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Fuel Cells: Alternative Energy Sources for Stationary, Mobile and Automotive Applications

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Abstract

This paper presents a classification and also an overview of fuel cells, including the working principles, the equations of the governing reactions, and the main applications. A brief exposure of thermodynamics and electrochemical theory describe the functioning of the fuel cells. Further, the proton exchange membrane fuel cells assembly, starting with the schematic presentation of the main components, the role of each component in fuel cell, the specific materials and their requested properties, and the way of assembling the components into device will be detailed. In conclusion, the challenges related to reliability and the cost and the targets for future development of the proton exchange membrane fuel cells for mobile and stationary applications will be presented.

Keywords: fuel cells, proton exchange membrane, catalyst layer, gas diffusion layer, membrane electrode assembly, bipolar plate

1. Introduction

The stringent request for green energy sources and technology turned the attention of the scientific world to the chemical energy conversion systems known as fuel cells (FC). The possibility to convert chemical energy to electricity was discovered in the first half of nineteenth century and the invention of the fuel cells was attributed to Sir William Grove [1, 2].

Fuel cells are electrochemical devices able to convert chemical energy to electricity through controlled oxidation-reduction (REDOX) processes. They behave as open systems which produce electricity as long as they are fed with fuel and oxidant. Commonly fuels, hydrogen (H_2) and methanol (CH_3OH) are compounds with small molecules and high density of chemical energy, considered energetic vectors. Basically, a fuel cell consists in two electrodes, anode and cathode, separated by an electrolyte. The cathode is always the positive electrode and the anode is the negative one as the electrons flow from negative to positive electrode. During operation the fuel is continuously fed to the anode while oxidant (oxygen or air) is continuously fed to the cathode.

Fuel cell systems are used as power sources for mobile, automotive and stationary applications including back-up power systems [3]. They can be single energy conversion devices (the low temperature operating fuel cells) or can operate in co-generation electrical/thermal energies (the high temperature fuel cells).

The advantages of fuel cells are the high efficiency and the decrease or even absence of harmful emission. Wang et al. [3] give a value up to 60% of efficiency in electrical energy conversion and for systems in co-generation of electrical and thermal energies the global efficiency reach 80%, both applications yielding less than 10% pollution. Particularly, the electrochemical reactions from inside the hydrogen fuel cells yield just water and heat.

Hydrogen can be produced in many ways: reforming of fossil fuels, hydrolysis of hydride type compounds or water electrolysis. It can be stored in special tank, under pressure, absorbed in hydride or metal organic framework, included into the structure of organic liquid compounds, or compactly stored in cryogenic form. The oxidant is gaseous oxygen extract from air or even purified air.

An economy based on fuel cell should be the economy of the future, free of greenhouse emissions and independent of fossil fuel. There are still many challenges related of materials and processes optimization for reaching the targets of operating life 5000 hours for automotive and 40,000 hours for stationary application [4] in terms of cost reduction.

2. Classification

According to the type of electrolyte and fuel which determine the electrodes reactions there are several kinds of fuel cells which differs by the electrolyte and others behaviors: Alkaline Fuel Cells (AFC), Proton Exchange Membrane Fuel Cells (PEMFC), Alkaline Fuel Cell (AFC), Direct Methanol Fuel Cells (DMFC), Microbial Fuel Cell, Phosphoric Acid Fuel Cells (PAFC), Solid Oxide Fuel Cells (SOFC), Molten carbonate Fuel Cells (MCFC).

The **Proton Exchange Membrane Fuel Cells (PEMFC)** use protons (H^+) as available mobile ions and a hydrated proton exchange membrane with the role of electrolyte. PEMFCs operate at temperatures between 30 and 100°C, with platinum electro-catalyst and carbon based electrodes.

The half reactions at each electrode are:

- oxidation of hydrogen to anode:



- reduction of oxygen to cathode:



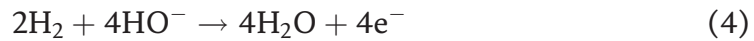
- The overall reaction is:



where Q is thermal effect—heat—produced in reaction.

In **Alkaline Fuel Cells (AFC)** the charge carriers are hydroxyl ions (HO^-) and the electrolyte is alkaline solution, usually 30–45 wt% KOH in water. Particularly, electrolyte solution is immobilized in a solid matrix, typically asbestos. The operating temperature range varies between 65 and 220°C and with platinum or transition metal catalysts to electrodes [5].

At the anode, hydrogen is oxidized in reaction with mobile hydroxyl ions, releasing electrons and producing water:



Resulted electrons pass to cathode through an external electrical circuit and generate electrical current. The reaction at the cathode consists of oxygen reduction with the electrons coming from the anode, in the presence of water, forming HO, which keep going the charge transport:



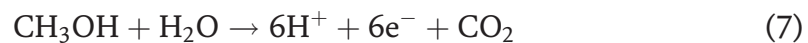
The overall reaction is:



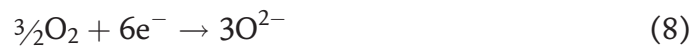
Even that the overall reaction is the same as that in the PEMFC the half reactions to each electrode differ.

Direct Methanol Fuel Cells (DMFC) is a special kind of polymer electrolyte fuel cell which is fed direct with methanol. Both Acid and Alkaline Fuel Cells could be feed direct with methanol, but there differ considering the mobile ions and the electrode reactions.

In an acid fuel cell a mixture of methanol and water is supplied at anode where methanol oxidation takes place [5, 6]:



The half electrochemical reaction at the cathode is oxygen reduction:



In the Alkaline Fuel Cell, methanol oxidation occurs to anode in the presence of hydroxyl ion:



To cathode, the oxygen reduction occurs in the presence of water and results hydroxyl:



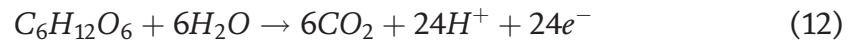
For both fuel cells, the overall reaction is:



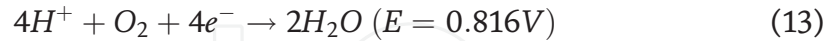
Microbial Fuel Cells (MFCs) are bio-electrochemical systems that can use microorganisms to produce electricity from a wide variety of organic compounds [7], being considered a promising source of sustainable energy, and thus they are considered a fast growing [8, 9] area of fuel cells research. Since the abiotic fuel cells are using platinum as catalyst (expensive), while MFCs are using microorganisms as biocatalysts, MFCs may be potentially more advantageously than abiotic fuel cells [10]. In a MFC, the transfer of electrons to anode surface occurs firstly via transformation of organic substrates from anodic chamber usually to CO_2 and generating electrons, eventually discharged on surface of the anode, and also protons. The excess of protons migrate to the cathode via a separator (i.e., Nafion) [11], while oxidizing species like oxygen are accepting electrons at the cathode surface, thus generating an electrical current through an external circuit. The electrochemical

processes within a typical MFC can be described by the following generic chemical equations:

Anode:



Cathode:



Nevertheless, since the voltage generated by a MFC is relatively small (in most cases between 0.5 and 0.8 V), multiple MFC systems can be stacked in series to increase the overall voltage and power [12], or in parallel to increase the overall current intensity. Nevertheless, this technical approach is challenging due to voltage reversal [13, 14] and other problems (e.g., energy losses, fluctuation of power outputs, etc.) associated with the non-linear nature of biological systems [15] (i.e., variability in exponential growth of microorganisms, etc.). Therefore, further research is needed in the field of MFCs in order to make them reliable tools in generating sustainable energy.

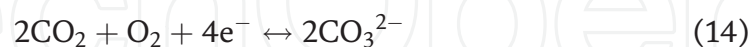
Phosphoric Acid Fuel Cell (PAFC) is acid type fuel cell with ionic conduction provided by protons (H^+) transport. The electrolyte is concentrated (100%) phosphoric acid, immobilized, in the liquid phase, into a silicon carbide (SiC) matrix. Phosphoric acid has poor ionic conductivity at low temperature under $100^\circ C$ but express the optimum conductivity between 150 and $220^\circ C$ [5]. At this temperature, platinum electro-catalyst is tolerant at CO poisoning. Both anode and cathode catalysts are Pt/C and Pt alloys on carbon.

Reactions occurring at the electrodes are the same that occurs in PEMFC (Eqs. (1)–(3)).

Major applications of PAFC are in stationary power plants and on-site cogeneration power plants [6].

In **Molten Carbonate Fuel Cells (MCFC)**, the electrolyte is a binary mixture of molten carbonate salts, such as lithium and potassium/sodium carbonate. These salts, highly conductive in the molten state at 600 – $700^\circ C$ are included into a ceramic matrix of double oxide $LiAlO_3$. The mobile ion is carbonate $(CO_3)^{2-}$, produced from carbon dioxide fed to cathode. The electrodes half reactions are:

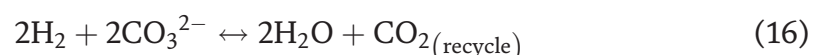
Cathode reaction:



Anode:



Overall reaction:



At this high temperature the Ni (anode) and NiO (cathode) are suitable catalysts to promote the electrochemical reactions, and the noble metal catalysts are not required. The MCFCs can use common hydrocarbon fuels as sources able to provide hydrogen and CO_2 by internal reforming. Severe corrosive electrolytes and high operating temperatures require special materials as nickel or high-grade stainless steel for cell hardware [5, 6].

Solid Oxide Fuel Cells (SOFC) is total solid devices operating in the high temperature range of 600°C -1000°C. However, in the last few years it is a noticeable effort to decrease the operating temperatures. A metal catalyst is not needed because the reaction kinetics are improved using the high operating temperatures which constitute an advantage of these fuel cells technology. Compared to other types of fuel cell, SOFC are relatively resistant to small quantities of sulfur in the fuel therefore can be used with coal gas.

The ion conduction is accomplished by the oxygen ions O^{2-} , which pass through an electrolyte composed from zirconia (ZrO_3) doped with 8–10% mole ratio of yttria (Y_2O_3).

The major components of an individual SOFC cell include the electrolyte, the cathode, and the anode and the following reactions take place: Anode reaction:



or



Cathode reaction:



Overall reaction:



The electrolyte, such as zirconium oxide stabilized with yttrium oxide, determines the operating temperature of the fuel cell and is used to prevent the two electrodes to come into electronic contact by blocking the electrons. It also allows the flow of charged ions from one electrode to the other to maintain the overall charge balance.

The operating principle of such a cell is illustrated in **Figure 1**.

At anode, electrochemical oxidation of fuel gas such hydrogen H_2 or carbon monoxide CO takes place (Eqs. (17) and (18)). The anode scatters the hydrogen gas over its whole surface and conducts the electrons that are freed from hydrogen molecule, to be used as power in the external circuit.

The oxygen, usually carried by air, is reduced by reaction taking place the cathode, described in equation from above (Eq. (19)). The cathode distributes the oxygen fed to it onto its surface and conducts the electrons back from the external

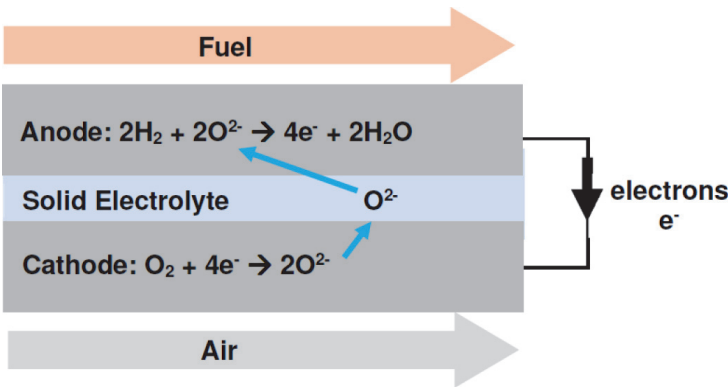


Figure 1.
Working principle of a solid oxide fuel cell (SOFC).

circuit where they can recombine with oxygen ions, passed across the electrolyte, and hydrogen to form water. The overall reaction (Eq. (20)) generates water.

Anode materials are based on metal ceramic mixture, named cermet, typically Ni-ZrO₂, Co-ZrO₂ and cathode materials is a p-type semiconductor usually LaMnO₃ doped with strontium. Both electrodes have highly porous structure for rapid transport of gaseous reactants or products.

The choice of these materials is a compromise between a number of factors necessary to meet some requirements: chemical, phase and morphological stability, chemical compatibility and with other components, dense electrolyte, etc.

For the electrolyte, in addition to the yttria stabilized zirconia mentioned above, have been considered compositions such as gadolinium doped ceria and scandium doped zirconia [16]. These compositions are more conductive than yttria stabilized zirconia, permitting a further reduction of the operating temperature by 50–100°C.

Currently, most cathodes are based on doped lanthanum manganites such as strontium doped lanthanum manganite or other materials with the perovskite structure [17–21]. Most used for the anode material is a cermet of nickel and yttria stabilized zirconia [22]. This material is sensitive to contaminants like sulfur and requires desulfurization of the anode feed. Some other materials such as copper—cerium oxide anodes are being developed.

Planar and tubular are the different geometries of solid oxide fuel cells [23–26]. The air and hydrogen flow through the unit of flat stacks via channels built in to the anode and cathode in the planar design. The tubular design has the advantage of much easier to seal air from the fuel. In this geometry the flow of air or fuel is through the inside of the tube and the other gas is passed along the outside of the tube. From the performance perspective the planar design is at this time better than the performance of the tubular design.

SOFCs are extremely useful in wide ranging applications such as stationary fuel cell applications and for transportation systems.

3. Fuel cells: thermodynamic and electrochemistry

Equation of overall reaction into Proton Exchange Membrane Fuel Cell (PEMFC) is:



According to first principle of thermodynamic, enthalpy of reaction (ΔG) is the sum of Gibbs free energy (ΔG) and a term depending on entropy (ΔS) (Eq. (22)):

$$\Delta H = \Delta G + T\Delta S \quad (22)$$

In terms of energies, the fraction able to generate useful work for a system evolving at constant pressure and temperature is variation of Gibbs free energy. In an operating fuel cell, the only work produced is electrical, described by (Eq. (23)):

$$\Delta G = -W = -q \cdot E, \quad (23)$$

where

q is electrical charge, $[q] = \text{C}$ (Coulomb)

E is electrical potential $[E] = \text{V}$ (Volt)

For 1 mole of hydrogen, the charge transferred in reaction is the product between the number of transferred electrons (n) and the molar charge of electrons ($F = 95,485 \text{ Coulombs/mol}$), so:

$$\Delta G = -nFE \tag{24}$$

where F, named Faraday’s constant represents the specific charge for 1 mole of electrons, $F = 96.485 \text{ C/mol}$;

The value of the maximum cell potential, obtained at constant, standard temperature and pressure is:

$$E^\circ = -\Delta G^\circ / nF \tag{25}$$

Gibbs free energy could be calculated from (Eq. (22)) taking into accounts the tabulated values of standard enthalpies and entropies of formation (**Table 1**) [1, 2]:

$$\Delta G = \Delta H - T\Delta S = \sum h_f^\circ - T \sum S_f^\circ \tag{26}$$

For water:

$$\Delta H_{H_2O}^\circ = h_f(H_2O) - h_f(H_2) - h_f(O_2) = -286.2 \text{ kJ/mol} \tag{27}$$

$$\Delta S_{H_2O}^\circ = s_f(H_2O) - s_f(H_2) - \frac{1}{2}s_f(O_2) = -0.163 \text{ kJ/mol} \cdot K \tag{28}$$

Hence, the standard Gibbs free energy for liquid water formation is:

$$\Delta G_{H_2O(l)}^\circ = \Delta H_{H_2O}^\circ - T\Delta S_{H_2O}^\circ = -237.42 \text{ (kJ)/mol} \tag{29}$$

Taking into account the expression of cell potential (Eq. (25)) and the value of $\Delta G_{H_2O(l)}^\circ$ calculated above (Eq. (29)) we obtain the theoretical value of potential of PEMFC:

$$E_{H_2O(l)}^\circ = -\frac{\Delta G}{nF} = \frac{237.42 \text{ kJ/mol}}{2 \times 96\,485 \text{ A}\cdot\text{s/mol}} = 1.23 \text{ V} \tag{30}$$

This is the theoretical value of PEMFC potential if the product is liquid water. If the water vapor results from electrochemical process, the value of theoretical potential is changed corresponding to values of standard enthalpy and entropy: $E_{H_2O(g)} = 1.18 \text{ V}$ [1].

The values of PEMFC potential are determined for reaction at equilibrium, in standard conditions: 1 mole hydrogen consumption, constant temperature, 25°C and pressure, 1 atmosphere (760 Torr). At equilibrium, the net current is equal to 0, although the reaction proceeds in both directions simultaneously.

The influence of reactants concentration on the cell potential is revealed by Nernst equation:

$$E = E^\circ - \frac{RT}{2F} \ln \frac{c_{H_2O}}{c_{H_2} \cdot (c_{O_2})^{1/2}} \tag{31}$$

Reactants	$h_f \text{ (kJ/mol)}$	$S_f \text{ (kJ/mol}\cdot\text{K)}$
H ₂	0	0.1306
O ₂	0	0.2051
H ₂ O(l)	-286.02	0.0699
H ₂ O(g)	-241.98	0.1888

Table 1.
The values of standard enthalpy and entropy of formation for reactants and products into PEM fuel cell reaction [2].

where

- E° is standard potential;
- R is the universal gas constant: $R = 8.314 \text{ J/(K}\cdot\text{mol)}$;
- T is the absolute temperature (K);
- 2 is number of electrons transferred in reaction;
- F is Faraday's constant;
- c_{H_2} , c_{CO_2} , $c_{\text{H}_2\text{O}}$ are concentrations of reactants and products of electrochemical reaction.

In the fuel cell, chemical energy of fuel is converted in electricity through electrochemical reactions. The intensity of electric current generated through an electrochemical process is proportional with the charge transfer and reactants consumption, according to Faraday's law:

$$i = nFj \quad (32)$$

where

- nF is the charge transferred in reaction for 1 mole of reactant consumption (C/mol), and
- j is the flow of reactant per unit area ($\text{mol/s}\cdot\text{cm}^2$).

Since electrochemical process within fuel cell is split in two electrode reactions, oxidation on the anode and reduction on the cathode, each reaction generates an electron transfer, from reactant to anode and from cathode to reactant. The net current generated into operating fuel cell is a sum of these two currents, from cathode (j_c) and to anode (j_a):

$$i = nFj_c - nFj_a \quad (33)$$

The intensity of anode current is negative because the current sense is opposite with the electrons flow.

The reactant flow is proportional to concentration of reactant species on the electrode. For PEMFCs, this could be expressed by the further equations:

$$j_c = k_{\text{ox}} \cdot (c_{\text{O}_2})^{1/2} \text{ and } j_a = k_{\text{red}} \cdot c_{\text{H}_2} \quad (34)$$

The current in the operating PEMFC is:

$$i = nFk_{\text{ox}} \cdot (c_{\text{O}_2})^{1/2} - nFk_{\text{red}} \cdot c_{\text{H}_2} \quad (35)$$

At equilibrium, the net current is equal to 0, but the reaction proceeds in both directions simultaneously with the same rate. Based on Arrhenius equation and the Transition State Theory, the rate constant in the electrochemical process depends on the potential of fuel cells, which rich the open circuit voltage for zero current.

$$k_{ox} = Ae^{\frac{-\alpha_{ox}FE_{eq}}{RT}} \quad (36)$$

$$k_{red} = Ae^{\frac{-\alpha_{red}FE_{eq}}{RT}} \quad (37)$$

where α_{ox} and α_{red} are the so called transfer coefficients.

The equilibrium flow of reactants gives so called the exchange current density (i_0):

$$i_0 = nFk_{o,ox} \left(c_{O_2}^0 \right)^{1/2} e^{\frac{-\alpha_{H_2}FE_{eq}}{RT}} = nFk_{o,red} c_{H_2}^0 e^{\frac{-\alpha_{O_2}FE_{eq}}{RT}} \quad (38)$$

The express of current density in the PEMFC could be written function of the exchange current density and the potential of the cell:

$$i = i_0 \left\{ e^{\left[\frac{-\alpha_{H_2}F(E-E_{eq})}{RT} \right]} - e^{\left[\frac{\alpha_{O_2}F(E-E_{eq})}{RT} \right]} \right\} \quad (39)$$

This equation, known as Butler-Volmer equation gives a relation between current density and the potential at the electrode of the PEMFC. Note that the reversible or equilibrium potential at the fuel cell anode is 0 V by definition, and the reversible potential at the fuel cell cathode is 1.229 V (at 25°C and atmospheric pressure) and it should vary with temperature and pressure [2].

4. Materials and components of proton exchange membrane fuel cell

Proton Exchange Membrane Fuel Cells (PEMFC), developed initial in USA by General Electric Company, was used in the U.S. Space Program at the beginning of 1960. The first electrolyte membrane was a polymer based on sulfonic acid substituted polystyrene. Few years later, in 1967, a new proton exchange membranes with better strength and chemical resistance came to improve the PEMFC [27]. This membrane was **Nafion**, from DuPont—a perfluorosulfonic acid membrane, based on polytetrafluoroethylene (PTFE) backbone, grafted with short ethylene-propylene chains terminated with sulfonic acid groups [28]. Until now, Nafion remains the standard proton exchange membrane.

Most of the PEMFCs work in the temperature range of 50–80°C generating between 0.35–0.7 W/cm² power densities in hydrogen-air systems at pressure levels varying from ambient pressure to 2.5 bar [29]. The power density can be multiplied by coupling more cells in a stack. In this way it is possible to attain the volumetric power density of 1 kW/l, target value for automotive applications.

In the study of the cost and expected future performance of PEMFCs for vehicles, Whiston et al. [30] presents the best cost life times and performances for current fuel cells stacks: costs between 40–500 \$/kW with power densities ranged from 0.5 to 4 kW/L and the lifetime varying between 1200 and 12,000 hours.

The architecture of Proton Exchange Membrane Fuel Cells (PEMFC) (**Figure 2**) shows a flat multi-layered structure with a polymer electrolyte membrane core and several specific layers ordered in pairs on both sides of the membrane. The two parts of the PEMFC placed in the mirror on both sides of the polyelectrolyte membrane have a generic name anode and cathode side. The anode side of the fuel cell contains the negative electrode, where fuel (H₂) is oxidized (hydrogen oxidation reaction HOR), while the cathode side is the half cell with the positive electrode, where the oxygen reduction reaction (ORR) occurs.

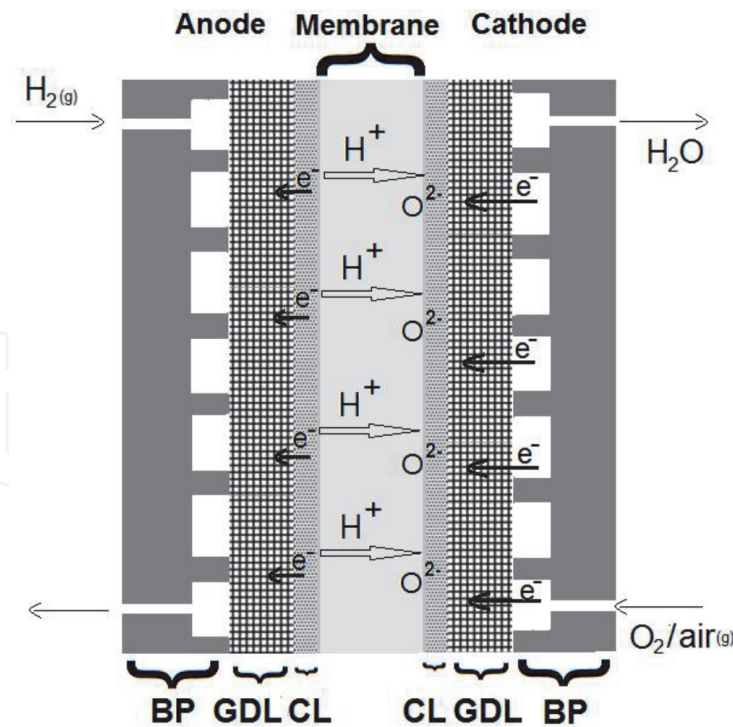


Figure 2.
Schematic presentation of PEMFC.

The role of each component of the PEMFC could be understood starting from the functioning principle of the device and its overall reaction: chemical energy of hydrogen molecule is converted into electricity through electrochemical processes. Using oxygen as oxidant into the REDOX process the only reaction product are water and heat.

Both reactants enter the PEMFC on their side: hydrogen (H₂) by the anode inlet and oxygen (O₂) by the cathode. The gases flow through the channels engraved on the Bipolar Plates (BP). From the flow channels, the reactants pass the Gas Diffusion Layers (GDL) toward the reaction sites in Catalyst Layers (CL). To the anode, hydrogen is oxidized yielding protons (H⁺) and electrons. The protons cross the Proton Exchange Membrane (PEM) and the electrons pass through an external circuit, yielding electrical current. On the cathode side catalyst layer, oxygen is reduced to O²⁻ ions by the electrons from external circuit. Oxygen ions react with protons resulting water.



Bipolar Plate (BP) connects two adjacent cells in the stack. BP consists in a graphite plate with flow channels engraved on both faces of the plate; one face contains the flow field from cathode side of one cell and the other contains the anode flow field of adjacent cell. Sometimes, the BP is composed by two flow plates from different materials. Flow field provides a pattern for even distribution of reactant gases by in plane direction of the device (**Figure 3**). At the same time it collects and removes the reactants and products into the flow channels, which has less than 1 mm depth and width separated between them by ribs of 1 mm width [31]. Furthermore, the conductive behavior of graphite plates enable electronic conduction and polarization, so that a face of BP has negative charge on the faces toward cathode side of a cell and positive charge to the other face toward the anode side of adjacent cell. This makes possible the serial connection of many cells result a cells stack with additive power character. Also the BP gives the stack solidity.

The Bipolar Plates requirements are [2, 4]:

- impermeable for gases, in order to minimize the gas leakage to 0% [$<2 \cdot 10^{-6} \text{ cm}^3 / (\text{cm}^2 \cdot \text{s})$];
- high electrical conductivity;

The resistance of the flow plate, including the flow channels should be less than $20 \text{ m}\Omega\text{cm}^2$;

- good thermal conductivity ($>20 \text{ W/mK}$);
- compressive strength ($>2 \text{ MPa}$);
- minimal thickness;
- high chemical resistance.

The structure of BP integrates the two flow field, one of each face of the plate, and also the cooling system. The geometry of distribution channels network considerable contributes to the fuel cell performance. Moreover, the material properties such as density and strength are important.

Bipolar plates operates in harsh chemical and electrochemical environment: highly oxidizing environment at the cathode under oxygen/air flux and 1 V potential versus the normal hydrogen electrode, or strong acid solution at the anode, due to the ions present in anode compartment H^+ , SO_3^- , F^- . Therefore, the BP should be resistant to oxidation, to acid and to hydrogen embrittlement.

Flow plates represent a major part in weight from total PEMFC and contribute to 80–90% to the weight and volume of entire stack, determining the power density of a PEMFC stack [29].

Gas Diffusion Layers (GDL) are important components of PEMFC, inserted between the bipolar plate and the catalytic layer on both side of the membrane, in order to ensure an uniform distribution of reactant gases, a properly management



Figure 3.
Bipolar plate pictures.

of water, both, who enters with humidified gases and that produced to cathode by electrochemical reaction.

GDL is composed from carbon fibers orderly arranged in carbon cloth (**Figure 4(a)**) or randomly in carbon paper (**Figure 4(b)**) forming a macro-porous layer with pore size between 10 and 30 μm and thickness between 200 and 400 μm [29]. The carbon fibers are produced mainly by electro-spinning of polyacrylonitrile (PAN) solution. The fibers network is treated with a hydrophobic agent in order to impede water retention. Usually the hydrophobic agent is polytetrafluoroethylene (PTFE) used in proportion of 5–30 wt% from total mass of GDL preserving a large void volume, typically 75–85% [28, 32].

On the inner face of the cathode GDL is deposited a thin, micro-porous layer (MPL), with porosity between 150 and 500 nm, allowing to enhance reactants transport and water removal. MPL consist in a thin layer of carbon black powder mixed with PTFE, with thickness around 30 μm [31], on GDL. MPL control water diffusion to cathode allowing an appropriate amount of water to be held at the interface MPL - catalyst layer to keep the membrane hydrated. MPL is applied also on the GDL from anode side in order to maintain catalyst active layer dried. The difference in permeability between the two layers (GDL and MPL) seems to be responsible to this water management behavior.

Main functions of GDL are:

- transport of reactant gases with uniform distribution toward catalytic sites;
- transport of electrons to (cathode) and from (anode) catalytic sites;
- removing the heat of reaction;
- rigid support for membrane and catalyst layers;
- water management.

Gas transport through GDL could be obstructing by liquid water, therefore the water removal is so important. A good transport rate and uniformity in gases distribution depend on both in plane and through plane gas permeability of GDL. In absence of flooding the oxygen transport is mostly diffusion driven and the permeability of material is sufficient for transport of gaseous reactants. Because the GDL is much thicker than MPL, the permeability of GDL is determinant in reactant gases transport.

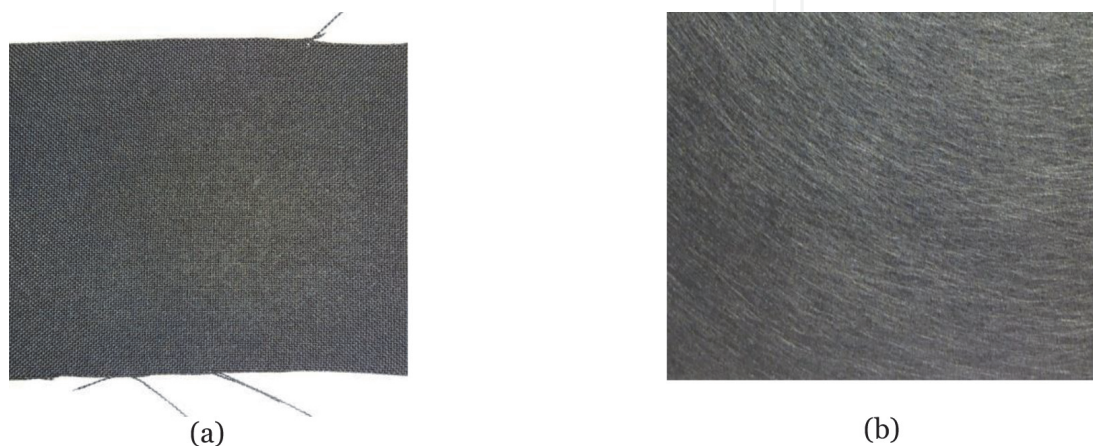


Figure 4.
Picture of the fragments from carbon cloth sample (a) and carbon paper (b).

Transport of electrons and heat occurs through carbon fibers which form GDL. In plane transport of electrons and heat are higher than through plane values. This anisotropy in GDL together different thickness of GDL and MPL are important factors for uniform in plan distribution of heat and potential.

Wet-proofing material increases the contact resistance. On the other hands, due to difference in thickness between GDL and MPL, the latter has a minor effect on the through-plane conductivity.

At the cathode GDL—gas flow channel interface, the interfacial resistance for reactant transport will be significantly increased due to the presence of liquid water. This happens mainly for oxygen transport through cathode GDL, where excess water could be yielded in cathode reaction.

Catalyst layer (CL) is one of the most important components of PEMFC assembly. While the bipolar plates and gas diffusion layers are responsible only for optimal mass, charge and heat transfer, the two catalyst layers together with the membrane, entitled Membrane Electrode Assembly (MEA) constitute the real heart of device. Therefore, catalysts are the center of the entire electrochemical process, playing an important role in accelerating electrochemical cell reactions: oxidation of the hydrogen gas and reducing the oxygen gas to water. The catalyst layer is often named electrode.

In order to achieve this function, the catalyst layer must provide three different pathways: one for reactant gases to catalytic centers, another for ions (H^+) transport from active site to membrane (to anode) and from membrane to active site (to cathode), and the third path is for electrons. The catalytic layers must have appropriate porosity and hydrophobicity for gas transport and water management. Moreover, ion and electron conductors together with the catalyst are mixed in composed material which form catalyst layer. There are three phases and three boundaries in the CL: between the gas phase reactant, the ion conductors and the electro catalytically active sites with electron conduction capacity. The catalyst particles must be in contact directly with the electron conductors therefore, the electro conductive carbon particles are used as support for catalyst nanoparticles. Hydrophobic substances, generally PTFE, serve as a catalyst binder and maintain the hydrophobicity in the catalyst layer, moreover polymer electrolyte, usually Nafion give the way for ionic transport.

With typically thickness between 5 and 100 μm and a porosity of 40–70%, the electrode consists of a metallic catalyst deposited on a carbon substrate, usually Pt/C. The catalytic particles with particle size of 1–10 nm are bonded in a compact layer by hydrophobic binder, usually PTFE, and an ionomer, usually, Nafion, provide pathway for proton transport. Also, the binder confers mechanical stability to catalyst [33].

The carbon-based materials used as catalyst substrates because of their high conductivity include carbon powder, graphite, and active carbon. In the last 10 years, new form of carbon based materials were synthesized and tested as carbon substrate in catalyst layer: nanotubes and graphene. The carbon substrate must have also larger porosity with average pores diameters in the range of mesoporous materials (2–50 nm).

From the initial design of PEMFCs in the 1960th, when the amounts of platinum at the electrode were 35 and 28 mg/cm^2 , this value decreased up to day at 0.5–0.1 mg/cm^2 [33]. For decreasing the amount of platinum, while maintain the desired performance of the catalyst material, several properties of the catalyst layer should be optimized including the level of adsorption of the reactants, the hydrophobicity level, and rate of transfer for ions and electrons. In addition, the catalyst durability is an important design constraint.

Because oxygen reduction reaction (ORR) is slower than the hydrogen oxidation reaction (HOR), the cathode catalyst layer requires high catalyst content in order to

maintain a tolerable response speed. The catalyst loading depends on thickness of the catalyst layer.

CL can be prepared by several methods, including casting, painting and brushing, injection molding, impregnation, spraying, thin layer deposition and electro deposition.

The first step in producing the electrode is the preparation of the catalytic ink. This must contain the main components of catalyst layer: metallic catalyst deposited on carbonic support, usually Pt/C, dispersed in appropriate solvents mixture, the hydrophobic binder (PTFE) and ionomer (Nafion), both in form of aqueous suspension. The ratio between catalyst particles and binder has major importance in optimization of electrode properties. B. Millington et al. prepare catalyst ink using Nafion as binder in the weight ratio of 2:1 supported catalyst to Nafion [34].

The catalyst ink is then spread on thin layer either on the membrane or on the gas diffusion layer. In the first case, the membrane with the two catalyst layers on both faces forms Catalyst Coated Membrane (CCM), in the second case the GDL with the catalyst layer is named Gas Diffusion Electrode (GDE). By putting together the CCM and the GDL or the GDE with the membrane obtain the Membrane Electrode Assembly (MEA).

However, platinum is an expensive metal catalyst and is easily poisoned. Platinum alloys are used to reduce the content of Pt catalysts without significantly decreasing the catalytic performance. Examples of Pt alloy catalysts that include other metals are Pt-Ru, Pt-Co, Pt-Pd, Pt-Ru-Co, Pt-Co-Cr and combinations of Pt with Fe, Co, Cu and Ni [33].

Proton Exchange Membrane or Polymer Electrolyte Membrane (PEM) is somehow a symmetry center of PEMFC and one of the main components of the PEMFC. PEM play the role of electrolytic bridge: it provide a conductive path for the ionic species (H^+ , H_3O^+ , etc.) and prevent unwanted phenomena: mixing of gaseous reactants and passing the electrons through membrane.

The membrane must fulfill several requirements in order to accomplish the operating functions and to maintain the integrity and stability in the PEMFC aggressive operating environment, including (i) chemical and electrochemical stability under acid and oxidizing environment; (ii) dimensional stability to water-uptake (in the range from liquid water to water vapors) while preserving the mechanical strength and durability; (iii) low gas permeability through membrane; (iv) high proton conductivity in the operating conditions [2, 4]; and (v) low cost and easy to recycle.

But the most important requirement is the highest ion conductivity/low resistance to ion transport. In general, the fuel cell performance is strongly dependent on the proton conductivity through membrane, the **value of proton conductivity for Nafion membranes being around 0.1 S/cm** [35]. The most important factor governing the efficiency of the fuel cell is the concentration of proton donor moieties, such as sulfonic or phosphonic groups. Other important factors that affect the proton conductivity of almost all PEM (except the acid-base complexes—based on polybenzimidazoles and inorganic acids) are the degree of hydration and the ionic channels morphology [36].

Distribution of the ionic channels inside the amorphous polymer matrix results from the polymer microphase separation into hydrophilic and hydrophobic domains. It is very important to control the physical balance between the hydrophilic and hydrophobic domains, because the first domain is responsible for proton, water and/or methanol transport, while the second one confers stability and mechanical strength against serious swelling. The rate of proton transport into PEM is directly influenced by the water content of the membrane.

Several parameters can characterize the protons transport capacity of PEM materials: Ion Exchange Capacity (IEC), Sulfonation Degree (SD) or Equivalent

Weight (EW), and the hydration degree (λ). IEC represents the milliequivalents of sulfonic acid groups per gram of dried polymer and the sulfonation degree (SD) is the average number of sulfonic acid groups corresponding to a monomer unit. IEC and SD were determined by titration method and by calculation, function of IEC, respectively. Also, EW is defined as mass of dried polymers (g) per number of sulfonic acid groups. The hydration degree of electrolyte polymer is often described as the number of water molecules per fixed ionic group (HSO_3^-) [37].

The value of proton conductivity of PEM is determined through potentiostatic measurement of PEM resistivity, either *ex situ* only for polymer electrolyte film, or *in situ*, in the MEA or in the PEMFC.

The state of the art proton exchange membrane still remains Nafion membrane from DuPont. Nafion is a perfluorosulfonic polymer, based on polytetrafluoroethylene backbone grafted randomly with short chain. The grafted chain is composed by 2–3 isopropylene oxide units followed by one ethylene oxide unit, capped on sulfonyl acid group (**Figure 5**).

There are several type of commercial Nafion varying by equivalent weight and thickness (**Table 2**).

Many other materials, polymer, polymer blends or polymer composites were tested for proton exchange membrane. Polymers used as proton exchange membrane can be classified in fluorinated and non-fluorinated backbone. Between non fluorinated materials, most of them are high performance sulfonated polyarylene: polystyrene (**Figure 6(a)**) and block polyethylene-block polystyrene, poly(phenylene oxide) (**Figure 6(b)**), poly(ether ketone) (**Figure 6(c)**), poly(ether sulfone) (**Figure 6(d)**), polyimide (**Figure 6(e)**) [39] and all. A lot of variation from this generic structure for example: polyether-ether ketone ketone, polyarylene substituted with different substituent was tested for improving the PEM properties.

For sulfonated polyarylene PEMs the transport of protons depends on the hydration degree, in other world depend on the amount of liquid water in the membrane. These PEMFCs work properly at temperature under 100°C.

However, working at high temperatures, above 120°C, improve catalytic activity and thermal management in PEMFC. An attempt to improve water retention inside the PEM uses the hybrid membranes, with inorganic fillers included inside the polymeric matrix. Moreover, fillers with hydrophilic behavior: silicates, titanium dioxide, zirconium dioxide, heteropolyacids (phosphotungstic, phosphomolibdenic) and carbon nanotube [39], also improve the ion conductivity, the thermal and mechanical properties.

Composite organic–inorganic PEM can be prepared through different techniques, involving direct mixing of inorganic fillers into polymer solution or melt, followed by recasting of the composite film or *in situ* techniques. Homogeneous distribution of the filler inside the polymer matrix is very important in order to obtain an isotropic distribution of material properties. In this respect, choosing the solvents and mixing procedure could enhance the degree of dispersion of the

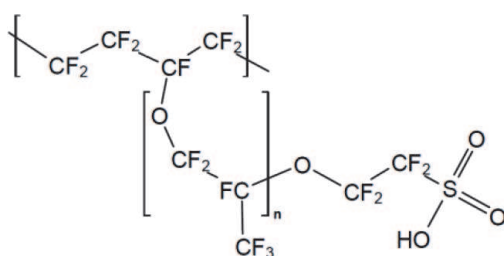


Figure 5.
 Structure of perfluorosulfonic ionomer Nafion.

Commercial Nafion membrane	Equivalent weight g/(-SO ₃ H)	Thickness (μm)
Nafion 112	1100	50.8
Nafion 117	1100	183
Nafion 211	1100	25.4
Nafion 212	1100	50.8

Table 2.
Characteristics of commercial Nafion membranes [27, 35, 38].

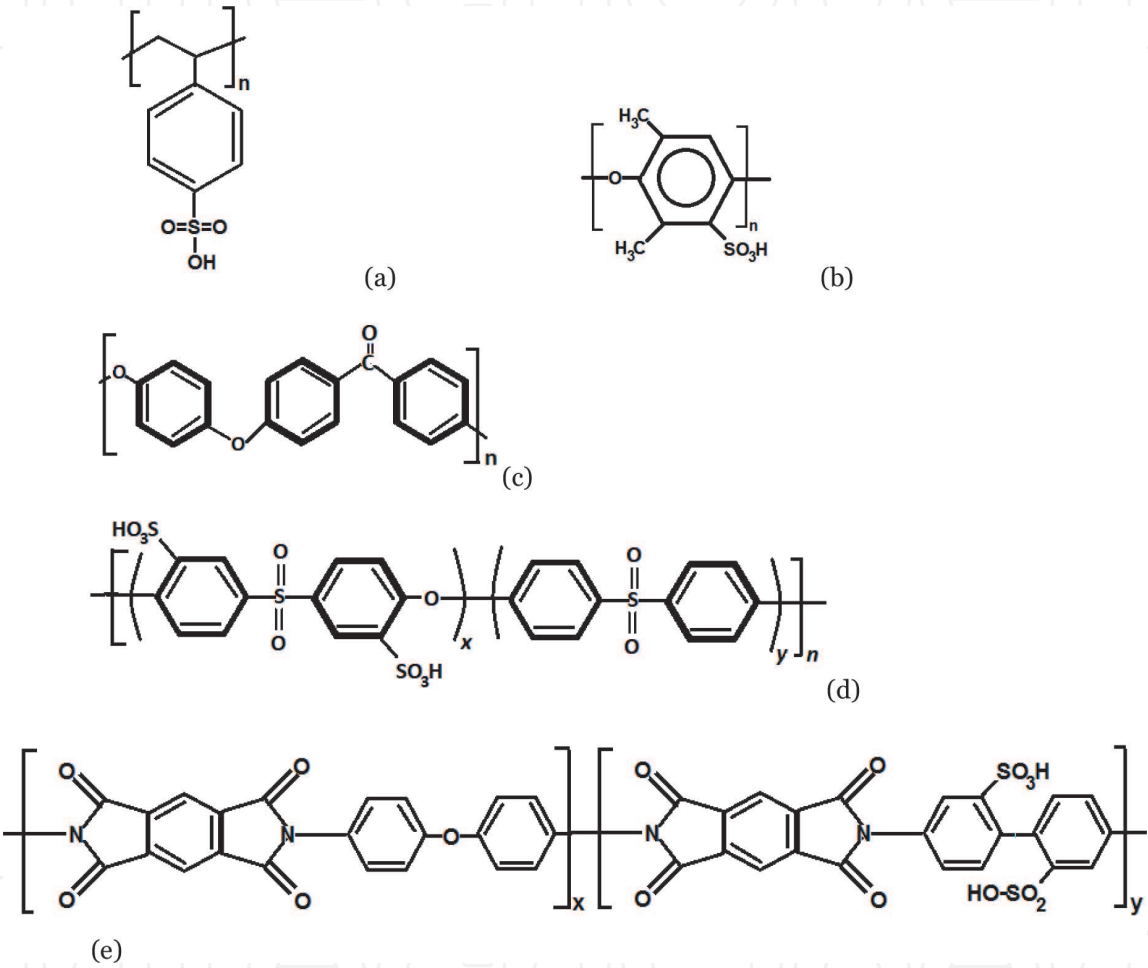


Figure 6.
Structure of several representative sulfonated polyarylene tested for PEM: (a) sulfonated polystyrene, (b) sulfonated polyphenylene oxide (dimethyl substituted), (c) polyetherketone, (d) sulfonated polysulfone, (e) sulfonated polyamide.

nanoparticles in the polymer matrix. Better dispersion depends on chemical compatibility between inorganic filler and polymer, too.

The in situ techniques for composite PEM preparation involve either the inclusion of the nanofiller into the polymer matrix during polymerization from mixed solution of filler—monomer, either the synthesis of the inorganic filler inside the polymer matrix by modified sol-gel technique [36].

Another kind of proton exchange membrane for high temperature PEMFC are acid-base membrane, which has a polybenzimidazole base structure (**Figure 7**) doped with phosphoric acid or heteropolyacids. These membranes expressed proton conductivity at temperature above 100°C even with low humidification or in the dry state.

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