Question:
  - How to convert the chemical energy of the fuel into electricity?
- Electrochemical route:
  - Direct transformation of the chemical energy into electric work
  - Efficiency = Quantity of energy theoretically recoverable / Quantity of Energy at play during the Transformation

$$\eta = \frac{\Delta G}{\Delta H}$$

Fuel Cell H2-O2:

$$\Delta G = -229 \ kJ/kmol$$
  

$$\Delta H = -242 \ kJ/kmol$$
  

$$\eta = \frac{\Delta G}{\Delta H} = 95 \ \%$$

**Direct conversion** 

- Electrochemical systems
  - Volta batteries:
    - Closed system, irreversibility
    - Consumption of the reactant chemicals
  - Rechargeable batteries
    - Closed system but reversible
    - Regeneration of reactants
  - Fuel Cells
    - Open system
    - Reactants are continuously supplied, while reaction products are continuously eliminated



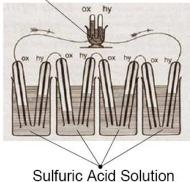




# Fuel Cell - History

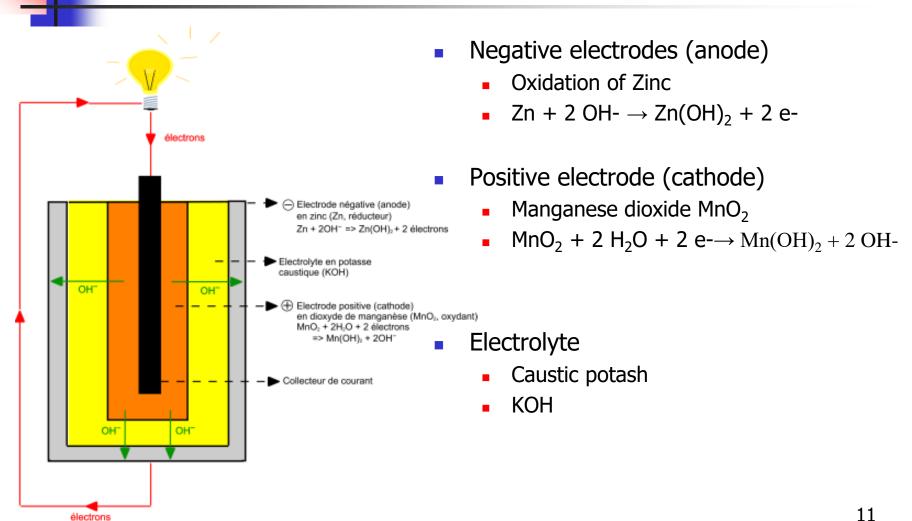


W. Groove Water



- In 1839 Christian Schönbein, a German scientist discovers the fuel cell effects
- From 1839 to 1842, The Welsh scientist William Groove makes the first lab implementation of a fuel cell
- From 1932, F. Bacon restarts study of fuel cells and shows prototypes of 1 kW in 1953 and 5 kW in 1959.
- Thomas Grubb and Leonard Niedrach from GE brings new improvements related to the sulfonated membranes and the platinum deposition on electrodes → Grubb-Niedrach fuel cell will be the basis for space exploration fuel cells developed by NASA and Mac Donell Aircraft for Gemini program.
- The first hydrogen fuel cell application was made by Roger Billing in 1991.

# Working principle of alkaline batteries



# Working principle of alkaline batteries

- Direct conversion of chemical energy into electrical energy
- Closed system:
  - At the beginning: given amount of reactants (oxidants and reductant)
  - At the end: the quantity of reactants is used, and the reaction product remain in the battery
  - Reaction stops when the materials are used
- Irreversible process
  - No recharge is possible

# What is a Fuel Cell?

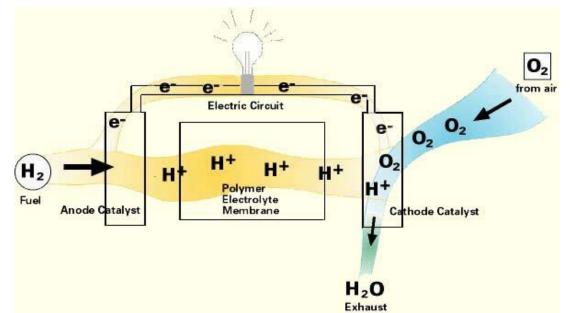
- Direct conversion of the chemical fuel into electricity using an electrochemistry process
  - Electrochemical reaction (oxidoreductase) without combustion (flame)
- Open system
  - Reactants are continuously fed, converted and then eliminated
  - Reaction products are removed continuously
- Electrolyte
  - Protons / ions are carried out from one electrode to the other one through the electrolyte (liquid or solid)

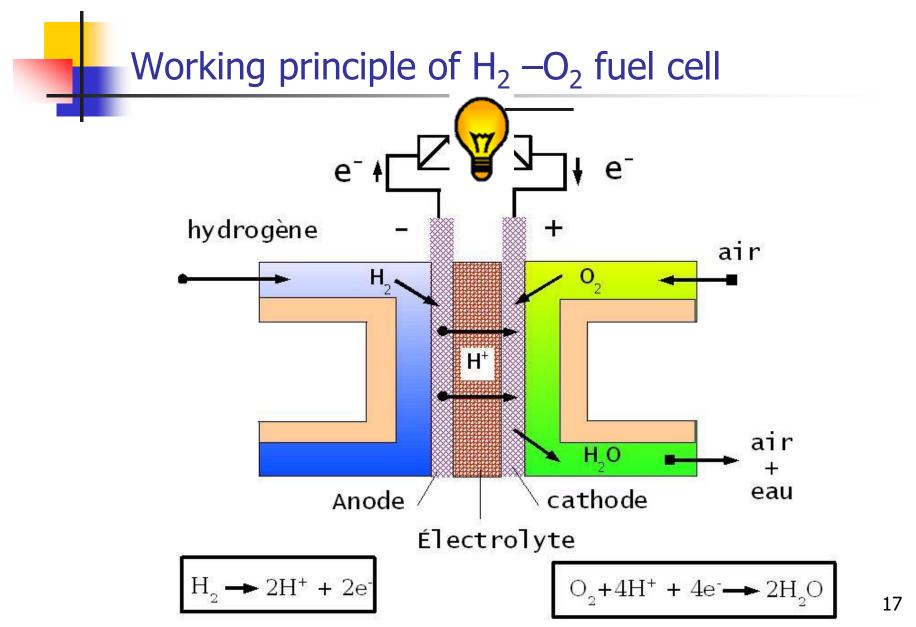
# What is a Fuel Cell?

- External circuit
  - Close to each electrode, highly conductive plates collect and drain the current to external circuit.
  - Electrons that are exchanged during the reaction are conducted through the external electrical circuit, creating a current in the external circuit.
  - Electrical work is developed by the external current in the circuit

# Working principle of fuel cells

- The  $H_2$ - $O_2$  fuel cell
  - The fuel: generally (di)hydrogen H<sub>2</sub>
  - Oxidizer: oxygen (often from air) O<sub>2</sub>
  - Hydrogen + Oxygen  $\rightarrow$  water (steam) + electricity + heat
  - Electricity: direct current





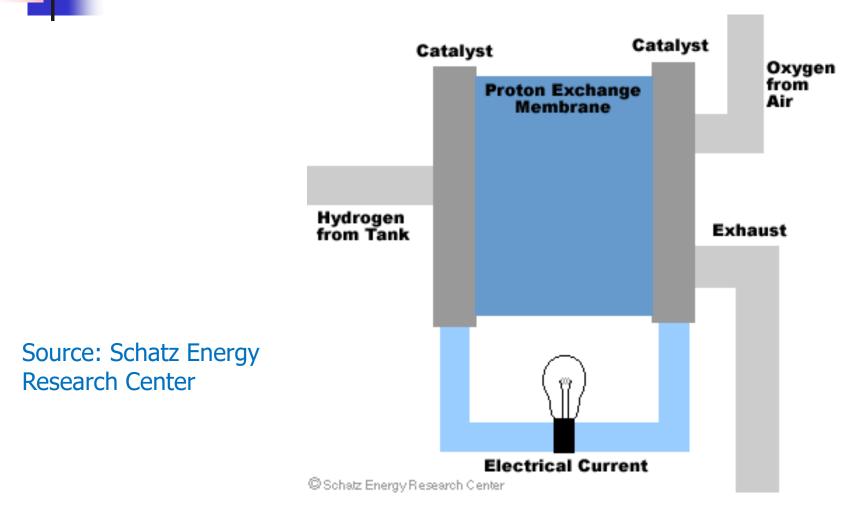
- <u>At anode</u>: oxidation of hydrogen (catalyzed reaction)
  - $H_2 \rightarrow 2 H^+ + 2 e^-$
  - $H_2 + 2 OH^- \rightarrow 2 H_2O + 2 e^-$
- Basic electrolyte

Acid electrolyte

- <u>At cathode</u>, reductase of oxygen (catalyzed reaction)
  - $1/2 O_2 + 2 H^+ + 2e^- \rightarrow H_2O$  Acid electrolyte
  - $1/2 O_2 + H_2O + 2e \rightarrow 2 OH^-$
- Basic electrolyte

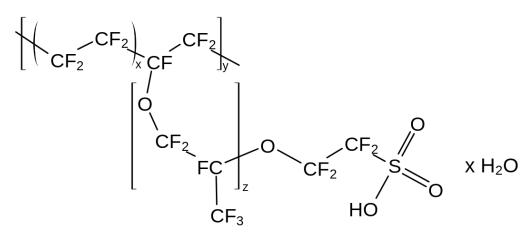
- Balance
  - $H_2 + 1/2 O_2 \longrightarrow H_2O + heat$

#### Work scheme of a single cell

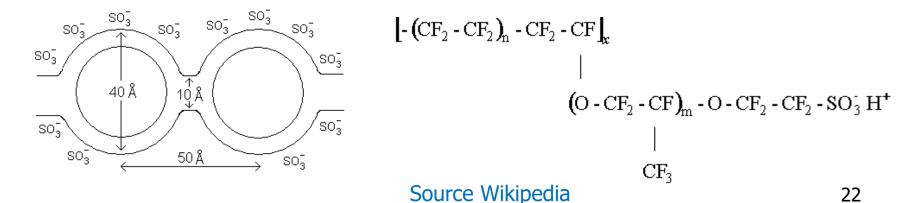


- The fundamental working principle is the inverse reaction of water electrolysis
- This chemical reaction is exothermic at 25 C.
- Free enthalpy of the reaction is -237 or -229 kJ/mol depending on the fact that the produced water is under liquid or gaseous form.
- This corresponds to theoretical voltages of 1,23 and 1,18 V. The voltage depends also of the temperature.
- The reaction requires the presence of catalyst (Pt or Pt/Ru) to activate (accelerate) the reaction speed.

- Every electrochemical systems require an electrolyte to transfer ions from one electrode to the other.
- For Proton Exchange Membrane (PEM) fuel cells
  - Solid electrolyte
  - Ions H+
  - Polymer membrane (Nafion)

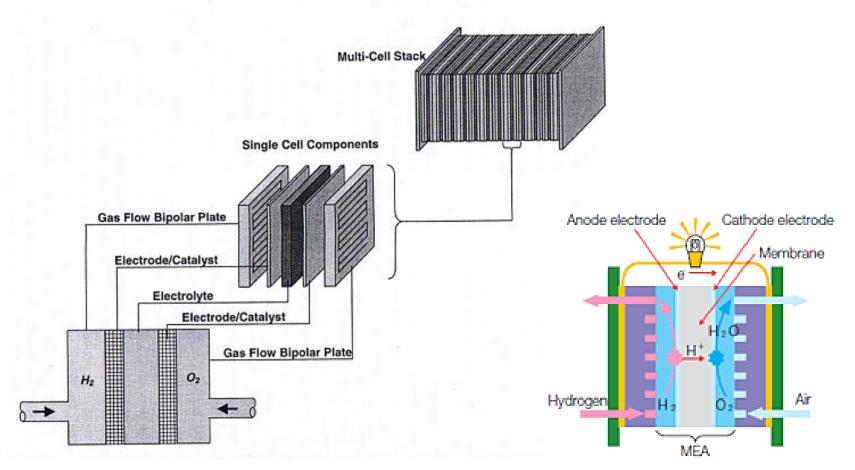


- Nafion is a sulfonated tetrafluoroethylene based fluoropolymercopolymer discovered in the late 1960s by Walther Grot of DuPont.
- First of a class of synthetic polymers with ionic properties which are called ionomers.
- Nafion's unique ionic properties are the result of incorporated perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon)



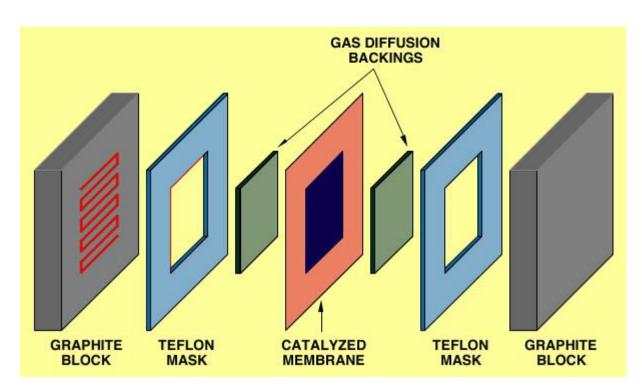
- Advantages:
  - Operating generally at low or moderate temperatures
  - Silent operation
  - High theoretical efficiency (η<sub>th</sub>~92%)
- Drawbacks:
  - Cost of electrodes (Pt)
  - Purity of the fuel
  - Limited power density

#### From MEA to single cell and fuel cell stack

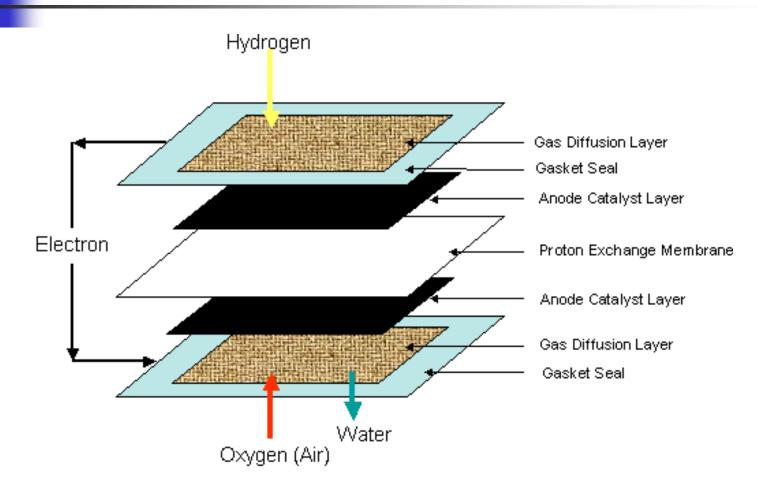




#### SINGLE CELL HARDWARE



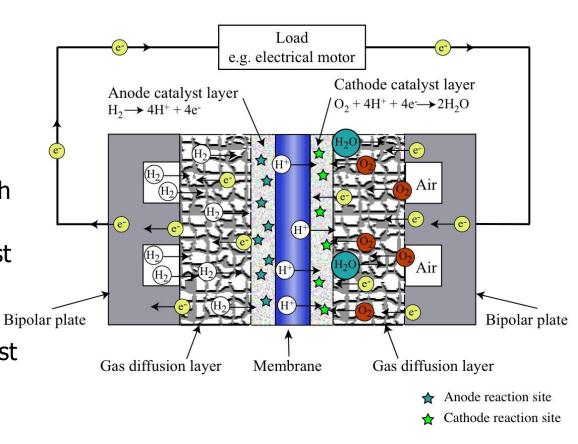
# Membrane Electrode Assembly (MEA)



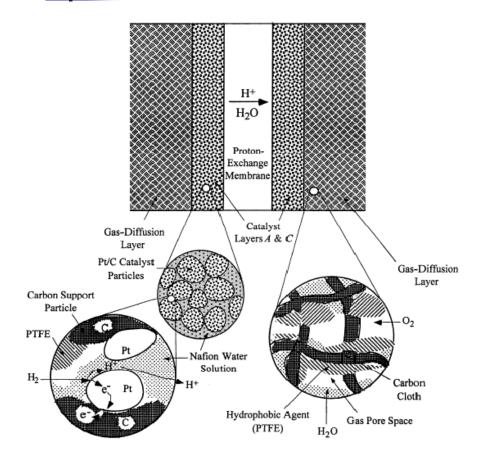
Construction of MEA (Membrane Electrode Assembly)

# Single cell mechanisms

- Mechanisms at electrodes:
  - Reactants are brought by convection
  - Diffusion towards the reaction anode sites through gas diffusion layer
  - Reaction of H<sub>2</sub> using catalyst
  - Dissolution into the electrolyte
  - Reaction H<sub>2</sub>-O<sub>2</sub> using catalyst
  - Diffusion of products towards the gaseous phase
  - Elimination by convection

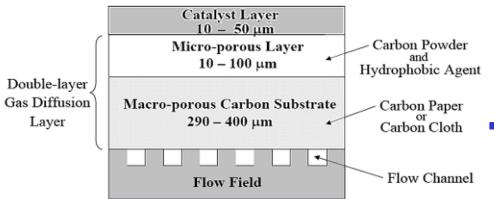


#### Membrane Electrode Assembly



- Considerable effort has been made in researching efficient electro catalysts.
- To date, the best PEM fuel cell anode and cathode catalysts are still platinum-based.
- To maximize platinum utilization and minimize cost, platinum is finely dispersed on an electrically conducting, relatively chemically inert support such as a *carbon black*. In this manner the amount of active platinum exposed to the reactants is maximized, greatly increasing power density.

#### Membrane Electrode Assembly



#### Gas Diffusion Layer

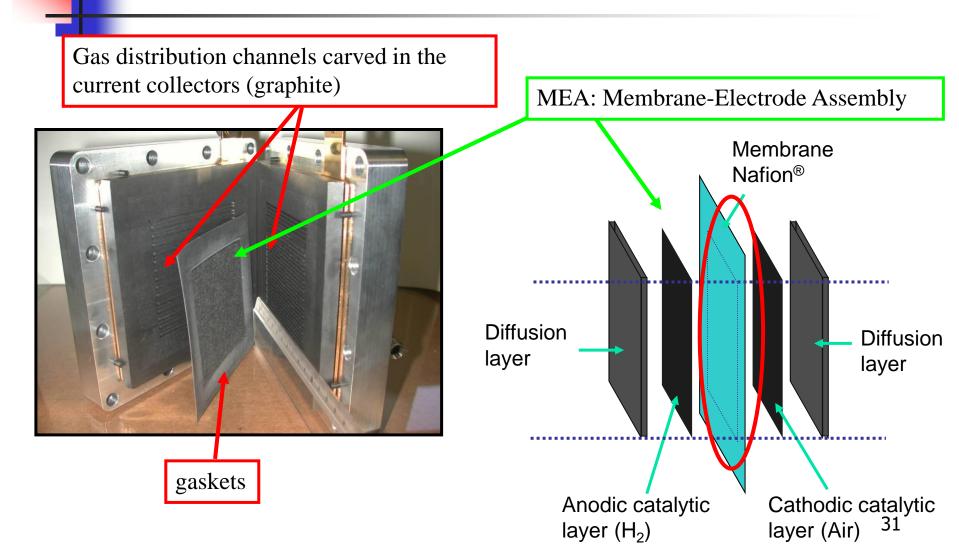
- The gas diffusion layer (GDL) or backing layer is a critical component in an MEA.
- GDL's main function is to distribute the reactant gases while providing a good electronic conductivity, porous conductors such as carbon cloth or paper are commonly used.

- Secondary functions: minimize water flooding and maximize the electronic contact at the interface with the catalyst layer.
- The GDL serves in water management as it removes product water away from the catalyst layer.
- The GDL usually has a dual layer structure :
- 1/ A microporous layer next to the catalyst layer and made from carbon powder and a hydrophobic agent (PTFE).
- 2/ The second layer is a macroporous carbon substrate consisting of the carbon paper or cloth.
   29

# Membrane Electrode Assembly (MEA)

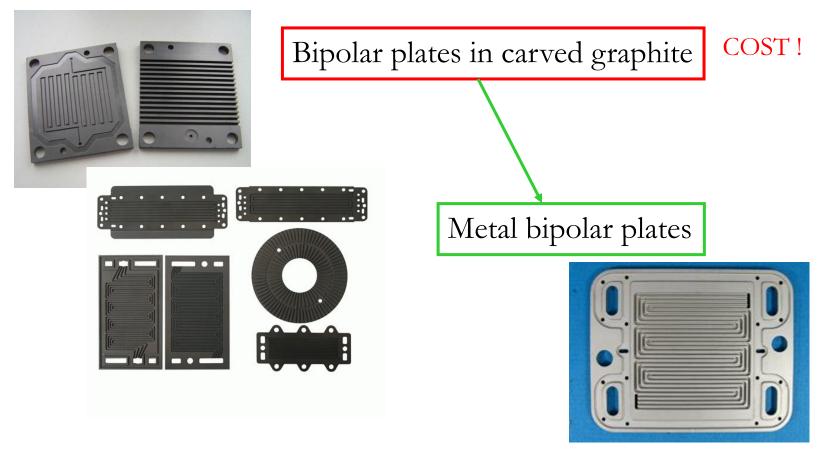
- Anodes:
  - Metal catalyst (Pt, Pd, Rh, etc.) supported on active C
  - Ni of Raney (alkaline fuel cells)
  - Fe, Co, Ni at high temperature (sintered metals or cermet)
- Cathodes:
  - Precious metals at low temperature
  - Ni sintered (or melted carbonates)
  - Mixed oxides (high temperature fuel cells)

### Design of Membrane Electrode Assembly (MEA)

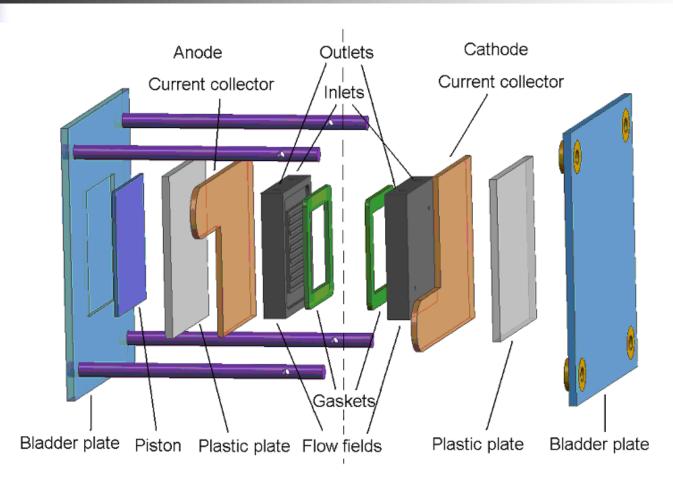


### Design of Membrane Electrode Assembly

#### Design



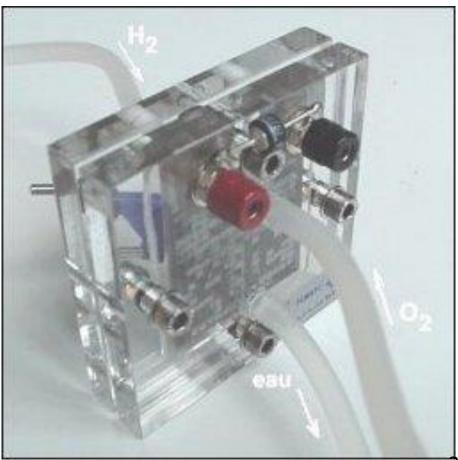
#### Fabrication of a single cell

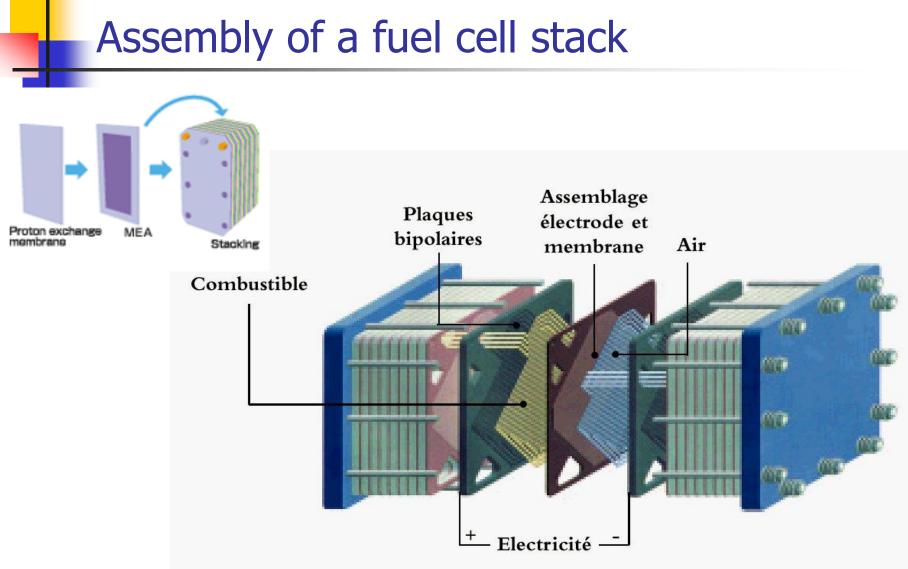


Exploded view of single PEM fuel cell.

# Fabrication of a single cell

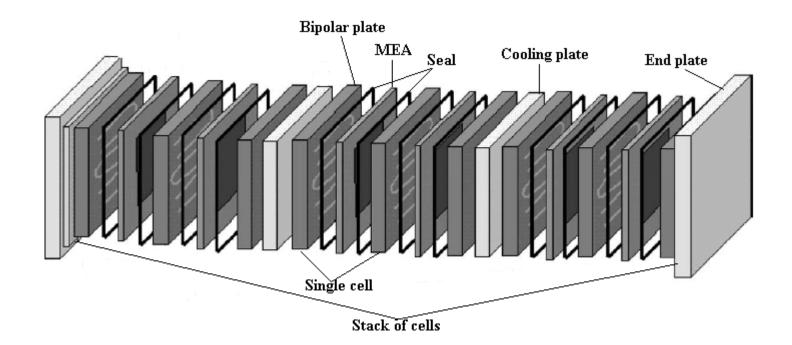






#### 

# Assembly of a fuel cell stack



Exploded view of PEM fuel cell stack

### Assembly of a fuel cell stack

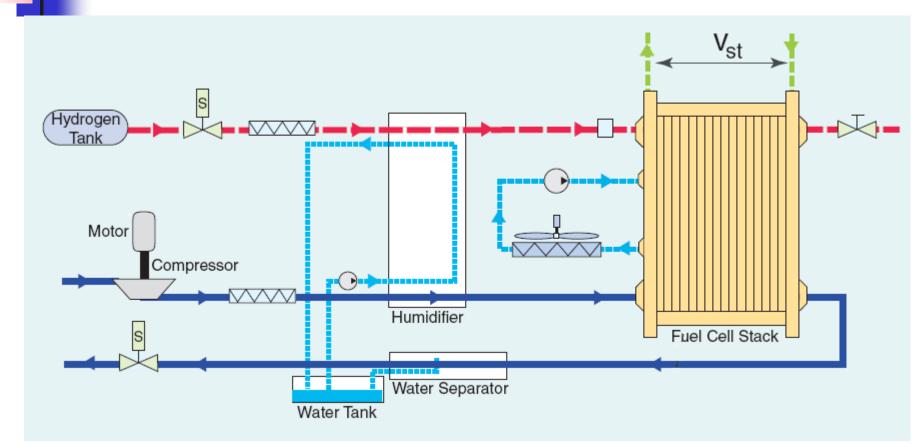
- In practice, the single cells are stacked in parallel or serial assembly to shape a fuel cell stack.
- The fuel cell stack power depends on the number and the surface of fuel cells that are compiled.
- The range of power of the stack can span from a few W to several MW.
- One can find miniaturized fuel cell stacks of a few Watts.







#### Fuel cell systems



Schematic of hydrogen PEM fuel cell system.

### Fuel cell systems

- Hydrogen reformer or hydrogen purification. Hydrogen gas rarely occurs naturally on the earth's surface and has to be made from other chemical fuels. Once the hydrogen fuel is made, impurities such as carbon monoxide poisons the cell, necessitating purification and detection systems.
- Air supply. Oxidant must be supplied to the cathode at a specific pressure and flow rate. Air compressors, blowers, and filters are used for this.
- Water management. The inlet reactant gasses must be humidified, and the reaction produces water. Management of water must also consider relative amounts of the two phases.
- Thermal management. Stack temperature must be monitored and controlled through an active or passive stack cooling systems as well as a separate heat exchanger in the case of an active system.

### Conversion efficiency of a Fuel Cell

• Work of the fuel cell = variation of free energy (Gibbs)  $W_{max} = -\Delta G$ 

$$W_{utile} = nF(E_a - E_c)$$
  $F = 96500 \text{ C/mol}$ 

Maximum voltage

$$(E_a - E_c) = -\frac{\Delta G}{nF}$$

• Example:  $H_2 + 1/2 O_2 \rightarrow H_2 O(g)$ 

△G = -229 kJ/mol H<sub>2</sub>(g)   

$$\Delta G$$
 = -237 kJ/mol H<sub>2</sub>(l)  
 $E_{max}$  = 1,18 V

 E<sub>max</sub> = 1,23 V

 The maximum voltage at the fuel cell depends also of the temperature. Indeed

$$\Delta G = \Delta H - T\Delta S$$

$$(E_a - E_c) = -\frac{\Delta H - T\Delta S}{nF}$$

- In case of a reduction of the number of molecules (case of fuel cells  $H_2/O_2$ ), there is a reduction of entropy  $\Delta S < 0$  and the absolute value of  $\Delta G$  is reduced with the temperature.
- Example H<sub>2</sub>/O<sub>2</sub>
   25°C: 1,18V
   650°C: 1,02V
   1000°C: 0,92V

Energy efficiency

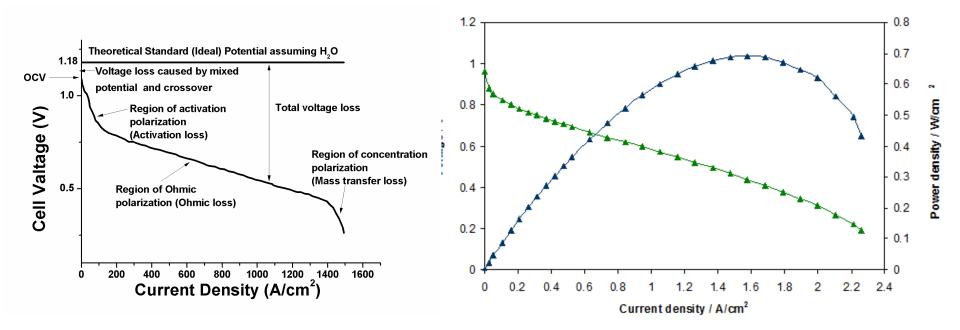
$$\eta = \frac{W_{elec}}{\Delta H} \qquad \qquad \eta = 1 - \frac{T \,\Delta S}{\Delta H}$$

- Example  $H_2 + 1/2 O_2 \rightarrow H_2 O(g)$ 
  - ∆H = -242 kJ/mol (PCI)
  - ▲G = -229 kJ/mol
  - η = 95% à 25°C (74% à 1000°C)
- In practice the efficiency is inferior to this theoretical value because of irreversibilities

Efficiency of the  $H_2/O_2$  fuel cell compared to the Carnot efficiency (Tu=300K)

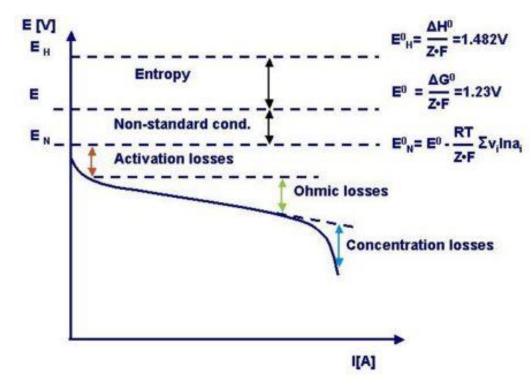
# Characteristics of fuel cells

- Real characteristics of fuel cells  $\rightarrow$  Limitations of fuel cells
- Irreversibility : gradients & friction
  - Gradient of concentrations
  - Gradient of temperatures
  - Gradient of pressure
  - Joule effects
  - Other factors



Polarization curve of the FC: voltage-current density curve

- Loss of efficiency due to over tension and polarization, and the reduction of voltage:
  - Open circuit losses: ∆G instead of ∆H (entropy) and nonstandard conditions (T≠T<sub>0</sub>, p≠p<sub>0</sub>).
  - Operational losses: Activation losses, Ohmic losses, Concentration polarization



$$U_{FC} = U_{rev} - U_{act} - U_{Ohm} - U_{conc}$$

$$F_{o} \qquad Thermodynamic voltage limit$$

$$Activation loss regime \qquad U_{micloss regime} \qquad U_{micloss reg} \qquad U_{micloss regime} \qquad U_$$

- Generally, on distinguishes three
  domains in the experimental
  voltage-current curves of FC. There
  are three main operational losses
  are often referred to as
  - Activation polarization: kinetic and activation energy related to the irreversibility of reactions
  - Ohmic losses: resistance of the ionic conduction
  - Concentration polarization losses: mass transfer resistance of reactants and products

Polarization curve of the FC: voltage-current density curve

- 1/ Activation loss regime: Even for zero and very low currents, there are irreversible losses. These stem from the activation energy of the electrochemical reactions at the electrodes [mainly at cathode electrode (oxygen)].
- These losses depend on the reactions at hand, the electro-catalyst material and microstructure, reactant activities (and hence utilization), and weakly on current density. They are related to the energy required to initiate the reactions and the finite speed (kinetic) of electrochemical reactions.
- The activation losses related to charge transfer are ruled by the Butler Volmer law. This law can be approximated by the semi empirical Tafel law

 $U_{act} = c_0 + c_1 \ln(i_{FC}(t))$ 

Or it's empirical approximation

$$U_{act} \simeq c_0 (1 - e^{-c_1 i_{FC}(t)})$$

- 2/ Ohmic loss regime: For intermediate current density, where the FC is generally used, the losses increase linearly with the current density. It is typical from ohmic losses due to internal resistance of the ion current across the electrolyte and the membrane, and the electronic resistance in the electrodes, current collectors and interconnects, and contact resistances.
- Ohmic losses are proportional to the current density.
- They depend on materials selection and stack geometry, and on temperature.

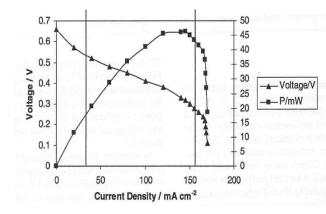
$$U_{Ohm} = i_{FC} \,\bar{R}_{FC}$$

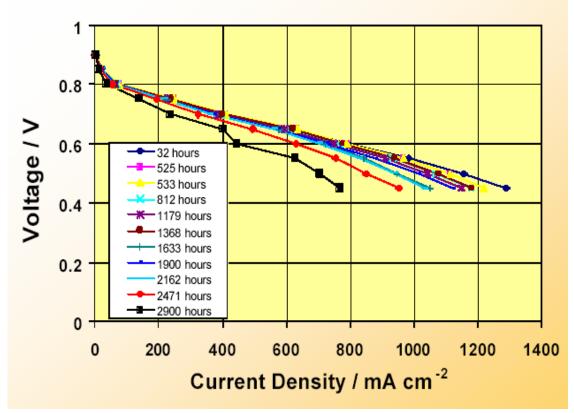
- 3/ Mass transfer loss regime: For high current densities, the losses increase drastically.
- The over tensions result from the finite mass transport limitations rates of the reactants and the products of the reaction to and from the electrodes.
- These losses depend strongly on the current density, reactant activity, and electrode structure. It is therefore also denominated as the concentration polarization.
- Concentration loss are generally expressed by the law

$$U_{conc} = c_2 \, i_{FC}^{c_3}(t)$$

Or alternatively

$$U_{conc} = c_2 e^{c_3 i_{FC}(t)}$$





### Loss of efficiency

The reversible efficiency is calculated as the ratio between the theoretical (reversible) voltage and the actual voltage measured at the ports:

$$\eta_{elec} = \frac{U}{E_{rev}}$$

 This efficiency also depends on the catalyst, the health state of electrodes, material selection, choice of oxidant (pure oxygen of from air), ambient conditions (temperature, pressure)

### Loss of efficiency

#### Faradic efficiency

- Take care of the number of electrons actually participating to the electrochemical reaction compared to the electrons liberated by the oxidoreductase per mole of fuel
- For hydrogen H<sub>2</sub>: efficiency is close to 1,0
- For methanol FC, one has secondary reactions (formaldehydes, formic acid) → efficiency can drop to 0,66 or even 0,33
- Account also for internal short circuits
- Material efficiency
  - Take into account for the (uncompleted) usage of the input fuel at the level of electrodes
  - Generally one admits more than the stoichiometric fraction ratio of air (1,7) and of H<sub>2</sub> (1,4)
  - H<sub>2</sub> is not fully utilized

### Loss of efficiency

- System efficiency
  - In mobile and stationary applications, the fuel cell does not work isolated.
  - Several auxiliaries are necessary: air compressors, control systems, thermal control, reforming and purification of H<sub>2</sub> (desulfuration, Hydrogen purification, heat exchangers)
  - Generally they have a global efficiency of 80%

### Global efficiency of the FC system

Global efficiency of the fuel cell

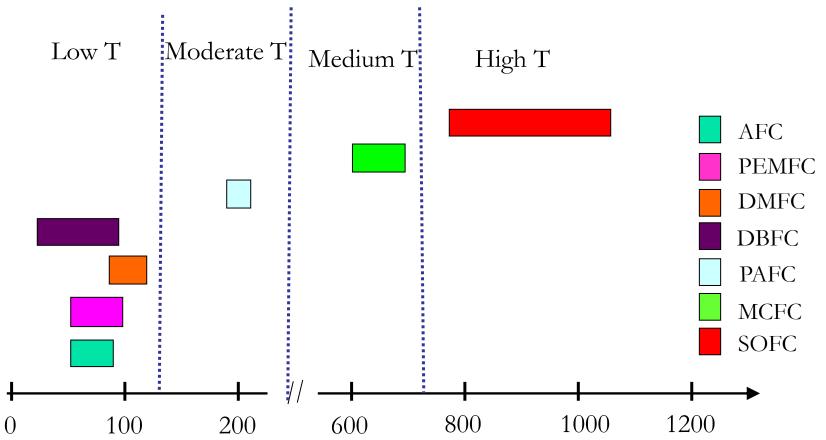
 $\eta_{FC} = \eta_{elec} \, \eta_u \, \eta_f \, \eta_m \, \eta_{sys}$ 

- Numerical example H<sub>2</sub>/O<sub>2</sub> @ 80°C, PEMFC with actual voltage of 0,7V for 350 mA/cm<sup>2</sup>
  - Reversible efficiency (thermodynamics) : 0,936
  - → Electrical efficiency : 0,60
  - Faradic efficiency: 1
  - Material efficiency: 0,9
  - System efficiency: 0,8
  - Total: 40,4%

- One distinguishes 6 types of fuel cells:
  - AFC: Alkaline Fuel Cell
  - PEMFC: Polymer Exchange Membrane Fuel Cell
  - DMFC: Direct Methanol Fuel Cell
  - PAFC : Phosphoric Acid Fuel Cell
  - MCFC: Molten Carbonate Fuel Cell
  - SOFC: Solid Oxide Fuel Cell

- The different fuel cell technologies are characterized by:
  - The type of fuel: hydrogen, methanol, natural gas
  - The nature of the electrolyte
  - The kind of the transported ions: H<sup>+</sup>, OH<sup>-</sup> or carbonate CaCO<sub>3</sub>--
  - The operating temperature
  - The architecture of the fuel
  - The size of the application (buildings, vehicle, electricity power plant, computer, portable communication equipment and by the nature of the application (mobile or stationary))
  - The typical power range
  - The conversion efficiency
  - The technology maturity or technological readiness level (TRL)
  - The cost per kW

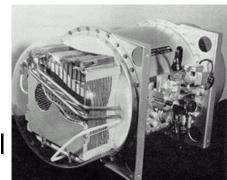
Fuel cell name	Electrolyte	Qualified power (W)	Working temperature (°C)	Efficiency (cell)	Efficiency (system)	Status	Cost (USD/W)
Direct borohydride fuel cell	Aqueous alkaline solution		70			Research	
Alkaline fuel cell	Aqueous alkaline solution	10 – 100 kW	< 80	60–70%	62%	Commercial / Research	
Direct methanol fuel cell	Polymer membrane (ionomer)	100 mW - 1 kW	90–120	20–30%	10–20%	Commercial / Research	
Reformed methanol fuel cell	Polymer membrane (ionomer)	5 W – 100 kW	250–300 (Reformer) 125–200 (PBI)	50–60%	25–40%	Commercial / Research	
Proton exchange membrane fuel cell	Polymer membrane (ionomer)	100 W – 500 kW	50–120 (Nafion) 125–220 (PBI)	50–70%	30–50%	Commercial / Research	30–35
Phosphoric acid fuel cell	Molten phosphoric acid (H <sub>3</sub> PO <sub>4</sub> )	< 10 MW	150-200	55%	40% Co-Gen: 90%	Commercial / Research	4–4.50
Molten carbonate fuel cell	Molten alkaline carbonate	100 MW	600-650	55%	47%	Commercial / Research	



- Low temperature T (80-90°C)
  - Proton Exchange membrane FC (PEM)
  - Alkaline fuel cell (AFC)
  - Direct methanol FC (DMFC)
- Moderate temperature (200°C)
  - Phosphoric Acid FC (PAFC)
- Medium temperature(600-700°C)
  - Melted Carbonate FC (MCFC)
- High temperature (900-1000°C)
  - Solid Oxide FC (SOFC)

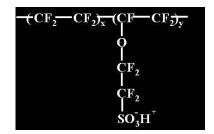
### Piles alkaline fuel cells

- Electrolyte: KOH solution 30-45%
- Temperature 60-90°C at atmospheric pressure (T higher at higher pressure)
- Electrodes: Ni or Pt at anode and coal +Ag at cathode
- Fuel: H<sub>2</sub> and oxidizer: O<sub>2</sub>
- Ions: OH<sup>-</sup>
- Power: 70-100 mW/cm<sup>2</sup>
- Low tolerance: a few ppm of CO and CO<sub>2</sub> in H<sub>2</sub> and air
  - CO is a poison of KOH  $\rightarrow$  K<sub>2</sub>CO<sub>3</sub>
- Developed in Belgium by HYDROGENICS
- Examples of application:
  - Spaceship vessels (Gemini, Apollo)
- Technological Readiness Level: industrial level



### Polymer exchange membrane

- Temperature 60-100°C; pressure between 1 and 5 bars
- Fuel: H<sub>2</sub> pure or from reforming Oxidizer: O<sub>2</sub> (air)
- Ions H<sup>+</sup>
- Electrolyte: conducting polymer membrane
  - Thickness: 50-100µm
  - Sulfonated tetrafluoroethylene based fluoropolymer-copolymer (Nafion)
  - High cost: 500€/m<sup>2</sup>
  - Hygrometric constraint: water saturation
- Catalyst of anode: Pt (0,5 2 mg/cm<sup>2</sup>)
- Inter connection plate: graphite machine tooled
- Tolerant of a few ppm of CO





### Polymer exchange membrane

- Power: 200-400 mW/cm<sup>2</sup>
- Examples of applications: vehicles, portable systems, cogeneration, marine
- Manufacturers: ex. Ballard (Canada), Horizon, MES...
- Development level : prototype or pre industrial level
- Prototypes 250 kW (env. 1kW / litre)

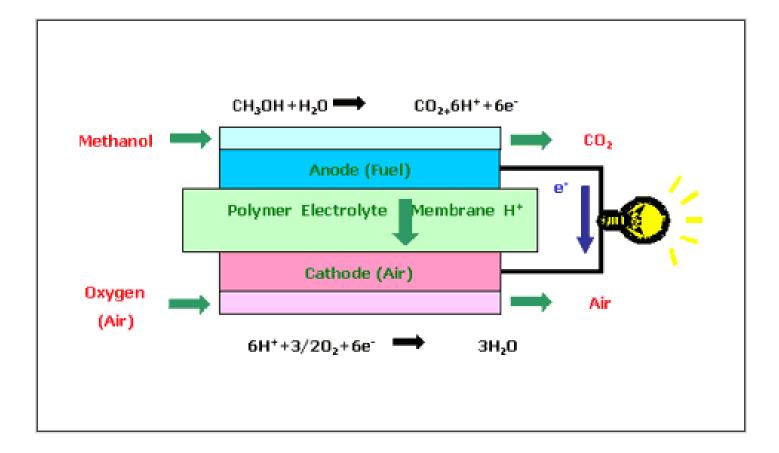
Application: Ballard 250 kW + heat Alsthom, Promocell



Anode: methanol supply (CH<sub>3</sub>OH)

 $CH_3OH + H_2O \to CO_2 + 6 H^+ + 6 e^-$ 

- Cathode: oxygen oxidizer (O<sub>2</sub>)
- Temperature 60-100°C; pressure between 1 and 5 bars
- Fuel: methanol Oxidizer: O<sub>2</sub> (air)
- Ions H+
- Electrolyte: polymer exchange membrane

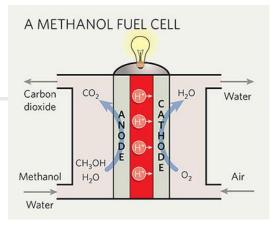


Liquid-feed DMFC, 90 C, 2M CH, OH, amb ient p ressure O,. E-TEK anode = Pt-Ru(1:1), 60 w/o on Vulcan XC-72 2 mg cm<sup>-2</sup> Pt. Cathode = 1.5 mg cm<sup>-2</sup> Rh<sub>3</sub>Ru<sub>113</sub>S<sub>43</sub>, 60 w/o Ketjen 600 50· Power density /mW cm<sup>-2</sup> 0.5 barg O<sub>2</sub> Pt,  $(A \text{ tm}, O_{3})$ 40 U.I barg O, 30 0.5 barg air 20·  $10 \cdot$ 100 200 300 0 Current density /mA cm

- Disadvantages:
  - Activity of methanol is lower than H<sub>2</sub>
  - Secondary reactions
  - Lower efficiency than PEMFC with  $H_2$  (2/3 à 1/3!)
- Advantages:
  - Methanol is liquid so that it is easier to transport, to store and to refuel compared to H<sub>2</sub> (gas)
- Applications: portable equipment (GSM, PC)
- TRL: prototype

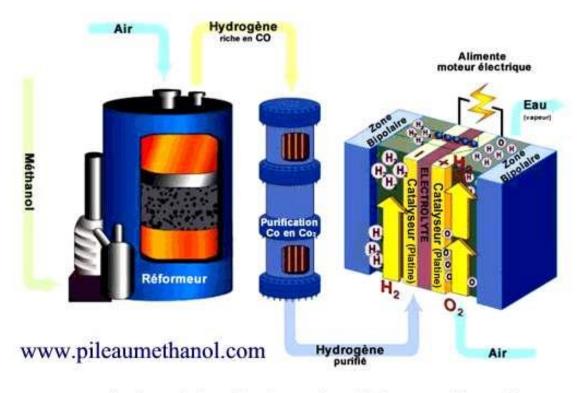






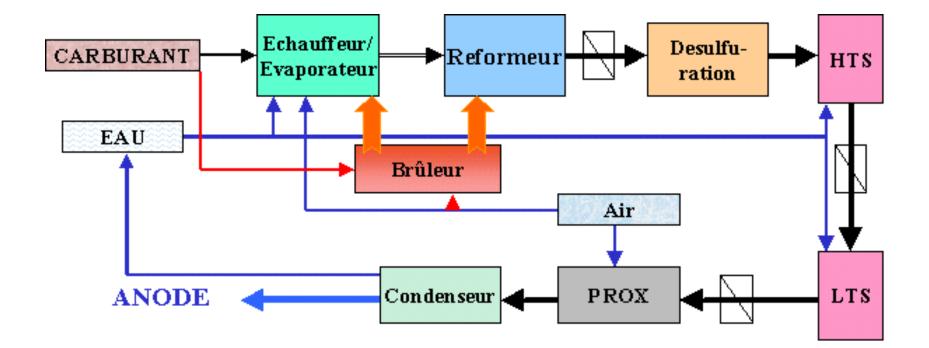
### Other H<sub>2</sub> supply: PEM with methanol reforming

Production of H<sub>2</sub> from methanol using reforming



Principe de la pile à combustible au méthanol

### Other H<sub>2</sub> supply: PEM with methanol reforming



# PAFC: phosphoric acid fuel cells

- Electrolyte: phosphoric acid H<sub>3</sub>PO<sub>4</sub> 100%
- Temperature 180-220°C
- Fuel: H<sub>2</sub> pure or from reforming Oxidizer: O<sub>2</sub> (air)
- Ions H<sup>+</sup>
- Power density: 100 300 mW/cm<sup>2</sup>
- Tolerance: 1% CO
- Applications: cogeneration
- TRL: mature technology

### PAFC: phosphoric acid fuel cells



Geometry of phosphoric Acid Fuel Cell

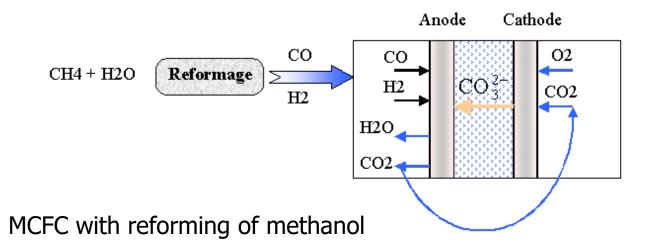
### PAFC: phosphoric acid fuel cells

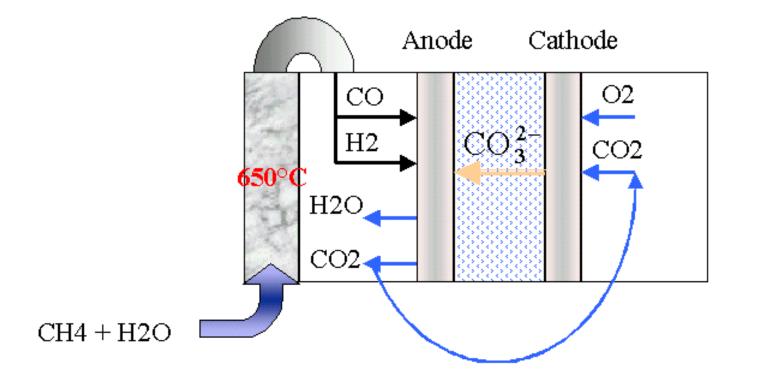


A fuel cell O.N.S.I. of 200 kWe and 200 kWth was installed in France in Celles by E.D.F. and G.D.F., for a demonstration project. It consumes natural gas provided by G.D.F and provides electrical energy as well as heat up to  $80^{\circ}$  C

- Molten Carbonate Fuel Cell : K<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub> melted in a matrix of LiAlO<sub>2</sub> (thickness 0,4 mm)
- Electrolytes: CO<sub>3</sub><sup>2-</sup>
- Fueling in  $H_2$  or natural gas  $CH_4$ :
  - Anode:  $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$
  - Cathode:  $\bar{O_2} + 2CO_2 + 2e^- \rightarrow 2CO_3^{2-}$
- Regeneration loop of CO<sub>2</sub> between anode and cathode
- Temperature : 600-660°C
- Catalysts:
  - Anode: Ni + Cr
  - Cathode: NiO + Li
- Connection plates made of Ni

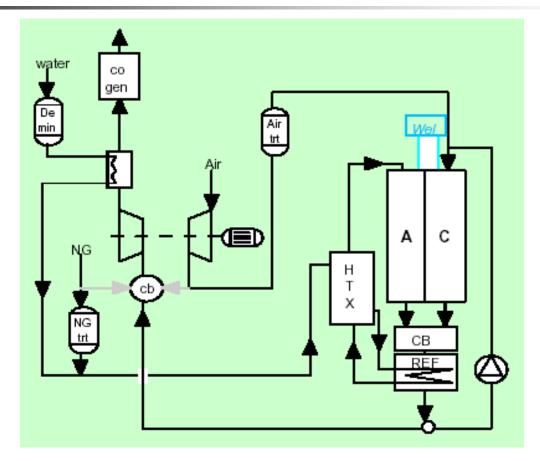
- Tolerant to CO
- Corrosion problems
- Stationary applications for high powers (800 kW to 2 MW) : cogeneration, centralized production of electricity, marine applications
- TRL: prototypes pre-industrial





MCFC with internal reforming

- Several advantages of MCFC
  - High electrical efficiency (60%),
  - Utilization of produced heat for cogeneration or internal reforming and combination with gas turbine,
  - Possible to use fuels as methane, methanol, ethanol or gasified coal...
  - Possible to use nonprecious metal as catalyst metals in electrodes.



Design of combined cycle (Ansaldo)



Application: MCFC of 2MW in Santa Clara, California. Operation time: 4000h. Other system: MCPower system of 250 kW used as a cogeneration unit in Miramar, California (See figure)

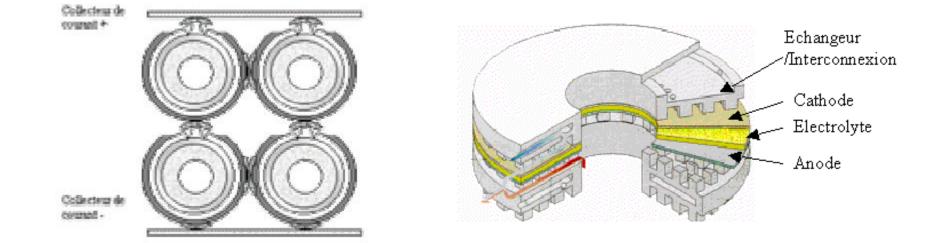
### Solid Oxide Fuel Cell : SOFC

- Conducting electrolyte: Zirconium doped with Yttrium:  $ZrO_2$  and  $Y_2O_3$ .
- Ions: O<sup>2-</sup>.
- Temperature: 700-1000°C
- Fuel: supply in pure H<sub>2</sub> or from reforming, natural gas CH<sub>4</sub>, CO or other fossil fuel (very interesting)
- Oxidizer: O<sub>2</sub> (air)
- Reactions:
  - Anode:  $H_2 + O^{2-} \rightarrow H_2O + 2e^-$
  - Cathode  $1/2 O_2 + 2 e^- \to O^{2-}$

## Solid Oxide Fuel Cell : SOFC

- Stationary and mobile application
- Vast application power (2,5 kW to 100 MW)
- Technical difficulties
  - Corrosion
  - Materials : fragile behavior and sensitivity w.r.t. to thermal shocks
  - Reduction of voltage with temperature T
- TRL: prototypes





SOFC fuel with a tubular structure SOFC Fuel Cell by Suzer Hexis

#### Hydrogen as a fuel

#### Fuel treatment

- H<sub>2</sub>: difficulty of storage and distribution network
- CH<sub>3</sub>OH: reforming process is a classical technology but remains costly
- Natural gas (CH<sub>4</sub>):
  - De sulfuration
  - Reforming
  - Elimination of CO<sub>2</sub> and of CO (except MCFC)
  - Utilization of unreacted H<sub>2</sub>
- Compression: energy loss
- Opportunity for partial oxidation-based systems

#### Hydrogen production paths

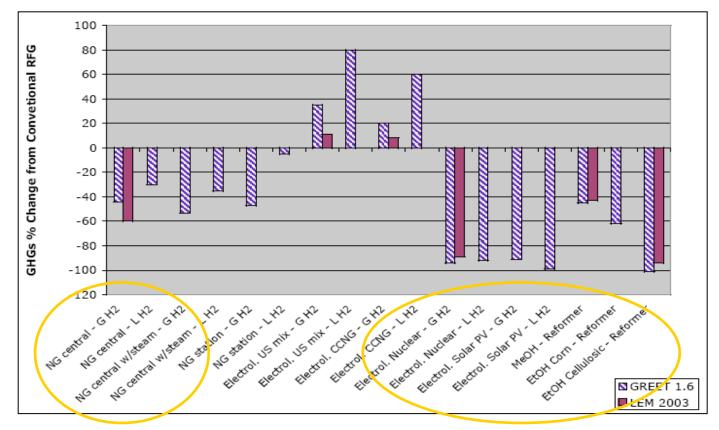
#### Water electrolysis

- Environmental impact depends on the CO<sub>2</sub> emission of electrical network
- Low overall efficiency (<60%)</li>
- Advantages: enables a massive energy storage of green electricity and allows to level the production peeks
- Reforming of fossil fuel from natural gas or oil
  - Production of CO<sub>2</sub> and dependency to oil
  - Emissions in upstream level
  - Is considered as the best option currently
- Hydrogen « lost » in industrial processes (chemical industry in processes)

#### Poly generation

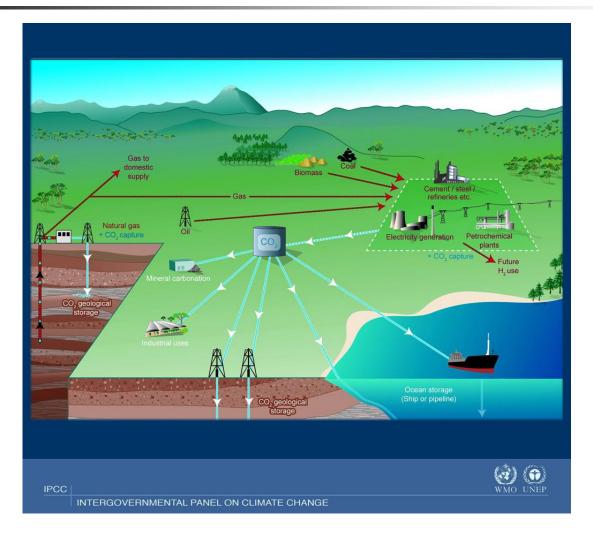
Production of heat, energy, and fuel in large scale energy systems.
 Possibility to perform Carbone capture & sequestration (CCS) as well as pollutants

#### Hydrogen production: GHG efficiency

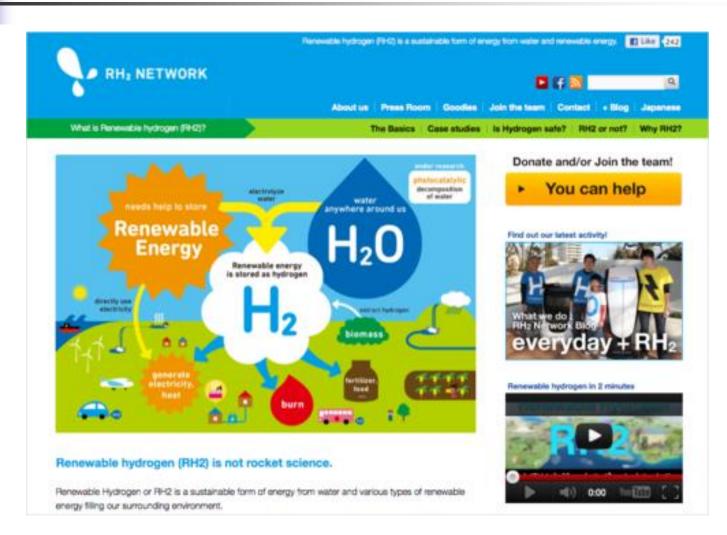


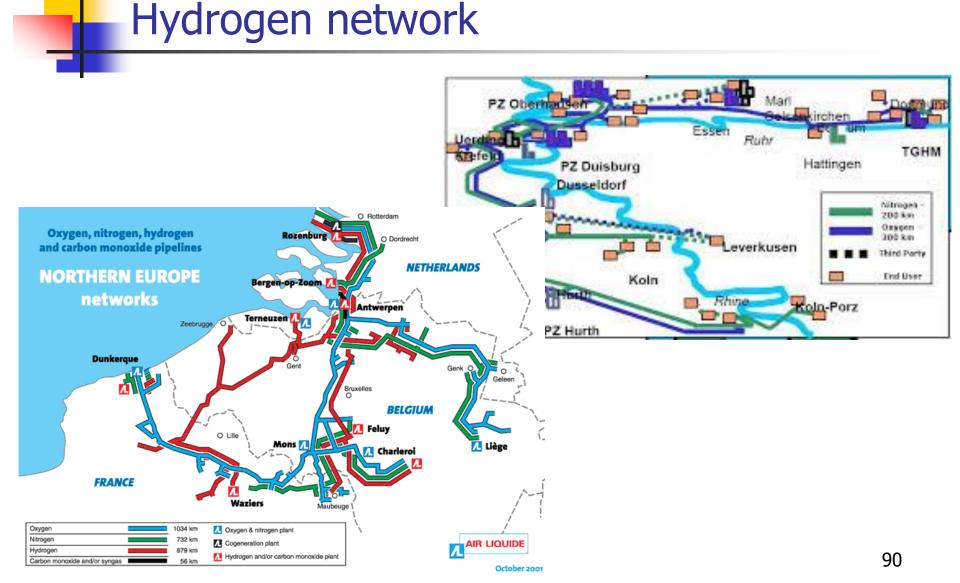
CO<sub>2</sub> and GHG emissions compared to the reforming in USA situation

#### Hydrogen production: the IPCC vision



#### Hydrogen route





#### IS HYDROGEN A SAFE FUEL?

Fuel leakage Simulation. Dr. Michael Swain. Experiment on fuel leakage and burning car conducted with the University of Miami at Coral Gables.

Lighter than air

Fuel tank punctured 0 seconds

Fuel set on fire 3 seconds Fuel tank burning 60 seconds







#### Hydrogen storages

# Hydrogen storage

	Specific energy	Energy density
	(Wh/kg)	(Wh/l)
H <sub>2</sub> compressed gas	33600	600
(T amb. et p=20 Mpa)		
H <sub>2</sub> liquefied	33600	2400
(T cryo. et p=0.1 Mpa)		
Mg-H2	2400	2100
Vanadium hydride	700	4500
Methanol	5700	4500
Petrol	12400	9100