





Thermomechanical Measurements for Energy Systems (MENR)

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Hydrogen Fuel Cells

Fuel cells are *electrochemical devices* capable of converting the <u>chemical</u> <u>energy of a fuel</u> (usually hydrogen) <u>directly into electricity</u> without the intervention of a thermal cycle, obtaining therefore higher conversion efficiency compared to conventional heat engines ...



A brief history of Fuel Cells

The first fuel cell was built by Sir William Grove in 1839, who used *platinum electrodes* and *sulphuric acid* as <u>electrolyte</u>. Later, starting in 1890, William White Jacques used phosphoric acid instead of sulfuric acid. These early devices were however characterized by a low current density (low efficiency).

Bacon, after 1930, replaced the first acid electrolyte of the cells with an *alkaline electrolyte* and continued to develop the system (cell of Bacon) today known by the acronym AFC (*Alkaline Fuel Cells*). The AFC were so popular that in the years' 60 they were chosen by NASA for the APOLLO lunar mission.



At the end of the years' 50 the use and the development of the PEMFC (*Proton Exchange Membrane Fuel Cells*) began; these cells use a special polymer membrane as electrolyte for exchanging protons. The production grew in the USA and was used by NASA for the space project GEMINI.

ELECTROLYSIS of WATER

The water is decomposed into its constituent elements, hydrogen and oxygen (the presence of salt Na_2SO_4 dissolved in the water serves to increase the conductivity of aqueous solution). At the **negative electrode** we have the **reduction** (**cathode**) of the water with formation of gaseous H₂, while the **positive pole** we have the **oxidation** (**anode**) with production of O₂ gas.



Anode (+) : oxidation	$2 H_2 O \rightarrow O_2 + 4H^+ + 4 e^-$
Cathode (-) : reduction	$4 H_2O + 4e^- \rightarrow 4 OH^- + 2 H_2$
Total reaction of the process :	$2 H_2 O \rightarrow O_{2 (g)} + 2 H_{2(g)}$ g = gas

CLASSIFICATION and WORKING SCHEME of the FUEL CELLS

- ✓ AFCAlkaline Fuel Cell
- ✓ PEMFC (SPFC)
 Proton Exchange Membrane
 Fuel Cell
- ✓ PAFC
 Phosphoric Acid Fuel Cell
- ✓ MCFCMolten Carbonate Fuel Cell
- ✓ SOFC Solid Oxide Fuel Cell



$H_2 + 1/2 \ O_2 \rightarrow H_2O + elettricità + calore$

PEM: polimeric electrolyte cell



PROS

- low operating temperature
- easy starting (order of minutes)
- high yield (power density)
- no corrosion problems (typical of other types of cells with liquid electrolyte)
- Quite simple construction

CONS

- poor tolerance to the presence of CO in the fuel
- difficult thermal integration between the fuel treatment system and the stack

As mentioned, there are various types of fuel cells. However, for automotive traction the best candidate appears to be the *Polymer Electrolyte Cell*.



In the figure are represented in order:

- 1. The **bipolar plates** which make up the cell's terminals, to them is connected the external electrical circuit that will use the current produced by the cell.
- 2. The **proton exchange membrane** which forms the electrolyte that allows ions to migrate.
- 3. The **electrodes** which represent the active sites where hydrogen oxidation and oxygen reduction happens; the membrane and electrode together is typically referred to as MEA (*Membrane Electrode Assembly*).
- 4. The **sealing system** which ensures the device sealing of the reagents and the cooling fluid.
- 5. The **gas diffusion layers** which convey the reagents to the active sites and are made up of tiny channels distributed close to the electrode.



Why don't we allow the reagents to pass directly through the catalytic layer ?

Why is the electrode substrate necessary ?

The substrate, being of porous material, allows access of the reagent gases under the structure of the bipolar plates. At the same time, it provides a conductive path to the patterned area of bipolar plates.

Bipolar plates must operate a balance between gas supply and electrons conduction. The best conductor, a solid sheet full, would not allow access to any gas while a completely open structure would not allow any current to flow.



Open Gas Channel Flow Field Plate

A FEW ELEMENTS OF THE CELL THERMODYNAMICS

The energy available at the equilibrium conditions (*constant pressure and temperature*) in a cell is given by the change of *free energy*:

$$\Delta G = -nFE_{rev} \qquad \begin{cases} H_2 \to 2H^+ + 2e^- \\ \frac{1}{2}O_2 + 2H^+ + 2e^- \to H_2O_2 \end{cases}$$

where:

- *n* number of electrons participating in the reaction = 2
- *F* Faraday constant = 96484 C/mol
- *E_{rev}* reversible cell potential

Nerst's equation determines the thermodynamic potential of the complete redox reaction; this potential represents the e.m.f. (electromotive force) of the cell in open circuit conditions :

$$\mathbf{E} = \frac{-\Delta \mathbf{G}_{\mathrm{E}}^{0}}{2 \cdot \mathbf{F}} + \frac{\mathbf{R} \cdot \mathbf{T}}{2 \cdot \mathbf{F}} \cdot \ln \frac{\mathbf{p}_{\mathrm{H2}} \cdot (\mathbf{p}_{\mathrm{O2}})^{\frac{1}{2}}}{\mathbf{p}_{\mathrm{H2O}}}$$

A fuel cell operating in standard conditions, that uses hydrogen and oxygen electrodes in open circuit, is capable of supplying a voltage E_{rev} of 1,229 V. When the cell delivers a current to an utilizer, polarization phenomena arise that cause localized voltage surges resulting in lowering of the measurable voltage at the electrodes.



The measurable voltage then has the following expression:

$$V_{FC} = E_{rev} - (V_{ohm} + V_{att} + V_{con})$$

where V_{FC} is the overall voltage measurable at the cell terminals and the three terms V_{ohm} , V_{att} , V_{con} summarize the effects of the cell polarization.

Cell polarization effects

Activation Polarization (activation loss)

it is correlated with the speed of the reactions at the electrodes. In the case of electrochemical reactions where V_{att} is in the order of 50-100 mV, it can be expressed by the *equation of Tafel* :



where α = charge transfer coefficient

*i*₀ = exchange current density

Activation polarization is correlated to the slow reaction parts, to this kind of polarization contribute processes involving adsorption of reagents, electron transfer towards the double layer, desorption of electronic products and the nature of the surface.

Ohmic Polarization (ohmic loss)

is caused by the resistance encountered by the ions to cross the membrane and by the resistance of the electrons moving along the electrode. It can be placed under the form:

$$V_{ohm} = i \cdot R$$

where R is the total resistance of the cell. The most significant loss occurs in the electrolyte and can be reduced by decreasing the distance between the electrodes and by using electrolytes with high lonic conductivity.

Concentration polarization (concentration loss)

is caused by mass transport phenomena of reactant gases and products that hinder the reactions at the electrodes: near these, given their limited porosity and the speed with which the reactants are consumed, concentration gradients are generated that, added to the difficulties of gases diffusion into the electrolyte and of the products movements to and from the areas of reaction, determines the occurrence of the phenomenon.

Mass transit speed can be described by the first Fick's law :

$$i = \frac{nFD}{\delta}(c_b - c_s)$$

diffusion coefficient of reagent species reagent species concentration in the bulk concentration on the electrode surface diffusion layer thickness

When the electrode is governed only by diffusion phenomena, we reach a current limit i_L which is defined as :

In the case where we can assume negligible the η_{att} , the concentration polarization V_{con} is expressed by:



$$V_{con} = \frac{RT}{nF} \ln \frac{c_s}{c_b} = \frac{RT}{nF} \ln \left(1 - \frac{i}{i_L}\right)$$

Polarizations always act in the sense of *raising the potential of the electrode* where the oxidation reaction runs (anode) and *lowering the electrode potential* where the reduction reaction runs (cathode). We have therefore:

D

C_S

 $c_b \delta$

$$V_{FC} = E_{rev} - V_{ohm} - V_{att} - V_{con}$$

FUEL CELL Efficiency

Thermodynamic efficiency :

the energy efficiency of a cell is defined as:



 $\begin{cases}
 L_u \\
 P_e \\
 n_{H2} \\
 F_{H2} \\
 \Delta H r_u
\end{cases}$

usable work [J] power output [W] number of hydrogen moles [mol] hydrogen moles consumed per second [mol/s] reaction enthalpy equal to 284.000 [J/mol]

Voltage efficiency :

when the cell produces electricity, the cell voltage (V) is less than the voltage that we would have with open circuit (E_{rev}). The voltage efficiency is defined by the ratio between the voltage output under load and the theoretical voltage :



Fuel utilization factor and theoretical efficiency :



- F_t theorical hydrogen flow rate [mol/s] which is responsible of the chemical reaction associated with the power supply of the cell
 F_a Faraday constant = 96484 C/mol , which is the electric charge (in Coulomb) associated with one mole of electrons
- N_{cell} umber of cells that make up the stack



$$\eta_{\text{teorico}} = \frac{V \cdot I}{F_{\text{t}} \cdot \Delta H} = \frac{V \cdot I}{\frac{N_{\text{cell}} \cdot I}{2 \cdot F_{\text{a}}} \cdot \Delta H} = k V$$

The constant "2" in the denominator is because for every mole of hydrogen, two protons and two electrons are formed !

The *theoretical efficiency* of a FC is proportional to the voltage that settles at its terminals !

Our lab experience :



- Determine the current-voltage characteristic curve and the power curve of the PEM fuel cell ...
- Determine the Energy efficiency of the PEM fuel cell ...



Figure 1.3.1.c: Voltage-current characteristic of fuel cell

Example (using the h-tec JuniorBasic Hydrogen Experimentation System):



Figure 1.3.1.a: Setup for determining current-voltage characteristic of fuel cell (FC = Fuel Cell)

R [Ω]	U [V]	I [A]	P [W] calculated: P=V·I
00	0.99	0.00 0.01 0.01 0.03	0.000 0.001 0.001 0.027 0.075 0.167 0.347
330	0.97		
100	0.94		
33	0.90		
10	0.84	0.08	
3.3	0.76	0.22	
1	0.62	0.56	
0.33	0.47	1.05	0.494
0.1	0.32	1.43	0.458
0	0.24	1.61	0.386

Figure 1.3.1.b: Table of measurements

Measurement of the voltage and current values of the fuel cell with different load resistances.

Example (using the h-tec JuniorBasic Hydrogen Experimentation System):

V _{H2} [cm ³]	t [s]	V [volts]	I [A]	P [W] calculated: P=V·I
20	0	0.813	0.128	0.104
15	281	0.770	0.120	0.092
10	605	0.678	0.106	0.072
Mean		$\overline{V} = 0.754$	$\overline{I} = 0.118$	$\overline{P} = 0.089$

Figure 1.3.2.b: Table of measurements

A fuel cell continuously converts hydrogen gas introduced as fuel into electrical energy. The values of time, voltage and current for certain hydrogen consumptions (5 cm³ increments) have been recorded in this table.

SELF-BREATHING and SELF-HUMIDIFYING Fuel Cells

The power generation of a fuel cell is *limited by the air flow,* by the pressure values of the incoming gas and by the amount of water supplied to the cell itself. To eliminate complicated controls on the system and simplify the functional schemes, sometimes we choose a *self-humidifying* and *self-breathing* cell. In fact, generally the cell oxidizing gas is supplied with a compressor by adjusting the oxygen incoming pressure, but this implies a substantial expenditure of energy to the power supply. On the other hand, the self-breathing cells suffer of a particular problem (*oxygen starvation*) that occurs when the partial pressure of oxygen falls below a critical level, in any place, within the cathode air ducts. This phenomenon results in a rapid decrease of the cell voltage, which in extreme cases, can also lead to the damage of the membrane of the cell itself.



CATENA DI MISURA DI UN BANCO PROVA PER UN SISTEMA DI TRAZIONE A CELLE A COMBUSTIBILE

- Linea Idrogeno
- Parte Elettrica
- Parte Meccanica

Parametri monitorati:

- Tensione e corrente erogate
- Flusso H₂
- Temperatura stack
- Velocità angolare albero motore
- Coppia torcente
- Potenza assorbita ausiliari
- Rendimenti





Cella a Combustibile

Caratteristiche:

- ✓ Potenza: 150W @ 15V
- ✓ Reagenti: idrogeno/aria
- ✓ P idrogeno: 2 psig
- ✓ T: 58°C
- ✓ Tipo di cella: PEM







Programma di acquisizione in LabView





Caratterizzazione statica



- Rendimento elevato ad alti giri
- Penalizzazione nel ciclo urbano

- Rendimento abbastanza costante in ampio range di potenze
- Lieve diminuzione del rendimento ad elevate potenze
- Tempo di avvio rapido (circa 5 min)

Ciclo urbano standard



Norma UNI-EN 1986-1



Calcolo del rendimento del sistema cella + motore elettrico



Risultati sperimentali

Rendimento istantaneo

Rendimento medio



$$\overline{p} = \frac{E}{n_{H_2}\Delta H} = \frac{\sum_{i} W_i \cdot \Delta t}{\sum_{i} F_i \cdot \Delta t \cdot \Delta H} = \frac{\sum_{i} W_i}{\sum_{i} F_i \cdot \Delta H} = \frac{W_{tot}}{F_{tot} \cdot \Delta H}$$

Incertezze associate:

$$\varepsilon_{\eta} = \sqrt{\left(\frac{\partial \eta}{\partial W} \varepsilon_{W}\right)^{2} + \left(\frac{\partial \eta}{\partial F} \varepsilon_{F}\right)^{2}} = \sqrt{\left(\frac{1}{F \cdot \Delta H} \varepsilon_{W}\right)^{2} + \left(-\frac{W}{F^{2} \cdot \Delta H} \varepsilon_{F}\right)^{2}}$$

$$\varepsilon_{\overline{\eta}} = \sqrt{\left(\frac{\partial \overline{\eta}}{\partial W_{tot}} \varepsilon_{W_{tot}}\right)^{2} + \left(\frac{\partial \overline{\eta}}{\partial F_{tot}} \varepsilon_{F_{tot}}\right)^{2}} = \sqrt{\left(\frac{1}{F_{tot}} \cdot \Delta H} \varepsilon_{W_{tot}}\right)^{2} + \left(-\frac{W_{tot}}{F_{tot}^{2}} \cdot \Delta H} \varepsilon_{F_{tot}}\right)^{2}}$$

dove: $\mathcal{E}_{W_{tot}} = \sqrt{\sum_{i} \mathcal{E}_{W_i}^2} \quad \mathcal{E}_{F_{tot}} = \sqrt{\sum_{i} \mathcal{E}_{F_i}^2}$

Potenza meccanica all'albero:



Rendimento meccanico istantaneo:



Rendimento meccanico medio:

$$\overline{\eta}_{mecc} = \frac{E}{n_{H_2} \cdot \Delta H} = \frac{\sum_i W_{i \ mecc} \cdot \Delta t}{\sum_i F_i \cdot \Delta t \cdot \Delta H} = \frac{W_{mecc \ tot}}{F_{tot} \cdot \Delta H}$$