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Bachelor Thesis

Water Management in Hydrogen Polymer Exchange Membrane Fuel Cells (PEMFC)

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Abstract

Current lifestyle makes energy to be essential beyond satisfying our basic needs. Nowadays, is not possible to talk about energy without dealing with its effect on the climate. The European Union (EU) consider that energy must be secure, competitive and sustainable [1] and the energy union and climate is a European Commission's priority [2].

The EU's Energy Union framework strategy was adopted back on February of 2015 and since then, the State of the Energy Union shows by its reports the progress made and the new targets and initiatives for the closest years [3]. The Energy Union's strategy is hold up by five key pillars mutually reinforcing which are: energy security, market integration, energy efficiency, decarbonisation of the economy and innovation [2]. The EU's Energy Union supports numerous cutting edge innovation projects where hydrogen is used. The main proposes related with hydrogen are for nuclear energy applications, energy storage and fuel cells.

Hydrogen, which is the most abundant element in the universe, can be converted to electricity through electrochemical processes in a fuel cell in a single step and without any moving part. In addition, in a fuel cell the by-products are waste heat and water. For these reasons, fuel cells technology (specially PEMFCs technology) have the potential to be a element to take into account in energy production satisfying the global warming targets. However, PEMFCs need more research and development and an H_2 large scale infrastructure. Nowadays, only the 4% of the hydrogen consumed is produced by electrolysis, the 96% left came from fossil fuels [4].

The present bachelor thesis focuses in one of the main current challenges in fuel cell industry: water management. A correct water management is a key factor for high PEMFC performance and durability. In order to achieve a global vision of water management and also to set a zone of stable operation in the UC3M PEMFC laboratory for upcoming works this bachelor thesis is divided in 5 main chapters. The first chapter focuses in fuel cell technology from its origin to its nowadays main applications. The second chapter deals with the PEMFC and its state of art. In the third chapter a simplified modelling of balance of mass and water is performed for a theoretical analysis of the experimental conditions. The fourth chapter summarizes all the experiments performed in the UC3M PEMFC laboratory and gives as a result a zone of stable operation that will be useful for further projects. Finally, a global conclusion of the results obtained over the bachelor thesis is presented. This present bachelor thesis involves the starting point for future hydrogen PEMFC investigation in the UC3M.

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Nomenclature

Superscript, Subscript, Variables and Symbols

\cdot	—	Flow Rate symbol
\sim	—	Dimensionless symbol
ΔG_{chem}	—	The chemical term of the Gibbs free energy [J]
$\alpha_{rd,ox}$	—	Transfer coefficient
v	—	Flux of reactant per unit area (unit-area reaction rate) [mol/(s cm ²)]
ξ	—	Initial molar fraction
ϕ	—	Stoichiometric ratio
χ	—	Molar fraction of specie k
ρ	—	Density [kg/m ³]
η_{act}	—	Activation Losses [V]
η_{ohm}	—	Ohmic Losses [V]
η_{conc}	—	Concentration Losses [V]
η	—	Global Efficiency
η_{th}	—	Theoretical Efficiency
Ω	—	Number of possible microstates of the system
a	—	Activity
\hat{A}	—	Dimensionless Advection Capacity of the Anode Stream
A	—	Advection Capacity of the Anode Stream [kg/s]
A	—	PEMFC Surface Area [cm ²]
<i>anode</i>	—	Anode Electrode
\widehat{BOW}	—	Dimensionless Balance of Water
\hat{C}	—	Dimensionless Advection Capacity of the Cathode Stream
C	—	Advection Capacity of the Cathode Stream [kg/s]
C	—	Surface concentration of reacting species [mol/cm ²]
<i>cathode</i>	—	Cathode Electrode
<i>cell</i>	—	Fuel Cell
<i>cons</i>	—	Consumption
E	—	Theoretical Potential [V]
E_r	—	Reversible Potential or Equilibrium Potential [V]
F	—	Faraday's constant [C/e ⁻ mol]
G	—	Gibbs Free Energy [J]
H	—	Enthalpy [J/mol]
h	—	Planck's constant [J s]
H_2	—	Hydrogen

H_2O	—	Water
h_f^0, k	—	Enthalpy of formation of specie k [J/kg]
$\overline{h_f^0}, k$	—	Enthalpy of formation of specie k [J/mol]
I	—	Current [A]
j	—	Current Density [A/cm ²]
k	—	Reaction rate coefficient [1/s]
k_B	—	Boltzmann's constant [J/K]
\dot{m}	—	Mass flow rate [kg/s]
M	—	Molar mass [kg/mol]
\dot{N}	—	Consumption/Production rate [mol/s]
n_{cell}	—	Number of cells in the fuel cell
n	—	Number of electrons per molecule
O_2	—	Oxygen
p	—	Pressure [Pa]
<i>partial</i>	—	Partial
<i>prod</i>	—	Production
\dot{Q}	—	Volume Flow Rate [m ³ /s]
Q	—	Heat [J]
R	—	Gas constant [J/K mol]
RH	—	Relative humidity [%]
S	—	Entropy [J/molK]
s, k	—	Specific Entropy of specie k [J/kgK]
s^0, k	—	Absolute Entropy of specie k [J/kgK]
\overline{s}, k	—	Specific Entropy of specie k [J/molK]
$\overline{s^0}, k$	—	Absolute Entropy of specie k [J/molK]
<i>sat</i>	—	Saturation
T	—	Temperature [K or °C]
t	—	Time [s]
U	—	Internal Energy [J]
V	—	Volume [m ³]
V_{cell}	—	Real Voltage [V]
V_m^{sc}	—	Standard Molar Volume [m ³ /mol]
W	—	Work [J]
Y	—	Mass fraction of specie k

List of Abbreviations

<i>APU</i>	—	Auxiliary Power Unit
<i>AVG</i>	—	Average. Mean Value
<i>BOP</i>	—	Balance of Plant
<i>CHP</i>	—	Combine Heat and Power
<i>CO</i>	—	Carbon monoxide
<i>DMFC</i>	—	Direct Methanol Fuel Cells
<i>DOE</i>	—	Department of Energy (USA)
<i>FCEV</i>	—	Fuel Cell Electric Vehicle
<i>FCH2JU</i>	—	Fuel Cell and Hydrogen Joint Undertaking (EU)
<i>GDL</i>	—	Gas Diffusion Layer

<i>HHV</i>	—	Higher Heating Value
<i>HOR</i>	—	Hydrogen Oxidation Reaction
<i>ICE</i>	—	Internal Combustion Engine
<i>JRC</i>	—	Joint Research Center (EU)
<i>LH2</i>	—	Liquidified Hydrogen
<i>LHV</i>	—	Lower Heating Value
<i>LOHC</i>	—	Liquid Organic Hydrogen Carriers
<i>MEA</i>	—	Membrane Electrode Assembly
<i>METI</i>	—	Japanese Ministry of Energy, Trade and Industry
<i>NIST</i>	—	National Institute of Standards and Technology (U.S.A.)
<i>NO_x</i>	—	Nitrogen Oxides
<i>NTP</i>	—	Normal Temperature and Pressure Conditions (T=20°C, p=1atm)
<i>ORR</i>	—	Oxygen Reduction Reaction
<i>PEM</i>	—	Polymer Electrolyte Membrane or Proton Exchange Membrane
<i>PEMFC</i>	—	Polymer Electrolyte Membrane Fuel Cell or Proton Exchange Membrane Fuel Cell
<i>PFSA</i>	—	Perfluorosulfonic acid
<i>PM2.5</i>	—	Particulate Matter of 2.5 micrometers diameter or less
<i>PM10</i>	—	Particulate Matter of 10 micrometers diameter or less
<i>RCS</i>	—	Regulations, Codes and Standards
<i>RCSSCG</i>	—	Regulations, Codes and Standards Strategy Coordination Group (EU)
<i>SOEC</i>	—	Solid Oxide Electrolysis
<i>SO_x</i>	—	Sulphur oxides
<i>SRS</i>	—	Standard Reference State (T=25°C, p=1atm)
<i>STD</i>	—	Standard Deviation
<i>STEM</i>	—	Science, Technology, Engineering and Mathematics
<i>STP</i>	—	Standard Temperature and Pressure Conditions (T=0°C, p=1bar)
<i>UPS</i>	—	Uninterruptible Power Supplies

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Fuel Cell Technology

1.1 Fuel Cell Technology

A fuel cell is a device able to transform the chemical energy of a fuel into direct current (DC) electricity in a single step and without any moving part. The name "fuel cell" may be a misleading term because by definition a fuel is a substance that provides heat or power normally by a combustion process. However, in case of fuel cells no combustion is produced. In order to generate electricity, the fuel cell's reactants (fuel and oxidant) are separated by at least two porous electrodes and a membrane, which is the electrolyte. In the interface between the electrodes and the electrolyte, a half reaction takes place splitting the atom into protons and electrons in the anode and combining the protons with the electrons in the cathode. After the reactions occur, the protons are able to flow through the electrolyte, however the electrons are blocked and must flow through an external electrical circuit generating electricity.

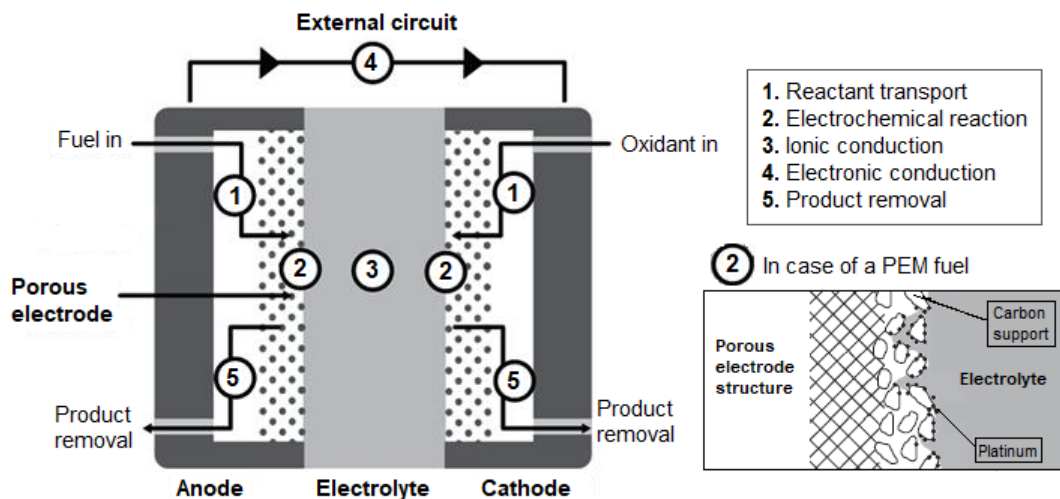


Figure 1.1. Fuel cell scheme [6] [5, page 11]. Edited

In a fuel cell the inlets are the reactants (fuel and oxidant) and the outlets are, apart from electricity, water (in liquid or vapor phase), excess reactants and heat.

Fuel cells, in order to generate electricity, needs a continuous supply of fuel and oxidant. In the case of proton exchange membrane fuel cells (PEMFCs), the typical reactants are hydrogen and oxygen but neither has to be in its pure form. The by-products (water, excess reactants and heat) must be handle out by a supporting system in order to keep the fuel cell manageable (for instance to keep stable the stack temperature).

Each cell generates about 1V [5, page 11], so in order to increase the fuel cell's voltage, and therefore its power, many cells must be stacked up in series. This versatility allows fuel cells technology be present from tiny devices, generating few watts, to large power plants generating great amount of power in the order of megawatts.

1.2 Types of Fuel Cells

Fuel cells are normally divided by the type of their electrolyte. Their main differences, apart from their type of electrolyte, are the catalyst used, the fuel used in the fuel cell, the operating temperatures and the electrical efficiency in low heating values basis (LHV). All these conditions must be taken into account when a fuel cell is chosen for a certain application.

In Table 1.1 the main features of the different fuel cells are exposed.

- **Polymer electrolyte membrane fuel cell (PEMFC)** They are also known as proton exchange membrane fuel cells. The electrolyte is a solid water-based acidic proton conductive polymer membrane, normally perfluorosulfonic acid (PFSA) (the one used in the experimental section is made by Nafion[®]). The fuel used in this kind of fuel cell is normally hydrogen (H_2), however new researches allows new kind of fuels such as methanol (CH_4O) and ethanol (C_2H_5OH). The catalyst used in PEMFC is typically carbon-supported platinum (Pt/C) being from 10% to 50% platinum [8]. If the hydrogen comes from a hydrocarbon fuel, the PEMFC needs an additional reactor in order to minimize the CO particles and avoid CO poisoning [9]. The PEMFCs' normal operating temperatures are from 60°C to 80°C when hydrogen is used [5, page 8]. The electrical efficiency is in the order of 60% if we use pure H_2 and in the order of 40% if we use a reformed fuel [10]. The main advantages of PEMFCs are the good start up behaviour at low temperatures, the high power density delivery and its size (small and compact) compared with other fuel cells. These features makes this type of fuel cell the most suitable for automobile applications but it is also applied in power plants generation and for portable power applications. Due to the wide range of PEMFC applications, the typical stack size used ranges from less than 1kW up to 100kW.

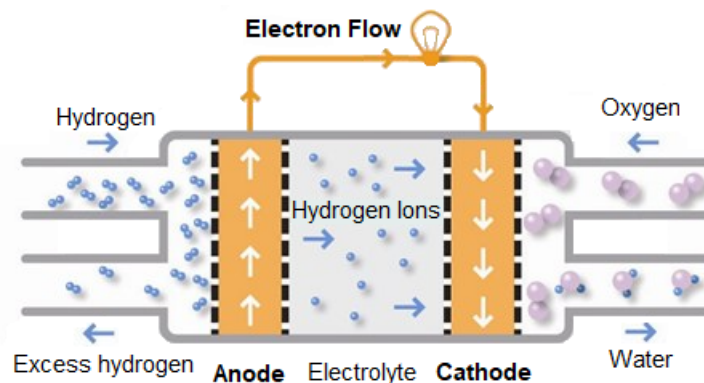


Figure 1.2. PEMFC scheme from Fuel Cell Today [11]. Edited

- Alkaline fuel cells (AFCs)** The electrolyte used is an aqueous solution of potassium hydroxide (KOH) commonly known as caustic potash retained in a porous matrix (usually asbestos). For high-temperature operation ($250^{\circ}C$) the KOH electrolyte is concentrated (85 wt%) and for low-temperature operation ($<120^{\circ}C$) the KOH electrolyte is diluted (35-50 wt%) [5, page 8]. New researches allow the use of a solid alkaline membrane as the electrolyte [9]; according to the division group criteria these alkaline membranes fuel cells (AMFCs) must be a new group, however they have the same properties than AFCs. The fuel used is pure hydrogen, or at least free of CO_2 particles because this type of fuel cell is very sensible to CO_2 poisoning in both sides of the fuel cell (even the amount present in air reduce its durability and efficiency). In order to speed up the reactions, AFCs can use as catalysts a wide range of non-precious metals such as nickel (Ni) and silver (Ag) for instance. AFCs' typical operational temperature range from $65^{\circ}C$ to $250^{\circ}C$ [5, page 8 & 9]. This kind of fuel cell has a great performance reaching a 60% electrical efficiency in space applications [9]. AFC typical stack size ranges from 1kW to 100kW [10] and it was the first cell technology developed in the 1960s. The main applications are military and space, been used in the U.S.A. space program (Apollo and Space Shuttle) to produce electrical energy and water on board the spacecraft [9].

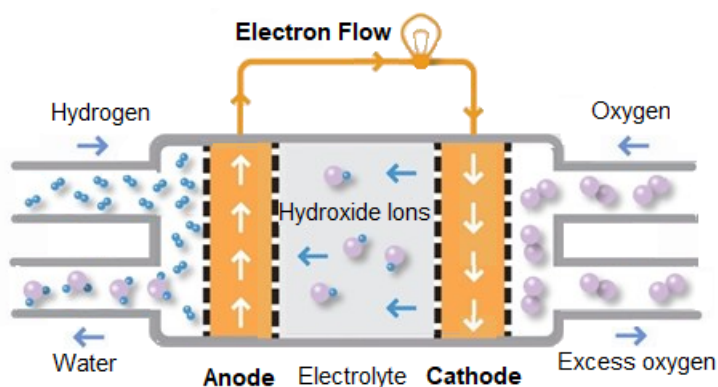


Figure 1.3. AFC scheme from Fuel Cell Today [12]. Edited

- Phosphoric acid fuel cells (PAFCs)** The electrolyte used is a concentrated liquid phosphoric acid (H_3PO_4) ($\sim 100\%$) [5, page 8] contained in a *Teflon*[®]-bonded silicon carbide (*SiC*) matrix [9]. The fuel used is hydrogen (H_2). The catalyst in the anode and cathode is platinum. The operational temperature is between 150°C and 220°C [5, page 9]. This high temperature operation allows this kind of fuel cell to be more tolerant to fuel impurities and a higher efficiency in combined heat and power (CHP). The electrical efficiency is around 40% which is slightly higher than a combustion engine efficiency (33%), however the PAFCs is normally used in co-generation processes reaching a 85% efficiency [9]. It is considered the first generation of modern fuel cells being the most mature fuel cell technology actually. PAFCs was the first type of fuel cell commercialized by late 1960s with a stack size of 4kW [13]. Actually, it is normally commercialized in container modules stack size of 200kW for stationary electricity generation [5, page 9].

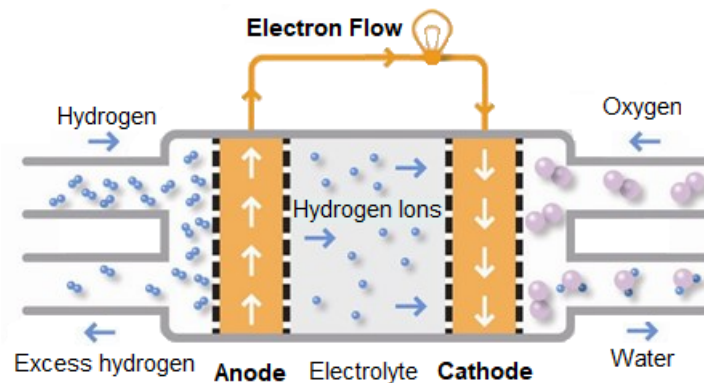


Figure 1.4. PAFC scheme from Fuel Cell Today [14]. Edited

- Molten carbonate fuel cells (MCFCs)** The electrolyte used is a molten alkali salt mixture contained in a lithium aluminium oxide ($LiAlO_2$) soaked matrix. The common alkali salts are lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3). The operation temperature is ranged between 600°C and 700°C [5, page 9]. Due to the high operational temperature of the MCFCs, this kind of fuel cell can use non-precious metals catalysts at the anode and at the cathode [9]. In addition, the temperatures are high enough to perform internal reforming. This term means that hydrocarbons fuels, such as syngas, are split in simpler elements obtaining hydrogen (H_2), carbon monoxide (CO) and other compounds. MCFCs, due to internal reforming, can use multiple fuels without the need of a external reformers as in the previous fuel cell types [9]. The main fuels used in MCFCs are light hydrocarbons, coal- derived fuel gas, methane (CH_4) or natural gas [15]. The electrical efficiency is between 50% [10] and 65% [9], however it can reach up to 85% in combined heat and power (CHP) applications [9]. The main disadvantage of this fuel cell is the durability. Actually, the current life is close to 40000 hours (~ 5 years) without decreasing performance due to the high temperature [9]. The high temperature corrode and breaks the fuel cells components. The MCFCs are commercialized

normally in modules of 300 kW, in ranges from 300kW up to 3 MW. The main applications of this kind of fuel cell are for distributed generation and for electrical utilities in natural gas and coal-based power plants [10] [9].

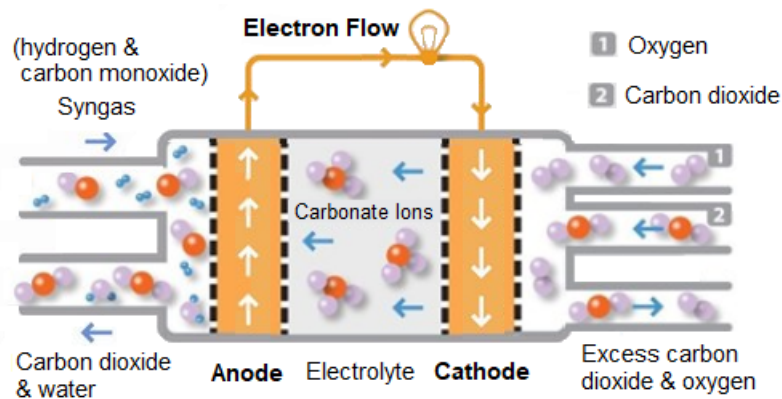


Figure 1.5. MCFC scheme from Fuel Cell Today [15]. Edited

- Solid oxide fuel cells (SOFCs)** The electrolyte used is a solid nonporous metal oxide, normally yttria (Y_2O_3)-stabilized zirconia (ZrO_2) also called *YSZ* [5, page 9]. In this fuel cell the mobile ions are oxygen. The operating temperature is ranged between 600°C up to 1000°C [5, page 9], being the fuel cell type with the highest operation temperature. As in the case of MCFCs, the high operating temperature produces internal reforming which allows SOFCs to use multiple fuels like natural gas, biogas and gases made from coal [9]. The main advantages of SOFCs are the high efficiency (60% alone and 85% with co-generation) [9] and the resistance to *CO* particles and sulfur compounds. The main disadvantages are the durability and the slow startup caused by the high temperatures. Thermal shielding is very important in this type of fuel cell to retain heat and for personnel protection. SOFCs are commercialized with a typical stack size ranged between 1 kW and 2 MW and it is used for auxiliary power applications, for distributed generation and for electric utility in natural gas and coal-based power plants [9] [10].

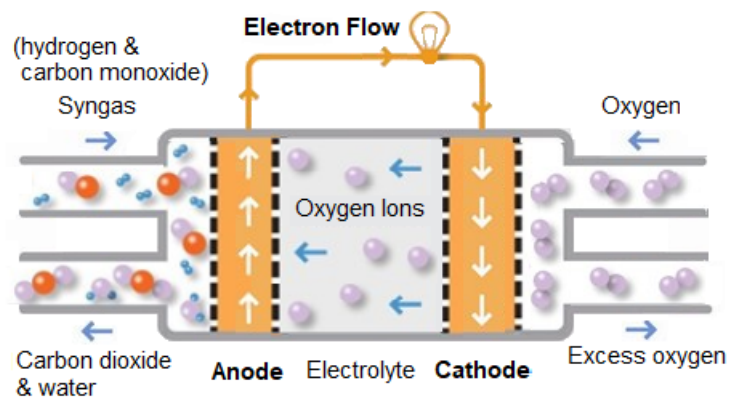


Figure 1.6. SOFC scheme from Fuel Cell Today [16]. Edited

Fuel Cell Type	Common electrolyte	Mobile Ion	Operational Temperature	Electrical Efficiency
PEMFC	Perfluorosulfonic Acid (PFSA)	H^+	60°C - 80°C	60% pure H_2 ; 40% reformed fuel
AFC	Potassium Hydroxide in water (KOH)	OH^-	65°C - 220°C	60% in space applications
PAFC	Phosphoric acid (H_3PO_4)	H^+	150°C - 220°C	85% co-generation; ~ 40% alone
MCFC	Molten Alkali Carbonate Salt	CO_3^{2-}	600°C - 700°C	85% co-generation; 50%-65% alone
SOFC	Yttria-stabilized zirconia (YSZ)	O^{2-}	600°C - 1000°C	85% co-generation; 60% alone

Table 1.1. Types of Fuel Cells

1.3 History of Fuel Cells

The origin of fuel cells date back to the first third of the 19th century with the scientific contribution of Christian Friedrich Shönbein and Sir William Grove. In 1838, the German-Swiss chemist Christian F. Shönbein made the first observation of the principles of the fuel cells which were published in the XIV volume of the *Philosophical Magazine*. Meanwhile, the Welsh barrister and scientist Sir William Grove demonstrated the first fuel cell in 1839 but it is not until 1842 when he developed the first fuel cell [5, page 4]. Grove is generally consider the inventor of the fuel cell in 1839 [18]. This first fuel cell, or *gaseous voltaic battery* as Grove called it, was able to produce electrical energy by combining hydrogen and oxygen over a platinum catalyst but not enough electrical energy for a practical use.

Fuel cell technology was mainly a scientific curiosity even though there were several attempts to make a practical device without significant successful. One of these trials were developed by the chemists Charles Langer and Ludwig Mond, which were the ones that give the current term "fuel cells" to the device in 1889 [17]. Langer and Mond were developing a fuel cell able to work with coal as fuel without meaningful success due to the catalyst poisoning. In 1893, the Nobel Prize winner Friedrich Wilhem Ostwald provided the theoretical understanding of the fuel cell and how it operates [5, page 4].

The reasons why fuel cells were not a practical device were mainly economical. By the time, the steam machine and the internal combustion engine were the references in order to obtain energy. These technology were less efficient in terms of energy than a fuel cell but more efficient in economical terms and more reliable.

It is not until the second third of the 20th, almost a century since the invention of the fuel cell, when progress in fuel cells are achieved. Francis Thomas Bacon, an English engineer, achieve a successful attempt in fuel cells. By modifying the equipment used by Langer and Mond, Francis T. Bacon was able to built the first AFC prototype in 1932 [18]. (However, it was not until 1959 when the AFC of Bacon was operational and shown publicly. The fuel cell had a 5 kW stack size In addition, the fuel cell developed by Bacon was patented and licensed by Pratt and Whitney, a United Technology Company (UTC) subsidiary, in the same year [19, page 39].

At the same time, in 1937, the swiss scientists Emil Baur and H. Preis were able to built the first SOFC which operated at 1050°C with a current density of 1 mA/cm² [19, page 226].

In 1955, General Electric developed the first PEMFC [19, page 425]. Willard Thomas Grubb is considered the inventor of the PEMFC and Leonard Niedrach improve Grubb device three years later by using platinum as a catalyst for PEMFC. The first PEMFC was able to generate 0.02 W.

In late the 1950s, the University of Amsterdam researchers G.H.J. Broers and J.A.A. Ketelaar started a series of experiments dealing with SOFCs. However, after realising that their solid oxide electrolyte was not solid at the operational temperature they decided to use molten carbonate salts instead. In 1960 they were able to build the first MCFC able to work continuously 6 months but the fuel cell showed some deterioration in electrolyte [19, page 138] [20].

The first practical application of fuel cells were in the U.S Space Program. PEMFC first application was in Project Gemini (1961-1966), in concrete Gemini 5 (1965), to provide electrical power to the spacecraft. In addition, the water generated as the by-product was used for drinkable water. However, the poor performance and scarce durability of the PEMFC at that time make the NASA to use instead AFC for the following space programs [19, page 426]. In Apollo Program a 1.5 kW AFC was used and in the Space Shuttle a 12 kW AFC was used. [18].

The last kind of fuel cell, the PAFCs, were first tested in 1961 by US scientists G.V. Elmore and H.A. Tanner. They published their results in an article called "Intermediate Temperature Fuel Cells" in the *Journal of the Electrochemical Society* [19, page 54]. In that article, they ensured that their PAFC during the 6 months's experiment was able to deliver a current density of 90 mA/cm² without reducing its performance [19, page 54].

Fuel cells were successful in spacial applications, were the cost was and is still not a problem however, for terrestrial applications, the cost is crucial. For the 1970s and 1980s the fuel cell technology was mainly used for space applications. During these decades, new researches and development in the R&D created new materials like Nafion, new designs like in the flow field and the reduction of material like the amount of platinum on the membrane. These improvements, among others, reduced the cost of fuel cells technology and in the 1990s fuel cells was considered economically feasible. An outcome of the researches in fuel cells made possible the development of the first direct methanol fuel cell (DMFC) in the early 1990s. It was developed by the NASA Jet Propulsion Laboratory and the University of Southern California. This kind of fuel cell uses the same electrolyte than PEMFC but its

importance is so notorious that sometimes is considered an independent kind of fuel cell.

During the 1990s almost every car manufacturer had built and proved at least one model of a fuel cell powered vehicle. These advances together with the wide range of applications boost the fuel cell industry optimism at the late 1990s with the promise of a new energy revolution which didn't occur (commonly called hydrogen hype [4]). At the beginning of the 2000s the fuel cell market went down. Many fuel cell companies bankrupt and went out of business. However, governments believed and still believe that the fuel cell industry will lead the energy sector. This thought is why nowadays governments keep investing in order to achieve the transition from R&D to commercialisation as the fuel cell industry will create jobs and generate a period of sustained growth. Actually, many fuel cell firms are far from being profitable but success in certain application segments such as backup power systems allows them to keep investing in R&D and improve fuel cell performances.

In general, the fuel cell industry has been dealing with extremely difficult times. Fuel cells have been always label as a very promising technology but it doesn't take the plunge. In order to become a real solution for the energy sector it must overcome the actual challenges which are to lower the cost, increase the durability, improve the electrocatalysts and the membrane properties.

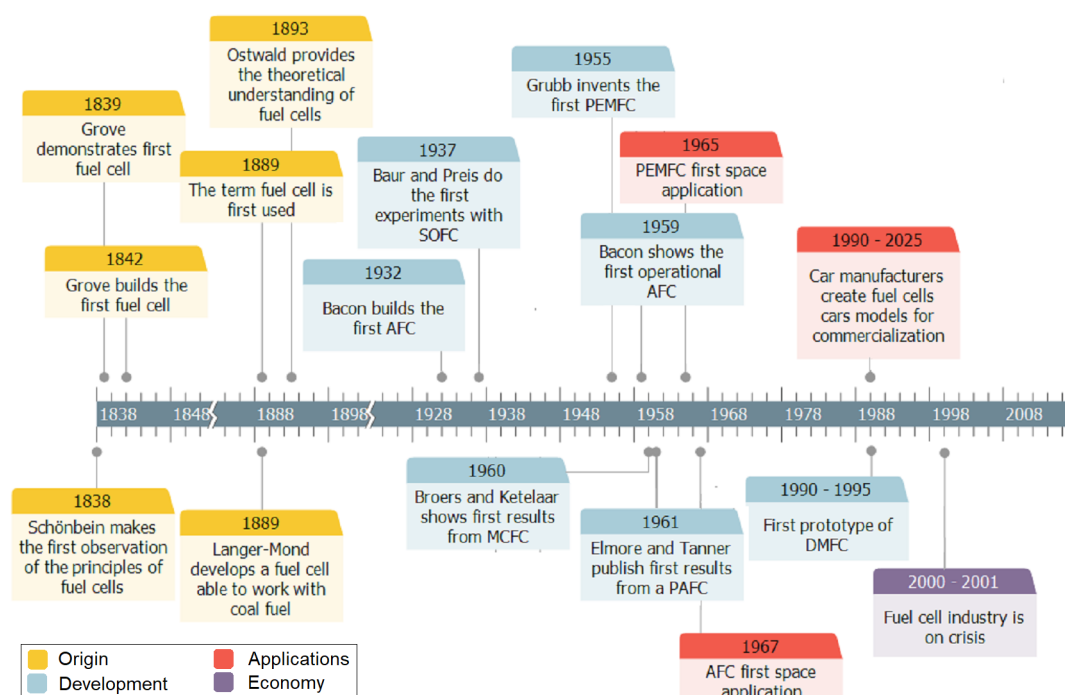


Figure 1.7. Fuel Cell's History Timeline

1.4 Fuel Cells' current situation: advantages, disadvantages and challenges

Fuel cells, like any other technology has its advantages and its disadvantages. In addition, as fuel cell technology is nowadays unmaturing, in this section some challenges and goals settled for the next years will be exposed. Some of the advantages and disadvantages have been said in previous sections.

1.4.1 Advantages

- **High efficiency:** Fuel cells electrical efficiency is much more higher than the internal combustion engines which reaches (33% ~ 35%). Whereas internal combustion engines is limited by the Carnot efficiency and involves several energy conversion steps (from chemical energy to thermal energy, from thermal energy to mechanical energy and from mechanical energy to electricity), fuel cells is not limited by the Carnot cycle as they are not heat engines and they directly transform the chemical energy from the fuel into electricity. For automobile applications, internal combustion engines car is less than 20% efficient while an electric motor powered by fuel cells car reaches an efficiency between 40% and 60% [21]. In addition, some fuel cells works at a very high temperature which allows co-generation reaching a global efficiency of 85%.
- **Low or zero emissions:** Fuel cells use as fuels hydrogen (PEMFC, AFC and PAFC), light hydrocarbons, methane, biogas and gases made from coal. The fuel cells which do not work with hydrogen fuel (MCFC and SOFC) generates as a by-product carbon dioxide. The generation of carbon dioxide can be capture as the fuel and oxidant streams in fuel cells are separated. This fact means that carbon emission levels can be easily reduce and don't require a significant cost. In the case of hydrogen, the by-products are water and heat; any pollutant is emit. However, nowadays in order to produce hydrogen a 96% is produced from gas, oil and coal [4] where the emissions of carbon dioxide is released to the atmosphere. A zero emission can be achieve if fuel cells use as fuel hydrogen and the hydrogen is generated by electrolysis.
- **Quiet:** Fuel cells have very low noise emissions as they don't have moving pieces or parts while they are working. Noise pollution is not a problem of fuel cells.
- **Modular:** Fuel cells are composed of small cells stacked together. The amount of power needed can be obtained adding more cells. This fact make fuel cell technology attractive because it can be mass-produced (and therefore reduce the cost of fuel cells) and the maintenance of the system is simple. Fuel cells can operate at almost constant efficiency independently of the number of cells connected. The modularity of fuel cells make this technology be present in a wide range of applications.
- **Facilitate distributed generation:** Due to its properties (clean, quiet and modular technology), fuel cells can promote the integration of distributed

generation and smart-grids in big cities where the energy actually is normally generated far away from the cities.

- **Expected to have a good reliability:** Fuel cells are expected to have a good reliability because it is not susceptible to outages caused by weather conditions or the capability of the grid, have few moving parts in its system so there is a low percentage of mechanical error and it can be installed in closer to the residential areas than actual power plants. However, R&D of fuel cell technology is still needed because of the durability of the devices.
- **Reduce energy dependency on foreign countries:** Nowadays there is a high dependency to fuel imports. In Europe the crude oil suppose the 69% and gaseous natural gas represents the 20% of the total imports in energy products in 2017 [22]. The possibility of obtaining hydrogen by electrolysis of the water and the flexibility of fuels offered by fuel cells reduce the dependency on energy exporting countries.

1.4.2 Current disadvantages

- **Cost:** It is the major obstacle to fuel cell implementation. It is vital to reduce fuel cells cost without reducing significantly their efficiency and durability. The main costs are located in the materials used, the balance of plant (BOP) components, and in the manufacturing costs [23, Technical Barriers]. In case of low temperature fuel cells (PEMFC and PAFCs), it is necessarily to implement a high cost catalyst composed normally by platinum in order to have a high performance. As it is shown in figure 1.14, the catalyst and its application constitutes from 26% up to a 41% of the total fuel cell stack cost depending of the volume of systems sold per year. In case of high temperature fuel cells, specially MCFCs and SOFCs, the materials required for the stack and BOP components must handle very high temperature without reducing the overall efficiency [23]. More information about the cost of a fuel cell and the cost evolution through the years and the cost targets are detailed in section 1.6.
- **Durability and reliability:** According to the latest Multi-Year Research, Development and Demonstration Plan published by the DOE (2016) fuel cells durability needs to be improve in order to be comparable with current technology and to be commercially available [23]. Durability and reliability tests with realistic conditions showed that the performance of the fuel cells is actually far away from the targets settled. In case of automotive applications, experiments show between 2500 and 3900 hours before a 10% voltage degradation occurs while in order to be competitive in the market a 5000 hours target is settled. In case of stationary applications, durability and reliability requirement is much higher being the target established in 60000 hours in order to be competitive with current technology and allow an attractive return for the consumer. However, most of the system failure ($\approx 90\%$ in automotive systems and micro CHP systems) takes place out of the stack, in the BOP components [23].
- **"Emerging" technology:** Even though fuel cells were invented almost two

centuries ago they are still developing and requires more R&D to fulfill the targets established.

- **Hydrogen Fuel difficulties:** Focusing in PEMFC technology, the hydrogen economy is not implemented yet. High cost of hydrogen production makes that approximately 96% of the hydrogen produced nowadays comes from fossil fuels [4]. A hydrogen economy must be settled for a successful fuel cell implantation in the market where hydrogen must be produced, delivered and storage achieving economical, security and reliability requirements.
- **Water and Thermal Management:** As it will be discussed along this bachelor thesis, water and thermal balance is one of the main problems inside the PEMFCs stack. An inadequate water balance leads to performance loss and durability decays as a result of permanent membrane degradation (lack of water), low membrane ionic conductivity (excess of water), non-homogeneous current density distribution (water is not distributed uniformly), delamination of components and reactants starvation (malfunction of the fuel cell stack) [25]. A correct thermal management is critical for the stack because the performance of the fuel cell is closely dependent to temperature.
- **Regulation, safety and public awareness:** Nowadays there are around 400 fuel cell and hydrogen standards around the world [24]. Due to the immaturity of fuel cell technology, there are not internationally-accepted codes and standards that guarantees the safety of this technology in terms of design, installation, operation, maintenance and fuel equipment. The regulation of fuel cell technology and hydrogen will allow a better perception of this alternative by the citizen and will facilitate its commercialization [25].

1.4.3 Challenges and pathways according to regions

In this section the main pathways and objectives of the main promoters of hydrogen and fuel cell technology will be discussed.

Actually, the main promoters are Japan, Europe (specially Germany) and United States.

In Japan the main organism in fuel cells technology is the Ministry of Energy, Trade and Industry (METI). In 2014 they settled a Strategic Roadmap for Hydrogen and Fuel Cells which was revised in 2016 adding new goals and the procedure to achieve them. The main highlights of the document are [26]:

- The price targets were settled for PEMFCs (800 thousand yen) by 2019 and for SOFCs (1 million yen) by 2021. In other words, the price for PEMFCs should be approximately 6000 euros and for SOFCs should be about 7500 euros.
- The fleet of vehicles is aimed to be 40 thousand by 2020, 200 thousand by 2025 and 800 thousand by 2030.
- The hydrogen infrastructure must count with 160 stations by 2020 and by 2025 is intended to increase its number up to 320 stations.

- Hydrogen power generation issues were discussed superficially. The main points were to have a large scale hydrogen power generation by 2030, achieve less than 30€/kWh (27 cents/kWh) by late 2020's and be able to store hydrogen in Liquid Organic Hydrogen Carriers (LOHC) or liquified hydrogen (LH2) [27].
- Technical and economic challenges needs to be discussed in the following years to achieve the totally hydrogen generation from renewable energy sources by 2040 [27].

In Europe the main organism involved in fuel cells technology is Fuel Cells and Hydrogen Joint Undertaking (FCH 2 JU) which was created in 2008. This entity is a public-private partnership between the European Commission, fuel cell and hydrogen industries which are represented by Hydrogen Europe and the research organizations represented by Hydrogen Europe Research. According to the Council Regulation 559/2014 the main objectives for 2020 are [28]:

- Reduce the manufacturing cost of fuel cell systems and increase its durability in transport applications in order to be competitive with current technology.
- Increase the electrical efficiency, reduce the cost and increase the durability for power production applications.
- Make competitive the hydrogen production and the hydrogen economy by increasing the energy efficiency of hydrogen's production from renewable sources and by reducing its cost.
- Consolidate the feasibility of the hydrogen infrastructure and economy in the renewable energy sources integration support.
- Reduce the use of *Critical raw materials* such as the platinum used in the catalyst in PEMFCs and PAFCs aiming a platinum-free fuel cells as last resort.

In this case, there are not specific targets for 2020 but general ideas. Nowadays, FCH 2 JU is involved in 227 projects which can be divided in two main application pillars. On one hand those projects related with energy and transport and on the other hand those projects related with cross-cutting activities.

In case of United States of America the main organization dealing with fuel cells is the Department of Energy (DOE) which has a Fuel Cell Technology Office department. Inside the Fuel Cell Technology Office, ten sub-programs interconnected are developed. These sub-programs covers every aspect that affects fuel cell technology, from the fuel (*Hydrogen Production; Hydrogen Delivery and Hydrogen Storage areas*) to the final applications (*Market Transformation and Fuel Cells sub-programs*) having betwixt the sub-programs of *Technology Validation; Manufacturing R&D; Education; Safety, Codes and Standards and finally System Analysis*. Even though they are linked between them, each one has its own targets. Focusing in the Fuel Cells sub-program we can find the following targets by 2020 [23].

- For transportation applications it is aimed to achieve a 65% peak-efficiency in an hydrogen fuel cell mass produced with a durability of 5000 hours (ultimate 8000 hours) at a cost of 40 \$/kW (ultimate 30 \$/kW) (in other words about 33 €/kW and 24 €/kW respectively).

- For distributed generation and micro-CHP fuel cell systems (5kW) it is aimed to achieve a 45% electrical efficiency in a natural gas fuel cell with a durability of 60000 hours and at a system cost of 1500 \$/kW (more than 1200 €/kW).
- For medium-scale CHP fuel cells systems (100 kW - 3 MW) it is aimed to achieve a 50% of electrical efficiency and a 90% CHP efficiency in the fuel cell with a durability of 80000 hours. The cost targets depends on the operating fuel, in case of natural gas it is settled a cost of 1500 \$/kW (more than 1200 €/kW) and in case of biogas a cost of 2100 \$/kW (approximately 1700 €/kW).

All the goals, objectives, technical targets, task and schedules are updated in the Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan.

Another countries/regions that are having a remarkable performance in their researches in fuel cells technology are China and South Korea in Asia, Canada in North America and France and UK in Europe.

1.5 Regulatory Framework for Fuel Cell Technology

Regulation is crucial for fuel cell technology success. In Europe, the main organization is the FCH 2 JU as it is previously mentioned. One of its initiatives is the Regulations, Codes and Standards Strategy Coordination Group (RCS SCG). The RCS SCG was funded in 2015 in order to ensure a good performance for fuel cells applications and systems in a safety environment. The RCS SCG is composed by members of Hydrogen Europe and Hydrogen Europe Research which are also supported by the Joint Research Center (JRC) and by the Programme Office.

The main goals of the RCS SCG are [29]:

- Recognise the main areas for RCS development and propose its analysis.
- Follow the FCH 2 JU projects development in order to update RCS needs.
- Transform pre-normative (PNR) conclusions into RCS documents.
- Achieve a strong status in European and international RCS regarding fuel cells and hydrogen technologies. In addition, to be able to contribute in the Annual Union Work Plans for Standardisation.

Actually, the RCS SCG is working to elaborate their firsts documents. Meanwhile, FCH 2 JU Programme Review 2017 had analysed and discussed 3 pre-normative projects during the Programme Review Days that took place on the 23-24 of November of 2017.

- **HySEA** [30]: The whole name of the project is *Improving Hydrogen Safety for Energy Applications (HySEA) through pre-normative research on vented deflagrations*. This project started in September 2015 and it is schedule to finish in August 2018. The main goal of this project is to provide harmonized standard vent sizing requirements for hydrogen energy systems in a secure and successful framework. HySEA project aims to provide guidelines

for vented explosions standards such as the European (EN-14994) and the American (NFPA 68) actual standards. This pre-normative project affects all applications and systems including fuel cells systems.

- **HyPactor** [31]: The whole name of the project is *Pre-normative research on resistance to mechanical impact of composite overwrapped pressure vessels*. This project started in April 2014 and finished in June 2017. The main goal of this project was to ensure security of hydrogen vessels in order to achieve fuel cell acceptance among the population. For that purpose, HyPactor project focused in the mechanical impact resistance of the composite pressure cylinders. The results of the HyPactor project were a list of recommendations to improve standards for periodic inspection and qualification testing.
- **SOCTESQA** [32]: The whole name of the project was *Solid oxide cell and stack testing, safety and quality assurance*. This project started in May 2014 and finished in April 2017. The main objective for this project was to test SOFC and SOEC assembly units present in diverse applications (μ -CHP and APUs for instance). The results of this project is nowadays analysed by standards developing organizations.

The main pre-normative projects developed by the FCH 2 JU affecting directly fuel cell technology without taking into account the previous projects are:

- **Hyindoor** [33]: The project consisted in a pre-normative research for indoor applications of fuel cells and hydrogen systems. This project started in January 2012 and finished in January 2014. This project contributed in the improvements of the RCS applied for fuel cells systems in early markets through safety guidelines and specific engineering tools to its appropriate operation. In addition, this project analyzed the expected socio-economic impact of indoor fuel cells systems.
- **HyLAW** [34]: This project is the most ambitious project for fuel cell technology in the regulatory framework. HyLAW started in January 2017 and is schedule to finish by December 2018. This project main objective is to remove the legal barriers which are limiting fuel cell and hydrogen applications and boost its market integration. HyLAW is an ambitious project because it brings together 23 partners from 18 European Countries where Spain is represented by *Foundation for the Development of New Hydrogen Technologies in Aragon*. By the end of this project a database, national policy papers and EU policy papers will be available. The database is expected to be fully operational at the end of June 2018 and will give information of the fuel cells and hydrogen system and applications. The national policy papers will state of art of fuel cells and hydrogen systems in each country and will propose solutions specifically for each country while the EU policy paper will give the recommendations from a community point of view for policymakers.

Besides these projects, more regulatory efforts must be done. Hydrogen Europe propose a list of regulatory encouragement measurements in order to make fuel cell technology a reality in Europe. These measurements are published in *The ultimate guide to fuel cells and hydrogen technology* and are divided in four groups (hydrogen production, handling and distribution; grid flexibility; stationary fuel

cells; and transport). The main measurements proposed are to apply an attractive tax regime for clean hydrogen in order to boost the market development, develop regulation to allow hydrogen flow through the natural gas actual network, include in the Network Code on Requirements for Generators document for the small scale fuel cell technology like μ -CHP and to define obligatory targets for Hydrogen Refuelling Stations Deployment for the Member State countries [35].

1.6 Social-economic Impact of Fuel Cell Technology and its Applications

This section is based mainly on two reports the *Report to the European Parliament on the Socio-Economic Impact of the FCH JU Activities* by the FCH JU and *The Fuel Cell Industry Review 2017* by E4tech consultancy. The bachelor thesis budget can be found in Appendix C.

According to FCH JU, the commercialization of FCH technologies for transport and energy areas will have multiple beneficial impacts for Europe. The main benefits are related with EU energy policy main goals which are sustainability, energy security and competitiveness [1]. Generally, in sustainability terms they can reduce drastically the CO_2 emissions (between 64% and 97% in 2050) substituting internal combustion engine (ICE) vehicles and current heating systems by fuel cell vehicles and stationary power and CHP products respectively. In the case of energy security, as hydrogen can be produced by numerous techniques and resources it can reduce the fuel imports to the EU meaning between 58 and 83 billion € a year savings by 2030. In the competitiveness field, hydrogen and fuel cells systems can be applied to a wide range of applications that will affect positively to the growth prospects and job creation.

The different applications for fuel cell technology can be divided in three big groups which are portable, stationary and transport. Portable and stationary applications are also called energy applications. The main difference between portable fuel cells and stationary power fuel cells is the ability to be moved, as its own name indicates. Both of them, portable and stationary, provide electricity from small batteries chargers to large stationary fuel cells able to reach power up to 2 MW. Transportation applications fuel cells provides the propulsive power or range-extending the capability of fuel cell electric vehicles or buses. In table 1.2 the different fuel cell applications are shown together with its typical power, type of fuel cell normally used by the industry and some examples.

These applications could involved according to FCH 2 JU report the following benefits in Europe:

- **Green-House Gas and pollutants emissions reduction and its concentrations in big cities:** Green-House Gas and pollutants emissions will be reduced because, depending on the fuel cell system used, the by-product is normally water and heat and in case of MCFCs and SOFCs which produce pollutants carbon capture and storage techniques can be applied. Actually the long exposure of CO , CO_2 , NO_x , SO_x , $PM_{2.5}$ and PM_{10} is damaging

Application	Typical FC type	Power Range	Examples
Portable	PEMFC DMFC SOFC	1 W - 20 kW	<ul style="list-style-type: none"> • Military applications (wearable power systems, skid mounted FC generators) • Portable products (cameras, battery chargers)
Stationary	PEMFC MCFC AFC SOFC PAFC	0.5 kW - 2 MW	<ul style="list-style-type: none"> • Large stationary power and CHP • Renewable Energy Storage • Uninterruptible Power Supplies (UPS)
Transport	PEMFC (DMFC)	1 kW - 300 kW	<ul style="list-style-type: none"> • FCEVs, Trucks, buses, trains, ferries • Materials Handling Vehicles (forklift)

Table 1.2. Types of Applications [37]

health. The *Air Quality Report 2015* published by the European Environment Agency estimated that *NOx* and *PM* were the cause of 403,000 and 72,000 early deaths respectively in the 28 Member States of the European Union.

Some examples of the pollution reduction are shown in figure 1.8 where it is estimated that FCEVs would generate 75% fewer emissions than diesel vehicles by 2030 and none by 2050 according to *UK H2 Mobility Phase 1 report* published in 2013 and 25-30% less *CO₂* using μ -CHP instead of current heating systems like gas boiler or district heating system published in *Advancing Europe's Energy Systems*. A recent study based in fuel cell electric buses *Fuel Cell Electric Buses - Potential for sustainable public transport in Europe 2015* shows that more than 2 million tonnes of *CO₂* could be saved in a year by replacing 2500 ICE buses by fuel cell electric buses.

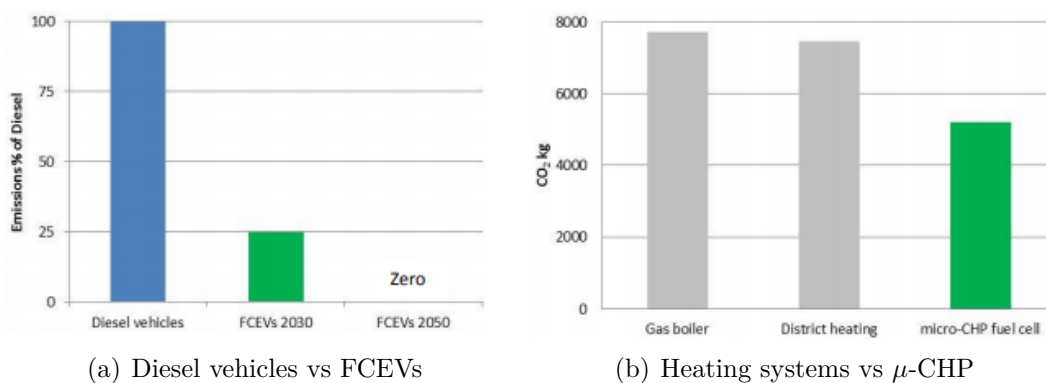


Figure 1.8. Green-House Gas emissions reduction examples

- **Boost of renewable energy systems reliability and energy security:** One of the main obstacle for renewable energy implementation is the reliability of the system and fuel cell technology could be a key factor to mitigate this problem. Fuel cells allows flexibility for the grid as a "energy switch". When the supply is higher than the demand hydrogen is produced and storage through electrolysis. Then, the hydrogen storage could generate electricity through fuel cells when renewable energy systems is not able to fulfill the demand requirements or deliver it for mobility or industry purposes.

A higher reliability on renewable energy will reduce the dependance on energy imports. The money saved by the energy imports is considered sufficient to cover both the fuel cell vehicle technology and the new hydrogen energy infrastructure [36].

- **Job creation:** The creation of a new whole market will allow European countries to develop a strong and competitive FCH sector and therefore high value level jobs through all the value chain areas from the production of hydrogen to commercialization of end-products. According to the report *Fueling Europe's Future* by Cambridge Econometrics the job creation only in the automotive sector will be between 500,000 to 1.1 million by 2030.
- **Stimulation of Smart-Grids and Smart-Cities:** Fuel Cells' properties are ideal for distributed generation reducing the electricity losses of current transmission grids. In addition, Smart-Citizens can be proactive in their electrical and heat consumption with their own fuel cell system at their homes.
- **Increase the interest in STEM and R&D projects:** Many companies are complaining that in Europe there is a Science, Technology, Engineering and Mathematics (STEM) workers shortage and it is challenging finding suitable candidates. The support for Europe's research and development community by European organizations, private companies and academic research institutions together with the dissemination of electro-chemistry concepts, energy engineering, computer modelling could partly rectify the lack of STEM skills.

The European Union through FCH 2 JU have invested more than 730 €million since 2008 [38] and by the 2018 the annual investment is settled in 73.2 €million [36]. Figure 1.9 shows the total amount of money invested in each area, the share of the investment, the number of projects developed with the budget assigned and some examples in each area.

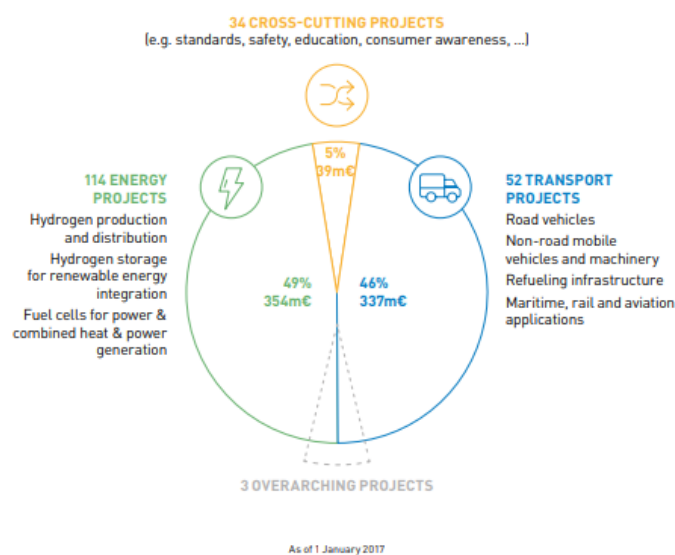


Figure 1.9. Total Budget of FCH 2 JU [38]

Because of these benefits Europe and the world is investing in fuel cell systems. In order to figure out the magnitude of fuel cells the report done by E4tech consultancy for 2017 shows the shipments by region, by application and by fuel cell type from 2012 to 2017 in figures 1.10, 1.11 and 1.12.

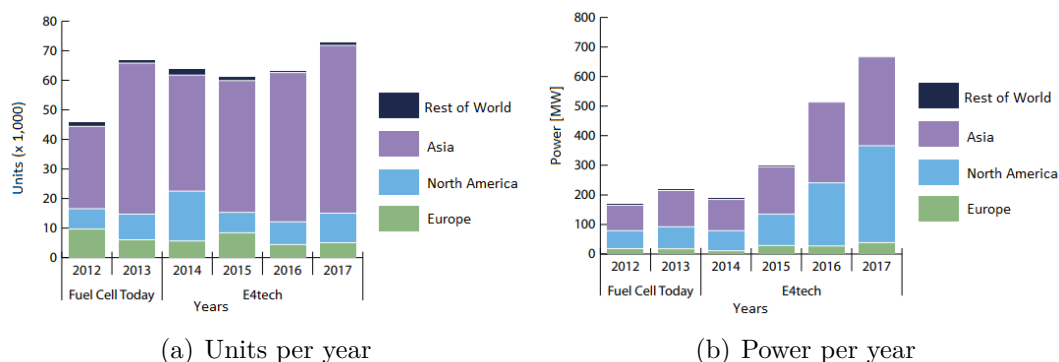


Figure 1.10. Fuel Cells Systems by Region [37]

As it is shown in figure 1.10, the Asian market is the strongest respect units sold however in power terms the Asian and the North America regions shares similar results. In fact, in power terms Asia and North America have approximately 95% of the world market. In Europe, the units of fuel cells increased mainly by residential and μ -CHP units and in a lesser extent by cars, large stationary systems and stationary back-up power systems. With respect the power installed in Europe, there was a slight increment but it is still below 50 MW in total [37].

If the fuel cells systems are analyzed according its applications as it is shown in figure 1.11, we can check two main ideas. The first idea is that stationary applications are consolidated and predominate the fuel cell market. The second idea is that the transport applications sales increased notably during the recent previous years since 2014 being the kind of application that requires more power. Toyota,

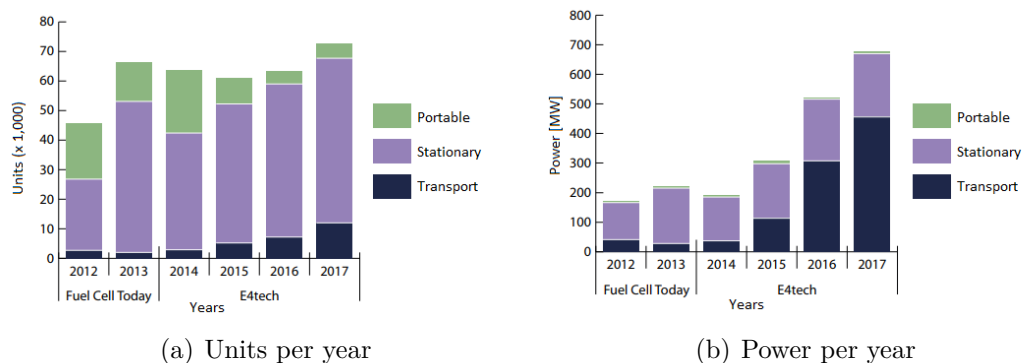


Figure 1.11. Fuel Cells Systems by Application [37]

Honda and Hyundai, three well-known car manufacturers, have more than 50% of the power in transport applications and their cars (around 3,000 cars) represent approximately 350 MW of the total [37].

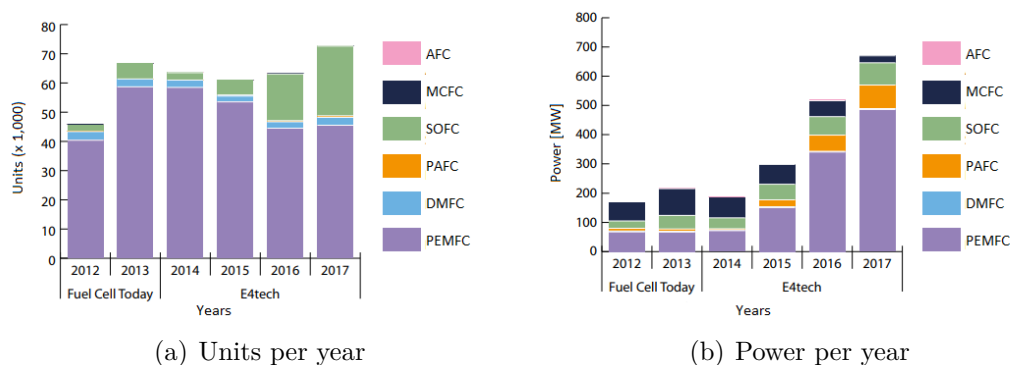


Figure 1.12. Fuel Cells Systems by Fuel Cell Types [37]

In order to figure out the importance of PEMFC in fuel cell technology is necessarily to observe figure 1.12. Actually, PEMFC represents approximately 62.7% of the total market (45,500 units out of 72,600 total fuel cell systems) [37]. Furthermore, more than 90% of PEMFCs were applied for transport applications. The other main fuel cell type which is sold are SOFCs. This kind of fuel cell is growing mainly because of the Japanese Ene-farm program (fuel cells for residential use).

In the following sections, the two main applications of fuel cells will be discussed showing commercial fuel cells examples.

1.6.1 Cars

PEMFCs cars provide a reliable solution to environmental targets in transport applications due to its properties. This kind of cars are quiet, emit zero pollutants, its by-products are water and heat as it is previously said. Furthermore, it can be refuelled in few minutes, similar as current diesel cars, and can travel long distances without refuelling (actually 500 km but it is estimated to reach 800 km in the next years) [38]. Nowadays, according to Toyota, more than 4,000 fuel cell vehicles are

operative in the world [39] and its number is going to increase exponentially in the following years.

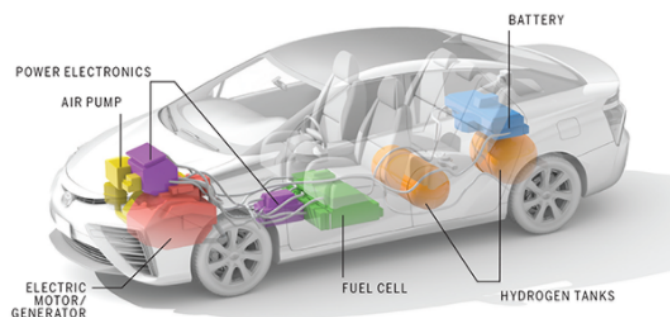


Figure 1.13. Toyota Mirai Schedule

According to the DOE Hydrogen and Fuel Cells Program Record 17007, the estimated cost to manufacture a fuel cell vehicle at 1,000 units annually is approximately 230\$/kW (186 €/kW) based on Toyota Mirai information [40]. In addition, in figure 1.14 it is projected how much the fuel cell stack cost components represents depending on the units produced per year.

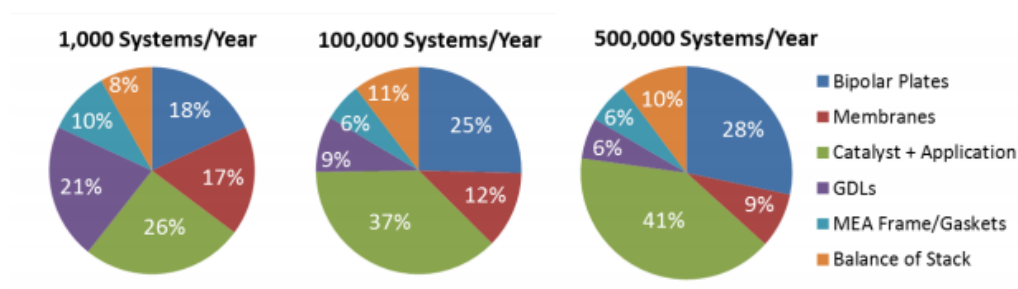


Figure 1.14. Estimations of fuel cell stack cost at different units per year [40]

Some examples of fuel cell cars are shown in figure 1.15 as the Toyota Mirai, the Honda Clarity Fuel Cell or the Hyundai Nexu.

1.6.2 Domestic Fuel Cell μ -CHP

Fuel Cell μ -CHP systems are able to supply and control the demand for heating, for sanitary hot water and for electricity in residential areas. The main type of fuel cell used are PEMFCs and SOFCs. One of the main advantages of using this technology are the high-efficiency as they offer 60% of electrical efficiency and up to 90% in heat and power combined efficiency [38]. In addition, this system can support and facilitate demand-aggregation concept, where in Spain is not allowed except for electrical vehicles, a very attractive concept for transmission system operators (TSO). By the demand-aggregation idea, the power generation can be modify in order to match the demand with the supply, specially useful for renewable sources integration.



Figure 1.15. Fuel Cell Cars

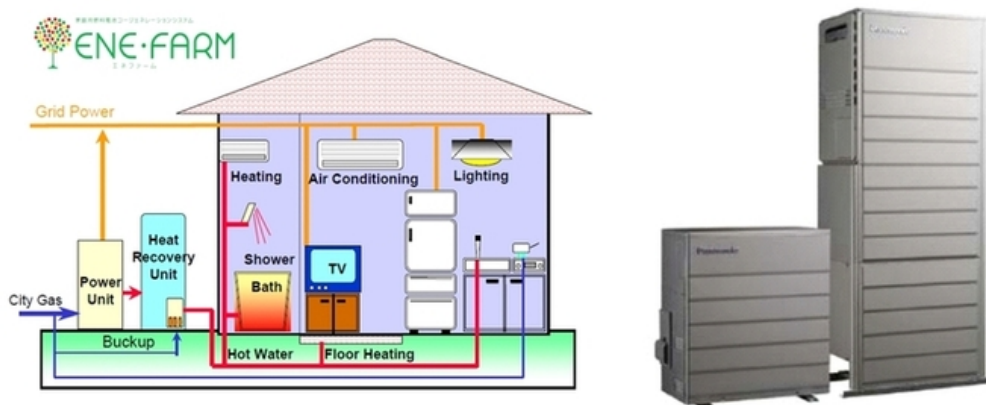


Figure 1.16. Fuel Cell μ -CHP Scheme

The Japanese Ene-Farm programme is the largest of the world. In figure 1.17, it can be checked out the evolution of this programme over the years since its beginning in 2009. In this graph we can observe that during the last years the annual sales have been around 50,000 units constantly and in order to achieve the Japan's targets an exponential boost is required. The programme has been subsidised by the Japanese government since its beginning. Actually, the subsidy corresponds to a 20% discount per 700 W unit (from 1.5 million ¥ to 1.2 million ¥) [37]. In other words, from around 11,300 € to approximately 9,000 €.

It is predicted prices are going to fall up to 800,000 ¥ (\approx 6,000 €) for PEMFC units by 2019 and up to 1 million ¥ (\approx 7,500 €) for SOFC units by 2021 [37]. The cost reduction together with the increase of durability (some models 90,000 hours) and the reduction of weight and size makes experts to forecast an exponential increase in sales.

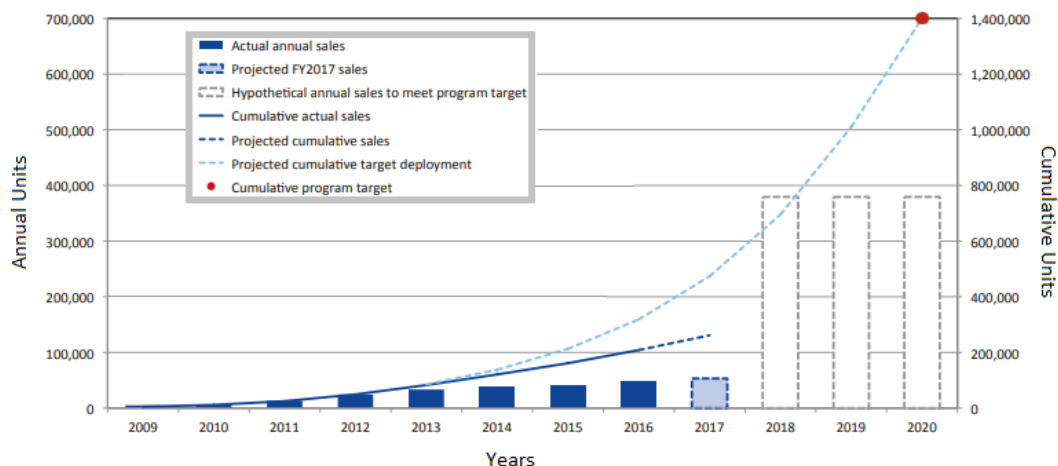


Figure 1.17. Ene-Farm Programme Annual Evolution and Forecast [37]

In figure 1.18, the main products analysed in the European ene.field Project are shown in order of power. The ene.field Project was the propeller of PACE project. The PACE project, which is actually in force, has as the main objective to deploy more than 2,500 units among the 11 European countries involved by 2021 [41]. These project are considered the most ambitious projects in fuel cell CHP systems in Europe.

Elcore 2400	Dachs InnoGen	Cerapower FC10 Logapower FC10	Vitovvalor	SteelGen	Galileo 1000 N	Vaillant G5+	PEMmCHP G5	BLUEGEN	ENGEN 2500	Inhouse 5000+
HT PEM 300W	LT PEM 700W	SOFC 700W	PEM 700W	LT SOFC 700W	SOFC 1kW	SOFC 1kW	LT PEM 2kW	SOFC 2kW	SOFC 2.5kW	LT PEM 5kW
Natural Gas	Natural Gas	Natural Gas, Gas	Natural Gas	Natural Gas	Natural gas + Biogas	Natural Gas	Natural Gas + Biogas	Natural Gas	Natural Gas	Natural gas + Biogas + H2
Wall	Floor	Floor	Floor	Wall	Floor	Wall	Floor	Floor	Floor	Floor
Elcore	SenerTec	Bosch Thermotechnik	Viessmann	Ceres Power	Hexis	Vaillant	Ballard Power	Solid Power		RBZ
<p>← Mostly one to two-family houses applications (but not limited to)</p>							<p>← Mostly small and medium commercial buildings, block of flats applications (but not limited to)</p>			

Figure 1.18. Fuel Cell μ -CHP units from ene.field Project (EU)

Polymer Electrolyte Membrane Fuel Cell (PEMFC)

This chapter deals with the theoretical background of polymer electrolyte membrane fuel cells (PEMFCs), which will be the basis of the following chapters related to the modelling and experimental campaign. Throughout this chapter the main components, the processes that take place inside and the fuel used are specifically discussed for a PEMFC. In addition, the thermodynamic and electrochemistry principles that are applied to the PEMFC and the PEMFC performance will be studied in depth. Finally, a remark dealing with water and thermal management in a PEMFC is included due to its importance in PEMFC efficiency and because they are the main theme of the present bachelor thesis.

2.1 PEMFC's Components

The function of main parts of the PEMFC will be discussed in this section. The main components are represented in figures 2.1 and 2.2. The components used in the laboratory will be analysed and described more detailed in chapter 4: experimental campaign.

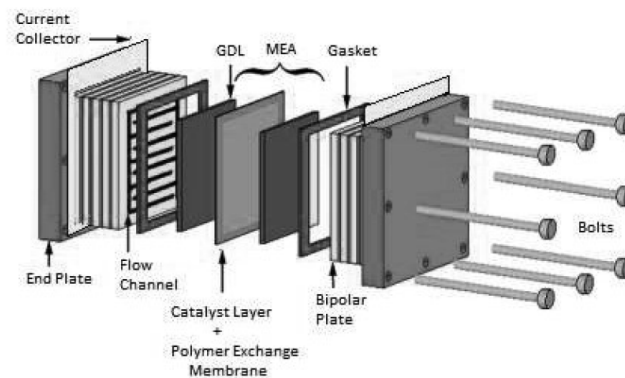


Figure 2.1. PEMFC stack components scheme [42]. Edited.

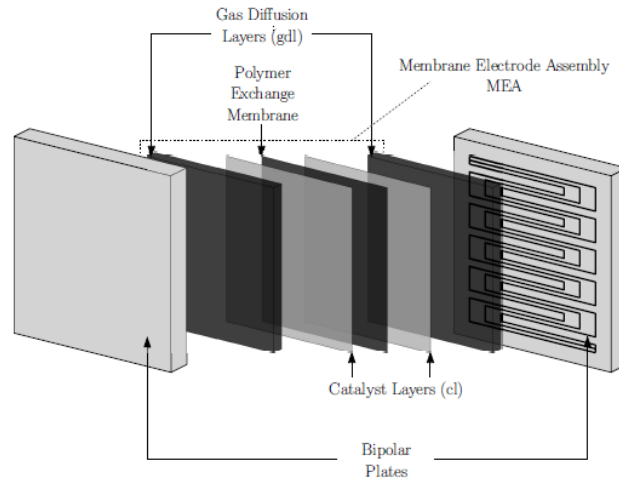


Figure 2.2. PEMFC single assembly scheme [60]

- **End Plate and Bolts:** The end plates, with their respective bolts, are used to fix the fuel cell together with an uniform pressure in order to avoid leakages in the stack. In addition, the inlet and outlet for the reactants and products are placed at the end plates. [44]
- **Current collector:** This item, as its name indicates, collects all the current generated by the PEMFC and delivers it through an external circuit. It is normally gold-plated because of the possible corrosion the fuel cell might suffer and in addition it allows a good electrical conduction with the bipolar plates. [44]
- **Gaskets:** They are placed between the membrane electrode assembly (MEA) and the bipolar plates. Its function is to seal properly the PEMFC to avoid leakages.
- **MEA:** It is consider the core element of fuel cells. In the MEA the electrochemical reactions process take place. It is composed normally by a polymer electrolyte membrane (PEM), two catalyst layers and two gas diffusion layers. This configuration is known also as 5-Layer MEA or MEA5.
 - **PEM:** It can stand to polymer electrolyte membrane or as proton exchange membrane, both have the same acronym PEM. This component is what makes the difference with other fuel cell technologies. The main function of this membrane is to allow only the flow of the hydrogen protons (H^+) from anode to cathode. Even though in the market are several kind of membranes normally, the membrane is made of Nafion® PFSA (a DuPont Co. product). The thickness of the membrane is a crucial variable for PEMFC performance. The membrane should be thin enough to reduce the proton conductivity losses (the thinnest the membrane is, the less distance protons must travel) but thick enough to ensure durability and therefore a long operating life (decelerate membrane degradation caused by crossover). The thickness of the membrane depends mainly on three parameters: the pressure difference between the hydrogen generation and the air coming in, the type of bracket the

membrane will have and the operating life in terms of hours and cycles [44]. In addition, a properly water balance management improves the hydrogen protons conductivity through the PFSA membranes [45]. The Nafion® PFSA membrane shows great resistance to chemical attacks (inert), it can be very thing due to its strong bonds and can absorb great quantities of water without reaching a flooding state which favours the conductivity of hydrogen protons through the membrane [43]. These properties make this kind of membrane the most popular in PEMFC systems.

The anode and cathode electrodes form part of the MEA and they include the catalyst layers and the gas diffusion layers [43]:

- **Catalyst layers:** The main function of the catalyst layers is to increase the electrochemical reaction rate of the fuel cell. These porous layers are made up of noble metal catalyst particles (normally platinum), ionomer and electric conductive phase (normally carbon) [60]. The catalyst particles are scattered through these layers in order to increase the surface area and therefore increase the contact with the reactants. The ionomer favours the proton conduction whereas the electric conductor favours the electron flow. The voids present in these layers enable the circulation of the reactants and products. The catalyst layers are expensive due to the amount of noble metals like platinum present however they are essential in order to achieve high efficiencies in the fuel cell. R&D is focused in creating a catalyst layer without noble metals which will lower the fuel cell stack prices significantly.
- **Gas diffusion layer:** The gas diffusion layer (GDL), as its own name indicates, allows the reactants and products to flow from the bipolar plates to the catalyst layers (and vice-versa). In addition, the GDL provides the removal of by-products in the MEA (water, electricity and heat) and ensures the mechanical strength to fix the MEA to avoid volume changes when water is absorbed. The GDL is made of macro-porous carbon fiber [60] which is an electric and thermal conductor. The GDL has a hydrophobic treatment, normally with Teflon®, in order to improve its water conduction to avoid water flooding. In addition, between the GDL and the catalyst layer a micro-porous layer is placed to minimize the contact between them and also to favour water conduction [44].
- **Bipolar plates:** The bipolar plates allow to distribute the reactants through the electrodes and therefore to flow over the MEA. In addition, they permit the flow of electrons from the MEA where the electrochemical reactions take place to the current collector. The bipolar plates are normally made of graphite which is a good electrical and thermal conductor, has good mechanical strength properties and has chemical stability [43]. The shape, size and pattern of the bipolar plate affects the performance of the PEMFC [6]. Some examples of PEMFC bipolar plates geometry and flow channels orientations are illustrated in figures 2.3 2.4.

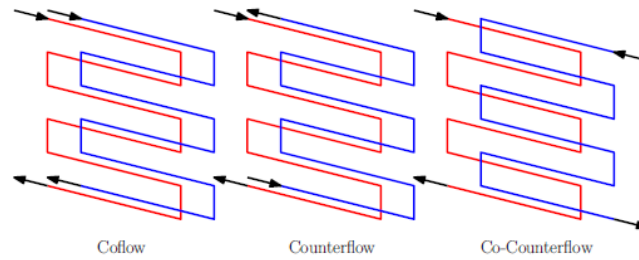


Figure 2.3. Schemes of typical flow directions through the bipolar plates [60]

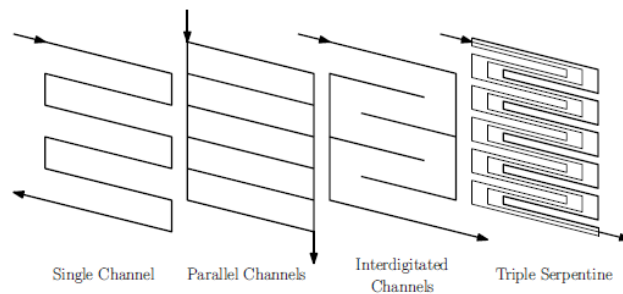


Figure 2.4. Schemes of different geometries in bipolar plates [60]

- **Thermal plates:** These plates are used to keep the PEMFC at a constant desired temperature by heating or cooling the fuel cell stack. The heating plates normally use electricity and resistances to heat the fuel cell. The cooling plates normally use external water which circulates through the fuel cell to cool it. [43]
- **Balance of plant (BOP) components** These components allow a correct functioning of the fuel cell system. They are in charge of fuel storage and processing, the water and thermal management and power conditioning among other tasks [43]. In chapter 4: experimental campaign, these components will be analysed in depth.

2.2 Processes inside a PEMFC

The PEMFC in order to generate electricity from the reactants goes through several processes. In general, these processes can be divided in 5 different stages as it is shown in figure 2.5.

1. **Reactant transport:** The reactants, which are the fuel and oxidant, are supply continuously to produce electricity. The more current the fuel cell is delivering, the more supply is required. In order to ensure the constant supply in an uniform mode, the bipolar plates are grooved in a meandering manner. The reactants flows from the bipolar plates to the catalyst layers by molecular diffusion and convection passing previously through the gas diffusion layers [60, page 5 & 6].

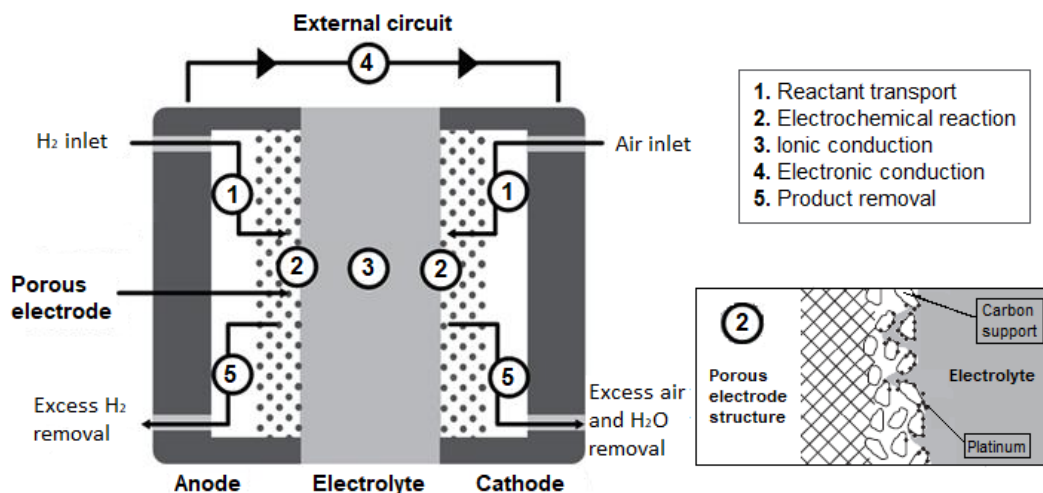


Figure 2.5. PEMFC Scheme [6] [5, page 11]. Edited

2. **Electrochemical reaction:** Once the reactants are in their respective catalyst layers the electrochemical reactions take place [60]. In the anode, oxidation reaction takes place and therefore hydrogen is divided into electrons and protons. The electrons flow through the external circuit while the hydrogen protons pass through the polymer exchange membrane (PEM) electrolyte. In the cathode, a reduction reaction takes place with the electrons flowing from the external circuit, the hydrogen protons coming in from the electrolyte and the inlet of air (only oxygen reacts) from the cathode's inlet. In order to speed up the electrochemical reactions platinum catalysts are used. The faster the reaction takes place, the more current is generated because more electrons are formed.
3. **Ionic conduction:** The ionic conduction, compared with the electronic one, is a more complex process. The complexity of this process relies in the fact that ions have a larger size and a higher mass than electrons. The ionic conduction occurs when there are both a voltage gradient and a concentration gradient as a result of the electrochemical reactions [6, page 95]. In the case of PEMFC, both gradients allow the flow of the positive ions of the hydrogen from the anode side to the cathode side. This conduction is possible because the polymer electrolyte membrane is only permeable by protons [60, page 6]. However, the ionic conduction is an issue R&D is dealing with because the ohmic loss (η_{ohm}) given by the membrane reduces the fuel cell performance [6, page 15]. This fact is the main reason why these membranes are as thin as possible, in order to reduce the distance protons must pass through from the anode to the cathode.
4. **Electronic conduction:** The electronic conduction occurs when there is a voltage gradient as a result of the electrochemical reactions [6, page 95]. In the case of PEMFC, the formation of electrons in the anode side flows through an external electrically conductive circuit to the cathode side. The flow of electrons, in other words the current, through the external circuit is used to generate electricity for the multiple applications the PEMFC technology offers.
5. **Product removal:** The excess of fuel and oxidant and the products formed

by the electrochemical reactions must be removed effectively. In the case of PEMFC, the only product generated is water. However, its removal is an issue that must be improve in order to avoid "flooding" which cause a water management failure. In the experimental campaign, it was very useful the purge gas (nitrogen gas (N_2)) to ensure the correct functioning of the PEMFC and avoid the presence of residues.

2.3 The Fuel: Hydrogen

Hydrogen is the simplest element in nature as its atom is formed by one proton and one electron. The name hydrogen is derived from the greek words "hydro" which means water and "genes" which means forming, both together results in "water- former" [48]. Hydrogen is the most abundant element in the universe, as it is estimated that 75% of the visible mass of stars and galaxies is hydrogen [46].

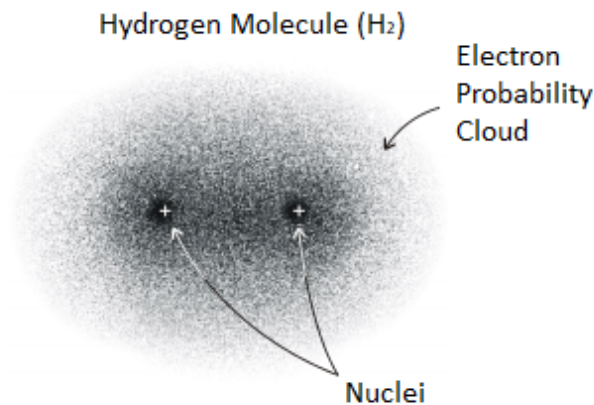


Figure 2.6. Atomic Structure of the Hydrogen Molecule [46]

The atomic structure of molecular hydrogen is formed by the nuclei and an electron probability cloud. The nuclei is 1800 times more massive than the electron while the radius of the electron probability cloud is around 100,000 times larger than the nucleus radius [46]. This facts changes with the deuterium and tritium isotopes, which have one and two neutrons in the nucleus respectively.

Hydrogen atoms are very reactive and this is the reason why in nature normally are combined with other elements to form water or organic compounds for instance. Hydrogen atoms can be also combined between them forming the stable hydrogen molecule (H_2) which is the fuel analysed in this section.

Property	Hydrogen	Propane	Natural Gas	Petrol	Diesel
Chemical formula	H_2	C_3H_8	Hydrocarbon Mixture CxHy (x=1-4)	Hydrocarbon Mixture CxHy (x=4-12)	Hydrocarbon Mixture CxHy (x=9-20)
Operational State	Gas	Gas	Gas	Liquid	Liquid
Boiling Point [°C]	-253	-42.1	-164 → -88	33 -221	250-360
Density NTP [kg/m^3]	0.0838	1.87	0.737	709-727	820-845
Liquid to gas expansion ratio	1:848	1:270	1:600	NA	NA
Lower Heating Values (LHV) at NTP [MJ/kg]	120.21	46.30	47.14	43.45	42.79
Higher Heating Values (HHV) at NTP [MJ/kg]	142.18	50.24	52.23	46.54	45.77
Volumetric energy densities [MJ/L]	5.6 (700 bar)	25.3	9 (250 bar)	34.2	34.6
Flashpoint [°C]	<-253	-104	<-188	-43	55
Flammability Range [%]	4-75	2.2-9.6	3.8-17	1-7.6	6-13.5
Auto Ignition Temperature [°C]	585	490	537	>200	210
Toxicological Information	Non - toxic (asphyxiant)	Non - toxic (asphyxiant)	Non - toxic (asphyxiant)	Poisonous, Irritant to lungs, skin and stomach	Poisonous, Irritant to lungs, skin and eyes

Table 2.1. Comparison between common fuels [52] [53] [54] [55] [57] [58] [46] [47] [49]

Among its physical properties, hydrogen gas stands out in its odorless, tasteless and colorless. Hydrogen is in gaseous state at ambient temperature with a boiling temperature of 20.271 K and a melting temperature of 13.99 K at atmospheric pressure [48]. Among its chemical properties, hydrogen gas stands out in its high energy content. Hydrogen gas is able to generate almost three times more energy than conventional fuels per kilogram (HHV and LHV). However, due to its very low density, hydrogen gas provides much less energy per volume compared with conventional fuels. The volumetric energy density depends on the operational state of hydrogen, if it is used in liquid state or in gaseous form and, if it is a gas, its pressure.

Hydrogen is an energy carrier which means that it can be stored and then delivered to produce energy but it must be created previously by a primary energy source. Hydrogen can be generated from different sources. The most common production procedures are through reforming fossil fuels process and the electrolysis process. The reforming process is a chemical reaction where the fossil fuel is first purified and later oxidized to form hydrogen rich gas (called reformat) and carbon oxides. When the reforming is applied to solid fossil fuels it is called gasification. Electrolysis process consists of applying electricity to water to decompose it into hydrogen and oxygen. Electrolysis process depends on the source of power, in order to be completely clean the electricity must come from non polluting energy sources. [46]

The low density of hydrogen together with its low boiling temperature make hydrogen storage challenging. In addition, the expansion ratio of hydrogen from liquid to gas is 1:848, which means that 1 liter of H_2 in liquid form occupies 848 liters when it is in gaseous state. Actually, there are two main options to store hydrogen: physical-based and material-based. The physical-based storage involves compressed hydrogen gas at ambient temperature, hydrogen in liquid state in cryogenic storage and a mixture of both of them, the cryo-compressed storage. The material-based storage covers the metal hydrides, the chemical hydrogen storage materials and the sorbent-based materials. This method relies on the fact that hydrogen can be adsorbed on the surface of these materials or form part of those components by absorption techniques [50]. The most common procedure to store hydrogen is through compressed hydrogen gas vessels. Hydrogen gas requires large size and pressure tanks between 300-700 bar and 15 times greater by size and 23 times by weight compared with gasoline tanks in vehicle applications meanwhile the hydrogen fuel weights approximately 50 kg which is almost negligible compared with the tank [46].

All fuels carry a degree of risk when they are used and hydrogen is not an exception. Among its numerous advantages, hydrogen presents several properties that must be taken into account. Hydrogen is a non toxic gas, however it can be asphyxiant when there are leakages in not vented spaces because hydrogen can displace the oxygen present in the air [46]. Moreover, hydrogen gas as a flammable fuel carries on certain risks when there is a source of ignition present causing a fire or an explosion. The flashpoint, which is the temperature at which the fuel produces enough vapor to be ignitable, is very low for hydrogen gas (below -253°C). In addition, hydrogen has a wide flammability range. It is necessarily at least 4% of hydrogen in the air to allow the spread of the flame, which is slightly higher

compared with other fuels but while the other fuels has a low upper flammability limit, hydrogen keep burning until there is a 75% of hydrogen in the air, where the fire starts to extinguish due to the lack of oxygen. Furthermore, the low electro-conductivity of hydrogen can generate electrostatic charges and therefore sparks when it is agitated or transported. For this reason, all components in the hydrogen system must be electrically grounded [49]. Also, hydrogen flames are almost invisible for the human eye, so it is required fire and leak devices in all hydrogen facilities.

Nevertheless, hydrogen gas is considered to be as safe as the main fuels in the market or even safer. In case of fire, hydrogen flames burn and dissipate rapidly due to hydrogen high diffusivity and buoyancy properties [46]. Hydrogen auto-ignition temperature is at 585 °C, far away from PEMFC operating temperatures and others fuels auto-ignition temperatures [49].

2.4 Thermodynamics in PEMFC

Thermodynamics is the study of the conversions and changes of energy in a system through physical and chemical processes. Thermodynamics are based on three laws which are detailed in Appendix A. In PEMFCs, thermodynamics analyze the transformation of the fuel from chemical energy to electrical energy. Through thermodynamics we can obtain the theoretical limits of a PEMFC, which in practice will never be achieved because of the losses in the PEMFC which are not considered in thermodynamics. In thermodynamics, the reference conditions of temperature and pressure is called the standard reference state (SRS) ($T = 25^{\circ}\text{C}, p = 1\text{atm}$) which is represented with a superscript $^{\circ}$.

The chemical energy contained in H_2 is quantified by the internal energy (U). Internal energy is the energy present in a system through the interaction between particles in a microscopic scale. PEMFCs are able to transform part of the whole internal energy present in hydrogen into electrical energy. This process is possible due to the electrochemical reactions that take place on each electrode of the PEMFC which are analyzed in-depth in section 2.5: electrochemistry in a PEMFC.

2.4.1 Theoretical Electric Work and Fuel Cell Potentials

The reactants contains all the energy stored in form of chemical energy. This energy is released when the electrochemical reactions are produced in the anode and cathode electrodes and its measured with the enthalpy of reaction. The enthalpy change (ΔH) of the chemical reaction produced in PEMFCs 2.18 can be calculated following equation 2.1. The specific enthalpy (h or \bar{h} depending if we are using massive or molar basis respectively) of the different compounds present in the reaction depends on temperature, pressure and physical state of each compound. The specific enthalpy of the different compounds is calculated applying formula 2.2 which is composed by the enthalpy of formation (\bar{h}_f°) and the specific enthalpy change ($\Delta\bar{h}$) from the reference (SRS) to the interested state. The enthalpy of formation is

the energy released or absorbed, depending on the sign, by the compound when is created from its elements at SRS. In some cases there are two enthalpy of formation for the same compound, like in the case of water, but with different physical state. In the case of water, at SRS it is in liquid state however it is useful to figure out the enthalpy of formation of water in vapour state at SRS even though it is not possible in practice. The enthalpy of formation of stable elements, in our case H_2 and O_2 , is considered zero. In addition, the specific enthalpy of stable elements is also zero at SRS as it can be checked in formula 2.2. The second term of the specific enthalpy ($\Delta\bar{h}$) refers to the gain or loose of energy when a different condition is applied, like in the case of PEMFCs, without modifying the composition.

$$\Delta H = \underbrace{\bar{h}_{H_2O}}_{\bar{h} \text{ products}} - \underbrace{\left(\bar{h}_{H_2} + \frac{1}{2}\bar{h}_{O_2}\right)}_{\bar{h} \text{ reactants}} [J/mol] \quad (2.1)$$

where:

$$\bar{h} = \bar{h}_f^0 + \underbrace{\left(\bar{h}_{(T_A)} - \bar{h}_{(T_{ref})}^0\right)}_{\Delta\bar{h}} [J/mol] \quad (2.2)$$

In this reaction, enthalpy will be always negative. The negative sign means that the process is exothermic, in other words the reaction releases heat.

In chemical reactions, entropy (S) is also generated. Entropy is defined in the second and third law of thermodynamics explained in Appendix A. In general, entropy is a thermodynamic measurement of the molecular disorder of a system. Applying the third law of thermodynamics, in case of pure crystalline structure substances, at 0 K the entropy is equal to zero. This is why the entropy reference is settled at 0 K. The absolute entropy (s^0 or \bar{s}^0 depending if we are using massive or molar basis respectively) is the change in entropy from the reference state ($T = 0K$) to the SRS temperature. As in the case of enthalpy, water has 2 different values of absolute entropy depending if it is considered in liquid or gaseous state. The specific entropy (\bar{s}) can be calculated by adding to the absolute entropy the difference between the entropy of the temperature of interest (T_A) and the absolute entropy of the compound at SRS temperature.

$$\Delta S = \underbrace{\bar{s}_{H_2O}}_{\bar{s} \text{ products}} - \underbrace{\left(\bar{s}_{H_2} + \frac{1}{2}\bar{s}_{O_2}\right)}_{\bar{s} \text{ reactants}} [J/K \text{ mol}] \quad (2.3)$$

$$\bar{s} = \bar{s}^0 + \underbrace{\left(\bar{s}_{(T_A)} - \bar{s}_{(T_{ref})}^0\right)}_{\Delta\bar{s}} [J/K \text{ mol}] \quad (2.4)$$

As it has been said previously in every chemical reaction some entropy is produced. This entropy formation generates irreversible losses in the transformation

of all the chemical energy contained in the reactants into electrical energy in the PEMFC and therefore reduce the production of useful work. The maximum amount of electric work the PEMFCs can deliver theoretically (the work potential) corresponds to Gibbs free energy (G) (equation 2.5) when the pressure is constant. The demonstration of equation 2.5 is shown in Appendix A. For Gibbs free energy, like in the case of enthalpy and entropy, there are two different values for water depending on its physical state. Following the concept that Gibbs free energy represents the maximum electric work a fuel cell delivers theoretically, for PEMFC reaction, water is considered in liquid state because the formation of liquid water releases more energy than vapour water formation.

$$\Delta G = \Delta H - T\Delta S \Leftrightarrow \Delta G = -\Delta W_{electric} \quad (2.5)$$

The electrical work can be expressed as:

$$W_{electric} = nFE \quad (2.6)$$

where:

- n = number of electrons per molecule (In case of PEMFCs $n=2$)
- F = Faraday's constant [C/e⁻mol]
- E = Potential [V]

Therefore, we can express the theoretical electrical reversible potential (E) in terms of Gibbs free energy. When the SRS conditions are applied, the theoretical potential obtained from the PEMFC is called the standard reversible potential of the reaction (E_0) which its value is 1.23 volts as shown in equation 2.7.

$$E = \frac{-\Delta G}{nF} \Rightarrow E_0 = \frac{-237000[J/mol]}{2[e^-/mol \text{ reactant}] \cdot 96400[C/mol]} = 1.23 [V] \quad (2.7)$$

Another parameter related with potential is the thermoneutral potential (E_{th}). The thermoneutral potential represents the maximum fuel cell potential in case no irreversible losses are produced, or in other words, when there is no entropy formation.

$$E_{th} = \frac{-\Delta H}{nF} [V] \quad (2.8)$$

The thermoneutral potential parameter is used to calculate the total heat produced (Q) by the PEMFC as shown in equation 2.8.

$$Q = I(E_{th} - V) [J] \quad (2.9)$$

where:

- Q = Total heat produced by the PEMFC [J]
- I = Current [A]
- E_{th} = Thermoneutral potential [V]
- V = Real Voltage [V]

2.4.2 Effect of Temperature and Pressure in PEMFC Thermodynamics

The theoretical PEMFC potential varies with temperature and pressure. Temperature changes have been considered in previous section however, if the PEMFC operates at different pressure than the atmospheric pressure, the previous formulas are not longer valid. PEMFC operates from atmospheric pressure up to 7 bars and from 60°C to 80°C normally [5]. Therefore, for PEMFC operational conditions (pressure and temperature different than the SRS conditions) the van't Hoff isotherm and the Nernst equations are required. The van't Hoff isotherm equation (equation 2.10) calculates the Gibbs free energy meanwhile the Nernst (equation 2.11) establishes the theoretical electrical reversible potential. Both equations are related between them by equation 2.7 and introduces a new variable called activity (a).

$$\Delta G = \Delta G_0 + RT \ln \left(\frac{\prod_{products} a_k^{v_k}}{\prod_{reactants} a_k^{v_k}} \right) [J/mol] \quad (2.10)$$

$$E = E_T - \frac{RT}{nF} \ln \left(\frac{\prod_{products} a_k^{v_k}}{\prod_{reactants} a_k^{v_k}} \right) [V] \quad (2.11)$$

where:

$$E_T = E_0 + \frac{\Delta S}{nF} \cdot (T - T_0) [V] \quad (2.12)$$

The activity of a chemical species (a_k) depends on its chemical nature [6, page 46]. The chemical nature can be categorised in ideal gas, non-ideal gas, dilute solution, non-ideal solution and pure components. In this analysis, the PEMFC's reactants have been considered ideal gas. The activities of interest are:

$$a_k = \begin{cases} \frac{p_k}{p_0} & \rightarrow \text{Ideal Gases} & H_2, O_2 \\ 1 & \rightarrow \text{Pure Components} & \text{Liquid water is normally considered as 1 [6]} \end{cases}$$

For hydrogen PEMFC, van't Hoff isotherm and Nernst equations (equations 2.11

and 2.10) lead to:

$$\Delta G = \Delta G_0 + RT \cdot \ln \left(\frac{a_{H_2O}}{a_{H_2} \cdot a_{O_2}^{1/2}} \right) \Rightarrow \Delta G = \Delta G_0 + RT \cdot \ln \left(\frac{1}{\frac{p_{H_2}}{p_{\sigma}^1} \cdot \left(\frac{p_{O_2}}{p_{\sigma}^1} \right)^{(1/2)}}} \right) [J/mol] \quad (2.13)$$

$$E = E_T - \frac{RT}{nF} \cdot \ln \left(\frac{a_{H_2O}}{a_{H_2} \cdot a_{O_2}^{1/2}} \right) \Rightarrow E = E_T - \frac{RT}{2F} \cdot \ln \left(\frac{1}{\frac{p_{H_2}}{p_{\sigma}^1} \cdot \left(\frac{p_{O_2}}{p_{\sigma}^1} \right)^{(1/2)}}} \right) [V] \quad (2.14)$$

$$E_T = 1.23 + \frac{\Delta S}{2F} \cdot (T - 298) [V] \quad (2.15)$$

These equations are able to predict the theoretical potential of the PEMFC under any conditions of temperature and pressure. When temperature increases, the theoretical potential decreases according to equations 2.11 and 2.14 because for temperatures below 100°C (PEMFC operation temperature) variations of enthalpy and entropy are small compared to the increase of temperature. However, in practice we can observe that an increment of temperature leads a higher cell potential. The reason for this contradiction is because the voltage losses of the PEMFC lessen when the temperature is higher, compensating the decrease of the theoretical potential. When pressure increases, the theoretical potential also raises as it is shown in equations 2.11 and 2.14. When air is used instead of pure oxygen the theoretical potential decreases proportional to its concentration. For this analysis it is supposed that there is 21% of oxygen in air, therefore the partial pressure of oxygen in equations 2.11 and 2.14 will be the pressure of air multiplied by the oxygen factor (0.21).

2.5 Electrochemistry in a PEMFC

In the PEMFC, the following electrochemical reactions takes place simultaneously in the anode's and in the cathode's sides of the membrane. The electrochemical reactions is the most important process in the fuel cell and for them to happen they must overcome the activation energy barrier. Through the electrochemical half-reactions, electric charges are obtained through *redox* (reduction-oxidation) reactions. The *redox* reactions in a PEMFC consist of a oxygen reduction reaction (ORR) which takes place in the cathode and an hydrogen oxidation reaction (HOR) which takes place in the anode.

At the anode:



At the cathode:



In general:



It is important to remark that in reality some intermediate steps and side reactions might occur, being sometimes unwanted for the correct functioning of the PEMFC. [5, page 17]

2.5.1 Reaction Rate

The reaction rate is the speed at which the electrochemical reactions occur. The higher the reaction rates are, the faster the reactants turn into products and more current is produced by the PEMFC. However, in PEMFC electrochemistry, current density (j) is used instead of current. Current density is the current per the PEMFC's surface area where the electrochemical half-reactions take place (equation 2.19). In addition, current density can be expressed in terms of net reaction rate (v) or flux of reactant per unit area [5, page 33-34].

$$j = \frac{i}{A} = nFv = nF \underbrace{(v_{forward} - v_{backward})}_v [A/cm^2] \quad (2.19)$$

Lets consider a generic electrochemical reversible reaction:



In the case of the PEMFC, the forward reaction belongs to the cathode electrode reduction reaction (ORR) and the backward reaction belongs to the anode electrode oxidation reaction (HOR). It is important to note that when the electrodes are in equilibrium, the oxidation and reduction happen at the same reaction rate [5, page 34]. The reaction rate is proportional to the surface concentration of the reactants as shown in equation 2.21.

$$v = kC \Rightarrow \begin{cases} v_{forward} & = k_f C_{ox} & [mol/s \text{ cm}^2] \\ v_{backward} & = k_b C_{rd} & [mol/s \text{ cm}^2] \end{cases} \quad (2.21)$$

where:

- k = Reaction rate coefficient [1/s]

- C = Surface concentration of reacting species [mol/cm²]

In addition, we have to consider that Gibbs free energy for electrochemical reactions, beyond what it has been said previously, have two components: a chemical term and a electrical term. For the PEMFC analysis, the Gibbs free energy for the ORR and HOR reactions will consist of:

$$\Delta G_{ORR} = \Delta G_{chem} + \alpha_{rd}FE \text{ [J/mol]} \quad (2.22)$$

$$\Delta G_{HOR} = \Delta G_{chem} - \alpha_{ox}FE \text{ [J/mol]} \quad (2.23)$$

where:

- ΔG_{chem} = The chemical term of the Gibbs free energy [J]
- $\alpha_{rd,ox}$ = Transfer coefficient
- F = Faraday's constant [[C/mol]]
- E = Potential [V]

For PEMFC electrochemical reactions, the charge transfer coefficient (α) is used instead of the symmetry factor because the PEMFC reactions involves several steps and electrons. The transfer coefficients for the hydrogen/oxygen PEMFC conditions (Pt catalyst) has a value according to F. Barbir of 1, however, other researchers estimates the transfer coefficient in a range between 0.2 and 2 [5]. This variation of the transfer coefficients is caused by the experimental nature of this variable. At steady state we can assume all the steps have the same rate. This rate is determined by the slowest step of the reaction and it is called the rate-determining step.

The reaction rate coefficient can be expressed it terms of the Gibbs free energy previously mentioned. The general equation which relates the reaction rate coefficient with the Gibbs free energy is obtained through the Transition State Theory [5, page 35].

$$k = \frac{k_B T}{h} \exp \left[\frac{-\Delta G}{RT} \right] \text{ [1/s]} \quad (2.24)$$

where:

- k_B = Boltzmann's constant [J/K]
- h = Planck's constant [J s]
- T = Temperature [K]
- R = Gas constant [J/K mol]

The reaction rate coefficient for the forward and backward reactions applying the Gibbs free energy concept shown in equations 2.23 and 2.22 are:

$$k_f = \underbrace{\frac{k_B T}{h} \exp\left[\frac{\Delta G_{chem}}{RT}\right]}_{k_{0,f}} \exp\left[\frac{-\alpha_{rd} F E}{RT}\right] \quad [1/s] \quad (2.25)$$

$$k_b = \underbrace{\frac{k_B T}{h} \exp\left[\frac{\Delta G_{chem}}{RT}\right]}_{k_{0,b}} \exp\left[\frac{\alpha_{ox} F E}{RT}\right] \quad [1/s] \quad (2.26)$$

2.5.2 Reaction rate, current density and potential: Butler-Volmer Equation

Returning to the concept of the net current density generated by the PEMFC (equation 2.19), it can be expressed as:

$$j = nF(k_f C_{ox} - k_b C_{rd}) \quad [A/cm^2] \quad (2.27)$$

And in turn, including the equations developed in equations 2.25 and 2.26:

$$j = nF \left(k_{0,f} C_{ox} \exp\left[\frac{-\alpha_{rd} F E}{RT}\right] - k_{0,b} C_{rd} \exp\left[\frac{\alpha_{ox} F E}{RT}\right] \right) \quad [A/cm^2] \quad (2.28)$$

The net current density at equilibrium is equal to zero [5, page 35] as the reaction rate in the electrodes are the same. The current density in the forward and backward reactions at this state, the thermodynamic equilibrium, is called the exchange current density (j_0) [6, page 69]. At the exchange current density state, the potential is called the reversible potential or equilibrium potential (E_r). The reversible potential is by definition 0 V at the anode electrode and at the cathode depends on the temperature and pressure at is shown in equation 2.14 [5, page 36]. The exchange current density shows how good the electrodes go by with the electrochemical reactions. A high exchange current density means that the surface of the electrode is very active.. In the case of a PEMFC, the anode electrode presents a larger exchange current density compared with the cathode electrode (several orders of magnitude) [5, page 39]. Applying these concepts, the exchange current density can be stated as:

$$j_0 = nF k_{0,f} C_{ox} \exp\left[\frac{-\alpha_{rd} F E_r}{RT}\right] = nF k_{0,b} C_{rd} \exp\left[\frac{\alpha_{ox} F E_r}{RT}\right] \quad [A/cm^2] \quad (2.29)$$

Finally, combining equations 2.28 and 2.29 together the Butler-Volmer equation is obtained 2.30. The Butler-Volmer equation is considered the basis of electrochemical kinetics [6]. This equation is able to relate the current with voltage in a electrochemical reaction by stating that the current produced by this kind of reactions increases exponentially with the overpotential (ϵ). The overpotential is the difference between the electrode potential and the reversible potential. The overpotential represents the amount of voltage lost to overcome the activation energy barrier and therefore generation of current in the PEMFC. The Butler-Volmer equation is valid for single-step electrochemical reactions and for multiple-step electrochemical reactions assuming that the rate-determining step is applied for all the steps, being the last case the conditions assumed for this analysis [6, page 74].

$$j = j_0 \left(\exp \left[\frac{-\alpha_{rd} F \overbrace{(E - E_r)}^{\epsilon}}{RT} \right] - \exp \left[\frac{\alpha_{ox} F \overbrace{(E - E_r)}^{\epsilon}}{RT} \right] \right) [A/cm^2] \quad (2.30)$$

The Butler-Volmer equation can be applied to each electrode independently. It must bear in mind that the overpotential (ϵ) on the anode is positive which makes the oxidation reaction predominant proving that electrons leave the anode electrode as its current density is negative. The opposite effect takes place in the cathode electrode. The overpotential in the cathode is negative which makes the reduction reaction predominant demonstrating that the electrons arrive the cathode electrode because the current density is positive. As a last observation, the overpotential on the anode and on the cathode are not necessarily the same, being normally the cathode overpotential much larger than the anode one [5, page 39].

2.6 PEMFC performance: Losses and Efficiency

As it can be expected, the theory shown in the previous sections doesn't match with the practice. The difference between the theoretical electric potential (E) and the real voltage (V) relies on the irreversible losses a PEMFC suffers. There are several kinds of factors that reduce the voltage of the PEMFC:

Activation Losses (η_{act}): Also called activation polarization. This loss is caused by the electrochemical reaction principle where the reactants need to overcome the activation energy barrier in order to turn into products. This loss is represented by the overpotential variable (ϵ) discussed in section 2.5.2 along the Butler-Volmer equation. This kind of loss affects both electrodes, being a more significant loss in the cathode as it requires a much higher overpotential as it is shown in figure 2.7. In order to reduce the activation losses, an increase of the exchange current density is required (figure 2.8). This is why the activation losses increases exponentially at low current densities but they smooth when the current density increases.

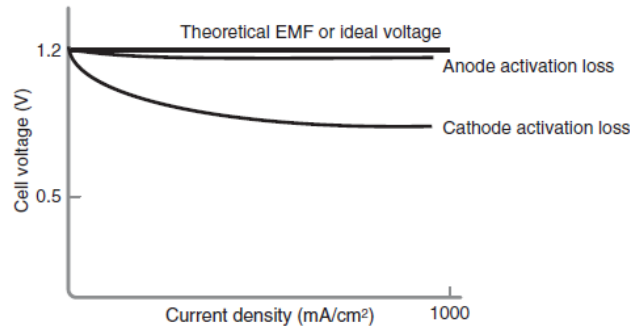


Figure 2.7. Activation loss effect on the PEMFC at both electrodes [6]

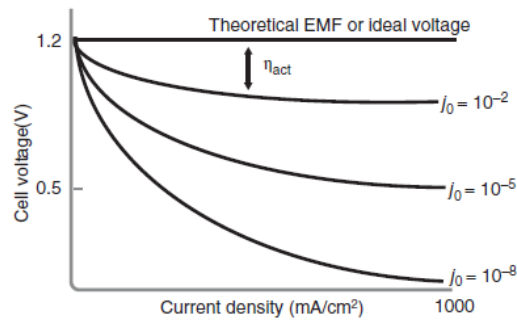


Figure 2.8. Activation loss effect on the PEMFC at different exchange current density [6]

Ohmic Losses (η_{ohm}): The ohmic losses represents the resistance of the PEMFC's components for the charge transport (ions and electrons). These losses are called ohmic losses because they fit in Ohm's Law, explained in Appendix A. The resistance for the ionic charge in PEMFC's components is much greater than the resistance for electrons due to its size and mass. For this reason, sometimes the electronic contribution for the PEMFC internal resistance is negligible. The value of the addition of all the resistances present in the PEMFC (R_{ohmic}) is typically between 0.1 and $0.2 \Omega \text{ cm}^2$ [5, page 45]. In figure 2.9 is shown the effect of the ohmic loss in the PEMFC performance at different internal resistance values. In order to minimize the ohmic losses, the thickness of the components (specially the membrane) should be as thin as possible and with a low contact resistance between the electrolyte and the electrode.

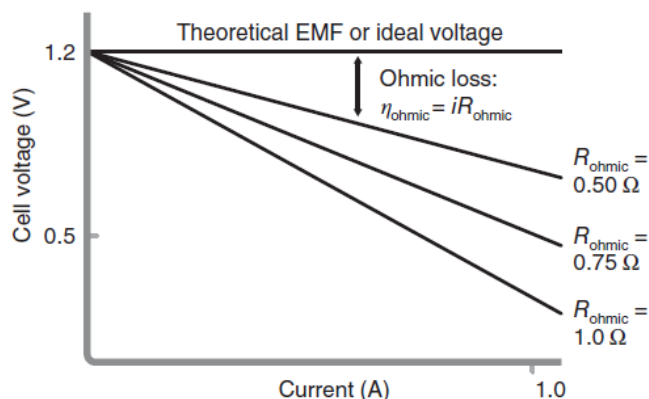


Figure 2.9. Ohmic loss effect on the PEMFC at different internal resistance values [6]

Concentration Losses (η_{conc}): Also called mass transport losses. The concentration losses represent the deficiencies of the reactants and products transport among the PEMFC. The concentration loss can be caused because there is a high current density overcoming the PEMFC finite reactant concentrations at the catalyst layer surface (reactant depletion) and/or there is inefficient removal of the products blocking the catalyst layer surface (product accumulation). The maximum current density a PEMFC can deliver is called the limiting current density [5]. The closer the current density is to the limiting current density, the greater are the concentration losses (figure 2.10). In order to reduce the concentration losses a correct flow structures are required.

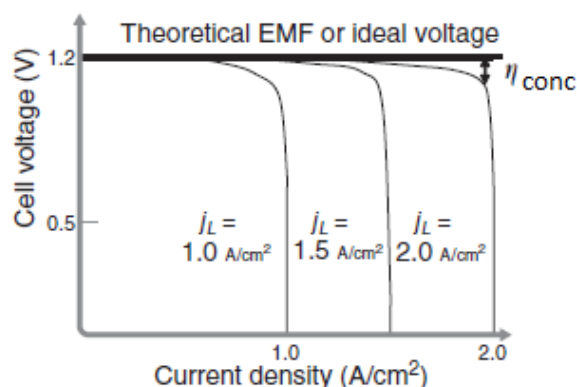


Figure 2.10. Concentration loss effect on the PEMFC at different current densities values [6]

Crossover Losses: Hydrogen fuel may diffuse through the polymer electrolyte membrane without reacting even though the membrane is theoretically impermeable to reactant gases. Both hydrogen and oxygen/air may permeate the membrane, however oxygen permeation rate is negligible compared with the hydrogen one [5, page 44]. Focusing in the hydrogen molecule, when it reaches the cathode side it reacts with the oxygen present meaning that the PEMFC has lost 2 electrons in the generated current per

molecule. The crossover effect is significant at open circuit potential or low current density, however at operating current densities, the permeation rate reduces significantly and therefore the crossover losses can be neglected.

In general, the real voltage can be expressed as the theoretical voltage minus the losses produced in the PEMFC (equation 2.31 and figure 2.11). The net PEMFC performance can be displayed by the polarization curve, which will be analyzed in detail in chapter 4: experimental campaign.

$$V = E - \eta_{act} - \eta_{ohm} - \eta_{conc} [V] \quad (2.31)$$

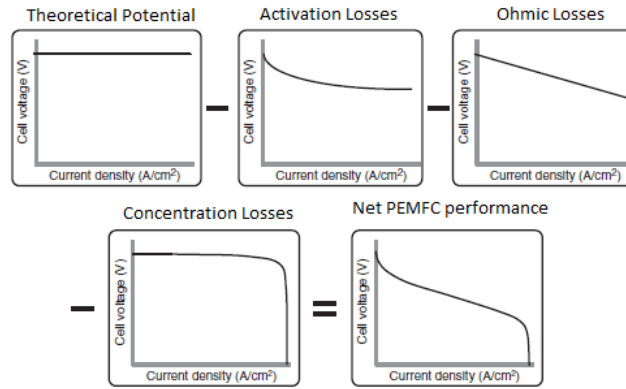


Figure 2.11. Fuel Performance considering the voltage losses [6]. Edited.

The PEMFC efficiency is the ratio between useful energy or work output and the energy employed, or in other words, the energy output versus the energy input. The two main efficiency parameters in PEMFC are the theoretical efficiency (η_{th}) (equation 2.32) and the global efficiency (η) (equation 2.33). In the case of PEMFC, the useful energy is the electrical energy obtained and the employed energy is the hydrogen enthalpy (ΔH). The theoretical efficiency is the maximum possible efficiency of the PEMFC.

$$\eta_{th} = \frac{\Delta G}{\Delta H} = \frac{\frac{-\Delta G}{nF}}{\frac{-\Delta H}{nF}} = \frac{E}{E_{th}} \quad (2.32)$$

$$\eta_{th} = \frac{W_{elec}}{W_{H_2}} = \frac{V \cdot \mathcal{I}}{E_{th} \cdot \mathcal{I}} = \frac{V}{E_{th}} \quad (2.33)$$

2.7 Water and Thermal Management in PEMFC

Water and thermal management are two of the main R&D challenges for PEMFC stack development and commercialization, specially for transport applications [23]. Both plays a key role in the performance and durability of the fuel cell.

In the case of water management, the fuel cell membrane needs enough water in order to maintain a high proton conductivity which is closely linked to the performance of fuel cell. On one hand, if the water content is not enough, the membrane gets dry leading to a lower conductivity of the membrane and therefore a lower performance. In addition, a dry membrane can develop pinholes which can shorten the lifespan of the membrane. On the other hand, an excessive amount of water can block the gas diffusion layers or the pores of the catalyst reducing the reactant mass transport, which, in turn, reduce the performance of the fuel cell, an inhomogeneous cell operation or even a cell reversal. In order to have the higher efficiency in the fuel cell a balance of water must be done: allow enough water in the membrane for a high proton conductivity and remove the condensed water that can block or reduce the fuel mass transport [59] [60]. Water maldistribution and accumulation can be detected experimentally because at those conditions the PEMFC stability analysis shows an oscillatory behaviour along time in PEMFC. The reason is because of the transit state between hydrated and excessive hydrated or dehydrated membrane states. Several studies has observed PEMFC oscillatory behaviour at low cathode inlet relative humidity gases and high anode inlet relative humidity values

In the case of thermal management, there is a high heat generation that must be removed for durability and performance reasons. The heat generation in a PEMFC is caused by the electrochemical reactions, entropy generation, ohmic losses and water condensation [61]. In the case of the electrochemical reactions and the entropy generation, the heat is generated at both electrodes being greater at the cathode electrode. This fact impose a thermal management challenge for maintaining temperature constant across the MEA [61]. PEMFC generates high amount of waste heat when it operates at high power densities. In addition, PEMFC is not able to remove the waste heat by its own because there is a low temperature driving force (the operational temperature of a PEMFC (60-80°C) results in a small temperature differential with ambient temperature) and because the product removal process in PEMFC is inefficient in heat removal. For these reasons, a cooling system is required for PEMFC which can modify the PEMFC size and limit the operating power density [61] [23].

In order to improve water and thermal management, variations in temperature and relative humidity are made in the inlet streams (hydrogen and air/oxygen). The inlet streams can hydrate or dehydrate the cell preventing flooding/dry membrane and non-uniform temperature distribution [60] [61].

2.8 Objectives

In the present bachelor thesis has raised as its main objective to set, for the first time, a zone of stable operation for future projects based on water balance for the fuel cell UC3M laboratory . In order to do so:

1. A global mass balance and a water balance will be described in order to achieve a better understanding of the challenge of fuel cell water management at low temperatures.

2. A dimensionless analysis will be performed in order to observe the theoretical effect of humidity on each side of the PEMFC.
3. Several simulations will be performed at different pressure, stoichiometries and relative humidities for the cathode and anode gases to observe its theoretical effect in PEMFCs.
4. A characterization experiment will be performed for the UC3M PEMFC.
5. Several tests were performed in order to observe and analyse the effect of the cathode inlet relative humidity variation in the stability performance of the UC3M PEMFC. This experimental procedure is based on the experiments performed by Juan Sánchez Monreal in DLR-Stuttgart.

Global Balances of Mass and Water in PEMFC

3.1 Introduction

In this chapter a balance of mass will be presented. The great importance of water accumulation/depletion in the performance of the PEMFC makes the balance of water (BOW) an interesting topic to analyze outside the balance of mass. The model described in this chapter is based in the doctoral thesis done by Juan Sánchez Monreal [60]. In addition, the figures presented in this chapter of this bachelor thesis are obtained from Juan Sánchez Monreal Matlab codes.

Several assumptions, listed below, have been made in these balances analysis:

- The PEMFC's operating conditions are at steady state.
- The PEMFC at a whole is considered as a system. The mass balance for the PEMFC has been calculated under the control volume shown in figure 3.1.
- The water production inside the PEMFC is considered completely saturated ($RH_{production} = 100\%$).
- The transportation of the reactants through the membrane is constant.
- The PEMFC stack have 1 cell.
- The pressure at the anode and cathodes electrodes are equal to the pressure of the PEMFC.
- The only side reactions that takes place at the PEMFC are the ones described in section 2.5: Electrochemistry in a PEMFC.

At the anode:



At the cathode:



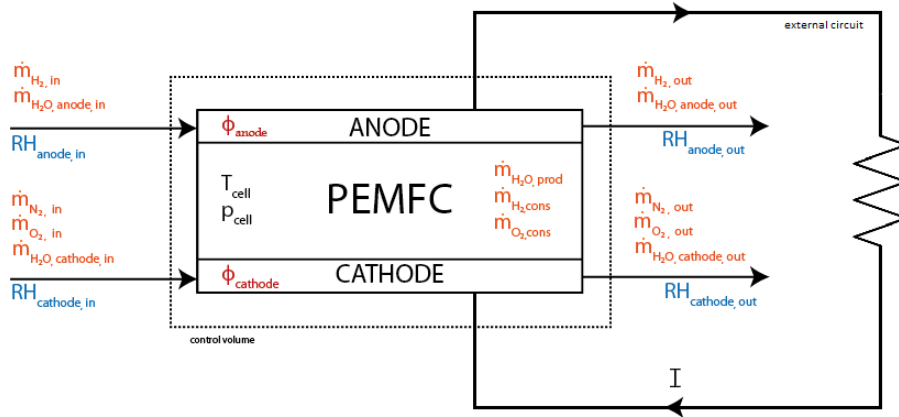


Figure 3.1. Schematic representation of the control volume and the variables considered for the PEMFC mass balance

In addition, the stoichiometric ratio and the relative humidity terms are essential to understand and develop the model studied in this chapter.

The stoichiometric ratio (ϕ) of the reactants is the ratio between the reactant's flow rate injected to the fuel cell and the consumption rate in the fuel cell. It is important to remark that the reactants' flow rate must be at least equal to the PEMFC's consumption ($\phi \geq 1$). For a PEMFC, there are three possible different modes of reactant supply depending on the stoichiometric ratio: the dead-end mode ($\phi = 1$), the flow-through mode ($\phi > 1$) and the recirculation mode ($\phi \approx 1$). Normally, fuel cells work with higher reactants' inlet flow rates than the consumption flow rate, particularly at the cathode, to improve the fuel cell performance as they facilitate the removal of water produced by the fuel cell away and in addition they keep oxygen concentration high [5, page 128].

The relative humidity (RH) present in the inlets and outlets flow rates is the ratio between the amount of water vapour present in the gas and the maximum amount of water vapour that could be in the gas. The relative humidity is calculated using pressure (p), following equation 3.3.

$$RH = \frac{p_{\text{partial}}}{p_{\text{sat}}} \quad (3.3)$$

The formula 3.3 will be useful not to know the relative humidity but the partial pressure. The saturation pressure of water can be calculated applying the following formula [62].

$$\log_{10} p_{\text{sat}} = -2.1794 + 0.02953 \cdot T_{\text{cell}} - 9.1837 \cdot 10^{-5} \cdot T_{\text{cell}}^2 + 1.4454 \cdot 10^{-7} \cdot T_{\text{cell}}^3 \quad (3.4)$$

where:

- p_{sat} = Saturation pressure of water [atm]
- T_{cell} = Temperature of the cell [°C]

3.2 Mass balance in a PEMFC

The global mass balance of the PEMFC applying all the assumptions previously described is divided in three different sections. Firstly, it is necessarily to know the consumptions and the production of the PEMFC. Secondly, according to the consumption/production and the stoichiometric ratios, the reactant supply can be calculated. Then, the output streams can be obtained finishing all the unknowns related with the mass balance. Finally, a global balance of water is explained and studied. It is important to notice that all the flow rates involving the fuel cells are proportional to current (I) and the number of cells (n_{cell}) [5, page 144], however in this mass balance analysis the number of cells in the fuel cell is considered 1.

3.2.1 PEMFC consumptions

The fuel cell consumption and production can be calculated by applying Faraday's Law:

$$\dot{N}_{H_2,cons} = \frac{I}{2 \cdot F} \cdot n_{cell} \quad [mol/s] \quad (3.5)$$

$$\dot{N}_{O_2,cons} = \frac{I}{4 \cdot F} \cdot n_{cell} \quad [mol/s] \quad (3.6)$$

$$\dot{N}_{H_2O,prod} = \frac{I}{2 \cdot F} \cdot n_{cell} \quad [mol/s] \quad (3.7)$$

where:

- F = Faraday's constant [C/mol]
- I = Current [A]
- \dot{N} = Consumption/Production rate [mol/s]
- 2; 4 = Number of electrons required to form 1 mole of the substance studied. It appears in the side reaction equations 3.1 and 3.2.
- n_{cell} = Number of cells in the fuel cell. In this analysis the number of cells in the fuel cell is considered 1.

Once we know the consumption of the reactants and the water production, we can express them in mass flow rates:

$$\dot{m}_{H_2O,prod} = \dot{N}_{H_2O,prod} \cdot M_{H_2O} = \frac{I}{2 \cdot F} \cdot M_{H_2O} \quad [kg/s] \quad (3.8)$$

$$\dot{m}_{H_2,cons} = \dot{N}_{H_2,cons} \cdot M_{H_2} = \frac{I}{2 \cdot F} \cdot M_{H_2} \quad [kg/s] \quad (3.9)$$

$$\dot{m}_{O_2,cons} = \dot{N}_{O_2,cons} \cdot M_{O_2} = \frac{I}{4 \cdot F} \cdot M_{O_2} \quad [kg/s] \quad (3.10)$$

where:

- \dot{m} = Mass flow [kg/s]

- M = Molecular weight [kg/mol]

3.2.2 Reactant Supply

The reactants flow rates depend on the reactants supply, which in this case is a flow-through mode ($\phi > 1$), and the reactant consumption by the fuel cell. In the anode's side, it is consider a supply of pure hydrogen (H_2) and in the cathode side the reactant supply is air. From both sides some water is coming in due to the relative humidity of both gaseous flows.

3.2.2.1 Anode's Inlet

The anode's inlet consist of:

$$\dot{m}_{anode,in} = \dot{m}_{H_2,in} + \dot{m}_{H_2O,anode,in} \quad [kg/s] \quad (3.11)$$

The hydrogen mass flow rate is:

$$\dot{m}_{H_2,in} = \dot{m}_{H_2,cons} \cdot \phi_{anode} = \phi_{anode} \cdot \frac{I}{2 \cdot F} \cdot M_{H_2} \quad [kg/s] \quad (3.12)$$

The water mass flow coming from the anode side is not trivial, several steps must be done. In order to obtain the mass flow of water coming in it is needed the mass fraction of the species, which requires the molar fraction of the species which in turn requires the partial pressures. Therefore, in order to know the partial pressure of water in the anode inlet feed, equation 3.3 together with 3.4 can be applied (changing the units from atm to Pa).

$$p_{H_2O,anode,in} = RH_{anode,in} \cdot p_{sat} \quad [Pa] \quad (3.13)$$

Next, as the anode gas feed consist only of hydrogen and water, Dalton's Law of partial pressure can be applied to obtain the partial pressure of hydrogen. Notice that Dalton's Law of partial pressure is included in Appendix A.

$$p_{H_2,in} = p_{cell} - p_{H_2O,anode,in} \quad [Pa] \quad (3.14)$$

Once the partial pressures of hydrogen and water are known, its molar fraction (χ) can be calculated applying also Dalton's Law.

$$\chi_{H_2,in} = \frac{p_{H_2,in}}{p_{cell}} \quad \chi_{H_2O,anode,in} = \frac{p_{H_2O,anode,in}}{p_{cell}} \quad (3.15)$$

After that, the mass fraction (Y) is calculated.

$$Y_{H_2,in} = \frac{\chi_{H_2,in} \cdot M_{H_2}}{\chi_{H_2,in} \cdot M_{H_2} + \chi_{H_2O,anode,in} \cdot M_{H_2O}} \quad (3.16)$$

$$Y_{H_2O,anode,in} = \frac{\chi_{H_2O,anode,in} \cdot M_{H_2O}}{\chi_{H_2,in} \cdot M_{H_2} + \chi_{H_2O,anode,in} \cdot M_{H_2O}} \quad (3.17)$$

It is important to notice that the mass fraction can be also expressed in terms of mass flow rates:

$$Y_{H_2,in} = \frac{\dot{m}_{H_2,in}}{\dot{m}_{anode,in}} \quad Y_{H_2O,anode,in} = \frac{\dot{m}_{H_2O,anode,in}}{\dot{m}_{anode,in}} \quad (3.18)$$

Finally, solving equations 3.18 the mass flow rate of water through the anode feed inlet can be expressed as:

$$\begin{aligned} \dot{m}_{H_2O,anode,in} &= \dot{m}_{H_2,in} \cdot \frac{Y_{H_2O,anode,in}}{Y_{H_2,in}} = \\ &= \phi_{anode} \cdot \frac{I}{2 \cdot F} \cdot M_{H_2O} \cdot \frac{\chi_{H_2O,anode,in}}{\chi_{H_2,in}} \quad [kg/s] \end{aligned} \quad (3.19)$$

In general, the anode inlets are:

$$\dot{m}_{H_2O,anode,in} = \phi_{anode} \cdot \frac{I}{2 \cdot F} \cdot M_{H_2O} \cdot \frac{\chi_{H_2O,anode,in}}{\chi_{H_2,in}} \quad [kg/s] \quad (3.20)$$

$$\dot{m}_{H_2,in} = \phi_{anode} \cdot \frac{I}{2 \cdot F} \cdot M_{H_2} \quad [kg/s] \quad (3.21)$$

3.2.2.2 Cathode's Inlet

The cathode's inlet consist of:

$$\dot{m}_{cathode,in} = \underbrace{\dot{m}_{O_2,in} + \dot{m}_{N_2,in}}_{\dot{m}_{air,in}} + \dot{m}_{H_2O,cathode,in} \quad (3.22)$$

In order to know the amount of air coming in from the cathode side, is necessarily to calculate previously the minimum amount of air required in the fuel cell.

$$\dot{m}_{min \text{ air},in} = \dot{m}_{O_2,cons} + \dot{m}_{N_2,min} \quad (3.23)$$

where either $\dot{m}_{min \text{ air},in}$ or $\dot{m}_{N_2,min}$ can be calculated using Amagat's Law and the ideal gas mixture assumption (A.1) since for this bachelor's thesis it has been assumed that air is composed by 79% of nitrogen and 21% of oxygen.

$$\dot{N}_{min \text{ N}_2,in} = \dot{N}_{O_2,cons} \cdot \frac{\xi_{N_2}}{\xi_{O_2}} \quad [mol/s] \quad (3.24)$$

$$\dot{m}_{min \text{ N}_2,in} = \dot{N}_{min \text{ N}_2} \cdot M_{N_2} \quad [kg/s] \quad (3.25)$$

$$\dot{N}_{min\ air,in} = \dot{N}_{O_2,cons} + \dot{N}_{min\ N_2} = \dot{N}_{O_2,cons} \cdot \left(1 + \frac{\xi_{N_2}}{\xi_{O_2}}\right) \quad [mol/s] \quad (3.26)$$

$$\dot{m}_{min\ air,in} = \dot{N}_{min\ air,in} \cdot M_{air} = \dot{N}_{O_2,cons} \cdot \left(1 + \frac{\xi_{N_2}}{\xi_{O_2}}\right) \cdot M_{air} \quad [kg/s] \quad (3.27)$$

where:

- $\dot{N}_{min\ air,in}$ = Minimum amount of air needed in the fuel cell [mol/s]
- $\dot{N}_{O_2,cons}$ = Amount of oxygen consumed by the fuel cell [mol/s]
- $\dot{N}_{min\ N_2,in}$ = Minimum amount of nitrogen needed in the fuel cell [mol/s]
- ξ_k = Initial molar fraction of specie k
- $\dot{m}_{min\ air,in}$ = Minimum mass flow of air needed in the fuel cell [kg/s]
- $\dot{m}_{min\ N_2,in}$ = Minimum mass flow of nitrogen needed in the fuel cell [kg/s]

Once the minimum amount of air needed for the fuel cell is obtained the amount of air coming into the fuel cell can be calculated using the stoichiometric ratio assigned for the cathode ($\phi_{cathode}$). And, as it is indicated in equation 3.22, air mass flow can be divided into oxygen and nitrogen mass flows:

$$\begin{aligned} \dot{m}_{air,in} &= \dot{m}_{min\ air,in} \cdot \phi_{cathode} = \\ &= \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot \left(1 + \frac{\xi_{N_2}}{\xi_{O_2}}\right) \cdot M_{air} \quad [kg/s] \end{aligned} \quad (3.28)$$

$$\dot{m}_{O_2,in} = \dot{m}_{O_2,cons} \cdot \phi_{cathode} = \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot M_{O_2} \quad [kg/s] \quad (3.29)$$

$$\dot{m}_{N_2,in} = \dot{m}_{min\ N_2,in} \cdot \phi_{cathode} = \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot \frac{\xi_{N_2}}{\xi_{O_2}} \cdot M_{N_2} \quad [kg/s] \quad (3.30)$$

The water vapour coming in from the cathode stream, like in the case of the anode stream, is not trivial because several steps are needed. In order to obtain the mass flow of water coming in, it is needed the mass fraction of the species, which requires the molar fraction of the species which in turn requires the partial pressures. Therefore, in order to apply the partial pressure of water in the cathode inlet feed it is apply equation 3.3 together with 3.4 (changing the units from atm to Pa).

$$p_{H_2O,cathode,in} = RH_{cathode,in} \cdot p_{sat} \quad [Pa] \quad (3.31)$$

Next, as the cathode gas feed consist of air and water, we can apply Dalton's partial pressure Law to obtain the partial pressure of air.

$$p_{air,in} = p_{cell} - p_{H_2O,cathode,in} \quad [Pa] \quad (3.32)$$

Then, also applying Dalton's Law, we can obtain the molar fraction (χ) of water and air.

$$\chi_{H_2O,cathode,in} = \frac{p_{H_2O,cathode,in}}{p_{cell}}; \quad \chi_{air,in} = \frac{p_{air,in}}{p_{cell}} = \chi_{O_2,in} + \chi_{N_2,in}; \quad (3.33)$$

$$\chi_{O_2,in} = \chi_{air,in} \cdot \xi_{O_2}; \quad \chi_{N_2,in} = \chi_{air,in} \cdot \xi_{N_2} \quad (3.34)$$

After that, the mass fraction (Y) can be calculated:

$$Y_{air,in} = \frac{\chi_{air,in} \cdot M_{air}}{\chi_{air,in} \cdot M_{air} + \chi_{H_2O,cathode,in} \cdot M_{H_2O}} \quad (3.35)$$

$$Y_{H_2O,cathode,in} = \frac{\chi_{H_2O,cathode,in} \cdot M_{H_2O}}{\chi_{air,in} \cdot M_{air} + \chi_{H_2O,cathode,in} \cdot M_{H_2O}} \quad (3.36)$$

The mass fraction can be also expressed in terms of mass flow rates:

$$Y_{air,in} = \frac{\dot{m}_{air,in}}{\dot{m}_{cathode,in}} \quad Y_{H_2O,cathode,in} = \frac{\dot{m}_{H_2O,cathode,in}}{\dot{m}_{cathode,in}} \quad (3.37)$$

Finally, solving equations 3.37 the mass flow rate of water through the anode feed inlet can be expressed as:

$$\begin{aligned} \dot{m}_{H_2O,cathode,in} &= \dot{m}_{air,in} \cdot \frac{Y_{H_2O,cathode,in}}{Y_{air,in}} = \\ &= \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot \left(1 + \frac{\xi_{N_2}}{\xi_{O_2}}\right) \cdot \frac{\chi_{H_2O,cathode,in}}{\chi_{air}} \cdot M_{H_2O} \quad [kg/s] \end{aligned} \quad (3.38)$$

In general, the cathode inlets are:

$$\dot{m}_{H_2O,cathode,in} = \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot \left(1 + \frac{\xi_{N_2}}{\xi_{O_2}}\right) \cdot \frac{\chi_{H_2O,cathode,in}}{\chi_{air,in}} \cdot M_{H_2O} \quad [kg/s] \quad (3.39)$$

$$\dot{m}_{air,in} = \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot \left(1 + \frac{\xi_{N_2}}{\xi_{O_2}}\right) \cdot M_{air} \quad [kg/s] \quad (3.40)$$

$$\dot{m}_{O_2,in} = \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot M_{O_2} \quad [kg/s] \quad (3.41)$$

$$\dot{m}_{N_2,in} = \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot \frac{\xi_{N_2}}{\xi_{O_2}} \cdot M_{N_2} \quad [kg/s] \quad (3.42)$$

3.2.3 Reactant Output

The reactant output will be the excess of hydrogen, nitrogen and oxygen and its quantities of water contained on its streams. In the previous section 3.2.2, a

flow-through mode has been assumed, therefore the reactant output can be calculate as the difference between the reactant supply and the PEMFC consumptions. Although in the initial assumptions is written that the relative humidity for the outlets (RH_{out}) is considered 100%, for this analysis it is consider a general one, as if the relative humidity at the outlet is a variable. In addition, as it is proven during these section, the reactant outlet flow is lower compared with the reactant supply. This fact leads to a reduction in the amount of water contained in the reactant output at the same relative humidity [60].

3.2.3.1 Anode's Outlet

The anode's outlet consist of:

$$\dot{m}_{anode,out} = \dot{m}_{H_2,out} + \dot{m}_{H_2O,anode,out} \quad [kg/s] \quad (3.43)$$

The amount of hydrogen coming out of the PEMFC is the one which has not reacted with the fuel cell. Therefore, the mass flow of the excess of fuel using equations 3.12 and 3.8 is expressed as:

$$\dot{m}_{H_2,out} = \dot{m}_{H_2,in} - \dot{m}_{H_2,cons} = \frac{I}{2 \cdot F} \cdot M_{H_2} \cdot (\phi_{anode} - 1) \quad [kg/s] \quad (3.44)$$

The amount of water contained in the anode outlet is calculated similarly as in the anode inlet section, the same steps are required. First, the partial pressure of both hydrogen and water are calculated.

$$p_{H_2O,anode,out} = RH_{anode,out} \cdot p_{sat} \quad [Pa] \quad (3.45)$$

$$p_{H_2,out} = p_{cell} - p_{H_2O,anode,out} \quad [Pa] \quad (3.46)$$

Once the partial pressures are known, Dalton's Law can be applied to obtain their respective molar fractions (χ).

$$\chi_{H_2O,anode,out} = \frac{p_{H_2O,anode,out}}{p_{cell}}; \quad \chi_{H_2,out} = \frac{p_{H_2,out}}{p_{cell}} \quad (3.47)$$

Then, the mass fraction (Y) is calculated.

$$Y_{H_2,out} = \frac{\chi_{H_2,out} \cdot M_{H_2}}{\chi_{H_2,out} \cdot M_{H_2} + \chi_{H_2O,anode,out} \cdot M_{H_2O}} \quad (3.48)$$

$$Y_{H_2O,anode,out} = \frac{\chi_{H_2O,anode,out} \cdot M_{H_2O}}{\chi_{H_2,out} \cdot M_{H_2} + \chi_{H_2O,anode,out} \cdot M_{H_2O}} \quad (3.49)$$

The mass fraction can be also expressed in terms of mass flow rates:

$$Y_{H_2,out} = \frac{\dot{m}_{H_2,out}}{\dot{m}_{anode,out}}; \quad Y_{H_2O,anode,out} = \frac{\dot{m}_{H_2O,anode,out}}{\dot{m}_{anode,out}} \quad (3.50)$$

Finally, solving equations 3.50 the mass flow rate of water through the anode feed outlet can be expressed as:

$$\begin{aligned} \dot{m}_{H_2O,anode,out} &= \dot{m}_{H_2,out} \cdot \frac{Y_{H_2O,anode,out}}{Y_{H_2,out}} = \\ &= (\phi_{anode} - 1) \cdot \frac{I}{2 \cdot F} \cdot M_{H_2O} \cdot \frac{\chi_{H_2O,anode,out}}{\chi_{H_2,out}} \quad [kg/s] \end{aligned} \quad (3.51)$$

In general, the anode outlets are:

$$\dot{m}_{H_2O,anode,out} = (\phi_{anode} - 1) \cdot \frac{I}{2 \cdot F} \cdot M_{H_2O} \cdot \frac{\chi_{H_2O,anode,out}}{\chi_{H_2,out}} \quad [kg/s] \quad (3.52)$$

$$\dot{m}_{H_2,out} = (\phi_{anode} - 1) \cdot \frac{I}{2 \cdot F} \cdot M_{H_2} \quad [kg/s] \quad (3.53)$$

As it can be checked, the anode outlets equations 3.52 are very similar to equations 3.20, except for the $(\phi_{anode} - 1)$ term which represents the consumption of hydrogen at the anode electrode. From the anode outlets expressions it can be proven that in a dead-end operation mode ($\phi_{anode} = 1$) the anode outlet flow will be non-existent.

3.2.3.2 Cathode's Outlet

The cathode's inlet consist of:

$$\dot{m}_{cathode,out} = \dot{m}_{O_2,out} + \dot{m}_{N_2,out} + \dot{m}_{H_2O,cathode,out} \quad (3.54)$$

Notice that the mass flow of air is not longer valid for the cathode's outlet. The reason is because the proportions of oxygen and nitrogen at the outlets are not longer 21% and 79% respectively. As nitrogen is not involved in the electrochemical reactions (equation 3.2), there is not a consumption of it and the nitrogen mass flow remains the same (equation 3.55).

$$\dot{m}_{N_2,out} = \dot{m}_{N_2,in} = \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot \frac{\xi_{N_2}}{\xi_{O_2}} \cdot M_{N_2} \quad [kg/s] \quad (3.55)$$

The amount of oxygen coming out of the PEMFC is the one which has not reacted with the fuel cell. Therefore, the mass flow of the excess of fuel using equations 3.39 and 3.8 is expressed as:

$$\dot{m}_{O_2,out} = \dot{m}_{O_2,in} - \dot{m}_{O_2,cons} = (\phi_{cathode} - 1) \cdot \frac{I}{4 \cdot F} \cdot M_{O_2} \quad [kg/s] \quad (3.56)$$

In order to know the water contained at the cathode outflow different steps compared with the cathode inlet flow steps are done. The first thing needed is the partial pressure of water at the outlet of the cathode which is similar to equation 3.31. The partial pressure of water is necessarily to calculate the molar fraction of water for the cathode outlet flow.

$$p_{H_2O,cathode,out} = RH_{cathode,out} \cdot p_{sat} \quad [Pa] \quad (3.57)$$

$$\chi_{H_2O,cathode,out} = \frac{p_{H_2O,cathode,out}}{p_{cell}} \quad (3.58)$$

For the cathode output stream, solve the partial pressures of oxygen and nitrogen together with its molar fractions are not trivial. In this case, the mass fraction equation can be applied directly and it is not necessarily to know the mass fraction of oxygen and nitrogen. Notice that the following procedure can be applied for the cathode inlet with its respective variables.

$$\begin{aligned} \chi_{H_2O,cathode,out} &= \frac{\frac{Y_{H_2O,cathode,out}}{M_{H_2O}}}{\frac{Y_{H_2O,cathode,out}}{M_{H_2O}} + \frac{Y_{N_2,out}}{M_{N_2}} + \frac{Y_{O_2,out}}{M_{O_2}}} = \\ &= \frac{\frac{\dot{m}_{H_2O,cathode,out}}{\dot{m}_{cathode,out}}}{\frac{\dot{m}_{H_2O,cathode,out}}{\dot{m}_{cathode,out}} + \frac{\dot{m}_{O_2,out}}{\dot{m}_{cathode,out}} + \frac{\dot{m}_{N_2,out}}{\dot{m}_{cathode,out}}} \end{aligned} \quad (3.59)$$

The only unknown in this equation is the mass flow of water content in the cathode outlet. Solving equation 3.59, we obtain the following expression:

$$\begin{aligned} \dot{m}_{H_2O,cathode,out} &= \frac{\chi_{H_2O,cathode,out}}{1 - \chi_{H_2O,cathode,out}} \cdot M_{H_2O} \cdot \left(\frac{\dot{m}_{N_2,out}}{M_{N_2}} + \frac{\dot{m}_{O_2,out}}{M_{O_2}} \right) \\ &= \frac{\chi_{H_2O,cathode,out}}{1 - \chi_{H_2O,cathode,out}} \cdot M_{H_2O} \cdot \left(\frac{\phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot \frac{\xi_{N_2}}{\xi_{O_2}} \cdot \cancel{M_{N_2}}}{\cancel{M_{N_2}}} + \right. \\ &\quad \left. + \frac{(\phi_{cathode} - 1) \cdot \frac{I}{4 \cdot F} \cdot \cancel{M_{O_2}}}{\cancel{M_{O_2}}} \right) \quad [kg/s] \end{aligned} \quad (3.60)$$

In general, the cathode outputs are:

$$\dot{m}_{H_2O,cathode,out} = \frac{\chi_{H_2O,cathode,out}}{1 - \chi_{H_2O,cathode,out}} \cdot M_{H_2O} \cdot \frac{I}{4 \cdot F} \cdot \left(\phi_{cathode} \left(\frac{\xi_{N_2}}{\xi_{O_2}} + 1 \right) - 1 \right) \quad [kg/s] \quad (3.61)$$

$$\dot{m}_{O_2,out} = (\phi_{cathode} - 1) \cdot \frac{I}{4 \cdot F} \cdot M_{O_2} \quad [kg/s] \quad (3.62)$$

$$\dot{m}_{N_2,out} = \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot \frac{\xi_{N_2}}{\xi_{O_2}} \cdot M_{N_2} \quad [kg/s] \quad (3.63)$$

In this analysis of the flow leaving the cathode the PEMFC water production has not been considered, although the water production removal is carried out through the cathode outlet.

3.3 Balance of Water (BOW)

This section is aside from the mass balance section due to the great importance of the balance of water in PEMFC and in the present bachelor thesis. The net amount of water added or removed from the PEMFC depends on the mass flows coming in and out of the PEMFC and the water they content and the water production rate as a result of the electrochemical reactions inside the PEMFC. The net amount of water can be expressed as:

$$BOW = \frac{\partial \dot{m}_{H_2O,cell}}{\partial t} = \dot{m}_{H_2O,prod} + \underbrace{\dot{m}_{H_2O,anode,in} - \dot{m}_{H_2O,anode,out}}_A + \underbrace{\dot{m}_{H_2O,cathode,in} - \dot{m}_{H_2O,cathode,out}}_C \quad [kg/s] \quad (3.64)$$

where:

- A = Advection capacity of the anode stream [kg/s]
- C = Advection capacity of the cathode stream [kg/s]

The steady state is only possible at ($BOW = 0$). On one hand, if the BOW value is positive it means that the PEMFC is hydrating and accumulating water. On the other hand, if the BOW value is negative it means that the PEMFC is dehydrating. However, the PEMFC can either work stable with a close to zero positive or a negative values of the BOW. In the case of water accumulation, the PEMFC can achieve a new stable regime when the accumulated water is condensed and the droplets of the excess of water leaves the PEMFC through the cathode outlet. In the case of absence of water, the stable regime is achieved because the relative humidity of the outlets are below 100% ($RH_{out} < 100\%$).

The advection capacity of the anode and cathode streams (A and C respectively) is defined as the net mass of water that each electrode stream is able to add or remove from its corresponding side to the fuel cell. As in the case of the global balance of water, a positive advection capacity means that the stream is hydrating its fuel cell side whereas a negative value means that the stream is drying its side. The advection capacity can be an illustrative parameter, however the effect of water and humidity must be supported by the BOW as it includes the water production [60].

In order to have a more general idea of the balance of water that could be applied to more general conditions, a dimensionless balance of water has been done.

3.3.1 Dimensionless Balance of Water

A dimensionless analysis will be helpful in order to obtain results and conclusions independently from the current applied to the PEMFC. For this analysis, the BOW has been done at the water production rate scale. Therefore, the BOW equation expressed previously (equation 3.64) turns into:

$$\widehat{BOW} = \frac{\dot{m}_{H_2O,prod}}{\dot{m}_{H_2O,prod}} + \underbrace{\frac{\dot{m}_{H_2O,anode,in} - \dot{m}_{H_2O,anode,out}}{\dot{m}_{H_2O,prod}}}_{\hat{A}} + \underbrace{\frac{\dot{m}_{H_2O,cathode,in} - \dot{m}_{H_2O,cathode,out}}{\dot{m}_{H_2O,prod}}}_{\hat{C}} \quad (3.65)$$

where the $\hat{}$ symbol represents the dimensionless variables.

In addition, the dimensionless anode and the cathode advection capacity can be expressed following equations 3.8, 3.20, 3.39, 3.52 and 3.61 as:

$$\hat{A} = \phi_{anode} \cdot \left(\frac{\chi_{H_2O,anode,in}}{\chi_{H_2,in}} - \frac{\chi_{H_2O,anode,out}}{\chi_{H_2,out}} \right) + \frac{\chi_{H_2O,anode,out}}{\chi_{H_2,out}} \quad (3.66)$$

$$\hat{C} = \frac{1}{2} \left(\phi_{cathode} \cdot \left(\frac{\xi_{N_2}}{\xi_{O_2}} + 1 \right) \cdot \left(\frac{\chi_{H_2O,cathode,in}}{\chi_{air,in}} - \frac{\chi_{H_2O,cathode,out}}{1 - \chi_{H_2O,cathode,out}} \right) + \frac{\chi_{H_2O,cathode,out}}{1 - \chi_{H_2O,cathode,out}} \right) \quad (3.67)$$

Furthermore, for a correct interpretation of the graphs, the dimensionless anode and the cathode advection capacity can be expressed by the graphs variables following equations 3.66 and 3.67 together with equations 3.15, 3.33, 3.47 and 3.58.

$$\begin{aligned}
\hat{A} &= \phi_{anode} \cdot \left(\frac{\frac{RH_{anode,in} \cdot p_{sat}}{p_{cell}} - \frac{RH_{anode,out} \cdot p_{sat}}{p_{cell}}}{\frac{p_{cell} - RH_{anode,in} \cdot p_{sat}}{p_{cell}}} \right) + \frac{\frac{RH_{anode,out} \cdot p_{sat}}{p_{cell}}}{\frac{p_{cell} - RH_{anode,out} \cdot p_{sat}}{p_{cell}}} \\
&= \phi_{anode} \cdot \left(\frac{RH_{anode,in} \cdot p_{sat}}{p_{cell} - RH_{anode,in} \cdot p_{sat}} - \frac{RH_{anode,out} \cdot p_{sat}}{p_{cell} - RH_{anode,out} \cdot p_{sat}} \right) + \\
&\quad + \frac{RH_{anode,out} \cdot p_{sat}}{p_{cell} - RH_{anode,out} \cdot p_{sat}} \tag{3.68}
\end{aligned}$$

$$\begin{aligned}
\hat{C} &= \frac{1}{2} \left(\phi_{cathode} \cdot \left(\frac{\xi_{N_2}}{\xi_{O_2}} + 1 \right) \cdot \left(\frac{\frac{RH_{cathode,in} \cdot p_{sat}}{p_{cell}} - \frac{RH_{cathode,out} \cdot p_{sat}}{p_{cell}}}{\frac{p_{cell} - RH_{cathode,in} \cdot p_{sat}}{p_{cell}}} \right) + \right. \\
&\quad \left. + \frac{\frac{RH_{cathode,out} \cdot p_{sat}}{p_{cell}}}{\frac{p_{cell} - RH_{cathode,out} \cdot p_{sat}}{p_{cell}}} \right) \\
&= \frac{1}{2} \left(\phi_{cathode} \cdot \left(\frac{\xi_{N_2}}{\xi_{O_2}} + 1 \right) \cdot \left(\frac{RH_{cathode,in} \cdot p_{sat}}{p_{cell} - RH_{cathode,in} \cdot p_{sat}} - \frac{RH_{cathode,out} \cdot p_{sat}}{p_{cell} - RH_{cathode,out} \cdot p_{sat}} \right) + \right. \\
&\quad \left. + \frac{RH_{cathode,out} \cdot p_{sat}}{p_{cell} - RH_{cathode,out} \cdot p_{sat}} \right) \tag{3.69}
\end{aligned}$$

According to equation 3.4, the saturation pressure only depends on the temperature of the PEMFC (T_{cell}) which in this case it is assumed constant at 80°C. The value of (p_{sat}) is constant and for this case its value is 0.47311 bars or 0.4669 atm, therefore it is always much lower than the pressure applied to the PEMFC.

3.4 Effect of pressure and stoichiometry in PEMFC Balance of Water

The analysis of the effect of pressure and the anode and cathode stoichiometry in the advection capacities and in the general BOW will be studied under dimensionless conditions as shown in equation 3.65. These effects will be studied in addition under several outlet streams relative humidities.

The points of study are not chosen aleatory. The pressure values are $p = 1$ atmosphere, which is the pressure at the UC3M PEMFC, $p = 1.5$ bars, which is the pressure used by the experiments in DLR facility and discussed by the Doctoral Thesis of Juan Sánchez Monreal [60], and $p = 2$ bars because it gives more information than a value between 1 atmosphere and 1.5 bars. In addition, the stoichiometry values are $\phi_{anode} = 1.2$ and $\phi_{cathode} = 2$ following the experiments done and analyzed by Juan Sánchez Monreal, $\phi_{anode} = 1.8$ and $\phi_{cathode} = 3$, which are values that were considered to apply for UC3M PEMFC facility and represents a 50% more of the DLR facility stoichiometry values, and $\phi_{anode} = 2.82$ and $\phi_{cathode} = 4.69$ which were the values finally adopted to the experimental campaign.

The present bachelor thesis focuses on the temperature typical operating conditions of the PEMFC which is $T = 80^\circ\text{C}$.

Because typically the relative humidity of the outlet streams are considered fully humidified ($RH_{out} = 100\%$) and that the relative humidity of the outlet gases are not controlled by the UC3M PEMFC facility, the dimensionless anode and cathode advection capacity (\hat{A}, \hat{C} respectively) are represented as a function of the relative humidity of the inlet gases RH_{in} . However, as it can be observed in figures 3.2 and 3.3, the relative humidity of the outlet gases are also represented by $RH_{out} = 50\%$ and $RH_{out} = 100\%$, which are the two theoretical limit values of the range considered for the experimental campaign, and $RH_{out} = 70\%$. It must be noticed that the relative humidity is included in the advection capacity equations as they form part of the molar fractions that appears in equations 3.68 and 3.69.

Figure 3.2 shows the dimensionless anode advection capacity as a function of the anode inlet relative humidity of the fuel gas at different stoichiometries, different pressures and different anode outlet relative humidity of the fuel gas. As it can be observed for each graph and from equation 3.68, the anode advection capacity increases when the inlet relative humidity increases for all the cases when the rest of the variables are fixed. The variation of the outlet relative humidity tends to move the anode advection capacity curve to the left when the outlet relative humidity value is reduced as a consequence of a lower water removal from the cell. The stoichiometry affects principally the slope of the advection capacity curves, the higher the stoichiometry, the higher the slope. The effect of the PEMFC pressure, as the stoichiometry value, affects the slope of the anode advection capacity curve. However, unlike in the case of the stoichiometry value, the higher the PEMFC value the lower the slope.

In addition, notice that when the relative humidity is equal for the inlet and for the outlet gases the advection capacity curves matches. This is because according to the equation 3.68, at equal relative humidities for the inlet and outlet gases, the stoichiometry has no effect and the advection capacity value at that point only depends on the cell pressure and the relative humidity. At this point ($RH_{anode,in} = RH_{anode,out}$), several conclusions can be made. First, the higher the relative humidity the higher the hydration of the anode side. The reason is because the inlet water rate of the inlet fuel gas is always higher than the water removal rate without taking into account the water production of the PEMFC. Second, the PEMFC without taking into account the water production will be always hydrating no matter the value of the relative humidity. In the theoretical case of ($RH_{anode,in} = RH_{anode,out} = 0$) the PEMFC will be at steady state. Finally, at this point, for a rough good approximation the increase of the relative humidity can be considered to be linearly dependent however, in reality, it is exponentially dependent. This assumption is possible because of the great difference between the cell pressure and the saturation pressure.

Figure 3.3, similarly to figure 3.2, shows the dimensionless cathode advection capacity as a function of the cathode inlet relative humidity of the air at different stoichiometries, different pressures and different cathode outlet relative humidity of the gas. The main differences between the anode advection capacity and the cathode advection capacity are in the stoichiometry values are caused by the presence of

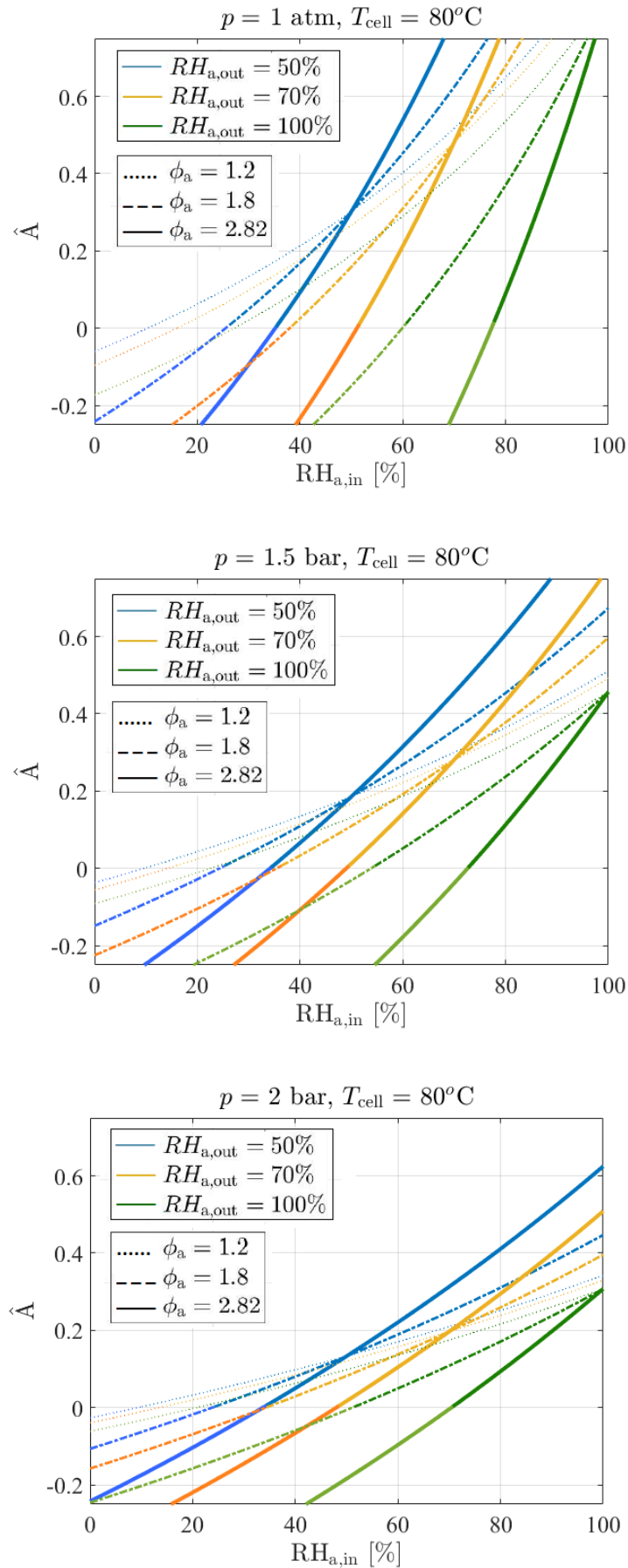


Figure 3.2. Dimensionless anode advection capacity under different conditions

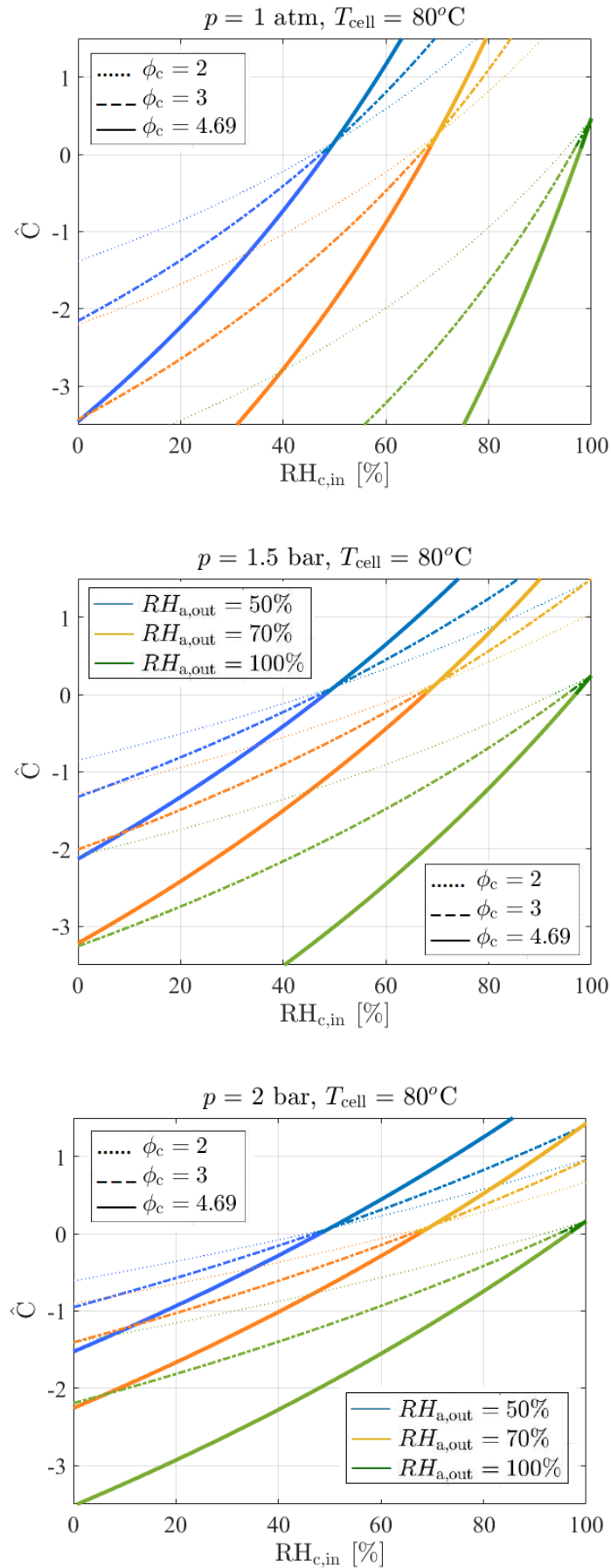


Figure 3.3. Dimensionless cathode advection capacity under different conditions

nitrogen in the air. The presence of nitrogen causes larger mass flow rates and larger stoichiometry and a constant factor ($\frac{\xi_{N_2}}{\xi_{O_2}}$) which its value is 3.76 which affects part of the cathode advection capacity equation and means that for each oxygen molecule introduced, almost 4 nitrogen molecules are introduced as well [60]. Therefore, the effect of the inlet cathode relative humidity has higher effects in the cathode advection capacity compared with the anode case. In addition, as it has been said previously, is in the cathode side where the water production is removed from the PEMFC. Because of these reasons the cathode side is more relevant for a correct balance of water and stability in a PEMFC.

Both figures 3.5 and 3.4 display the effect of different values of stoichiometry and different values of pressure have in the general balance of water. The results are presented under the anode and cathode inlet relative humidities axes ($RH_{anode,in}$ vs $RH_{cathode,in}$). At BOW=0, the outlet relative humidities are considered fully hydrated ($RH_{anode,out} = RH_{cathode,out} = 100\%$) and it is represented by a bold black line. At lower humidity, instead of considering a dehydration of the PEMFC, it has been esteemed also a BOW=0 but at a lower outlet relative humidity. This estimation, which includes the outlet relative humidity from 90% to 50%, represents better the reality as it is observed in the experimental campaign and is represented by the black curves. Finally, the positive dimensionless BOW are represented with the blue curves.

Figure 3.4, shows the differences between the initially expected experimental configuration and the final experimental configuration shown in chapter 4. At the UC3M PEMFC facility conditions, the curves at which the BOW=0 are shifted to the right in all the cases. This shift makes the PEMFC to operate at drying conditions if the relative humidity of the outlet gases are assumed fully humidified, or what actually happens in the experimental campaign, the PEMFC relative humidity of the outlet gases are below 100%. In addition, the positive BOW curves are very close to steady state condition, therefore at high relative humidities the PEMFC may behave at flooding state. Furthermore, the increase of the PEMFC pressure shifts the curves to the left but not as much as the original stoichiometry values. The increase of the fuel cell pressure achieves to increase the distance between the curves, but again not as much as the original stoichiometry values.

Figure 3.5 shows which stoichiometry has a bigger impact in the BOW. The comparison between them has been done with the graphs shown in figure 3.4 which has a ($\phi_{anode} = 1.2$) and ($\phi_{cathode} = 2$) which were the conditions applied in the Doctoral Thesis presented by Juan Sánchez [60]. Both anode and cathode stoichiometry values ($\phi_{anode} = 1.8$ and $\phi_{cathode} = 3$) represent an increase of 50% of the DLR facility stoichiometry values. The BOW curves change their slope as a function of both anode and cathode stoichiometry. However, the cathode stoichiometry has a bigger impact in the BOW. On one hand, if the anode stoichiometry is increased it can be observed that the BOW curves tend to reduce its slope being this effect more notorious at lower anode inlet relative humidities. On the other hand, if the cathode stoichiometry is increased the slope is notable more gradient and the curves are shifted to the right. In addition, the positive curves of the BOW are closer, therefore the PEMFC has a greater probability of behave at a flooding state compared with the previous case. An increase in the

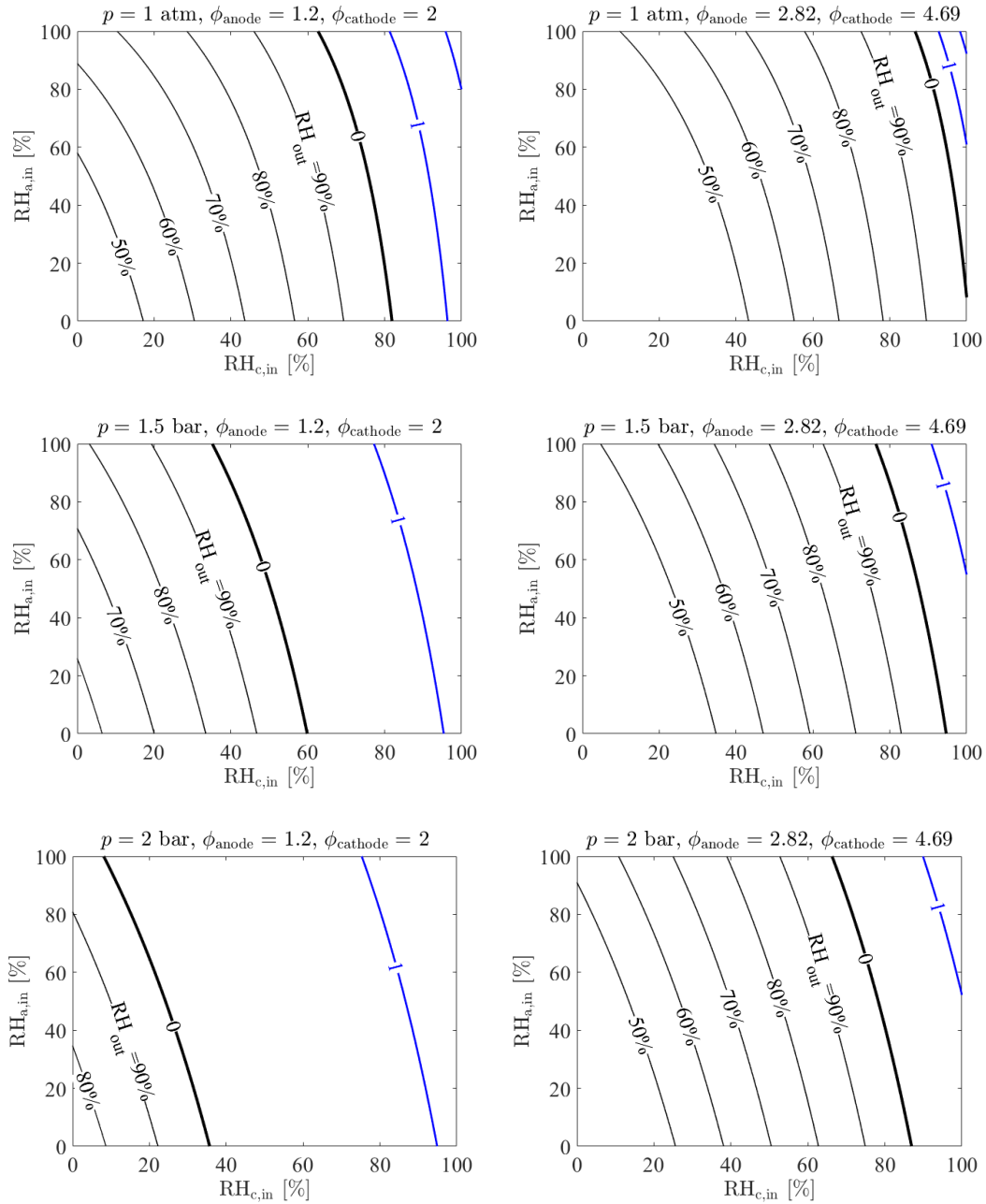


Figure 3.4. Dimensionless BOW comparing the experimental conditions between the DLR facility and the UC3M facility at different pressures

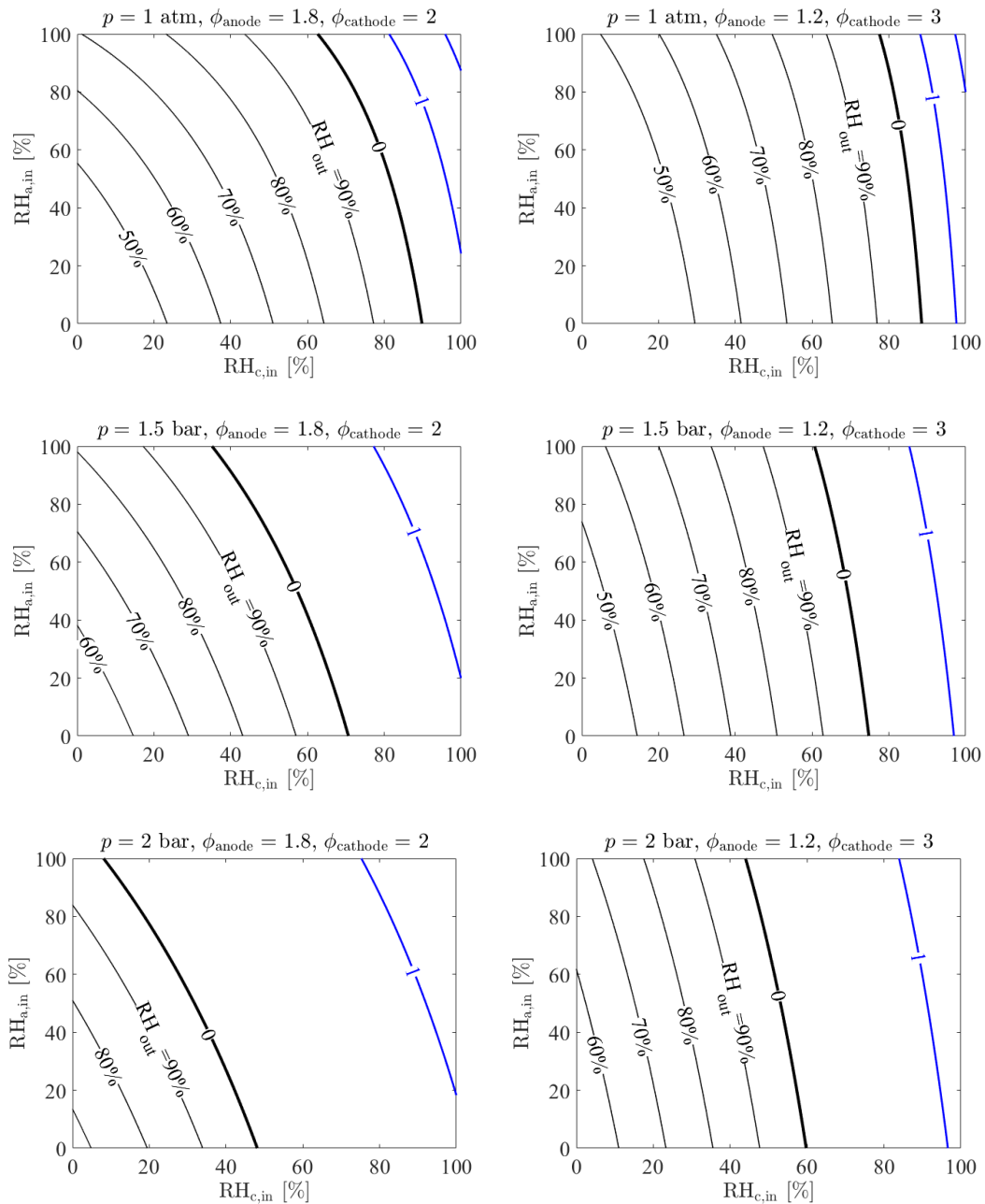


Figure 3.5. Dimensionless BOW with alternative stoichiometry configuration at different pressures

PEMFC pressure has a lower effect in the cathode stoichiometry increase case than in the anode stoichiometry increase. When the cell pressure increases, the BOW=0 curves shift to the left while the positive curves tend to keep constant. However, in reality the positive curves of BOW are shifted to the right and therefore there is more space between these positive lines as it can be observed in [60]. Therefore, at higher PEMFC pressure a better fuel cell stability is achieved avoiding a flooding behaviour.

From figures 3.5 and 3.4, it can be stated that in order to achieve a better performance a high pressure must be applied to the PEMFC. Even though, based on these graphs, a high value of the anode stoichiometry looks that favor the PEMFC stability, in reality the gain in stability is low and the fuel mass rate increases significantly which means a higher cost of the facility and also it can cause a flooding behaviour at the anode side of the PEMFC (which is visible in figure 3.2). Therefore, for a good PEMFC performance it can be observed from the figures 3.66, 3.67, 3.5 and 3.4 that it is preferable to choose low stoichiometry values and high PEMFC pressure in order to avoid great dehydration/hydration in the anode side and restrict the effect of the relative humidity of the inlet gases.

The experiments performed in chapter 4, concretely the second part of the experimental campaign, were performed at $p = 1$, $RH_{anode,in} = 50\%$ and a $RH_{cathode,in}$ sweep. (Table 4.4). At those values, the value of the dimensionless BOW goes from closely 1 at $RH_{cathode,in} = 100\%$ to a relative humidity of the outlet streams closely to 50%. These results give a first impression of a stable PEMFC behaviour. In order to ensure these conditions will be valid for the experimental campaign, the anode and cathode advection capacities must be also checked. According to figures 3.66 and 3.67, at $RH_{anode,in} = 50\%$ the anode advection capacity value range for $RH_{anode,out} = 50 - 70 - 100\%$ are between 0.3 and -0.5. These values of the anode advection capacity are closely to zero and therefore it can be assumed that the anode side is operating at normal operation. In addition, at the fixed anode relative humidity it is considered to operate at steady state at a $RH_{anode,out} = 70\%$. At the cathode side some problems might appear. At the cathode stoichiometry value chosen, the cathode advection capacity curves are very gradient and if the relative humidity of the outlet cathode gas could be fixed several problems might appear with slight changes in the inlet relative humidity. Since the experimental facility does not allow to fix the outlet relative humidity, the PEMFC is expected to work stable at least at high cathode inlet relative humidity values which have an estimated outlet relative humidity values between 50% and 100%, as it has been considered for the dimensionless BOW graphs. In general, the values of the stoichiometry chosen are not the best ones based on the theory but it is expected to have a stable performance in the experimental campaign.

Experimental Campaign

This chapter deals with the experimental campaign carried out in the UC3M laboratory were based on the experiments described in Doctoral Thesis of Juan Sánchez Monreal B. The Doctoral Thesis experiments were performed at the Department Electrochemical Energy Technology of DLR located in Stuttgart.

In this experimental campaign, the PEMFC behaviour at different relative humidity values at the electrodes will be studied. In order to achieve this objective, the PEMFC laboratory counts with different equipment which will be discussed in detail during this chapter. In addition, for a valid comparison of the different results, a operating condition and a reference condition (summarized in tables B.2 and 4.4) have been established. The PEMFC stability behaviour will be studied at the conditions illustrated in figure 4.13. Furthermore, a PEMFC characterization have been done at the operating conditions, which will allow to observe the performance of the PEMFC.

4.1 PEMFC Laboratory Equipment

The equipment used in the experiments are located in room 1.0T08 inside the Thermal and Fluid Mechanics Engineering Laboratory. The laboratory equipment, as it can be observed in figures 4.1 and 4.2, is composed by a test station, a single fuel cell, a hydrogen gas generator, a purge gas cylinder, an air intake system and a computer.



Figure 4.1. UC3M Fuel Cell Laboratory

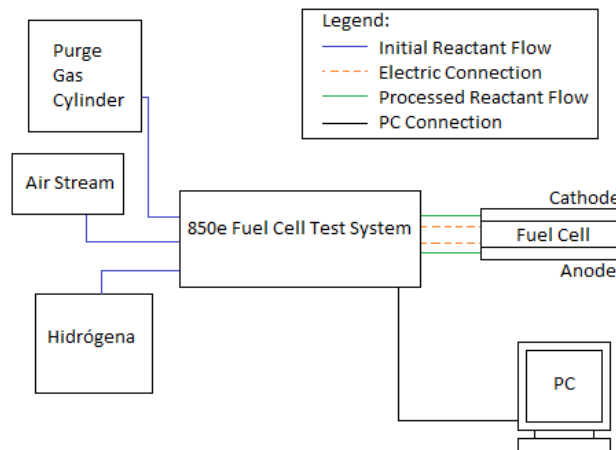


Figure 4.2. UC3M Fuel Cell Laboratory Scheme

4.1.1 Test Station

The test station used is the model 850e Fuel Cell Test System by Scribner Associates. This control system allows to change the PEMFC inlet variables like temperature, flow rates and relative humidity among others and to collect all the data that can be studied later. This test station is focused for PEMFC and DMFC. The test station works together with FuelCell 4 software, also by Scribner Associates, described later. The main specifications of the model 850e Fuel Cell Test System is highlighted in table 4.1 and its internal components are shown in figure 4.3.

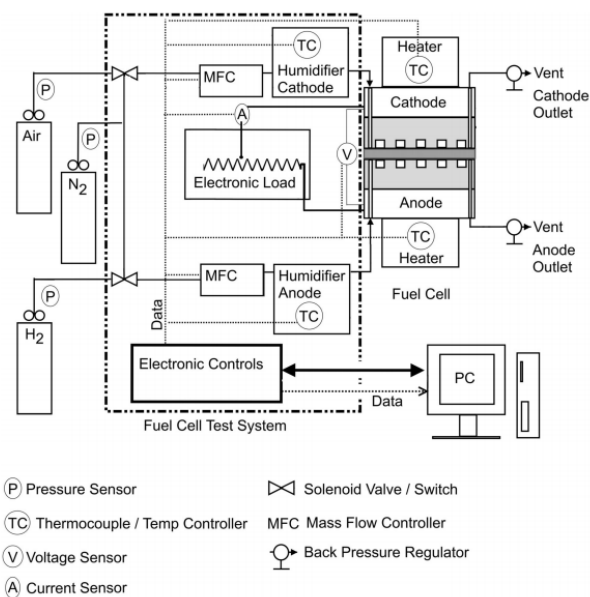


Figure 4.3. Schematic of a Fuel Cell Test Station [63]

Dimensions	46x28x48 [cm] (Height x Width x Depth)
Weight	23 [kg]
Maximum Load Current	5/25/50 [A]
Maximum Load Power	100 [W]
Minimum Load Resistance	< 2 [mΩ]
Maximum Voltage	20 [V]
Current Accuracy	3% of full scale
Voltage Accuracy	± 3 [mV]
Maximum Temperature	95 [°C]
Temperature Accuracy	± 0.1 [°C]

Table 4.1. Test Station Specifications



Figure 4.4. UC3M Fuel Cell Test System

The control station is composed by the following components and features [64]:

- Mass Flow Controllers:** As its name already indicates, the control station regulates the mass flow of the reactants with these controllers, one per electrode. The desired reactant flow is one of the only variables that the user can modify.
- Bubblers:** There are two bubblers in the test station, one per electrode. The inlet streams which are completely dry are heated and humidified by the bubbler. The bubbler is made of stainless steel and they must be filled with ionized water with a resistivity lower than $18\text{ M}\Omega\text{cm}$.
- Electronic Controls:** This component is the connection between the control station and fuel cell with the software. The test station is connected to the computer by a GPIB-USB by National Instruments. The electronic controls allow to apply the changes of the variables by the software and to avoid non safety operational conditions for the fuel cell or the test station; first by an alarm and finally with disconnection to avoid damages. The user can stop the operation of the test station by pressing the emergency button.
- Electronic Load:** Is the external circuit at which the free electrons circulates from the anode to the cathode side. The load is modified automatically depending on the amount of current generated by the fuel cell. The electronic load can be operated in galvanostatic or potentiostatic mode. The main parameters of the electronic load is summarised in table 4.1.
- Temperature Controllers:** There are three temperature controllers which determines and fixes the operational temperature of the fuel cell and the temperature of the reactants located in each humidifier. There is a maximum temperature ($95\text{ }^{\circ}\text{C}$) (Table 4.1) at which the temperature controller is not able to work in order to avoid damages in the system and in the fuel cell membrane. The desired temperatures in the cell and in the reactants are the only variables that the user can modify.

- **Pressure Sensors:** The control station has pressure sensors that control the pressure of the reactants. It is important to remark that in the experiments performed at the present bachelor thesis the fuel cell reactants are at 4 bars and the fuel cell works at atmospheric pressure. An auto back pressure unit can be implemented in order to increase the fuel cell operational pressure and achieve a better performance.

4.1.2 Hidrógena: The hydrogen generator

The hydrogen generator is the Hart 250 model, from Hidrógena Desarrollos Energéticos SL. The hydrogen is produced by electrolysis of deionized water. The hydrogen gas obtained has a purity of 99.9999 % [65]. This model is able to generate 8 liters per hour at 7 bars maximum. In the experiments, the hydrogen generation was at 3.8 bars, the same pressure as air and nitrogen.



Figure 4.5. Hydrogen Generator

4.1.3 Fuel Cell

The components of a PEMFC are described in section 2.1. All the fuel cell components were delivered by Alphaomega Electronics. The main properties are listed in table 4.2.

UC3M PEMFC Components	
Component	Model
MEA	Naffion ©XL (Ion Power Inc)
Catalyst Layer	0.3 mgPt/cm ² /side
GDL	SIGRACET 10 BB
Bipolar Plate	POCO SA Graffite
Flow Channel	Serpentine Flow pattern

Table 4.2. UC3M PEMFC Characteristics

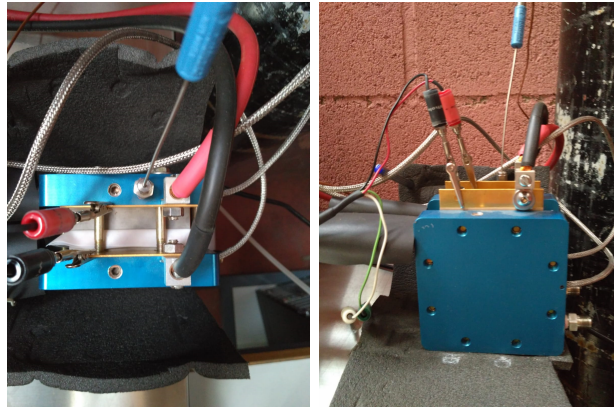


Figure 4.6. UC3M PEMFC



Figure 4.7. UC3M PEMFC Components

4.1.4 Software

The software used in the experimental proceeding is Fuel Cell 4, developed by Scribner Associates. This software allows the user to set the conditions and parameters for the fuel cell. In addition, it has several programming routines which favor more automated experiments. The main characteristics of the software are listed below:

- Guarantees the optimal state of the fuel cell and its connections.
- Set the input variables.
- Activate/deactivate the flow inputs.
- Activate/deactivate the temperatures inputs.
- Activate/deactivate the load inputs.
- Schedule experiments.

- Choose which variables are monitored.
- Establish security limits and its alarms.
- Real time graphic representation.
- Record in a file all the data obtained.

The data obtained by Fuel Cell 4 is saved in a ".fcd" file extension. This kind of file is opened by FuelCellView, which is an analysis and postprocessing software. The main function of this software is to plot different graphs with all the data stored.



Figure 4.8. UC3M PEMFC laboratory computer facility

4.1.5 Purge Gas Cylinder

The purge gas is compressed nitrogen (N_2). This nitrogen, which is delivered at 4 bars, is connected to the test system. Its main function is to remove the reactant and by-product residues. In addition, the purge gas has a safety factor. The purge gas allows the fuel cell to be at an optimum condition and avoids the crossover effect, therefore the membrane is not damaged.



Figure 4.9. Purge gas cylinder

4.1.6 Air intake stream

The laboratory has access to an air intake connection. The air is compressed up to 3.5 bar and it is connected to the test system.

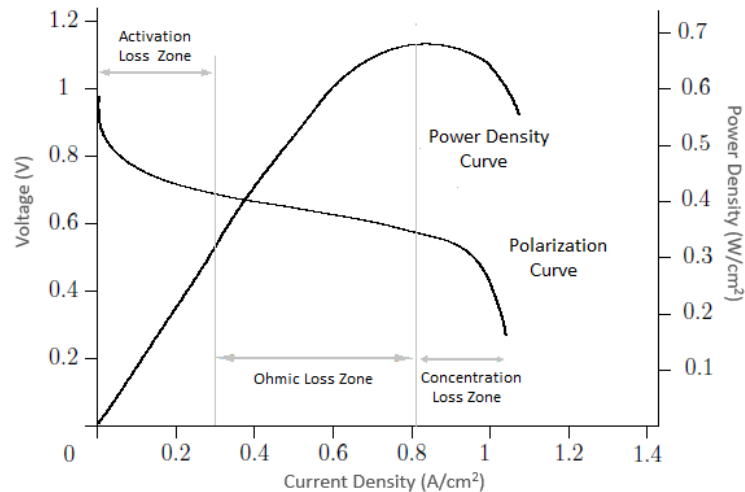


Figure 4.11. Typical Polarization and Power Density Curve [64]



Figure 4.10. UC3M PEMFC laboratory air intake

4.2 PEMFC characterization at reference conditions

The characterization of the UC3M PEMFC will be done by a polarization curve and a power density curve. These two characterization techniques are performed in situ, show the PEMFC overall performance and are commonly plotted together [6, page 237].

The polarization curve shows the voltage performance and is obtained by subtracting the activation, ohmic and concentration losses that takes place in the fuel cell to the theoretical potential as it is shown in figure 2.11. The power density curve shows the maximum power that can be obtained from the PEMFC. The maximum power value is the most important value because it is the desired point of operation. Any point beyond the maximum power is not optimum because it means that the same power output could be obtained at a lower current and higher voltage [5, page 62]. A theoretical typical polarization and power density curve is illustrated in figure 4.11.

Experimental Conditions	
Temperature (T_{cell})	80 °C
Pressure (p_{cell})	1 atm
Surface Area (A)	5 cm ²
Anode Flow Rate (Hydrogen Stream)	29.47 ml/min
Cathode Flow Rate (Air Stream)	116.75 ml/min
Anode Inlet Relative Humidity ($RH_{anode,in}$)	50%
Cathode Inlet Relative Humidity ($RH_{cathode,in}$)	76%

Table 4.3. Bachelor Thesis Experimental Characterization Techniques Conditions

4.2.1 Current-Voltage Measurement

Current, time and voltage are the variables the user can manage in the characterization techniques. In addition, current and voltage cannot be modified independently at the same time, a change in current affects the real voltage and viceversa. Therefore, in order to obtain the polarization and power density curves two different techniques can be used.

- Potentiostatic Technique: where the user control the voltage and the current is given by the software.
- Galvanostatic Technique: where the user controls the current and the voltage is given by the software.

For this part of the experimental procedure the galvanostatic technique was used in a steady state, that means that the current was fixed independently of the variable time. The main reason is because the PEMFC at different conditions takes longer or shorter to settle in and if the measurement is done before the steady state voltage value is acquired, the polarization and the power density curves will present errors. The experimental operating conditions are listed below in table 4.3. These conditions have been established having as a reference the conditions mentioned in Appendix B.

For a successful data obtention, a warm-up procedure of minimum 1 hour at low current is required. The warm-up procedure allows the fuel cell to heat up and fix the temperature of the PEMFC, the air and the fuel, the flow rates and achieve steady state behaviour [6, page 245]. Notice that the anode inlet relative humidity is fixed to 50% in order to link the experimental campaign together. At this anode inlet relative humidity, in order to achieve a BOW=0 with fully humidified outlet gases, the cathode inlet relative humidity has been fixed at 76% (figure 3.4).

4.2.2 Experiment results

The results of this experiment are illustrated in figures 4.12.

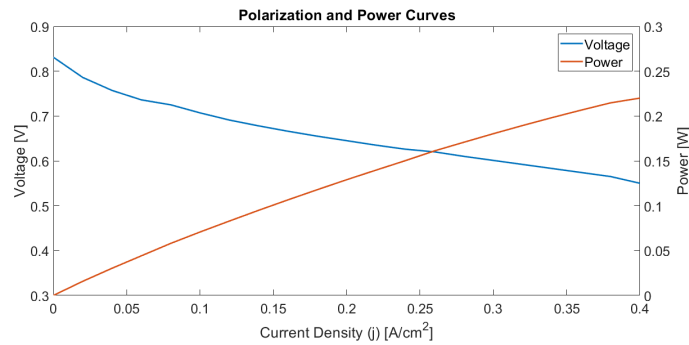


Figure 4.12. UC3M PEMFC Polarization and Power Density Curves

At higher current densities, the PEMFC becomes unstable reaching potential cell under limits. The experiment set-up configuration was settled assuming that the PEMFC could reach to current densities close to 1 A/cm^2 as it is showed in figure 4.11. At first, comparing the values of the current density obtained in the experiment with the theoretical typical values, it can be considered that the PEMFC has not reached the concentration loss zone. However, when a deeper analysis is done, it can be concluded that the results gives a full polarization curve but the performance of the PEMFC is very low. Once these results were obtained, several modifications in the flow rates were made. At higher flow rates, the gain in the current density was little and in addition the increase in the anode and cathode stoichiometry values compromise the global PEMFC stability. At lower flow rates, the current density maximum value was even smaller.

For these reasons it was thought that the MEA might be dry and a hydrating technique was performed. The hydrating technique followed was a stack break-in proposed by the Auto-Stack Core Project, which forms part of the European FCH 2 JU. The test conditions and test procedure can be checked in Appendix D.1. Unfortunately, the hydrating technique was not completely done because some steps were out of the limits of the PEMFC. The PEMFC after the partial hydrating technique showed practically the same results. For future works a solution might be found if the MEA5 is substituted.

4.3 Gas Humidity influence on the performance stability of PEMFCs

4.3.1 Introduction

One of the main challenges of PEMFCs is the water management. A good water management, as it has been previously discussed, allows a hydrated membrane which is essential for a high proton conductivity. A high proton conductivity is synonym of a stable and high performance in the PEMFC. In chapter 3 it has been discussed that water is supplied into the PEMFC through the anode and cathode inlet gases, there is also a water generation inside the PEMFC (concretely in the cathode side) as a result of the electrochemical reactions and finally water is removed from the

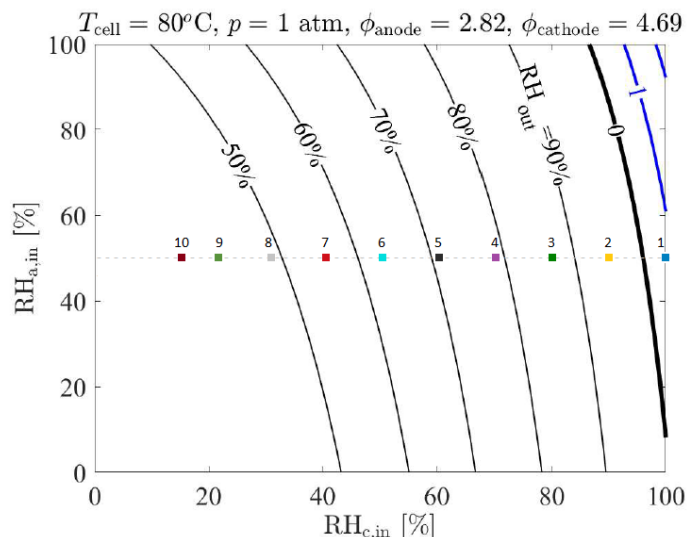


Figure 4.13. The different RH conditions at which the PEMFC has been studied

PEMFC through the anode and cathode outlet gases. The higher importance of the cathode side of the fuel cell with respect to water accumulation and removal has motivated the following experimental analysis. The experiment conditions are listed in table 4.4.

The objective of this experiment is to observe the effect of the cathode relative humidity inlet gases and establish a zone of stable operation conditions for future work. In order to do so, the experiment has been divided in 10 different tests where the only variable modified was the inlet relative humidity at the cathode side, or in other words the temperature of the cathode inlet gas. The relative humidity of the anode side was settled to 50% based on the experimental conclusion achieved in Juan Sánchez Monreal Thesis [60], where the PEMFC has better stability performance at 50 % compared with a fully hydrated anode inlet gas. The current value was fixed at 1.5 A even though the maximum power is achieved at $I=2$ A. The current value set for this experimental procedure is somewhat inconsistent with what it has been discussed in the previous section, where the maximum power is seek in order to obtain the most efficient current value. However, this experiment is not focused on the PEMFC optimization and at $I=1.5$ A it is ensured that the possible experiment instability is only caused by the cathode inlet relative humidity. The flow rates have been kept equal to the ones employed at the characterization techniques experiment. The main reason is because it has been studied how the PEMFC behaves at those flow rates. Finally, the stoichiometry values are obtained from the flow rates and current values. The formula relating flow rates, current and stoichiometry is found in Appendix A.

4.3.2 Experimental Results

Figure 4.15 shows the results obtained from the experimental campaign. These results were obtained after performing the different tests mentioned in table 4.4 during at least 1800 seconds. After the test was done, the more stable 1500 seconds interval was chosen in order to compare all the test together as it is shown in figure

Experimental Conditions	
Temperature (T_{cell})	80 °C
Pressure (p_{cell})	1 atm
Surface Area (A)	5 cm ²
Current (I)	1.5 A
Current Density (j)	0.3 A/cm ²
Anode Flow Rate (Hydrogen Stream)	29.47 ml/min
Anode stoichiometry (ϕ_{anode})	2.82
Cathode Flow Rate (Air Stream)	116.75 ml/min
Cathode Stoichiometry ($\phi_{cathode}$)	4.69
Anode Inlet Relative Humidity ($RH_{anode,in}$)	50%
Temperature Anode Stream ($T_{gas,anode}$)	63.7 °C
Cathode Inlet Relative Humidity ($RH_{cathode,in}$)	50 - 100 %
Temperature Cathode Stream ($T_{gas,cathode}$)	38.8 - 80 °C
Test 1: ($RH_{cathode,in}$, $T_{gas,cathode}$)	100 %, 80.0 °C
Test 2: ($RH_{cathode,in}$, $T_{gas,cathode}$)	90 %, 77.4 °C
Test 3: ($RH_{cathode,in}$, $T_{gas,cathode}$)	80 %, 74.7 °C
Test 4: ($RH_{cathode,in}$, $T_{gas,cathode}$)	70 %, 71.4 °C
Test 5: ($RH_{cathode,in}$, $T_{gas,cathode}$)	60 %, 67.8 °C
Test 6: ($RH_{cathode,in}$, $T_{gas,cathode}$)	50 %, 63.7 °C
Test 7: ($RH_{cathode,in}$, $T_{gas,cathode}$)	40 %, 59.0 °C
Test 8: ($RH_{cathode,in}$, $T_{gas,cathode}$)	30 %, 53.1 °C
Test 9: ($RH_{cathode,in}$, $T_{gas,cathode}$)	20 %, 44.9 °C
Test 10: ($RH_{cathode,in}$, $T_{gas,cathode}$)	15 %, 38.8 °C

Table 4.4. Experimental Conditions applied for the Stability Study

4.14. In addition, figure 4.15 shows the mean value and the standard deviation for each test performed (AVG and STD respectively) which will be very useful to observe its stability performance.

The peaks of voltage observed at $RH_{cathode,in} = 100\%$, $RH_{cathode,in} = 80\%$ and $RH_{cathode,in} = 70\%$ are most likely produced because of water accumulation in the PEMFC, concretely in the cathode side. The peaks of voltage are momentary and, as it is observed by the figure 4.15, the voltage tends to come back to its steady value. In addition, at $RH_{cathode,in} = 20\%$ a constant voltage drop is observed which is more notorious if the relative humidity is reduced as it is shown at $RH_{cathode,in} = 15\%$ test. Therefore, at these conditions, it can be concluded that the membrane is under severe drying conditions and these conditions must not be consider for future projects.

Therefore, it can be stated that the PEMFC operates at stable state from $RH_{cathode,in} = 100\%$ to $RH_{cathode,in} = 30\%$. At lower cathode inlet relative humidities the PEMFC stability is not ensured. According to the experimental results, the best PEMFC stability performance conditions are obtained when $RH_{cathode,in} = 60\%$ because its standard deviation (STD) is the lowest of all the tests. This conclusion matches with the conclusion done in the experimental campaign performed by Juan Sánchez Monreal where better results were obtained at $RH_{cathode,in} = 50\%$ compared with a fully humidified cathode gas inlet

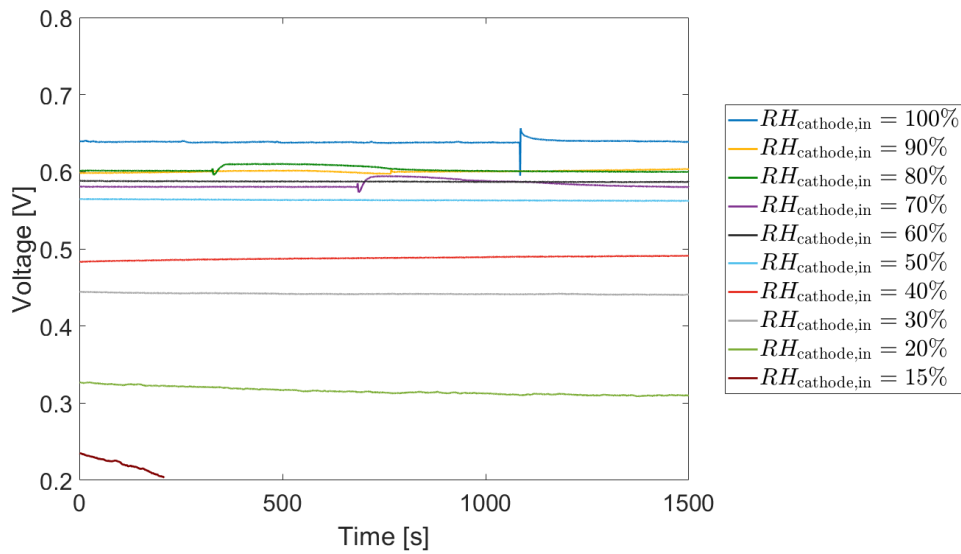


Figure 4.14. Stability Performance Experiment

($RH_{cathode,in} = 100\%$).

The main difference between both experimental campaigns is found in the voltage value mean. The experimental results obtained in this present bachelor thesis show a tendency in which a reduction of the relative humidity of the cathode gases affects significantly the voltage mean value and the PEMFC performance (figure 4.14) whereas this effect is not appreciated in the experimental campaign detailed in Juan Sánchez Monreal thesis. This difference is caused because voltage has a highly nonlinear dependence to operating conditions [68]. The difference of the PEMFC behaviour is caused by the different values in pressure, stoichiometry values and current density between both experiments. In addition, the cell size and the different bipolar path design could also affect PEMFC behaviour.

In general, according to the results, the operational PEMFC conditions should be between $RH_{cathode,in} = 60\%$ and $RH_{cathode,in} = 30\%$ if the objective is PEMFC stability performance. In case the PEMFC efficiency is seek, the PEMFC conditions should be between $RH_{cathode,in} = 100\%$ and $RH_{cathode,in} = 50\%$, where $RH_{cathode,in} = 100\%$ test shows the highest voltage mean and therefore the highest power.

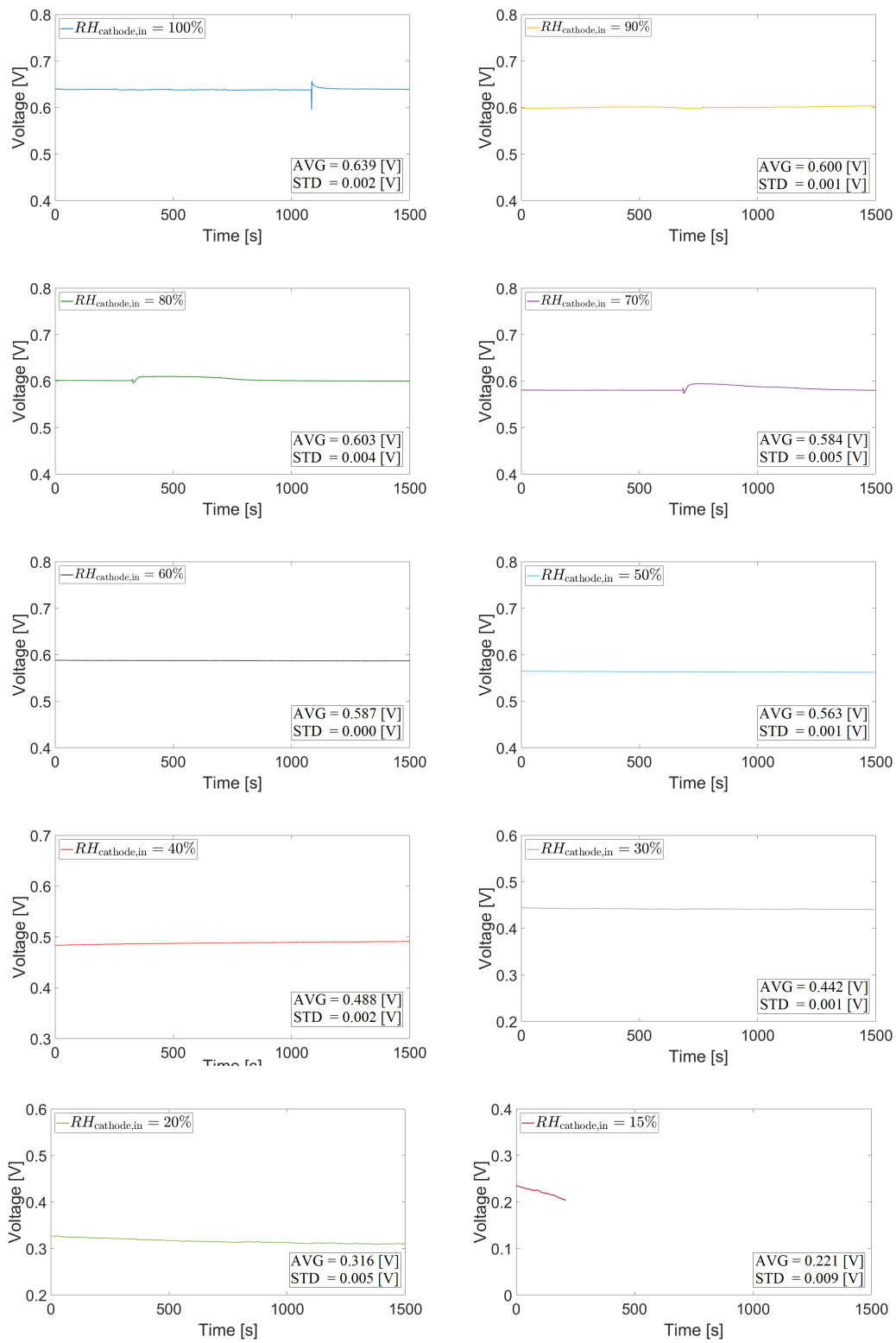


Figure 4.15. Stability Performance Tests Results at different Cathode Inlet Relative Humidities

Conclusions and Future Works

Through the present bachelor thesis the main objective initially proposed has been achieved: to set a zone of stable operation for the fuel cell UC3M laboratory. This zone of stable operation has been achieved thanks to the conclusions obtained through the modelling and experimental chapters. During the time in which this bachelor thesis was performed, the hydrogen generator and the anode mass flow controller broke down. These events increased the budget of the project and the working hours.

The global balances of mass and water have shown the different flow rates that intervene in the PEMFC. These balances are the start point for the whole project and have been very useful in order to have a clear global image of the processes happening inside the PEMFC. It is important to remark that water management inside the PEMFC involves many complex processes out of the scope of this bachelor thesis.

The dimensionless analysis performed from the balance of water has been done in base of the water produced in the PEMFC. This dimensionless analysis allows to take conclusions independently from current and therefore it can be applied to any PEMFC. From the equations 3.68 and 3.69 it can be observed that the variables that are able to modify the anode and cathode advection capacities are the stoichiometry, the relative humidity, the cell pressure and temperature. Because the UC3M fuel cell laboratory doesn't count with a back-pressure component, the cell pressure was limited to 1 atm. In order to compensate the pressure limiting condition it was decided to modify the stoichiometry. For this reason several simulations were performed in order to check good conditions for the experimental campaign.

According to the simulation results, the best configuration for the PEMFC is a high cell pressure and low stoichiometry values being the cathode stoichiometry more determinative than the anode one. However, due to the cell pressure is limited to 1 atm, the best configuration based on the experimental results was the one using stoichiometry values of $\phi_{anode} = 2.82$ and $\phi_{cathode} = 4.69$. These stoichiometry values match with the volumetric flow used in the DLR experimental campaign described in the Doctoral Thesis of Juan Sánchez Monreal. The PEMFC at $\phi_{anode} = 2.82$ and $\phi_{cathode} = 4.69$ shows that a change in the relative humidity conditions could compromise the stability performance of the fuel cell by flooding or dehydration of the membrane. However, as the output relative humidity parameters can not be

fixed the PEMFC has a large margin of manoeuvre and stability is ensured at least at high relative humidities of the anode and cathode inlet gases.

The characterization experiment was performed for the different stoichiometry values analyzed by the modelling chapter and finally the best configuration was considered the one using $\phi_{anode} = 2.82$ and $\phi_{cathode} = 4.69$. The main reasons were the high voltage and current densities obtained from the UC3M PEMFC compared with the other set-up configurations. Operating the PEMFC at a higher stoichiometry values of the ones chosen is not recommended because the gain in current density is little and the risk of flooding or dehydration inside the fuel cell increases significantly. The polarization and power densities curves show that the UC3M PEMFC has a low performance. Because the PEMFC performance is closely depending on the MEA performance, it is suspected that the actual MEA is worn and a change should be consider for future works.

Finally, once the experimental configuration was chosen a PEMFC stability performance experiment was done. In order to observe the response of the PEMFC at different cathode inlet relative humidities each test was performed at least 1800 s and the results show the best 1500 s interval. As it is observed in figure 4.14, the PEMFC behaviour is stable from $RH_{cathode,in} = 100\%$ to $RH_{cathode,in} = 30\%$. At lower cathode inlet relative humidity values the PEMFC is under severe dehydrated condition and it must be excluded for PEMFC operation to avoid membrane damages. These results are in accordance with the modelling results, in which the PEMFC performance stability is ensured for high cathode inlet relative humidity values. In addition, as it was suspected in the modelling chapter, the PEMFC output relative humidity values vary with the inlet relative humidity values in order to achieve a balance of water. Moreover, the voltage values in the UC3M PEMFC is more sensible to the inlet cathode relative humidity than the one used at DLR facility. The main reason is because the voltage has a highly nonlinear dependency to the current density, temperature, cell pressure and stoichiometry values. By trying to compensate the pressure limiting condition a new scenario was created.

For future works, a change of the MEA and the installation of a back-pressure component should be considered. New experiments at higher pressures than the atmospheric pressure should give better PEMFC behaviour in the fuel cell UC3M laboratory. The reason is because higher pressures reduce the effect of the relative humidity in the anode and cathode advection capacity values and therefore in the balance of water as it is shown in the modelling chapter. In addition, the increase in pressure would avoid the change in stoichiometry values and the PEMFC would operate at a higher efficiency. Furthermore, the change of the MEA should give a better performance of the PEMFC and the next experiments could operate at maximum power conditions at the stable zone of operation settled by this bachelor thesis.

APPENDIX A

Formulas in the Bachelor's thesis

In this appendix a list of external formulas and explanations will be listed. The following equations has been useful to calculate the main parameters of this bachelor thesis.

Amagat's Law, Dalton's Law and Ideal Gas Mixture Assumption

$$pV = nRT \rightarrow \text{Ideal Gas Law} \quad (\text{A.1})$$

$$p_{total} = \sum_{species} p_{partial} \quad (\text{A.2})$$

$$\chi_k = \frac{n_k}{n_T} = \underbrace{\frac{V_k}{V_T}}_{\text{Amagat's Law}} = \underbrace{\frac{p_k}{p_T}}_{\text{Dalton's Law}} \quad (\text{A.3})$$

$$Y_k = \frac{\chi_k \cdot M_k}{M_{total}} = \frac{\dot{m}_k}{\dot{m}_{total}} \quad (\text{A.4})$$

where:

- Y_k = Mass fraction of specie k
- n_k = Moles of species k [mol]
- n_T = Moles of the mixture [mol]
- V_k = Volume of specie k [m^3]
- V_T = Total volume of the mixture [m^3]
- p_k = Partial pressure of specie k [Pa]
- p_T = Total pressure of the mixture [Pa]
- χ_k = Mole fraction of specie k
- M_k = Molar mass [kg/mol]
- \dot{m}_k = Mass flow of specie k [kg/s]

Laws of Thermodynamics

There are three fundamental assumptions, in deed there are four, that are necessarily to understand and develop formulas that predicts how a system change when a physical or/and chemical process is involved.

Zeroth Law: When two systems are in thermal equilibrium with a third one, we can state that each system is in thermal equilibrium with the other systems, or in other words the three systems are at the same temperature. Assuming there are 3 different systems called A, B and C, if A and B are in thermal equilibrium with C, we can state that A and B are also in thermal equilibrium. This law enhance temperature variable and the use of a temperature scale.

First Law: Also known as the law of conservation of energy. It states that energy can not be created or destroyed but just change its form. In other words, internal energy variation of a system equals the heat (Q) added to the system by the surrounding minus the work (W) done by the system to the surroundings.

$$d(\text{Energy})_{system} = dU = dQ - dW \quad (\text{A.5})$$

Second Law: The second law deals with the irreversibility of spontaneous processes. This law prevent certain thermodynamic processes to occur even though these processes are allowed by the first law. In case of heat transfer, the heat only flows from higher to lower temperature systems and not viceversa. In addition, the second law also denotes that the entropy of an isolated system never decreases.

Third Law: The entropy of a perfect crystal of an element at absolute zero (0 K) is equal to zero. This law allows to scale entropy setting a reference point. Entropy is the number of possible microstates in a system, the higher the entropy, the higher the "disorder" of the system. Entropy can be defined in an isolated system as:

$$S = k_B \cdot \log \Omega \quad (\text{A.6})$$

where:

- S = Entropy [J/K]
- k_B = Boltzmann's constant [J/K]
- Ω = Number of possible microstates of the system.

Gibbs Free Energy and Electrical Power [6]

Gibbs free energy (G) can be expressed as:

$$\Delta G = \Delta H - T\Delta S \quad (\text{A.7})$$

where:

- S = Entropy [J/K]
- H = Enthalpy [J]
- T = Temperature [K]

In addition enthalpy (H) can be formulated as:

$$\Delta H = \Delta U + p\Delta V + V\Delta p \quad (\text{A.8})$$

where:

- U = Internal Energy [J]
- p = Pressure [Pa]
- V = Volume [m^3]

Applying the 1st Law of Thermodynamics:

$$\Delta U = \Delta Q - \Delta W \Rightarrow \Delta U = T\Delta S - \underbrace{p\Delta V}_{\Delta W_{mechanic}} - \Delta W_{electric} \quad (\text{A.9})$$

where:

- Q = Heat [J]
- W = Work [J]

$$\Delta Q = T\Delta S \quad (\text{for reversible transfer of heat at } p=\text{cte})$$

$$\Delta W = \Delta W_{mechanic} + \Delta W_{electric}$$

$$\Delta W_{mechanic} = p\Delta V$$

If we combine equations A.8 and A.9 together we obtain:

$$\Delta H = \underbrace{T\Delta S - p\Delta V - \Delta W_{electric}}_{\Delta U} + p\Delta V + \cancel{V\Delta p}^{cte} \Rightarrow \Delta H = T\Delta S - \Delta W_{electric} \quad (\text{A.10})$$

Finally, we can express Gibbs free energy as:

$$\Delta G = \underbrace{T\Delta S - W_{electric}}_{\Delta H} - T\Delta S \Rightarrow \Delta G = -\Delta W_{electric} \quad (\text{A.11})$$

Ohm's Law and its effect in the Ohmic Losses

The Ohm's Law establish that the voltage difference between two points of a conductor is proportional to the amount of current flowing through it.

$$V = I \cdot R \quad (\text{A.12})$$

The charge resistance of the components present in the PEMFC represents a voltage loss which is called ohmic loss. This voltage drop (η_{ohm}) can be estimated by Ohm's Law as:

$$\eta_{ohm} = j \cdot R_{ohmic} \Rightarrow \eta_{ohm} = j \cdot (R_{elect} + R_{ionic}) \quad (\text{A.13})$$

where:

- j = Current density [A/cm²]
- R_{ohmic} = PEMFC internal area-specific resistance [Ω cm²]
- R_{elec} = PEMFC internal area-specific resistance belonging to the flow of electrons [Ω cm²]
- R_{ionic} = PEMFC internal area-specific resistance belonging to the flow of ions [Ω cm²]

Dew Point Calculator

The dew point is closely related with the relative humidity. For the experimental campaign it has been necessary to calculate the different relative humidity for the anode and cathode flow inlet streams. In addition, the software used in the experimental campaign (FuelCell®) shows the relative humidity at both electrodes in real time. The relative humidity can be modified by changing the anode and cathode temperatures streams in the fuel setup. In order to obtain a good initial approximation for the different relative humidities the dew point has been calculated. The dew point is the atmospheric temperature at which the water present in the gas is saturated. Below the dew point, the gaseous water condensates and forms dew. It can be checked in equation 3.3 that the relative humidity is related with the saturation conditions. In order to calculate the dew point the Magnus equation has been used.

$$T_{dew\ point} = \frac{c \cdot \gamma}{b - \gamma} \quad (A.14)$$

where:

$$\gamma(T_{cell}, RH_{desired}) = Ln\left(\frac{RH_{desired}}{100}\right) + \frac{b \cdot T_{cell}}{c + T_{cell}} \quad (A.15)$$

and the constants:

- $b = 18.678$
- $c = 257.14$ [°C]

The real electrodes streams temperatures were slightly different than the theoretical dew point temperature. For the experiments the temperatures were modified until the desired relative humidity was obtained and showed by the software.

Volume Flow Rates of the Inlet Gases

The anode and cathode volume flow rate equations have been very useful for the experimental campaign because the software (FuelCell4) works with volume flow rates instead of mass flow rates.

There is a close relationship between the volume flow rate and the mass flow rate as it is shown in equation A.16

$$\dot{Q} = \frac{\dot{m}}{\rho} \quad [m^3/s] \quad (\text{A.16})$$

where:

- \dot{Q} = Volume Flow Rate [m^3/s]
- \dot{m} = Mass Flow Rate [kg/s]
- ρ = Density [kg/m^3]

For the hydrogen and air volume flow rate the equations are:

$$\dot{Q}_{H_2} = \phi_{anode} \cdot \frac{I}{2 \cdot F} \cdot V_m^{sc} \quad [m^3/s] \quad (\text{A.17})$$

$$\dot{Q}_{air} = \phi_{cathode} \cdot \frac{I}{4 \cdot F} \cdot V_m^{sc} \cdot \frac{1}{\xi_{O_2}} \quad [m^3/s] \quad (\text{A.18})$$

where:

- ϕ = Stoichiometry rate
- I = Current [A]
- F = Faraday constant [C/e⁻mol]
- V_m^{sc} = Standard Molar Volume [m^3/mol]
- ξ = Molar fraction

APPENDIX B

Reference Conditions

The conditions applied to the experimental campaign was based on the conditions implemented in the Doctoral Thesis of Juan Sánchez Monreal [60]. These conditions are listed below:

Juan Sánchez Monreal Experimental Conditions	
Temperature (T_{cell})	60/80 °C
Pressure (p_{cell})	1.5 bar
Surface Area (A)	142 cm ²
Current (I)	100 A
Current Density (j)	0.704 A/cm
Flow Rate Hydrogen	840 ml/min
Anode stoichiometry (ϕ_{anode})	1.2
Flow Rate Air	3320 ml/min
Cathode Stoichiometry (ϕ_{cathode})	2

Table B.1. Juan Sánchez Monreal Experimental Conditions

These configuration values can be applied to the UC3M PEMFC facility, obtaining:

Initial Experimental Conditions	
Temperature (T_{cell})	60/80 °C
Pressure (p_{cell})	1 atm
Surface Area (A)	5 cm ²
Current (I)	3.52 A
Current Density (j)	0.704 A/cm
Flow Rate Hydrogen	29.4 ml/min
Anode stoichiometry (ϕ_{anode})	1.2
Flow Rate Air	116.8 ml/min
Cathode Stoichiometry (ϕ_{cathode})	2

Table B.2. Juan Sánchez Monreal Experimental Conditions applied for UC3M facility. Reference Experimental Conditions

APPENDIX C

Bachelor Thesis Budget

This appendix shows the budget allocated for the elaboration of this bachelor thesis. The different costs are detailed in tables C.2, C.3 and C.4.

Bachelor Thesis Budget	
Item	Total Cost for the Project
Equipment Costs	11473.95 €
Tools Costs	9.63 €
Labour Costs	9500 €
Transport Costs	120 €
SUBTOTAL	21103.58 €
<i>Additional 15 % bearing the costs produced in the UC3M</i>	3165.54 €
TOTAL	2426.12 €

Table C.1. Summary of the Bachelor Thesis Budget

Labour Cost			
Item	Hours	Salary per hour	Total Cost for the Project
Dr. Marcos Vera	20	30 €/hour	600 €
Dr. Juan Sánchez	30	30 €/hour	900 €
Student	400	20 €/hour	8000 €
TOTAL			9500 €

Table C.2. Labour Costs

Transport Cost			
Item	Months	Cost per month	Total Cost for the Project
Abono Joven Card	6	20 €/month	120 €
TOTAL			120 €

Table C.3. Transport Costs

Equipment Cost						
Item	Units	Cost per unit	Total Cost (21% VAT included)	Expected useful life	Time of Use	Total Cost for the Project
Hydrogen Generator: Hart 250	1	5500 €/unit	6655.00 €	10 years	4 months	221.83 €
Software FUELCELL4	1	-	-	15 years	4 months	Included
Fuel Test: Model 850e	1	26500 €/unit	32065.00 €	15 years	4 months	712.56 €
Flow field pack	1	780 €/unit	943.80 €	7 years	4 months	44.94 €
MEA + GDL	1	140 €/unit	169.40 €	1 year	4 months	56.47 €
Gaskets	2	105 €/unit	254.10 €	2 years	4 months	42.35 €
Installation of the equipment and Transportation	1	1980 €	2395.80 €	-	-	2395.80 €
Reparations	2	-	8000.00 €	-	-	8000.00 €
TOTAL			50483.10 €			11473.95 €
Tools Cost						
Item	Units	Cost per unit	Total Cost (21% VAT included)	Expected useful life	Time of Use	Total Cost for the Project
Asus Personal Computer	1	412.39 €/unit	499 €	5 years	400 hours	4.62 €
Matlab and Other Softwares	1	-	-	-	-	Included
Other materials (notebooks, pens...)	-	4.14 €/unit	5.00 €	-	-	5.00 €
TOTAL			504.00 €			9.63 €

Table C.4. Equipment and Tools Costs

Auto-Stack Project Proposed Stack Break-In

In this appendix the test conditions and procedure to follow are summarized for a PEMFC stack break-in.



Proposed Stack Break-In, Overview...

Break-In

Test Conditions	T.Si.CI	73°C
Break-In	DPT.S.A / C	72 / 72°C
	Stoic.A / C	2.0 / 2.8
	p.So.A / C	200 / 200 kPaabs
	conc.Si.A	100% H2
	i.S./minFlowA/C	0.5 A/cm²

Test Procedure

Step	Action	Load-Level	dwell-time	Ramp time	Step-time	Comment
1	Steady-State	0.5 A/cm²	2 hrs	1 hr	2 hrs	
2	Load Cycling	0.2 - 0.9 A/cm²	2 min	15 sec	2-4 hrs	Step is finished when cell voltage levels do not significantly increase from one cycle to the following
3	Polcurve	0 - 1.2 A/cm²	6 min	15 sec	~ 3.5 hrs	
4	ShutDown and Cold Soak		min. 4 hrs		min. 2 hrs	
5	Startup and Polcurve	0 - 1.2 A/cm²	6 min (2 min @ OCV)	15 sec	~ 4 hrs	Repeat Steps 5 - 6 until no significant cell voltage increase from one polcurve to the following is observed
6	ShutDown and Cold Soak		min. 4 hrs		min. 2 hrs	



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Figure D.1. Auto-Stack Project Proposed Stack Break-In

Bibliography

- [1] European Union, "Topics of the European Union: Energy". [Online]
(website link: www.europa.eu/european-union/topics/energy_en)
- [2] European Commission, "Priority: Energy union and climate". [Online]
(website link: www.ec.europa.eu/commission/priorities/energy-union-and-climate_en)
- [3] European Commission, "Second Report on the State of the Energy Union", 1-02-2017. [Online]
(website link: www.ec.europa.eu/commission/second-report-state-energy-union_en)
- [4] Nils Anders Rokke, "Hydrogen is on a mission to decarbonise the world", SINTEF's blog (An independent research organization), 3-10-2017. [Online]
(website link: www.sintef.no/en/latest-news/hydrogen-is-on-a-mission-to-decarbonise-the-world/)
- [5] F. Barbir, *PEM Fuel Cells: Theory and Practice*, 2nd edition. Waltham (MA) USA: Elsevier, 2013.
- [6] R. O'Hayre, S.W. Cha, W. Colella, F. Prinz, *Fuel Cell Fundamentals*. New York: John Wiley and Sons, 2016.
- [7] Fuel Cell Today, "Fuel Cells Basics: Technology Types" [Online]
(website link: www.fuelcelltoday.com/media/1637138/fc_basics_technology_types.pdf)
- [8] C. He, S. Desai, G. Brown, S. Bollepalli, "PEM Fuel Cells Catalysts: Cost, Performance and Durability" *The Electrochemical Society Interface*, vol. 14, n°3, pp. 41-44, fall 2005.
- [9] U.S.A. Department of Energy: Fuel Cells Technologies Office, "Types of Fuel Cells". [Online]
(website link: www.energy.gov/eere/fuelcells/types-fuel-cells)
- [10] U.S.A. Department of Energy: Fuel Cells Technologies Office, "Comparison of Fuel Cell Technologies". [Online]
(website link: www.energy.gov/eere/fuelcells/comparison-fuel-cell-technologies)
- [11] Fuel Cell Today, "PEM Fuel Cells" [Online]
(website link: www.fuelcelltoday.com/technologies/pemfc)

- [12] Fuel Cell Today, "Alkaline Fuel Cells" [Online]
(website link: www.fuelcelltoday.com/technologies/afc)
- [13] J. Ferro, "UTC Power presentation: PAFC History and Successes". [Online]
(website link: www.energy.gov/sites/prod/files/2014/03/f11/mcfc_pafc_workshop_ferro.pdf)
- [14] Fuel Cell Today, "Phosphoric Acid Fuel Cells" [Online]
(website link: www.fuelcelltoday.com/technologies/pafc)
- [15] Fuel Cell Today, "Molten Carbonate Fuel Cells" [Online]
(website link: www.fuelcelltoday.com/technologies/mcfc)
- [16] Fuel Cell Today, "Solid Oxide Fuel Cells" [Online]
(website link: www.fuelcelltoday.com/technologies/sofc)
- [17] FuelCell CO, "History of Fuel Cells", 2010. [Online]
(website link: www.fuelcell.co.uk/history-of-fuel-cells/)
- [18] Fuel Cell Today, "History of Fuel Cells" [Online]
(website link: www.fuelcelltoday.com/history)
- [19] N. Hikosaka, *Fuel Cells: Current Technology Challenges and Future Research Needs*, 1st edition. Elsevier, 2013.
- [20] E. Ortiz-Rivera, A. Reyes Hernandez and R. Febo, *Understanding the History of Fuel Cells*, Newark (NJ) USA: IEEE, 2008.
- [21] U.S. Department of Energy Hydrogen Program, "Hydrogen Fuel Cells Fact Sheet" [Online]
(website link: www.hydrogen.energy.gov/pdfs/doe_fuelcell_factsheet.pdf)
- [22] Eurostat, "EU imports of energy products - recent developments". [Online]
(website link: www.ec.europa.eu/eurostat/statistics-explained/index.php/EU_imports_of_energy_products_-_recent_developments)
- [23] Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan "Chapter 3.4 Fuel Cells" (Updated May 2017) [Online]
(website link: www.hydrogen.energy.gov/pdfs/15015_fuel_cell_system_cost_2015.pdf)
- [24] Hydrogen Tools, "Codes and Standards". [Online]
(website link: www.h2tools.org/content/hydrogenfuel-cell-codes-standards)
- [25] O. Sharaf and M. Orhan, "An overview of fuel cell technology: Fundamentals and applications" *Renewable and Sustainable Energy Reviews*, vol 32, pp. 810-853, April 2014.
- [26] METI, "Strategic Roadmap for Hydrogen and Fuel Cells" [Online]
(website link: www.meti.go.jp/english/press/2016/0322_05.html)
- [27] E. Akiba, "Hydrogen energy R&D: The Roadmap and State-of-Art of Japan, and Activities of Kyushu University", August 2017. [Online]
(website link: www.wretc.in/presentation/2017/Day2/Session-7/Akiba.pdf)

- [28] Council of the European Union, "Council Regulation No 559/2014 of 6 May 2014". [Online]
(website link: www.publications.europa.eu/en/publication-detail/-/publication/2f0375fc-ee10-11e3-8cd4-01aa75ed71a1/language-en)
- [29] FCH JU, "Regulations, Codes and Standards Strategy Coordination Group" [Online]
(website link: www.fch.europa.eu/page/rcs-strategy-coordination-group)
- [30] HySEA Project. [Online]
(website link: www.hysea.eu)
- [31] HyPactor Project. [Online]
(website link: www.hypactor.eu)
- [32] SOCTESQA Project. [Online]
(website link: www.soctesqa.eu)
- [33] Hyindoor Project. [Online]
(website link: www.hyindoor.eu)
- [34] Hyindoor Project. [Online]
(website link: www.hyindoor.eu)
- [35] Hydrogen Europe, "The Ultimate Guide to Fuel Cells and Hydrogen Technology". [Online]
(website link: www.hydrogeneurope.eu/wp-content/uploads/2016/02/FCH_Brochure_V2SP.pdf)
- [36] FCH JU, "Report To The European Parliament On The Socio-Economic Impact Of The FCH JU Activities", January 2016. [Online]
(website link: www.fch.europa.eu/sites/default/files/FCH%20JU%20report%20on%20socio-economic%20impact.pdf)
- [37] E4tech consultancy, "The Fuel Cell Industry Review 2017". [Online]
(website link: www.FuelCellIndustryReview.com);
(document available in: www.ap2h2.pt/download.php?id=74)
- [38] FCH JU, "Fuel Cell and Hydrogen Technology: Europe's Journey to a Greener World. 10th Stakeholder Forum FCH2 JU 2017". [Online]
(website link: http://www.fch.europa.eu/sites/default/files/2017_FCH%20Book_webVersion%20%28ID%202910546%29.pdf)
- [39] Toyota, "Mirai Brochure 2018". [Online]
(website link: www.ssl.toyota.com/mirai/assets/modules/carpagell/features/docs/MY18_Mirai_eBrochure_Lifestyle.pdf)
- [40] U.S. Department of Energy Hydrogen Program, "Fuel Cell System Cost 2017", Record 17007, September 2017. [Online]
(website link: www.hydrogen.energy.gov/pdfs/17007_fuel_cell_system_cost_2017.pdf)
- [41] PACE Project. [Online]
(website link: www.pace-energy.eu)

- [42] P. Zhou, C.W. Wu, G.J. Ma, "Influence of clamping force on the performance of PEMFCs", *Journal of Power Sources*, Volume 163, Issue 2, pp 874-881, 2007.
- [43] B. Gou, W. Na, B. Diong *Fuel Cells: Modeling, Control and Applications*, 1st edition. CRC Press, 2010.
- [44] FuelCellStore, "Fuel cell components". [Online] (website link: www.fuelcellstore.com/fuel-cell-components/)
- [45] D. Sanchez, T. Ruiu, K. A. Friedrich, J. Sanchez and M. Vera, "Analysis of the Influence of Temperature and Gas Humidity on the Performance Stability of Polymer Electrolyte Membrane Fuel Cells", *Journal of the Electrochemical Society*, Volume 163, Issue 3, pp 150-159, 2016.
- [46] A. Lanz, *Hydrogen Fuel Cell Engines and Related Technologies*, 1st Edition. Palm Desert (CA, USA): Colleague of the Desert, 2001.
- [47] National Center for Biotechnology Information, "Hydrogen". [Online] (website link: www.pubchem.ncbi.nlm.nih.gov/compound/Hydrogen)
- [48] Royal Society of Chemistry, "Hydrogen" [Online] (website link: www.rsc.org/periodic-table/element/1/hydrogen)
- [49] K. Mazloomi, C. Gomes, "Hydrogen as an energy carrier: Prospects and challenges", *Renewable and Sustainable Energy Reviews*, Volume 16, Issue 5, pp. 3024-3033, 2012.
- [50] DOE Fuel Cell Technology (USA), "Hydrogen Storage". [Online] (website link: www.energy.gov/eere/fuelcells/hydrogen-storage)
- [51] DOE Fuel Cell Technology (USA), "Safe Use of Hydrogen". [Online] (website link: www.energy.gov/eere/fuelcells/safe-use-hydrogen)
- [52] DOE Fuel Cell Technology (USA), "Safety, Codes and Standards - Basics". [Online] (website link: www.energy.gov/eere/fuelcells/safety-codes-and-standards-basics)
- [53] Hydrogen Tools, "Basic Hydrogen Properties". [Online] (website link: www.h2tools.org/hyarc/hydrogen-data/basic-hydrogen-properties)
- [54] Hydrogen Tools, "Comparative Properties of Hydrogen and Other Fuels". [Online] (website link: www.h2tools.org/hyarc/hydrogen-data/comparative-properties-hydrogen-and-other-fuels)
- [55] L. Wright, B. Boundy, P.C. Badger, B. Perlack and S. Davis, "Biomass Energy Data Book", *Office of the Biomass Program*, edition 2. Tennessee: UT-Battelle LLC, December 2009.
- [56] Repsol, "Technical Report 95 Petrol". [Online] (website link: www.imagenes.repsol.com/pe_es/gas95__168184_tcm18-208310.pdf)
- [57] Repsol, "Technical Report e⁺ Diesel". [Online] (website link: www.repsol.es/imagenes/repsolpores/es/fds_diesel_e__58083_tcm19-19929.pdf)

- [58] PGW, "Technical Report Natural Gas". [Online] (website link: www.pgworks.com/uploads/pdfs/NaturalGasSafetyData.pdf)
- [59] W. Dai et al. "A review on water balance in the membrane electrode assembly of proton exchange membrane fuel cells", *International Journal of Hydrogen Energy*, volume 34, issue 23, pp. 9461-9478, December 2009.
- [60] J. Sánchez Monreal, "Polymer Exchange Membrane Fuel Cells modeling: from kinetic models to water management", Thesis, UC3M, Madrid, España, 2017.
- [61] S.G. Kandlikar and Z. Lu, "Thermal management issues in a PEMFC stack - A brief review of current status". *Applied Thermal Engineering*, volume 29, issue 7, pp. 1276-1280, May 2009.
- [62] T.E. Springer, T.A. Zawodzinski and S. Gottesfeld, "Polymer Electrolyte Fuel Cell Model", *Journal of the Electrochemical Society*, volume 138, issue 8, pp. 2334-2342, 1991.
- [63] R.L. Edwards and A. Demuren, "Regression analysis of PEM fuel cell transient response", *International Journal of Energy and Environmental ENgineering*, volume 7, issue 3, pp. 329-341, September 2016.
- [64] P. Pérez Gallego, "Caracterización experimental de una pila de combustible con metanol directo". Bachelor thesis, Thermal and Fluids Engineering Department, UC3M, Madrid, Spain, 2013.
- [65] Hidrógena Desarrollo Energéticos SL [Online] (website link: www.hidrogena.com/en/)
- [66] D. Sánchez et al, "Oscillations of PEM fuel cells at low cathode humidification", *Journal of Electroanalytical Chemistry*, volume 649, issues 1-2, pp. 219-231, November 2010.
- [67] J. Benziger, E. Chia, J.F. Moxley, I.G. Kevrekidis, " The dynamic response of PEM fuel cells to changes in load", *Chemical Engineering Science*, volume 60, issue 6, pp. 1743-1759, March 2005.
- [68] C. Kunusch, P. Puleston and M. Mayosky, *Sliding-Mode Control of PEM Fuel Cells*, 1st edition. Springer, 2012.