

Chapter 2

PEM Fuel Cell Systems

2.1 An Introduction to PEM Technology

Among the many different technologies summarised in Chap. 1, Proton Exchange Membrane (PEM) fuel cells are extensively used for mobile and portable applications. This is due to their compactness, low weight, high power density and clean, pollutant free operation. From the operational point of view, a relevant aspect is their low temperature of operation (typically 60–80 °C), which allows fast starting times. In a PEM Fuel Cell, a hydrogen-rich fuel is injected by the anode, and an oxidant (usually pure oxygen or air) is fed through the cathode. Both electrodes are separated by a solid electrolyte that allows ionic conduction and avoids electrons circulation. Catalytic oxidation of H₂ and catalytic reduction of O₂ take place in the negative and positive electrodes, respectively.

The standard electrolyte used in PEM Fuel Cells is a perfluored solid polymer composed by Teflon-like chains. This material combines mechanical, chemical and thermal stability with a high protonic conductivity, when properly humidified. Electrodes are typically made of a porous carbon compound coated with a catalyst such as platinum or palladium, to improve the efficiency of electrochemical reactions. Catalysts are essential in this technology and constitute one of the most expensive components of the cell. Besides, they are very sensitive to CO contamination, which makes the use of high-purity hydrogen (CO \ll 20 ppm) mandatory. This is a serious limitation when H₂ is obtained from hydrocarbon reforming. Alternative alloys, like platinum/ruthenium, which are more resistant to CO poisoning, are currently under development.

The output of a PEM Fuel Cell is electric energy, with water and heat as the only by-products. Efficiency can be high, as previously said, due to the absence of a Carnot cycle. From the electrical point of view, the cell can be seen as a voltage source where the output impedance presents a highly nonlinear dependence to operating conditions such as temperature, electric current, partial pressures and humidity levels of the incoming gases. Due to this nonlinear, multi-variable dependent behaviour, precisely controlled conditions must be ensured for proper operation.

2.2 Basics of PEM Fuel Cells Operation

Catalytic reactions of hydrogen oxidation at the anode and oxygen reduction at the cathode produce an electric potential difference between electrodes, that can be used in an external circuit if the electrolyte allows ionic mass transport but isolates electrically both electrodes. On the anode side, the catalyst produces the dissociation of hydrogen molecules into protons (H^+) and electrons (e^-). Protons cross the polymeric membrane, while electrons are forced to the external electric network. In the cathode's surface the oxygen molecules react with electrons from the external circuit and protons from the membrane to produce water. In the process, the only by-product is water, in vapour and liquid phases. The membrane must be properly humidified, because its protonic conductivity depends directly on its water content. To accomplish this, input gases are previously humidified. The amount of energy produced in the electrochemical process can be calculated from changes on the Gibbs free energy (g_f), that is, the difference between the Gibbs free energy of products and reactants. In the particular case of PEM Cells fuelled with pure hydrogen, the product is distilled water (H_2O), the reactants are hydrogen and oxygen, and then

$$\Delta g_f = (g_f)_{prod} - (g_f)_{react} = (g_f)_{H_2O} - (g_f)_{H_2} - (g_f)_{O_2} \quad (2.1)$$

The Gibbs free energy represents the energy available for external work. The values of Δg_f depend on the reactants temperatures and pressures according to the following expression:

$$\Delta g_f = \Delta g_f^o - RT_{fc} \ln \left[\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \right] \quad (2.2)$$

where R is the universal constant for ideal gases, P_{H_2} is the hydrogen partial pressure, P_{O_2} is the oxygen partial pressure, P_{H_2O} the water vapour partial pressure, and Δg_f^o the change in the process g_f at a standard working pressure (1 bar), which in turn changes with the temperature of the fuel cell (T_{fc}). Values of the Gibbs free energy for standard pressure at different temperatures are shown in Table 2.1 [17]. A negative Δg_f^o implies that the reaction releases energy ($(g_f)_{react} > (g_f)_{prod}$).

If the electrochemical processes taking place in the cell were reversible, all the Gibbs free energy could be converted into electrical energy for the external circuit. In this ideal case, for each mol of hydrogen, two moles of electrons circulate by the electric circuit making an electric work (charge \times voltage) $-2FE$, where F is the Faraday's constant or, equivalently the charge of an electron mol (96485.309 C/mol), and E is the open circuit fuel cell voltage. This amount of electrical work is the net change in the Gibbs free energy:

$$\Delta g_f = -2FE \quad (2.3)$$

Therefore, the "reversible" voltage of a PEM cell is expressed as

$$E = -\frac{\Delta g_f}{2F} = -\frac{\Delta g_f^o}{2F} + \frac{RT_{fc}}{2F} \ln \left[\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \right] \quad (2.4)$$

Table 2.1 Changes in Δg_f for a standard 1 bar pressure

Water phase	Temperature °C	Δg_f^o (kJ/mol)
liquid	25	-273.2
liquid	80	-228.2
gaseous	80	-226.1
gaseous	100	-225.2
gaseous	200	-220.4
gaseous	400	-210.3
gaseous	600	-199.6
gaseous	800	-188.6
gaseous	1000	-177.4

Expression 2.4 is the so called *Nernst voltage* of a PEM fuel cell. In practice, however, the open circuit voltage is smaller than what Eq. (2.4) predicts. In fact, the term $\Delta g_f^o/2F$ varies with temperature, and differs from its value $E_0 = 1.229$ V at standard conditions (25 °C, 1 atm) according with the following expression:

$$-\frac{\Delta g_f^o}{2F} = 1.229 + (T_{fc} - T_o) \left(\frac{\Delta S^o}{2F} \right) \quad (2.5)$$

where T_o is the standard temperature of reference (298 K), and ΔS^o is the entropy change for the new operating conditions. Therefore, the last equation can be rewritten as

$$-\frac{\Delta g_f^o}{2F} = 1.229 - \frac{298\Delta S^o}{2F} + \left(\frac{\Delta S^o}{2F} \right) T_{fc} \quad (2.6)$$

Using the standard thermodynamical relations regarding entropy changes [17], Eq. (2.4) can be written as

$$E = 1.229 - 0.85 \times 10^{-3} (T_{fc} - 298) + 4.3 \times 10^{-5} T_{fc} [\ln(P_{H_2}) + 1/2 \ln(P_{O_2})] \quad (2.7)$$

Additionally, the cell voltage varies with electric load conditions. This is due to electric losses, which can be classified as *activation*, *ohmic* and *concentration or diffusion* losses.

- Activation losses are important at low currents and reflect the fact that the cell requires a certain amount of energy to start electron circulation and create/break chemical bondings, both in the anode and the cathode [19]. This produces an important voltage drop at low current densities in both electrodes. It is worth noting that hydrogen oxidation at the anode is considerably faster than oxygen reduction at the cathode. Therefore, the dynamics of activation losses are always dominated by the cathode. The relationship between activation losses and current density can be described using the Tafel equation [18]

$$V_{act} = A \ln \left(\frac{i}{i_0} \right) \quad (2.8)$$

where the constant A is higher for slow electrochemical reactions, and i_0 is higher for fast reactions. The value of i_0 can be considered as the current density from which the voltage drop becomes evident. It is called *exchange current density* and its typical values are in the 10^{-2} – 10^{-8} A range. The Tafel equation is only valid for $i > i_0$. For a pure hydrogen fuel cell, A is given by

$$A = \frac{RT}{2\alpha F} \quad (2.9)$$

The constant α is known as the *charge transfer coefficient* and represents the amount of electric energy applied that is harnessed in changing the rate of an electrochemical reaction. Its value depends on the reaction involved and the material of the electrode, and falls in the 0–1 range.

- Ohmic losses are due to the resistance of the polymeric membrane to proton circulation, and also to the electrical resistance of electrodes and current collectors. Therefore, these losses are proportional to electric current in a wide operational range:

$$V_{ohm} = i \cdot R_{ohm} \quad (2.10)$$

The value of R_{ohm} represents the internal resistance of the cell and has a strong dependency with the cell humidity and temperature levels. It depends on the membrane conductivity (σ_m) and dry thickness (t_m) according to the following expression [26, 30]:

$$R_{ohm} = \frac{t_m}{\sigma_m} \quad (2.11)$$

For standard operating conditions, the following empirical expression is frequently used [30]:

$$V_{ohm} = (R_0 - R_1 \lambda_m) i \quad (2.12)$$

where λ_m is the membrane water content, defined as the number of water molecules per sulfonate group in the ionomer, and R_0 and R_1 are values to be experimentally determined.

- Diffusion losses are the result of changes in the concentration of reactants as they are consumed by the electrochemical reaction. This effect is responsible of an important voltage drop at high current densities. The non-uniform conditions arising at the porous electrodes discourage this as a desirable operation zone. A semi-empirical expression for this effect is [15]

$$V_{conc} = m e^{(n \cdot i)} + b \ln \left(\frac{P_{O_2}}{a} \right) \quad (2.13)$$

where m and n are empirical coefficients with typical values close to 3×10^{-5} V and $8 \text{ cm}^2/\text{A}$, respectively [17]. The last term is included to take into account concentration losses due to low oxygen stoichiometry values.

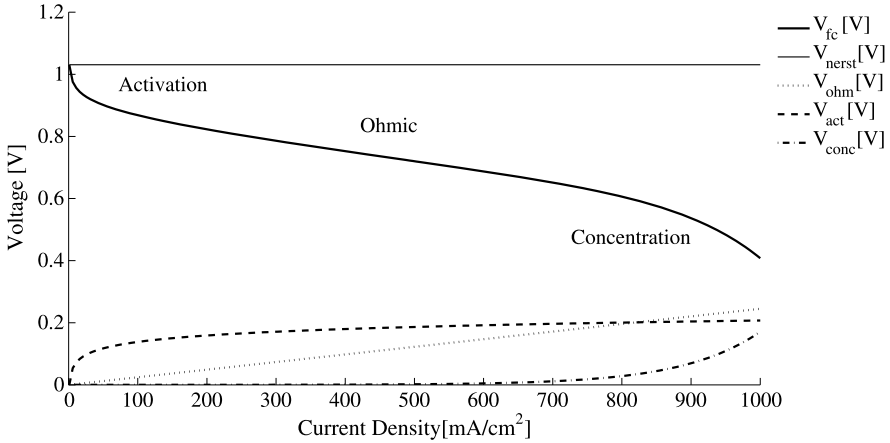


Fig. 2.1 Polarisation curve of a PEM fuel cell

Therefore, taking into account all the losses, the cell voltage can be written as

$$V_{fc} = E - V_{act} - V_{ohm} - V_{conc} \quad (2.14)$$

Replacing the values of the individual terms, the expression for (2.14) is

$$V_{fc} = E - \frac{RT}{2\alpha F} \ln\left(\frac{i}{i_0}\right) - (R_0 - R_1 \lambda_m) i - m e^{(n \cdot i)} + b \cdot \ln\left(\frac{P_{O_2}}{a}\right) \quad (2.15)$$

where α , i_0 , R_0 , R_1 , m , n , b and a are empirical parameters that take into account the different polarisation effects and are adjusted for a specific fuel cell stack, without loss of generality. A systematic procedure for the determination of these constants is outlined in Chap. 5. The resulting *polarisation curve* of a typical PEM fuel cell is shown in Fig. 2.1. It can be seen that the open circuit voltage is close to 1 V. In applications requiring higher voltage and power, several cells can be combined in series/parallel configurations to fulfil load demands.

2.3 Efficiency and Power Conversion

The efficiency of any energy conversion device is defined as the ratio between output and input useful energy. In the PEM fuel cell case, the available energy at the input of the device is the hydrogen's enthalpy (measured as the amount of heat that can be converted to work). If all the Gibbs free energy at the cell output is converted to electric energy, the efficiency results in

$$\eta_{max} = \frac{\Delta g_f}{\Delta H} = \frac{237.2}{286} = 0.83 \quad (2.16)$$

This is the maximum theoretical efficiency that a PEM fuel cell can reach at 25 °C. Using Faraday's constant and considering that there are two electrons involved in the reaction, the efficiency of a PEM fuel cell can be expressed as a quotient of voltages:

$$\eta_{max} = \frac{-\Delta g_f}{-\Delta H} = \frac{-\Delta g_f/2F}{-\Delta H/2F} = 1.229/1.482 = 0.83 \quad (2.17)$$

where $-\Delta g_f/2F = 1.229 \text{ V}$ is the theoretical voltage of an open circuit cell, and $-\Delta H/2F = 1.482 \text{ V}$ is the value of the thermoneutral voltage (that is, the resulting voltage if all the enthalpy of hydrogen is converted in electric energy). In this way, the efficiency of the cell at any condition can be obtained from the voltage at its output terminals (V_{fc}):

$$\eta = \frac{V_{fc}}{1.482} \quad (2.18)$$

2.4 State-of-the-Art in PEM Fuel Cells Technology

Current research efforts in PEM technology are mainly oriented to three basic directions: new components and materials, modelling of cell dynamics, and control.

- **Materials:** evolution of new components and devices, capable of efficient operation under wider ranges of temperature, humidity and gas purity is required to broaden the spectrum of applications currently devised for PEM fuel cells. This includes aspects related to fabrication and operation of membranes and electrodes, manufacturing processes, design and characterisation of components. Research in membranes is oriented to thermostable polymers (*polyetheretherketone*, *polysulphone*, etc.) and composite membranes capable to operate at temperatures above 100 °C and lower humidity levels than the actual commercial membranes [31]. Regarding electrodes, most efforts are centred on reducing the amount of platinum required in catalysts and improving gas diffusion layers. Advances in the production, transport and storage technologies are also necessary, to make hydrogen an economically viable alternative [15].
- **Cell Dynamics Modelling:** better understanding of the processes involved in fuel cell operation, both at the membrane level and the auxiliary subsystems (compressors, line heaters, humidifiers, etc.), is helping engineers to develop dynamic models suitable for the design of more reliable, compact and efficient devices. This is also widening the spectrum of applications of PEM fuel cells, making them attractive alternatives in fields traditionally reserved to other types of cells, for instance, in stationary, high-power installations. On the other hand, accurate models of gas distribution and fluid dynamics inside cells are improving the predictability of electrochemical processes, with direct impact on design strategies.
- From the *automatic control* perspective, efforts are conducted to the development of robust, nonlinear strategies capable to improve efficiency and reliability of PEM cells, avoiding permanent damage to membranes. Robustness is required

to take into account the intrinsic uncertainty in the system model and to avoid expensive or cumbersome (even impossible) measurement of certain variables. Additionally, nonlinear control strategies usually allow wider operation ranges than “local” approaches that linearise the system around equilibrium points. For commercial success, it is also important to develop models and strategies to diagnose and predict failure situations.

2.5 Components and Associated Devices

2.5.1 Polymeric Membranes

Membranes in a PEM fuel cell must have a relatively high protonic conductivity and also act as suitable mechanical barriers to avoid mixing of comburents and reacting gases. Additionally, they must be chemically stable for the entire operation range. Standard membranes are made of *perfluorosulfonic acid* (PFSA). This material is, essentially, a copolymer of tetrafluoroethylene (TFE) and several sulfonated perfluor monomers. The most popular commercial membrane is Nafion[®], made by Dupont, which uses *perfluoro-2-(2-fluorosulfonylethoxy) Propyl Vinyl Ether* (PSEPVE). Similar materials are produced by several companies, such as Asahi Glass (Flemion[®]), Asahi Chemical (Aciplex[®]), Chlorine Engineers (C Membrane[®]), etc. Dow Chemical has developed a composite membrane called GoreSelect[®], using a Teflon-like material.

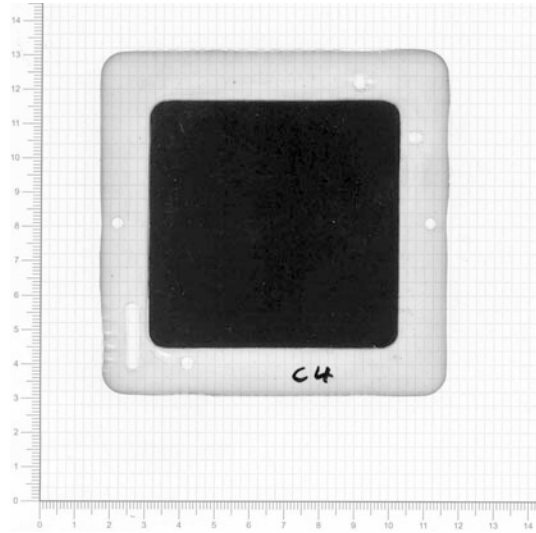
Important features of membranes suited for PEM fuel cells are protonic conductivity, water transport properties, gas permeability, mechanical resistance and dimensional stability. These parameters strongly depend on the membrane water content. The water content is usually expressed as the weight rate of water and dry polymer or, alternatively, the rate between the number of water molecules per sulfonic groups present in the polymer. The maximum amount of water in a given membrane depends heavily on its previous preparation [11].

Regarding its critical role on protonic conduction, it is important to keep a proper membrane water content at all possible operating conditions. Several mechanisms affecting water transport are present in a PEM fuel cell, and their combined effects determine the amount of water present. Among them, the most relevant are the following:

- Water generation on the cathode side, at a rate proportional to the electric current produced.
- Electro-osmotic drag, produced by water molecules dragged by the proton flow from anode to cathode.
- Diffusion, due to the water concentration gradient across the membrane.
- Water permeability, due to the pressure difference between anode and cathode channels.

In thin membranes, diffusion can be compensated by the drying effect produced by electro-osmotic drag at the anode. In thick membranes this drying effect can be

Fig. 2.2 PEM fuel cell Membrane and cathode. Effective area is 50 cm^2 . IRI (CSIC-UPC)



more important, especially at high current densities. An ideal electrolyte should be impermeable to reactant gases, to avoid gas mixing inside the cell. However, due to its porous structure, water content, and the solubility of hydrogen and oxygen in water, small amounts of reactant gases can pass through the membrane. It is worth noting that hydrogen has a permeability one order of magnitude higher than oxygen [4].

2.5.2 Electrodes

Electrodes in PEM fuel cells are basically catalytic layers placed between the polymeric membrane and an electrically conducting substrate. This is where the electrochemical reactions take place. Given that gases, electrons and protons react in the surface of electrodes, their efficiency can be improved increasing its rugosity (effective area), reducing catalyst particle size and/or incorporating ionomeric material (a one-ion polymer) in the catalyst. The later can be accomplished by painting the electrode with a PFSA solution in a mix of alcohol and water, or simply mixing the ionomer and catalyst in the preparation of the catalytic layer. A 30 percent ionomer content in the catalytic layer is typical.

The catalyst most usually employed in both electrodes of PEM fuel cells is platinum. In the early stages of PEM fuel cells development, important quantities of platinum were used (more than 28 mg/cm^2). By the end of the 1990s this amount was reduced to $0.3\text{--}0.4 \text{ mg/cm}^2$. Considering that the effective area of catalyst is of paramount importance, it is crucial to achieve a fine dispersion of catalyst particles in the support material, usually carbon powder [29].

The combination of electrodes and polymeric membrane is known as *Membrane-electrode assembly* (MEA). There are basically two different approaches for its con-



Fig. 2.3 Toray paper diffusion layers. IRI (CSIC-UPC)

struction. In the first one, the catalyst is deposited on a porous substrate called *gas diffusion layer*, which is typically a carbon fibre paper. These are then placed at both sides of the membrane using heat and pressure to ensure proper contact. In the second approach, the catalyst is deposited directly on the membrane, an arrangement known as *catalysed membrane*. A porous substrate is then added, resulting in a five-layer MEA (Fig. 2.2). Several techniques can be used for deposition of catalyst on diffusion layers and membranes (*spreading, spraying, sputtering, painting, screen printing, decaling, electro-deposition, evaporative deposition, impregnation reduction, etc.*), and many other proprietary approaches exist.

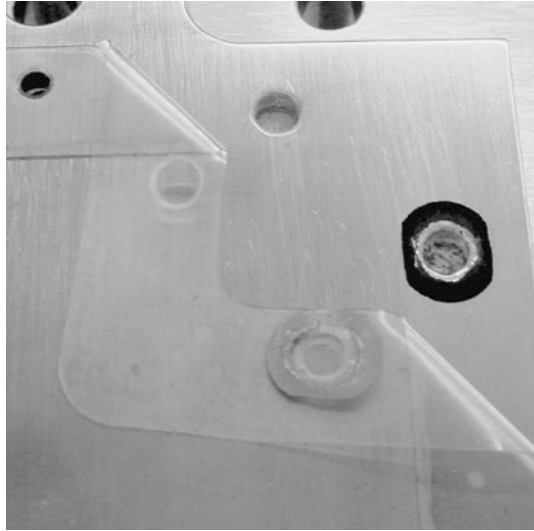
2.5.3 Gas Diffusion Layers

The main purpose of gas diffusion layers is conducting and spreading reacting gases from bipolar plate channels to the MEA. They are typically made of porous materials. Regarding desirable properties of diffusion layers, the following aspects must be considered:

- *Porosity* must be such that the flux of reactants and water is efficient. Note that both flows are in opposite directions.
- *Electrical and thermal conductivity* must be high. The contact resistance or interface is typically dominant versus the volume conductivity.
- Given that the catalyst is a discrete material (small particles), diffusion layer *pore size* cannot be excessively big.
- They must provide proper *mechanical support* to the membrane. However, some degree of flexibility is required to provide good electrical contact.

Although conflicting somewhat, these requirements are typically fulfilled with carbon fibre-based papers and cloths (Fig. 2.3). These materials are usually made hydrophobic to avoid flooding in the structure. To achieve this, diffusion layers are usually treated with polytetrafluorethylene (PTFE), a polymer similar to polyethylene. To improve electrical properties, a microporous layer made of carbon or

Fig. 2.4 Sealing gasket placed over a current collector. IRI (CSIC-UPC)



graphite particles mixed with PTFE is added, resulting on pore sizes of 0.1–0.5 μm , which are much smaller than the carbon fibre pores (20–50 μm) [21].

2.5.4 Sealing Gaskets

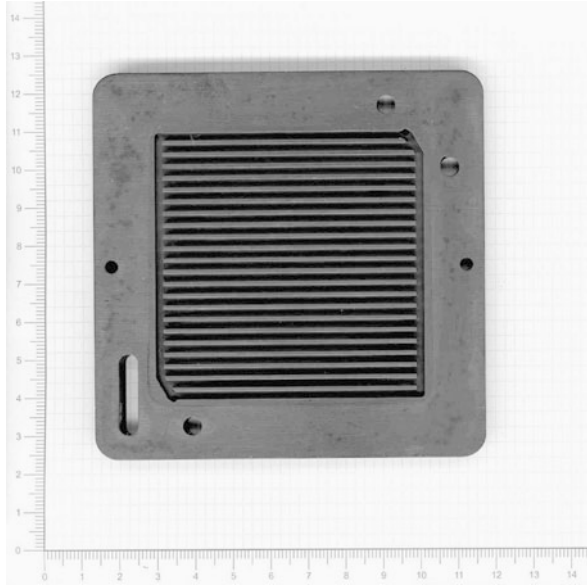
These components provide *mechanical sealing* among bipolar plates and diffusion layers. Their purpose is twofold: on one hand, minimising leaking of gases to the exterior of the cells and, secondly, avoiding the mixing of reactant gases near the catalyst areas (Fig. 2.4). However, it is worth noting that a certain amount of hydrogen is expected to pass through the membrane by diffusion. This can be computed from the number of cells, their width and type, effective area, partial pressures and working temperature. Sealing gaskets avoid direct combination of reactants, which in turn can produce irreversible damages to cell components [12]. Most sealing gaskets are made of silicone, neoprene or plastic polymers, with additional fibre materials to improve their mechanical properties.

2.5.5 Bipolar Plates

Bipolar plates, also called collectors or separators, have many functions in a fuel cell system [4]. Among others, the most relevant are the following:

- Electrical connection between individual cells of the stack.
- Separation of gases among adjacent cells. Thus in PEM fuel cells they must be impermeable to H_2 , O_2 and N_2 .

Fig. 2.5 Graphite bipolar plate. IRI (CSIC-UPC)



- Structural support to the cell. Robustness and light weight are mandatory.
- Efficient heat conduction.

In addition, bipolar plates must be corrosion resistant, which make them expensive. In most PEM cells pH is between 2 and 3, and temperatures are in the 60–80 °C range. These environmental conditions discourage the use of traditional choices like aluminum, steel, titanium or nickel. Corrosion produces ions of metal which can diffuse through the membrane, affecting its ionic conductivity, reducing its lifetime and increasing its electrical resistance. For this reason, metallic plates are usually coated with non-metallic conductive materials, such as graphite, diamond carbon, conductive polymers, organic polymers, noble metals, metallic nitrides, tin-doped indium, etc. Bipolar plates can also be made of thermoplastic materials, such as polypropylene, polyethylene and polyvinylidene fluoride. Thermosetting resins (phenolic, epoxy, etc.) are also used, with the addition of graphite and fibre reinforcing (Fig. 2.5).

An important property of bipolar plates is their electrical conductivity. In graphite composites, typical values range between 50 and 200 S/cm. Although pure graphite has a conductivity of 680 S/cm, metallic plates have values an order of magnitude higher. Note that the overall conductivity of the cell is always lower than the material conductivity, due to the contact resistance among components.

In Fig. 2.6, a schematic representation of a typical PEM fuel cells stack is presented, where all the components described above can be visualised.

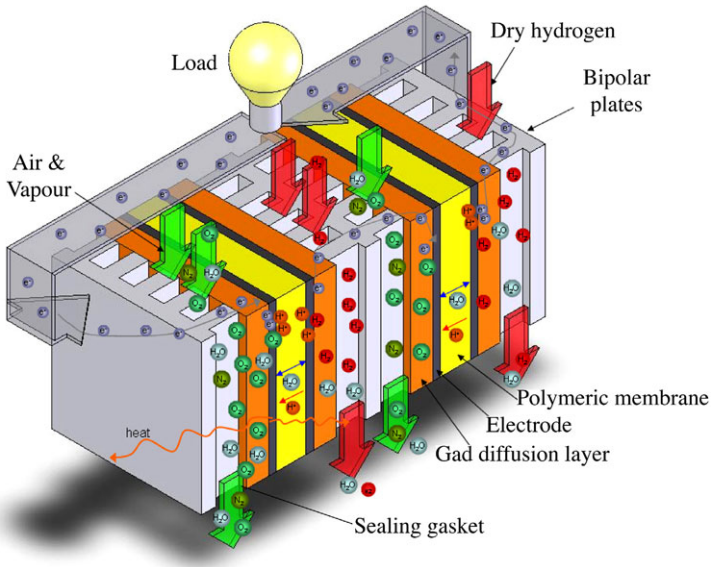


Fig. 2.6 PEM fuel cell stack scheme [13]

2.5.6 Auxiliary Devices

2.5.6.1 Air/Oxygen and Hydrogen Supplies

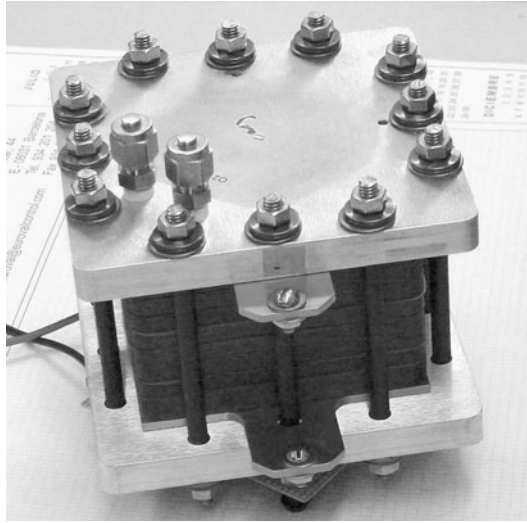
In PEM fuel cell stacks, air can be supplied by means of a compressor, a fan or a compressed air source, although the latter is mostly used only in laboratory settings. Fans are customarily used in open-cathode designs working at ambient pressure. Air compressors give autonomy and flexibility to the system, allowing precise control of working pressures. Usually, both compressors and fans are electrically connected to the stack, becoming part of its losses or parasitic loads and thus reducing the amount of energy available to external loads. This results in a significant reduction of the overall performance of the system as an energy conversion device.

At the time of this writing, PEM cells require a high-purity hydrogen supply ($\text{CO} < 20 \text{ ppm}$). Hydrogen storage for PEM cells is a matter of active research, the main options being compressed gas, cryogenic liquids and solid metallic hydrides.

2.5.6.2 Water and Heat Management

Water management in individual PEM cells and cell assemblies is a technological challenge. For proper operation, membranes must be totally saturated of vapour but, in order to ensure optimum performance, excess water must be efficiently removed (especially from the cathode line). Ionic conductivity in the polymeric membrane is directly related to its water content, which in turn affects the conversion efficiency

Fig. 2.7 A PEM fuel cell stack, showing the series connection of individual MEAs. IRI (CSIC-UPC)



at each operation point. The amount of liquid water and membrane humidification levels can be modified by controlling the relative humidity of the reacting gases, as well as their individual pressures and temperatures.

Temperature is as important as water content, and both magnitudes are closely related. PEM fuel cells are intended to operate at high power densities ($>0.5 \text{ W/cm}^2$), but, apart of new high-temperature membranes, the most widespread technology now prevents operation at temperatures above 100°C . This small gap between operational and ambient temperatures makes it difficult to remove the 1.3 W of heat produced for each watt of electric power generated.

2.5.6.3 Electrical Conditioning

Output power of a fuel cell is not regulated, and its stability is a relevant issue. The small voltage of each individual cell is heavily influenced by changes in electric current, partial gas pressures, reactants humidity level, gas speed and stoichiometry, temperature and membrane water content.

According to Eqs. (2.6) and (2.7), the maximum voltage of a single PEM cell is close to 1.229 V . Higher power and voltage is obtained connecting individual cells in series/parallel configurations (Fig. 2.7). Then, an electronic conditioning system is necessary to meet load requirements. For instance, DC/DC converters can be used to extend the range of operating voltages or provide specific voltage values. The combination of a DC/AC stage and a transformer can be used to ensure electric isolation between load and stack, converting DC to an intermediate AC frequency and using a decoupling transformer and a rectifier. Usually an auxiliary power source is necessary to start the stack operation. In the special case of autonomous systems, power converters associated with a supervisory electronic control are required to ensure proper management of batteries or super-capacitors charge/discharge cycles.

2.5.6.4 Humidification

Proper humidification of polymeric membranes is an important matter. At moisture levels below recommended values, ionomer water content falls, reducing conductivity and adversely affecting the kinetics of reduction and oxidation reactions.

Water content of an MEA depends on many factors and is closely related with operating conditions. For instance, in open circuit and also at low current densities, the small water production by oxygen reduction causes the MEA humidification levels to decrease, although the reacting gases are saturated with vapour. This is because water absorption in perfluoro-sulfonated membranes is lower when the membrane has been equilibrated with vapour instead of liquid water. Besides, at higher current densities, the electro-osmotic dragging of water through the membrane tends to dry the anode. An additional problem in this case is the eventual cathode flooding due to the excess of water produced by the electrochemical reactions.

Under certain conditions, the amount of water produced by oxygen reduction at the cathode suffices to keep proper membrane hydration. However, this fact does not ensure an equilibrium point in water content. In most cases, a gas humidification system is required, at least in the cathode line, to control this important performance variable. Humidity control is a challenging task, because moisture levels in both channels are coupled and many perturbation (known and unknown) exist. Besides, humidification requirements can be in conflict with other control objectives, such as oxidant stoichiometry. For instance, in certain situations the optimal humidity level could be incompatible with the most efficient reactant flux level required to satisfy electric load demands. In such a case, a problem arises because it is difficult to suspend instantaneously the cathode humidification if the cells start to flood. On the other hand, it is also impossible to increase hydration levels at low currents when the cell starts to dry.

Among the many techniques for gas humidification, the main alternatives are the following:

- **Gas bubbling.** This is a method mostly used in laboratory applications for relatively low flows, being seldom used in commercial devices. It involves circulating air or hydrogen through a porous tube immersed in liquid water at a regulated temperature. The resulting bubbles provide a relatively big contact area between gas and water, allowing proper humidity transfer. Moisture level is controlled by varying water temperature. In a well-designed system, emerging gases are saturated of vapour at the water temperature. The main drawback of this approach is the presence of water droplets in the outgoing gas. This affects gas diffusion in the MEAs, reducing the overall efficiency.
- **Direct vapour injection.** This is the most compact, efficient and easy to control method. A fine mist is injected in the gas stream using a small pump. An additional heat source is usually required to produce complete water evaporation if hot water enthalpy solely does not suffice. Moisture level is directly controlled by varying the amount of vapour injected [4].

- Water exchange through a permeable material. In this approach, gases are circulated on one side of a permeable membrane such as Nafion[®]. De-ionised, temperature-controlled water circulates on the other side of the membrane. During the process, a moisture gradient is established, which allows water transfer via diffusion through the membrane. The amount of water transfer is controlled by varying its temperature.
- Enthalpy wheel. In this passive method the water and heat content of a gas can be transferred to other gas using a thermal process. It comprises a cylinder that interfaces two parallel conducts, where gases at different humidity and temperature circulate in opposite directions. The cylinder is filled with a permeable material, to provide a large interface area for energy transfer. As the wheel rotates between the ventilation and exhaust gas streams, it takes heat energy and releases it into the colder gas stream. The driving force behind the exchange is the thermal gradient between the opposing gas streams. The enthalpy exchange is accomplished by the use of desiccants, which transfer moisture by adsorption. This effect is predominately driven by the difference in the partial pressure of vapour between the gas streams.

2.5.6.5 Gas Heating Lines

These devices are inserted in the gas path to provide temperature control, independently from the humidification process. Basically they are made of heating resistances, with protective stainless steel shielding. In PEM fuel cells, the main objective of the heating lines is keeping gas temperature high enough to avoid condensation inside cell channels.

The comprehensive block diagram presented in Fig. 2.8 shows a typical laboratory set up of a PEM-based generation system.

2.6 Available PEM Fuel Cell Models in the Open Literature

Accurate mathematical models of PEM cells behaviour are subject of current interest and active research. Dynamics of the electrochemical reactions that take place in the MEAs and the ancillary devices required for operation of the cell constitute a nonlinear, highly coupled multi-variable dynamic system. In control applications, the interest is focused on the development of *reduced-order* nonlinear dynamical models relating *smooth vector fields*. This is usually required in the design of many nonlinear control strategies.

A suitable model should be capable of predicting the dynamic and stationary behaviour of the fuel cell in a wide range of operating conditions. Important variables to be taken into account are temperature and relative humidity of interacting gases, partial pressures (hydrogen, oxygen, nitrogen and water vapour), velocities of flows in the MEAs channels, electric currents and voltages, etc. Although many models of PEM fuel cells have been reported, only a few are suitable for their use in nonlinear control design.

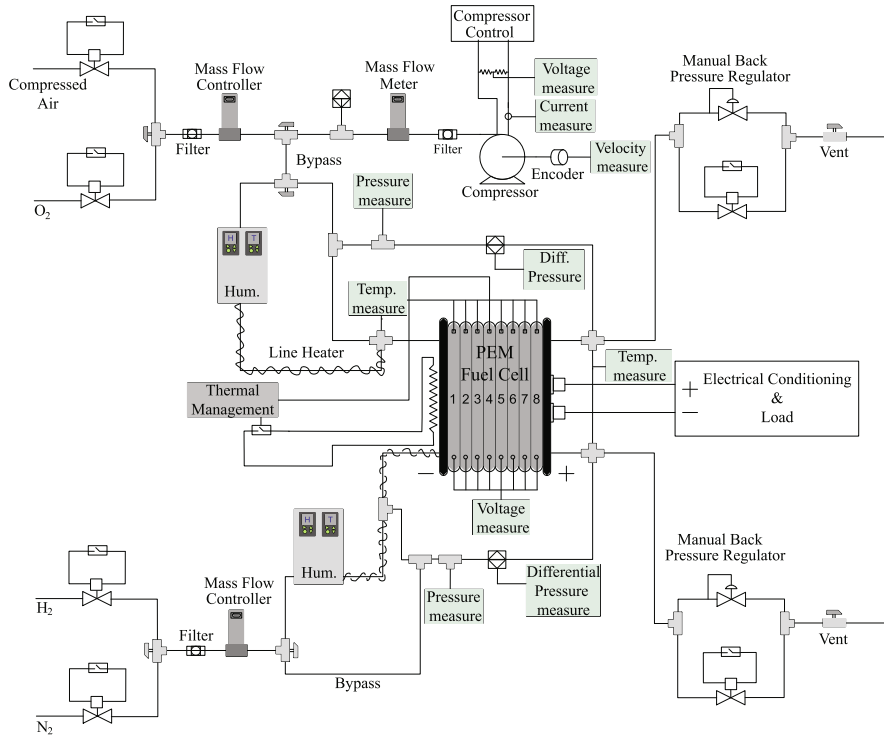


Fig. 2.8 PEM fuel-cell-based system scheme

2.6.1 Control Oriented Models

PEM fuel cell modelling has been studied by several recognised authors and with different approaches [2, 20, 27, 28]. However, many of these models have not been experimentally validated, and there is still a lack of rigorous studies on parameters identification and their association with performance variables. On the other hand, there are few models and methodologies specifically oriented to control design. For example, the first models from the open literature, as the ones presented in [2] and [30], are essentially electrochemical characterisations based on empirical relationships that do not consider gas dynamics. More recently, works such as [8, 9, 27, 28] have presented extended equations, including gas dynamics and temperature effects inside the cells. However, only [28] and [9] have proposed fully analytical control oriented models. In [9], the model considers only three of the six states of a typical air supply subsystem, the humidification phase is not included, and characterisation of the other subsystems is only briefly described. In [28] it is presented probably the first proposal of a PEM fuel cell stack model, fully validated and especially developed for control engineering, and it is the basis of numerous works such as [5, 14, 27]. Changes in the liquid water and oxygen concentrations, as well as temperature, have significant effects on the PEM fuel cell performance and may even affect its

durability. All these variables exhibit a spatial dependence along anode and cathode channels, and therefore it is necessary to incorporate control mechanisms to keep them within their nominal values [20].

2.6.2 Control Objectives and Challenges

PEM fuel cell systems have many advantages over traditional alternatives such as internal combustion engines. However, a number of technical issues must be faced to make them competitive. Among them, operational costs, lifetime and reliability are of vital importance.

From the automatic control perspective, a PEM fuel cell is a nonlinear multiple-input–multiple-output (MIMO) dynamical system with strongly coupled internal variables, external perturbations and parameter uncertainties. Its normal operation is always associated with the generation and transport of liquid water, vapour and gas mixtures, spontaneous electrochemical reactions, exothermic processes and thermal conduction. By their very nature, they are sensitive to changes on operation conditions (power demand, partial pressures and relative humidity of reacting gases, temperatures, etc.) and also susceptible to potential damage. Three basic degradation mechanisms can be clearly distinguished: mechanical, thermal and electrochemical. Among the mechanical processes that produce a significant degradation, the cycles of humidification/drying play a decisive role, as they cause membrane expansion/shrinking. This leads to mechanical stress of the membranes and gaskets. Additionally, the thin polymeric membranes currently used make the system potentially vulnerable to abrupt pressure changes between channels, excessive temperature and low relative humidity conditions.

Thermal degradation arises when considerable temperature variations occur in the stack, even within the range usually recommended by manufacturers of PEM fuel cells (60–80 °C). These thermal cycles, which in some cases can be extreme (e.g. those driven by cold starts and sudden high power demands), produce accumulative mechanical damages that affect the resistance contact between the membrane and electrodes, as well as the mechanical resistance, conductivity and permeability of the polymeric membranes. In fact, heat management is recognised as one of the most important issues in high-power PEM cells. This is due to the fact that under normal conditions, the cell produces as much heat energy as electricity. This means that in an automotive 100-kW fuel cell it is necessary to provide a structure capable of dissipating 100 kW of heat, which is particularly difficult if the operating temperature is only 80 °C. This operating temperature is a restriction imposed by the materials employed. Besides, temperature cannot be lower than 60 °C, to avoid water condensation inside cell channels, which would result in a voltage drop, caused by a reduction of gas mass transport to the membrane.

Regarding the electrochemical mechanisms of degradation, it is important to state that the chemical reactions on the catalysts produce small amounts of peroxide radicals (HO) or hydroperoxide (HOO) that are responsible for the chemical degrada-

tion of the membrane and its catalyst. The production of such radicals is accelerated when the fuel cells operate in open circuit or low humidity conditions.

Another issue which deserves special attention is oxygen control. If the oxygen flow is too low, undesirable hot spots appear in the membrane, and output power decreases because of the lack of reactants, a situation called *cathode starvation*. On the other hand, if oxygen flow is too high, an excessive amount of water is pushed to the cathode outlet, which in turn results in membrane drying, which affects its ionic resistance. Besides, an increase of the air flow results in higher power demand to the compressor that supplies it, reducing the overall system performance. Thus, an efficient control system must be capable of regulating air flow properly, avoiding irreversible damages to the membrane and delivering enough oxygen to meet the electric power demand in a reliable and efficient way.

2.6.3 Recent Advances on PEM Fuel Cell Control

During the last years, several control proposals have been made for PEM fuel-cell-based systems. Many examples can be mentioned. For instance, in [38] fuel cell power output is directly regulated by limiting its hydrogen feed. This is achieved using a PID control that varies the internal resistance of the membrane-electrode assembly in a self-draining fuel cell with the effluents connected to water reservoirs. In [35] cathode oxygen is regulated through a feedforward loop, and temperature is controlled using a proportional control, to ensure stack performance around an optimal operation point, where net power is maximised. In [23] a MIMO system is considered, with hydrogen and coolant as inputs and power density and temperature as outputs. Those variables were selected from a steady-state analysis using a relative gain array (RGA) technique. Two PID controllers were used, and simulation results suggest that the design can be accomplished from two decoupled SISO systems. In [34] and [3] predictive control approaches are considered, allowing improvements on the response of the air supply and efficiency optimisation in fuel cell stacks. In [28] a dynamic model of the air supply subsystem of a PEM cell is presented. Based on this model, an LQR controller was designed to decouple the air mass flow from cathode pressure. Reported results favourably compare against a standard PI controller. A substantial improvement was made in [37] where, from a linear identification of a fuel cell system, a H_∞ controller was designed to regulate the cell output resistance and control output voltage, manipulating input gases flows.

Alternatively, several proposals have been made regarding hybrid power generation configurations. In these systems, a fuel cell stack is usually combined with different energy storage devices, to provide a more reliable power source. Ultracapacitors [33] can be included to improve power transients using, for instance, PID controllers to regulate DC bus voltage. In [18] and [7] a hybrid system made from a fuel cell and batteries is proposed. In this approach, fuel cells are used for low power demands, while battery banks supply additional energy for higher power requirements, when the cell tends to reduce its output voltage. In such cases power

converters can also be used to improve efficiency and extend operating ranges of the stack. For instance, in [36] resonant soft-switching techniques are used to adjust the output voltage of a 250-W PEM fuel cell.

Most of the above approaches are based on linear models, providing interesting solutions that efficiently solve different control objectives [10, 27, 39]. However, an important issue such of robustness against parametric uncertainty and external perturbations have not been addressed in depth. Besides, the validity range of these controllers is local, and results do not extend to the entire operation range. Solutions to this problem can be found in the nonlinear control field, such as [1] and [24, 25], where strategies based on parametric cerebellar model articulation and exact linearisation were addressed, respectively. More recently, in [6] a methodology based on an energetic macroscopic representation of the fuel cell stack is proposed. Good global performances were attained with these nonlinear techniques, but, regretfully, their applicability in real systems is still limited because the algorithms demand considerable computational burden.

Therefore, despite these advances in fuel cell controllers, it is evident that to meet the expected enhanced capabilities, a substantial R&D work is still necessary, and a control approach particularly suitable to cope with their challenging features is of high interest. At this point, Sliding-Mode control emerges as an especially apt technique to tackle the complex characteristics inherent to fuel cell systems (e.g. high nonlinear dynamics, inaccessible variables, model uncertainties and disturbances). In addition, the on-line computational burden of the resultant algorithms can be conveniently low. Promising results have been obtained with sliding mode controllers for fuel cell systems [16, 22, 32], strongly encouraging the prosecution of research in this direction.

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