Fuel Cells
State of the Art

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1. Introduction

A fuel cell is an electrochemical device that has the ability to convert chemical energy of a reactant directly into electricity with high efficiency. When the fuel reacts with the oxidant, the electrochemical reaction takes place and some energy is released, usually low-voltage DC electrical energy and heat. The former is used to do useful work directly and the latter is wasted or can be used in cogeneration applications.

In the following sections, two concepts will be described: the unit cell and the fuel cell. The unit cell is the basic operating device that converts chemical energy into electricity. Multiple unit cells connected together in series make up the fuel cell, giving the desired voltage in a specific application.

Fuel cells are usually compared with other energy convertors, like reciprocating engines or batteries. In fact, batteries and fuel cells have the same operating principle, based on the electrochemical reaction between the anode, the cathode and the electrolyte. The operating principle of fuel cells and batteries will be described in section 1.4.

The most attractive feature of the fuel cells is that they have zero emissions. Nowadays, the energy demand is becoming a great problem because it is increasing continuously. Moreover, the more energy is produced, the more the environment is contaminated. For this reason, fuel cells could be a viable solution to that issue.

This report pretends to explain the state of the art of fuel cells and the applications focused on aviation, such as unmanned aerial vehicles (UAV).

1.1 History of Fuel Cells

The history of fuel cells began about 150 years, at the beginning of the 19th century. The picture below shows the main facts related with fuel cells, from their invention to the extensive research:

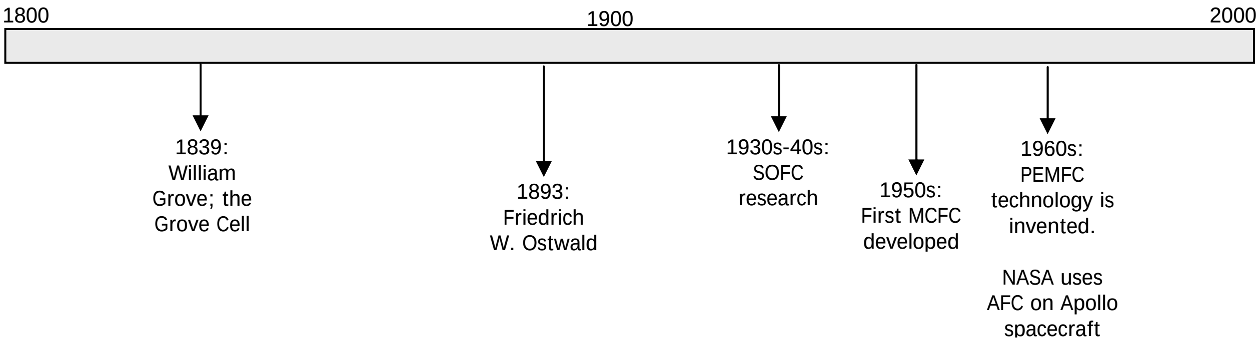

Figure 1 – History of fuel cells

In 1839, William Grove developed the first fuel cell (the “Grove Cell”). Grove read the notes that William Nicholson and Anthony Carlisle wrote in 1800 describing the process of water break using electricity, and thought about recomposing water by combining electrodes in a series circuit. The Grove cell operated with a platinum electrode immersed in nitric acid and a zinc electrode in zinc sulfate and it generated a current of about 12A and 1’8V of voltage.

In 1893, Friedrich Wilhelm Ostwald, one of the founders of physical chemistry, experimentally determined the roles of many fuel cell components.

In 1939, Francis Thomas Bacon built the first alkali electrolyte fuel cell (AFC) based on nickel gauze electrodes. He thought that these fuel cells could provide power for the Royal Navy submarines better than the batteries used at the time, which were dangerous to storage. Thus, he developed large-scale alkali fuel cells using potassium hydroxide as the electrolyte, instead of the acid electrolytes used in Grove cell. In the 1960s decade, NASA used alkali fuel cells for the Project Apollo and the Space Shuttle.

During the 1930s, Emil Baur and H.Preis experimented with high temperature solid oxide electrolyte fuel cells (SOFC), and O.K. Davtyan researched further in this field during the 1940s. In the latest years of the 50s decade, G.H.J. Broers and J.A.A. focused their studies on the electrolytes of molten carbonate salts and created the first molten carbonate fuel cell (MCFC).

In the early 1960s, Thomas Grubb and Leonard Niedrach invented proton exchange membrane fuel cell (PEMFC) technology at General Electric. It was a compact device, but platinum catalysts were expensive. NASA initially researched PEMFC technology for Project Gemini, but it required a power source that would last a long amount of time. That is the reason why NASA chose alkali fuel cells instead of PEM fuel cells.

From the 1990s to the present time, an extensive research is being done in order to improve fuel cells and make them suitable for commercial applications, like automobiles or cell phones.

1.2 Hydrogen as a Fuel. Properties

Hydrogen is the most abundant element in the universe, making up about 75% of the mass of all visible matter. Hydrogen atom is the simplest of all elements, composed by the nucleus (a single proton) and a single orbiting electron. The proton and electron charges are positive and negative respectively. Thus, hydrogen atom is electrically neutral because the mentioned charges cancel each other. However, this atom cannot stay alone because of the orbiting electron reactivity. That is the reason why hydrogen atoms combine into molecular pairs, known as H_2.

The most important properties of hydrogen are:

- It has the second lowest boiling and melting points of all substances. Hydrogen is a liquid below 20K (-253ºC) and a solid below 14K (-259ºC) at atmospheric pressure.
- Pure hydrogen is odorless, colorless and tasteless, which means that a leak cannot be detected even in daylight. Substances like mercaptan that provide smell are usually added to odorless gases (natural gas, for example) in order to avoid accidents. Compounds like this may not be added to hydrogen for fuel cells since they contain sulfur, a harmful element for fuel cells. Although hydrogen obtained from fossil fuels reforming has traces of nitrogen, carbon monoxide and dioxide, these gases are also odorless, colorless and tasteless.
- Hydrogen has the lowest density not only as a gas (0,08376kg/m^3; at 20ºC, 1atm) but also as a liquid (70,8kg/m^3; at normal boiling point, 1atm).

- Hydrogen is very reactive, especially with oxygen. For this reason, it is impossible to find it uncombined.
- At normal conditions, hydrogen has both the highest Higher Heating Value (141860kJ/kg) and Lower Heating Value (119930kJ/kg). These terms are compared with other typical fuels like methane, propane or gasoline.
- Is extremely flammable over a very wide range of concentrations in air (4-75%).
- When combined with oxygen, the only product of the reaction is water or steam water.

Some of these properties make hydrogen the perfect fuel, especially its energy content and the zero-emissions when burned. Nonetheless, hydrogen has some disadvantages, like are its low density or the high flammability, turning it into a very difficult and dangerous substance to be packaged.

More information can be found in [3], module 1.

1.3 Ideal and Actual Performance. Efficiency

To easily understand the ideal performance of a fuel cell, a few thermodynamic concepts should be defined previously. The maximum electrical work obtainable in a fuel cell is given by the change in Gibbs free energy of the electrochemical reaction:

$$W_{el} = \Delta G = - n \mathcal{F} E \tag{1-1}$$

where W_{el} is the electrical work, ΔG the change in Gibbs free energy, n the number of electrons participating in the reaction, $\mathcal{F}$ is the faraday's constant (96487C/g) and E is the Nernst potential. ΔG also can be written as:

$$\Delta G = \Delta H - T\,\Delta S \tag{1-2}$$

ΔH is the enthalpy change and it represents the total thermal energy available in a given system. Otherwise, the Nernst potential gives the ideal open circuit cell potential. In other words, is the upper limit or maximum performance achievable by a fuel cell. Every type of unit cell has its own value of Nernst potential, but at 300K is approximately 1,2V. This value is strongly influenced by the reactant concentrations, as it reaches the maximum value when the reactants at the anode and cathode are pure.

The thermal efficiency of a fuel conversion device is defined as the quotient between the useful energy produced and the enthalpy change. In the case of fuel cells, this useful energy corresponds to the change in Gibbs free energy. The ideal efficiency of a fuel cell can be expressed as:

$$\eta_{\text{ideal}} = \frac{\Delta G}{\Delta H} \tag{1-3}$$

The fuel cell efficiency is based on the change in standard free energy for the cell reaction:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(l)} \tag{1-4}$$

At standard conditions, the thermal energy in the reaction above is 285,8kJ/mol, and the free energy available is 237,1kJ/mol. Finally, the thermal efficiency of an ideal fuel cell operating on pure hydrogen and oxygen is:

$$\eta_{\text{ideal}} = \frac{237{,}1}{285{,}8} \cong 0{,}83 \tag{1-5}$$

A very important property of fuel cells is that efficiency is not related with size. Due to different types of irreversible losses, the actual cell potential is decreased from its ideal potential, as it does the efficiency. These losses can be summarized as:

- Activation-related losses. The electrochemical reactions at the electrodes need some activation energy, so a little amount of energy is consumed previously.
- Ohmic losses. These losses are caused by ionic resistance in the electrolyte and electrodes, electronic resistance in the electrodes, current collectors and contact resistances.
- Mass-transport-related losses. Mass transport losses are a result of finite mass transport limitations rates of the reactants.

The following picture shows the typical fuel cell performance curve at equilibrium:

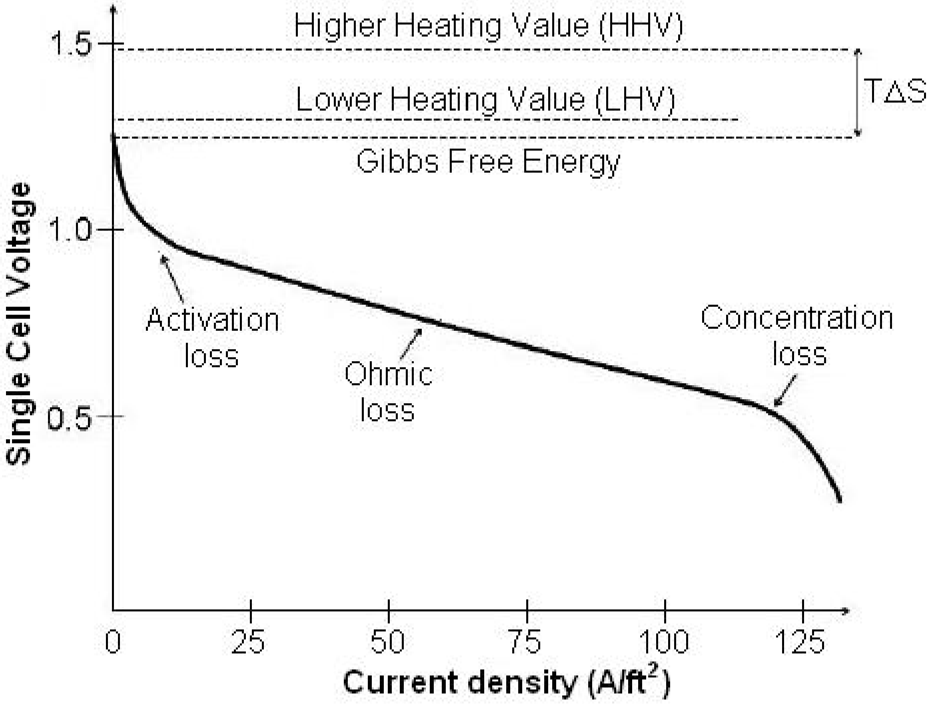

Figure 2 – Fuel cell performance curve at equilibrium

1.4 Architecture

A fuel cell is a collection of unit cells connected in series. Each unit cell can produce 1,2VDC so the more unit cells connected, the higher the fuel cell voltage. The unit cell is a very simple device compared with other energy conversion devices, like an engine, and it is made up by the following elements:

- Anode
- Cathode
- Electrolyte
- Catalyst

These elements and their functions will be explained in the following section. The next picture shows the unit cell architecture and how the different parts are distributed:

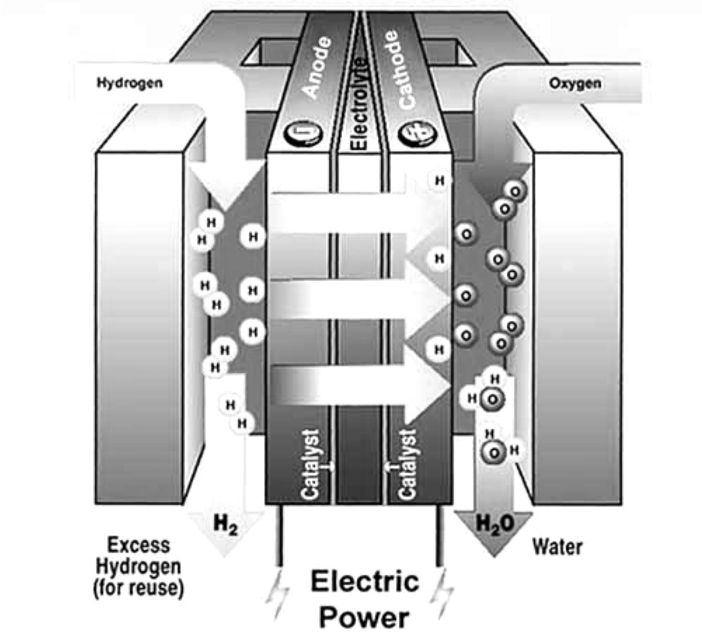

Figure 3 – Unit cell architecture

In this case, the cell is fed with hydrogen and oxygen, which are the fuel and the oxidant, respectively. The products are water and unreacted hydrogen (it can be reused).

1.5 Operating Principle

As it has been described before, a fuel cell is an energy conversion device that directly turns chemical energy into electricity. This is also the operating principle of the batteries. In fact, batteries and fuel cells are galvanic cells.

A galvanic cell is made up by two electrodes, an anode and a cathode, and an electrolyte. The anode is the negative electrode and is made of a substance that is readily oxidized, or in other words, that can release electrons. Conversely, the cathode is the positive electrode and is made of a substance that can accept electrons or that can be reduced. When put together, a spontaneous oxidation-reduction reaction occurs and electrons and ions are exchanged between both electrodes.

For this electrochemical reaction to happen, the reactive elements must be in contact with each other. However, if the electrodes are in direct contact, the reaction occurs in their surfaces and the electrons are exchanged directly, so no useful work results. In addition, all of the reaction energy is converted to heat. In order to perform useful work, these electrons must be forced to flow by an external path including a load, and the electrodes must be separated with an element that conducts ions but not electrons. This element is the electrolyte. Once the electrodes have been separated, the electrolyte lies between them and the external path flow is set, the red-ox reaction starts:

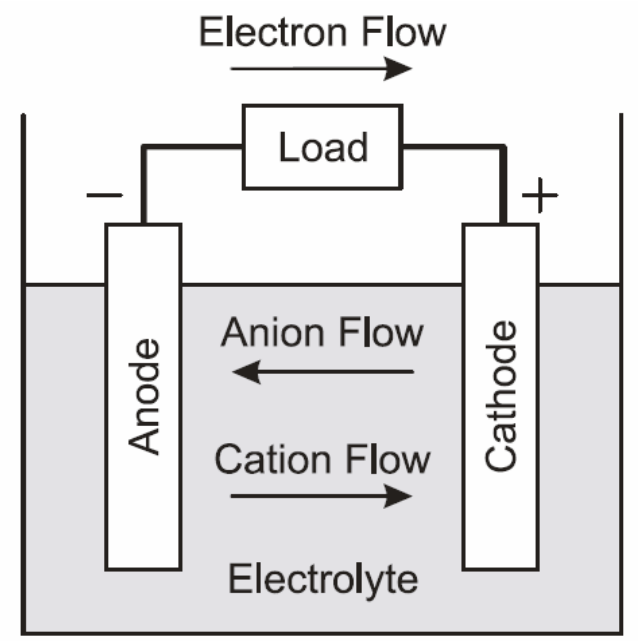

Figure 4 – Galvanic cell operating principle

In a battery, during the reaction the anode dissolves itself into the electrolyte forming positive charged ions and leaving behind an accumulation of electrons. The positive ions (or cations) will go through the electrolyte to the cathode and electrons will flow by the external path also to the cathode. This flow continues until the anode is consumed, the electrolyte is unable to furnish more cations or the load path is removed.

In a fuel cell, the fuel becomes the anode and the oxidant becomes the cathode. It means that in a fuel cell, the fuel and the oxidant gases are directed through flow channels to either side of the electrolyte, so they can performance the electrochemical reaction. While fuel and oxidant gases are supplied, the fuel cell won’t stop operating, in contrast of what happens in a battery.

Although a fuel cell can operate using different types of fuels and oxidants, hydrogen has long been recognized as the most effective fuel for practical fuel cell use since it has the higher electrochemical reactivity than other fuels like hydrocarbons or alcohols. Oxygen is the obvious choice of oxidant due to its high reactivity and its abundance on air. The electrolyte can be liquid or solid and is the distinguishing feature between different types of fuel cells, because different electrolytes conduct different ions.

Fuel cells also have a catalyst based on a noble metal, such as platinum, but only those that work at low temperature. The reason to add the catalyst is to encourage the electrode reactions.

2. Fuel Cell Types

In this section, the most important fuel cell types are described. The main difference between each type of fuel cell is the electrolyte, which dictates the operating temperature. A solid electrolyte is better than a liquid one since the latter involves handling problems.

High temperature fuel cells have enough energy to perform the internal reforming of the fuel and also have fast kinetic reactions, so expensive catalysts are not necessary. On the other hand, low temperature fuel cells do not require special materials and can be used in portable applications like cell phones or laptops.

2.1 Alkaline Fuel Cells (AFC)

Alkaline fuel cells operate between room temperature to 250ºC and a pressure about 1bar. Each cell can produce about 1,2VDC and the whole fuel cell has a power output between 300W to 15kW. Alkaline fuel cell stacks used in the Space Shuttle Orbiter have a power output of 12kW, their size is about 0,38x0,114x0,35m and they weigh 120kg approximately. The electrolyte used conducts hydroxyl ions (OH^-) from the cathode to the anode and is typically made up of a molten alkaline mixture such as potassium hydroxide (KOH). The electrolyte can be mobile (a continuously circulating fluid between the electrodes) or static (a thick paste retained by capillary forces within a porous support matrix such as asbestos).

The advantages of alkaline fuel cells are that they:

- Operate at low temperature
- Have fast startup times
- Have high efficiency
- Do not need expensive platinum catalyst
- Have minimal corrosion
- Have low weight and volume

The disadvantages are that they:

- Are extremely intolerant to CO_2 (about 350ppm maximum) and somewhat intolerant of CO
- Require complex water management
- Have a relatively short lifetime

The different reactions that take place in alkaline fuel cells are:

Anode reactions	**Overall cell reactions**
$H_2 + 2K^+ + 2OH^- \Rightarrow 2K + 2H_2O$ $2K \Rightarrow 2K^+ + 2e^-$	$H_2 + 2OH^- \Rightarrow 2H_2O + 2e^-$ $\frac{1}{2}O_2 + H_2O + 2e^- \Rightarrow 2OH^-$
Cathode reactions	
$\frac{1}{2}O_2 + H_2O \Rightarrow 2OH$ $2OH + 2e^- \Rightarrow 2OH^-$	

2.2 Molten Carbonate Fuel Cells (MCFC)

Molten carbonate fuel cells operate at about 650ºC and a pressure between 1 to 10bar. Each cell can produce between 0,7 to 1VDC and the whole fuel cell has a power output between 10kW to 2MW. For example, a MCFC with 250kW of power has a size of 1x1,5x3m.The liquid electrolyte used conducts carbonate ions (CO_3^{2-}) from the cathode to the anode and is typically made up of a molten mixture of lithium and potassium carbonates retained by capillary forces within a ceramic support matrix of lithium aluminate.

The advantages of MCFCs are that they:

- Support spontaneous internal reforming of light hydrocarbon fuels
- Generate high-grade waste heat
- Have fast reaction kinetics
- Do not need expensive platinum catalyst
- Have high efficiency

The disadvantages are that they:

- Are extremely intolerant to sulfur (about 1-5ppm maximum at the anode)
- Require materials that are corrosion resistant, dimensionally stable and have high endurance
- Require complex water management
- Have a relatively short lifetime

When a hydrocarbon is used as a fuel, such as methane, it absorbs heat and undergoes a steam reforming reaction:

$$CH_4 + H_2O \Rightarrow 3H_2 + CO$$

The different reactions that take place in molten carbonate fuel cells are:

Anode reactions	**Overall cell reactions**
$3H_2 + 3CO_3^{2-} \Rightarrow 3H_2O + 3CO_2 + 6e^-$ $CO + CO_3^{2-} \Rightarrow 2CO_2 + 2e^-$	$2H_2 + O_2 \Rightarrow 2H_2O$ $CO + \frac{1}{2}O_2 \Rightarrow CO_2$
Cathode reaction	
$2O_2 + 4CO_2 + 8e^- \Rightarrow 4CO_3^{2-}$	

2.3 Solid Oxide Fuel Cells (SOFC)

Solid oxide fuel cells operate at about 1000ºC and at 1bar of pressure. Each cell can produce between 0,8 and 1VDC and the whole fuel cell has a capacity range from 200kW to 25MW. For instance, a 250kW SOFC has a size of 1,5x2x4m. The used electrolyte conducts oxide ions (O^{2-}) from the cathode to the anode and is a solid-state electrolyte composed of zirconium oxide stabilized with yttrium oxide. These fuel cells are built trough sequential deposition, like computer chips, of various layers of material. The most common configurations are tubular and flat designs.

The advantages of solid oxide fuel cells are that they:

- Support spontaneous internal reforming of hydrocarbon fuels

- Generate high-grade waste heat
- Have very high efficiency
- Have fast reaction kinetics, so do not need noble metal catalysts

The disadvantages are that they:

- Have a moderate intolerance to sulfur (about 50ppm maximum)
- Require materials that have the specified conductivity, remain solid at high temperatures, are chemically compatible with other cell components, are dimensionally stable and have high endurance.

The different reactions that take place in these fuel cells are:

Anode reactions	**Overall cell reactions**
$H_2 + O^{2-} \Rightarrow H_2O + 2e^-$ $CO + O^{2-} \Rightarrow CO_2 + 2e^-$	$H_2 + \frac{1}{2}O_2 \Rightarrow H_2O$ $CO + \frac{1}{2}O_2 \Rightarrow CO_2$
Cathode reaction	
$\frac{1}{2}O_2 + 2e^- \Rightarrow O^{2-}$	

2.4 Polymer Electrolyte Membrane Fuel Cells (PEMFC)

These fuel cells, also called Proton Exchange Membrane FC, operate between room temperature to 100ºC and a pressure between 1 and 3bar. Each cell can produce about 1,1VDC of electricity, delivering an output power compressed between 1W and 2kW. These devices have a wide range of sizes because of the many types of applications, from cell phone batteries to motive power for vehicles. The used electrolyte conducts hydrogen ions (H^+) from the anode to the cathode and is composed of a non-corrosive solid polymer film that consists on a form of acidified Teflon, also known as Nafion.

The advantages of PEMFCs are that they:

- Operate at low temperature
- Are tolerant of carbon dioxide
- Have high voltage, current and power density
- Are compact and rugged

The disadvantages are that they:

- Can tolerate only about 50ppm carbon monoxide and a few ppm of total sulfur compounds
- Need reactant gas humidification
- Use an expensive platinum catalyst and an expensive membrane

The different reactions that take place in PEM fuel cells are:

Anode reaction	**Overall cell reaction**
$H_2 \Rightarrow 2H^+ + 2e^-$	$H_2 + \frac{1}{2}O_2 \Rightarrow H_2O$
Cathode reaction	
$\frac{1}{2}O_2 + 2e^- + 2H^+ \Rightarrow H_2O$	

2.4.1 Direct Methanol PEM Fuel Cells (DMFC)

These fuel cells are PEMFC using methanol as a fuel directly instead of hydrogen. The electrochemical reaction when using methanol releases less energy than when using pure hydrogen, but it is a safer technology because the fuel is liquid instead of pressured gas.

The advantages of DMFCs are that:

- Methanol is a widely available fuel and is easily reformed
- Using a liquid fuel means use a more secure technology

The disadvantages are that they:

- Can be poisoned by intermediate hydrocarbon species produced in the methanol oxidation
- Need a noble catalyst

The different reactions that take place in PEM fuel cells are:

Anode reaction	**Overall cell reaction**
$CH_3OH + H_2O \Rightarrow 6H^+ + CO_2 + 6e^-$	$CH_3OH + \frac{3}{2}O_2 \Rightarrow CO_2 + 2H_2O$
Cathode reaction	
$\frac{3}{2}O_2 + 6e^- + 6H^+ \Rightarrow H_2O$	

2.5 Phosphoric Acid Fuel Cells (PAFC)

Phosphoric Acid fuel cells operating temperature is in the range of 150 to 220ºC. Each cell can produce about 1,1VDC and the whole fuel cell has a power output between 50kW to 11MW. For example, a PAFC with 400kW of power output has a size of 2x2x3,5m.The electrolyte used conducts hydrogen ions (H^+) from the anode to the cathode and is made up of liquid phosphoric acid within a silicon carbide matrix material.

The advantages of phosphoric acid fuel cells are that they:

- Operate at low temperature
- Are tolerant of carbon dioxide
- Have stable electrolyte characteristics with low volatility

The disadvantages are that they:

- Only tolerate about 2% carbon monoxide and 50ppm of total sulfur compounds

- Use a corrosive liquid electrolyte
- Allow product water to enter and dilute the electrolyte
- Are large and heavy
- Cannot auto-reform hydrocarbon fuels
- Have to be warmed up before they are operated

The different reactions that take place in phosphoric acid fuel cells are:

Anode reaction	**Overall cell reaction**
$H_2 \Rightarrow 2H^+ + 2e^-$	$H_2 + \frac{1}{2}O_2 \Rightarrow H_2O$
Cathode reaction	
$\frac{1}{2}O_2 + 2e^- + 2H^+ \Rightarrow H_2O$	

2.6 Other fuel types

Due to the continuous research and investigation in this area, many other types of fuel cells have been developed:

- Zinc air fuel cells (ZAFC)
- Protonic ceramic fuel cells (PCFC)
- Biological fuel cells (BFC)
- Direct borohydride fuel cells
- Metal hydride fuel cells
- Formic acid fuel cells
- Direct ethanol fuel cells
- Regenerative fuel cells
- Microbial fuel cells
- Enzymatic fuel cells

The three first types have been improved in the latest years and have become as important as the fuel cell types described before.

For more information, see [1] pages 35-50.

2.7 Comparative table

The next table shows the main differences between each type of fuel cells:

	AFC	MCFC	SOFC	PEMFC	DMFC	PAFC
Fuel	H_2	H_2/CO	CO, H_2	H_2	CH_3OH + H_2O	H_2
Electrolyte	KOH	Li, Na and K_2CO_3	YSZ[1]	Nafion	Nafion	H_3PO_4
Ion transferred	OH^-	CO_3^{2-}	O^{2-}	H^+	H^+	H^+
Catalyst	Pt or Ni	Ni	Ni/YSZ	Pt	Pt/Ru	Pt
Temperature (°C)	RT[2] – 250	620 – 660	600 – 1000	RT – 100	RT – 100	150 – 220
Pressure (bar)	1 – 4	1 – 10	1	1 – 3	1 – 3	3 – 10
Contaminants (ppm)	CO_2	H_2S, HCl, As, NH_3, dust	S < 100	CO < 100, S, dust	CO < 100, S, dust	CO < 100, S, dust, NH_3
Maximum Efficiency (current)	64%	50%	65%	58%	40%	42%
Applications	Space programs, portable power	Stationary power	Stationary and distributed power, APU	Stationary, portable and vehicular	Portable electronics, APU	Stationary power

Table 1 – Comparative table between the different main types of fuel cells

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[1] Yttria stabilized zirconia

[2] Room Temperature

3. Applications

Once the different types of fuel cells have been described, it is easier to see which application match better to each fuel cell type.

3.1 Stationary Plants

As it has been explained in section 1.2, the fuel cell efficiency does not depend on its size. Consequently, small and high power generators can be built without giving up efficiency. As a result, stationary plants have been developed to produce between a hundred kW to few MW.

Smaller plants are sited within the user's facility and produce heat in addition of electricity. In other words, smaller plants are designed for cogeneration operation. Larger plants, on the other hand, are normally used for distributed generation and soon will be considered as base-load plants because of their high efficiency. Stationary fuel cells are suitable for many applications, such as:

- Primary power source
- Grid support
- Cogeneration
- Hybrid power systems

The first commercial on-site plant is the PC-25, a 200kW PAFC developed by UTC Fuel Cells, and it has been installed in hospitals, hotels and in large office buildings. The main characteristics of the plant are:

- Its dimensions are 3m wide by 3m high by 5,5m long
- The plant weight is approximately 17000kg
- Power capacity 0 to 200kW with natural gas fuel
- 480/277V at 60Hz, 400/230V at 50Hz
- 740000kJ/h at 60ºC of thermal energy

Another interesting application could be the hybrid fuel cell/gas turbine plant developed by Siemens Westinghouse Power Corporation. In this hybrid plant, the fuel cell replaces the combustion chamber of the gas turbine, producing together about 1MW of power with 60% efficiency when using natural gas.

For further information see [2] pages 1-15 – 1-20 and [1] pages 72 – 85.

3.2 Vehicles

Due to the wide range of power outputs, fuel cells can be the motive power of many different types of vehicles:

- Automobiles
- Buses
- Utility vehicles
- Scooters and bicycles
- Unmanned aerial vehicles

3.2.1 Automobiles

During the last decade, fuel cell automobiles have been developed because their low emissions and their efficiency. These vehicles normally use compressed hydrogen as a fuel, but other hydrocarbon fuels like methanol can be used. PEMFC and DMFC are the most commonly used fuel cell types because of their low operating temperature.

Despite all the improvements made in these vehicles, fuel cell automobiles are still very expensive so they are not a viable option. In order to enhance the production of automotive fuel cells, the next issues must be addressed:

- New techniques for mass fabrication and new materials must be created to lower the production cost
- The catalyst must be replaced if other fuels than hydrogen are used
- The size and weight of the fuel tanks must be reduced

Although hydrogen seems to be the perfect fuel since does not generate any pollution, its production and storing are important problems to attend. First of all, fuel cell automobiles need hydrogen refueling stations, which means that a hydrogen infrastructure must be established. However, many hydrogen stations already exist in USA, Japan or Germany.

Hydrogen can be stored in different forms, such as compressed gas, liquid or metal hydrides. Tanks that store compressed gases are usually bulky, so a reduction in the size is needed. Liquid hydrogen tanks less bulky, but they must be stored at extremely low temperatures as seen in section 1.1.

It seems that a viable solution is to use different fuels than hydrogen and reform them onboard, eliminating both onboard storage and hydrogen infrastructure problems. Nevertheless, onboard reforming carries many problems:

- Vehicles have low emissions instead of zero emissions
- Reformed hydrogen is not pure, decreasing then fuel cell’s efficiency
- Increased complexity, size, weight and cost of the entire propulsion system

3.2.2 Buses

Although buses need more power than automobiles, they are the best candidates to introduce fuel cells into the commercial market.

Automobiles cannot carry heavy and bulky hydrogen tanks, which is not a problem for buses. Usually, these tanks are located in the bus floor, far enough from the engine. Furthermore, buses can store a larger amount of hydrogen and can be refueled once a day in a central facility.

The commercialization of fuel cell buses it is still difficult because of the fuel cell cost and lifetime. However, in the latest ten years some bus manufacturers have demonstrated a few fuel cell bus models that have been running in cities like Amsterdam, Barcelona or London.

The most common fuel types used are compressed hydrogen, methanol and zinc, and the fuel cell types used are PEMFC, DMFC, PAFC and ZAFC.

3.2.3 Utility vehicles

Most of these vehicles already run with electricity; therefore, they can be easily adapted with fuel cell technology. Some examples of fuel cell-powered utility vehicles are

- Forklifts
- Wheelchairs
- Unmanned vehicles
- Boats
- Golf cars

Many demonstrations of utility vehicles operating with fuel cells have proved that they have lower operating costs and less maintenance. Another advantage is that these vehicles can operate indoors because they have zero emissions.

The most common fuel types used are compressed hydrogen, methanol, metal hydrides and sodium borohydride. The fuel cell types commonly used are PEMFC, DMFC and AFC.

3.2.4 Scooters and bicycles

Scooters and bicycles are the best forms of transportation in high populated cities. Due to the low power that they demand, fuel cells can be used in these vehicles. Although many models have been positively demonstrated, fuel storage is still a great challenge. The most commonly used fuels are compressed hydrogen and methanol.

3.2.5 Unmanned Aerial Vehicles

Unmanned aerial vehicles (UAV) are airplanes that can perform many tasks, such as reconnaissance and remote sensing missions. These aircrafts are powered by gas turbine powerplants, but currently investigations are focusing on power them with compressed or liquefied hydrogen PEMFC instead of gas turbine.

Proton exchange membrane fuel cells have high specific energy and have also high efficiency in comparison to other technologies available. In fact, liquid hydrogen fuel cells have greater specific energy than hydrocarbon fuelled internal combustion engines. However, fuel cells are characterized by low specific power, which is an indicator of aircraft performance. Thus, the first challenge is to maximize the fuel cell specific power. Other challenges are that fuel cell systems applied in UAV must have high efficiency and also that the aircraft structure shall have low weight.

The Georgia Tech Research Institute at the Georgia Institute of Technology in Atlanta has developed a fuel cell aircraft [7]. This aircraft has 3m length and 7m width approximately and is the largest fuel cell aircraft yet build that is fueled by compressed hydrogen. Furthermore, this aircraft can set the basis for large scale commercial fuel cell aircrafts.

Boeing has developed a manned airplane powered by fuel cells. More information can be found in [9].

3.3 Auxiliary Power Systems

Fuel cells not only supply primary power like in stationary plants or in vehicles, but also can be used in secondary applications such as auxiliary power units (APU). Auxiliary power units are devices that provide the non-propulsion power for vehicles, like refrigeration, lightning or communication equipment. APUs can be used in trucks, airplanes, trains or automobiles.

In contrast of what happens in propulsion systems for vehicles, APU applications do not require challenging performance and a low cost. For these reasons, APU applications market is becoming more and more attractive.

Many systems have been designed and build, so there is a lot of information in this area. Some detailed information can be found in:

- [2], pages 1-23 to 1-32
- [6], pages 99 to 102, 277 to 282, 358 and 359.
- [10] and [11].

3.4 Portable Power

Portable power applications are specially focused in compact and small fuel cells. Using this kind of devices has the great advantage of having a long-lasting, portable power source that enhance the time that a device can run without recharging. Portable fuel cells replace rechargeable batteries in many applications because they are light and practical. The most important applications for portable fuel cells are:

- Laptops
- Power tools
- Cellular phones
- Video cameras
- Military equipment
- Battery chargers
- Computers
- Unattended sensors
- Unmanned aerial and underwater vehicles

Once again, the most critical issue of these devices is the fuel storage. Because of the low density of hydrogen, its storage container would be too much big for a portable application. A viable solution is to use methanol or ethanol, instead of hydrogen, as a fuel. Both fuels can feed the fuel cell directly or can be reformed before being used.

For the time being, the only type of fuel cell that is suitable for these applications is the DMFC.

4. Fuel Cell Modeling and Characterization

The previous sections have exposed an overall idea of what are the fuel cells, their classification and their different applications. This section is an accurate description of fuel cells and all the different processes that take place within them. Once the fuel cell is properly described, it might be modeled in order to optimize its performance and reach the maximum efficiency.

4.1 Fuel Cell Electrochemistry

The following section will describe the basic electrochemistry of fuel cells, explaining the reaction speed, the creation of products and the energy losses that take place during the reaction. Thus, the fuel cell net output voltage will be accurately predicted, and so will the electrode kinetics.

As it has been described in section 1.2, the electrochemical reaction is actually electron transference between the electrode and the chemical species involving a Gibbs free energy change. This reaction takes place at the interface between the electrode and the electrolyte. Every charge must overcome an activation energy barrier in order to move through the electrolyte and the electrode.

The rate of the electrochemical reactions is measured by the fuel cell current. The transferring charge rate is:

$$i = \frac{dQ}{dt} \tag{4-1}$$

Where Q is the charge. Each electrochemical reaction can be written as the transference of n electrons per unit of time:

$$i = nF\frac{dN}{dt} \tag{4-2}$$

The term $\frac{dN}{dt}$ is the rate of the electrochemical reaction measured in mol/s and F is the Faraday constant, which value is 96487C/mol. Integrating equation (4-2) gives

$$\int_0^t i dt = Q = nFN \tag{4-3}$$

The electrochemical reaction can be represented as

$$Ox + e^- \leftrightarrow Re \tag{4-4}$$

Depending on the electrode potential, the reaction will form more Re or more Ox. Both forward and backward reactions take place simultaneously. The flux for the former reaction is

$$j_f = k_f C_{Ox} \tag{4-5}$$

Where k_f is the forward reaction rate coefficient and C_{ox} is the surface concentration of the reactant species. The backward reaction of the flux is described similarly:

$$j_b = k_b C_{Rd} \tag{4-6}$$

The difference between the electrons released and consumed equals the net current generated

$$i = nF(k_f C_{Ox} - k_b C_{Rd}) \tag{4-7}$$

At equilibrium, the net current should equal zero. The reaction rate at equilibrium is called the current exchange density.

4.1.1 Electrode Kinetics

Every reaction needs to overcome an energy barrier before proceeding. This energy barrier corresponds to the Gibbs free energy change between the reactant and the product, which varies depending on the distance from the interface:

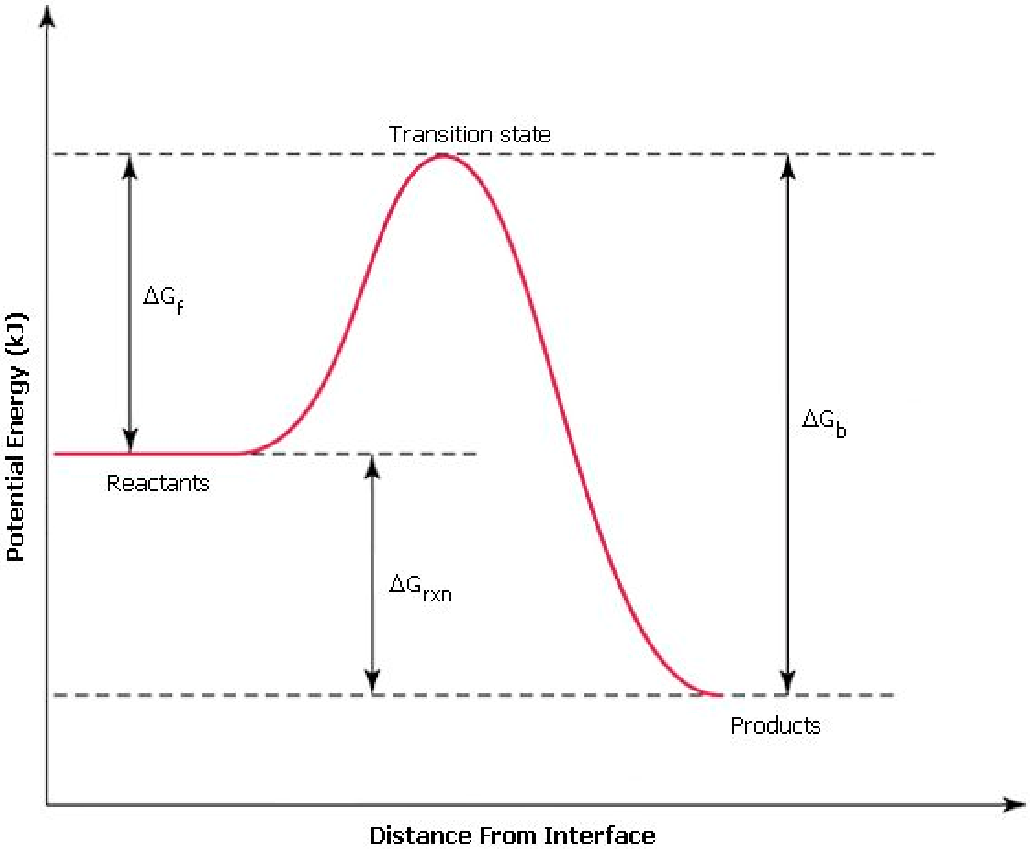

Figure 5 – Gibbs free energy change compared with distance from the interface

The heterogeneous rate coefficient, k, can be calculated for an electrochemical reaction that is function of the Gibbs free energy:

$$k = \frac{k_B T}{h} e^{\left(\frac{-\Delta G}{RT}\right)} \tag{4-8}$$

Where k_B is the Boltzmann's constant (1,38049 x 10^{-23} J/K) and *h* is Plank's constant (6,621 x 10^{-34} Js). The Gibbs free energy can be considered to consist of both chemical and electrical terms because it occurs in the presence of an electrical field. For a reduction and an oxidation reaction:

$$\Delta G = \Delta G_{AC} + \alpha_{Rd} FE \tag{4-9}$$

$$\Delta G = \Delta G_{AC} - \alpha_{Ox} FE \tag{4-10}$$

Where ΔG_{AC} is the activation complex of the Gibbs free energy, α is the transfer coefficient, F is the Faraday's constant and E is the potential. The value of α depends upon the activation barrier and is typically between 0 and 1. However, for must electrochemical reactions is specifically between 0,2 and 0,5. α_{Rd} and α_{ox} are related as:

$$\alpha_{Rd} - \alpha_{Ox} = \frac{n}{\nu} \tag{4-11}$$

Where n is the number of electrons transferred and ν is the number of times the stoichiometric step must take place for the reaction to occur. The forward and backward oxidation reaction rate coefficients are:

$$k_f = k_{0,f} e^{\left(\frac{-\alpha_{Rd} FE}{RT}\right)} \tag{4-12}$$

$$k_b = k_{0,b} e^{\left(\frac{-\alpha_{Ox} FE}{RT}\right)} \tag{4-13}$$

Introducing these equations into equation (4-7), the net current is:

$$i = nF\left(k_{0,f} C_{Ox} e^{\left(\frac{-\alpha_{Rd} FE}{RT}\right)} - k_{0,b} C_{Rd} e^{\left(\frac{-\alpha_{Ox} FE}{RT}\right)}\right) \tag{4-14}$$

The net current at equilibrium is equal to zero because the reaction proceeds in both directions simultaneously. The reaction rate at equilibrium is called the current exchange density and it is equal to:

$$i_0 = nFk_{0,f}C_{Ox}e^{\left(\frac{-\alpha_{Rd} F E_r}{RT}\right)} = nFk_{0,b}C_{Rd}e^{\left(\frac{-\alpha_{Ox} F E_r}{RT}\right)} \tag{4-15}$$

The current density and the potential are related in the Butler-Volmer equation:

$$i = i_0\left(e^{\left(\frac{-\alpha_{Rd} F(E-E_r)}{RT}\right)} - e^{\left(\frac{-\alpha_{Ox} F(E-E_x)}{RT}\right)} \right) \tag{4-16}$$

This equation is valid for both anode and cathode reactions in a fuel cell. It means essentially that the more current is needed, the more voltage is lost. The exchange current density is a function of temperature, catalyst loading and catalyst specific surface area. The effective exchange current density at any temperature and pressure is given by the following equation:

$$i_0 = i_0^{ref} a_c L_c \left(\frac{P_r}{P_r^{ref}}\right)^{\gamma} e^{\left(-\frac{E_c}{RT}\left[1-\frac{T}{T_{ref}}\right]\right)} \tag{4-17}$$

Where i_o^{ref} is the reference exchange current density per unit catalyst surface area (A/cm^2), a_c is the catalyst specific area, L_c is the catalyst loading, P_r is the reactant partial pressure (kPa), P_r^{ref} is the reference pressure (kPa), γ is the pressure coefficient, E_c is the activation energy, R is the gas constant, T is the temperature and T_{ref} is the reference temperature.

The exchange current density measures the readiness of the electrode to proceed with the electrochemical reaction.

4.1.2 Voltage Losses

The most important fuel cell voltage losses have been explained in section 1.2. The single cell voltage strongly depends on operating conditions like temperature, applied load and fuel/oxidant flow rates. When the current is drawn, electrical energy can be obtained from the fuel cell, but then the cell voltage drops because of irreversible losses. The fuel cell voltage can be defined as:

$$V(i) = V_{rev} - V_{irrev} \tag{4-18}$$

Where V_{rev} is the theoretical potential and V_{irrev} is the deviation of the cell potential from V_{rev}. Thus, the actual open circuit voltage of a fuel cell is lower than the theoretical voltage due to different types of losses, as seen on section 1.2. Consequently, equation (4-18) can be rewritten as:

$$V(i) = V_{rev} - v_{act}^{anode} - v_{act}^{cathode} - v_{ohmic} - v_{conc}^{anode} - v_{conc}^{cathode} \tag{4-19}$$

Where v_{act}, v_{ohmic}, v_{conc} are activation, ohmic and mass concentration losses, respectively. Both activation and concentration losses occur at both the anode and cathode. Substituting the equations for activation, ohmic and concentration polarization into equation (4-19) it gives:

$$E = E_r - \frac{RT}{\alpha_c F}\ln\left(\frac{i}{i_{0,c}}\right) - \frac{RT}{\alpha_a F}\ln\left(\frac{i}{i_{0,a}}\right) - \frac{RT}{nF}\ln\left(\frac{i_{L,c}}{i_{L,c} - i}\right) - \frac{RT}{nF}\ln\left(\frac{i_{L,a}}{i_{L,a} - i}\right) - iR_i \tag{4-20}$$

Or:

$$E = E_r - \frac{RT}{\alpha F}\ln\left(\frac{i_{ext} + i_{loss}}{i_0}\right) - \frac{RT}{nF}\ln\left(\frac{i_L}{i_L - i}\right) - iR_i \tag{4-21}$$

This equation shows the relationship between the fuel cell potential and current density, as illustrated in the following picture:

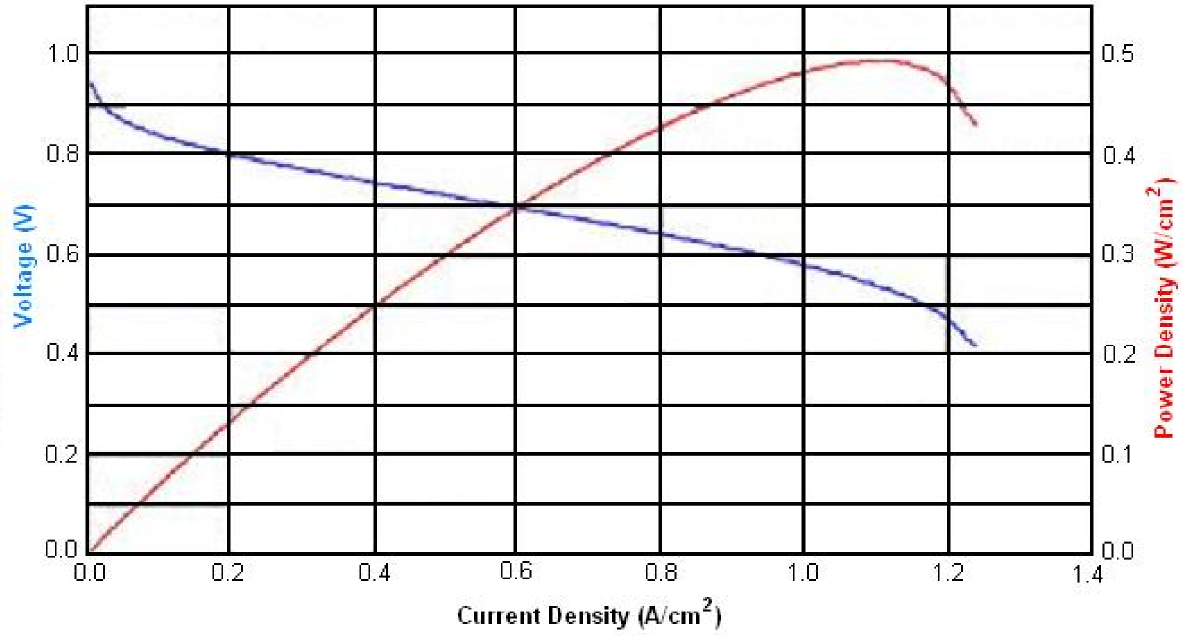

Figure 6 – Polarization curve for a hydrogen PEM fuel cell

Activation polarization is the voltage overpotential required to overcome the activation energy of the electrochemical reaction on the catalytic surface. At low current densities, this type of polarization dominates losses and measures the catalyst effectiveness at a given temperature. This is a complex interface problem since the gaseous fuel, the solid metal catalyst and the electrolyte must make contact. Although the catalyst reduces the height of the activation barrier, a loss in voltage remains due to the slow oxygen reaction.

As it can be seen in Figure 1, the total activation polarization overpotential is 0,1 to 0,2V, which reduces the maximum potential to less than 1V. The activation overpotential can be expressed as:

$$\Delta V_{act} = E_r - E = \frac{RT}{\alpha F}\ln\left(\frac{i}{i_0}\right) \tag{4-22}$$

The activation losses can be expressed simply as the Tafel equation:

$$\Delta V_{act} = a + b\ln(i) \tag{4-23}$$

Where $a = -\frac{RT}{\alpha F}\ln(i_0)$ and $b = -\frac{RT}{\alpha F}$.

The ohmic and concentration polarization regions are discussed in detail in section 4.2 and 4.3 respectively.

4.1.3 Internal Currents and Crossover Currents

The electrolyte, as seen in section 1.4, is a substance that is not electrically conductive and is usually impermeable to gases. However, some hydrogen and electrons diffuse through the electrolyte. Each hydrogen molecule that diffuses through the electrolyte results in fewer electrons that travel to the external circuit.

These losses are normally minor during fuel cell operation, but can sometimes be significant when the fuel cell operates at low current densities or when it is at open circuit voltage. Thus, it can be written that:

$$i = i_{ext} + i_{loss} \tag{4-24}$$

i.e., the total electrical current is the sum of useful current and the lost current. Using the total current density in equation (4-22), then:

$$E = E_r - \frac{RT}{\alpha F}\ln\left(\frac{i_{ext} + i_{loss}}{i_0}\right) \tag{4-25}$$

The second term represents the activation potential, also shown in equations (4-20) and (4-21). When hydrogen diffuses through the electrolyte, it forms water and reduces the cell potential. This phenomenon, hydrogen crossover, depends on electrolyte properties, like permeability or thickness.

4.1.4 Improving Kinetic Performance

The fuel cell kinetics can be improved using different methods:

- Increase the temperature
- Increase the reactant concentration
- Decrease the activation barrier
- Increase the number of reaction sites

More detailed information can be found in [1].

4.2 Fuel Cell Charge Transport

This section will explain the fuel cell electronic and ionic charge transport and voltage losses due to transport resistance. Electronic charge transport describes de movement of charges from the electrode (where they are produced) to the load (where they are consumed). The main types of charged particles are ions and electrons.

Ionic transport is more difficult to predict than fuel cell electron model. The ions transference occurs when O^{2-}, OH^-, CO_3^{2-} or H^+ ions travel trough the electrolyte, as it has been explained in section 1.4.

Resistance to charge transport leads to voltage loss for fuel cells (ohmic loss). Ohmic losses can be minimized by making electrolytes as thin as possible and employing high conductivity materials which are connected well to each other.

4.2.1 Voltage Loss Due to Charge Transport

All conductors have the inherent feature of being resistant to charge flow, known as ohmic polarization, producing a loss in cell voltage. The cell components that have electrical resistance are the electrolyte, the catalyst layer, the gas diffusion layer, bipolar plates, interface contacts and terminal connections.

Ohmic losses are the reduction in fuel cell voltage and include de electronic (R_{elec}) and ionic (R_{ionic}) resistances. Ohmic polarization can be written as:

$$v_{ohmic} = IR_{ohmic} = I\left(R_{elec} + R_{ionic}\right) \tag{4-26}$$

R_{ionic} dominates the reaction because ionic transport is more difficult than electronic charge transport. The term R_{iocinc} represents the ionic resistance of the electrolyte and the term R_{elec} includes the electrical resistance of bipolar plates, cell interconnects and contacts.

In contrast of the resistance, the conductivity of a material is the ability to support the flow of charge trough itself. The electrical resistance of the fuel cell components is expressed as conductance (σ) which is the reciprocal of resistance:

$$\sigma = \frac{1}{\rho} \tag{4-27}$$

Where σ is the electrical conductivity (Ω^{-1} cm^{-1}) and ρ is the resistivity. Resistance can be expressed as:

$$R = \frac{L_{cond}}{\sigma A_{cond}} = \frac{L_{cond}\,\rho}{A_{cond}} \tag{4-28}$$

Where L_{cond} is the length (cm) of the conductor and A_{cond} is its cross-sectional area (cm^2). The current density can be defined as:

$$i = \frac{I}{A_{cell}} \tag{4-29}$$

Or

$$i = n_{carriers}\, q\, v_{drift} = \sigma\,\xi \tag{4-30}$$

Where A_{cell} is the active area of the fuel cell, $n_{carriers}$ is the number of charge carriers (carriers/cm^3), q is the charge on each carrier ($1{,}602 * 10^{-19}$ C), v_{drift} is the average drift velocity (cm/s) where the charge carriers move and ξ is the electric field. The conductivity for most materials is:

$$\sigma = nq\frac{v}{\xi} = nqu_i \tag{4-31}$$

The term u_i is the mobility (cm^2/Vs). A more specific equation for material conductivity is:

$$\sigma_i = F\sum |z_i|\, c_i\, u_i \tag{4-32}$$

Where c_i is the number of moles of charge carriers per unit volume and z_i is the charge number (valence electrons) for the carrier. Changing the cross-sectional area, the fuel cell resistance changes and its performance is improved. Resistances are usually compared on a per-unit basis using current density, so ohmic losses can be calculated as:

$$v_{ohmic} = i\left(ASR_{ohmic}\right) = i\left(A_{cell}\, R_{ohmic}\right) \tag{4-33}$$

Where ASR_{ohmic} is area specific resistance of the fuel cell. This parameter allows fuel cells of different sizes to be compared.

When the cell is designed properly, the ohmic polarization is typically dominated by electrolyte conductivity, which is primarily a function temperature and, in the case of PEMFC, water content.

Ohmic losses can be reduced trough advanced conductive materials, thinner electrolytes or an optimal temperature/water balance.

One of the most effective methods of reducing ohmic loss is to use a better ionic conductor for the electrolyte layer, or a thinner electrolyte layer since the electrolyte component of a fuel cell dominates ohmic losses. Since the ohmic overpotential for the fuel cell is mainly due to ionic resistance in the electrolyte, this can be expressed as:

$$v_{ohmic} = IR_{ohmic} = iA_{cell}\left(\frac{\delta_{thick}}{\sigma A_{cell}}\right) = \frac{i\delta_{thick}}{\sigma} \tag{4-34}$$

Where A_{cell} is the active area of the fuel cell and δ_{thick} is the thickness of the electrolyte. This equation shows that the ohmic potential can be reduced by using a thinner electrolyte layer and using a higher ionic conductivity electrolyte.

4.2.2 Microscopic Conductivity of Metals

The charge transfer of electrons depends on the electron conductivity of metals used in a fuel cell. Thus, this is a critical property to consider when choosing which metal is used in bipolar plates and current collectors. The equation of conductivity has been written before in expression (4-32). The term u_i is the mobility of free electrons in a metal conductor limited by some parameters, such as impurities, defects, lattice vibrations and photon scattering. The mobility equation is:

$$u = \frac{q\tau}{m_e} \tag{4-35}$$

Where τ is the time between collisions, also known as *relaxation* and m_e is the mass of the electron ($9{,}11 * 10^{-31}$ kg). Combining equations (4-32) and (4-35) it gives:

$$\sigma = \frac{|z_e| c_e q\tau}{m_e} \tag{4-36}$$

This equation means that the carrier concentration in a metal can be calculated from the density of free electrons.

4.2.3 Ionic Conductivity of Aqueous Electrolytes

There are different types of fuel cells that use aqueous electrolytes:

- MCFCs use molten K_2CO_3 or Li_2CO_3
- PAFCs use aqueous or concentrated H_3PO_4
- AFCs use an aqueous KOH electrolyte

As it has been explained in section 2, the electrolyte in many cases is held in a matrix material for support, preventing also crossover of reactant gases and creating a short distance between electrodes (usually 0,1–1mm).

The ions moving through the liquid find two kinds of opposing forces: an electrical force (F_ξ) and a frictional force (F_D). Thus, the ions quickly reach a terminal speed. The electric field force is given by:

$$F_\xi = |z_i| q \frac{dV}{dx} \tag{4-37}$$

Where $|z_i|$ is the charge number of the ion. On the other hand, the frictional force is:

$$F_D = 6\pi \mu r_{ion} v_{ion} \tag{4-38}$$

Where r_{ion} is the radius of the ion, μ is the viscosity of the liquid and v_{ion} is the ion velocity. The mobility can be predicted equaling these forces each other:

$$u_i = v_{ion} \frac{dV}{dx} = \frac{|z_i| q}{6\pi \mu r_{ion}} \tag{4-39}$$

This equation states that the mobility is a function of ion size and liquid viscosity, and gives an estimate for dilute aqueous solutions. Fore more concentrated ionic solutions, the conductivity is more difficult to calculate due to the multitude of electrical interactions that occurs. The conductivity can be written as:

$$\sigma_i = F \sum |z_i| c_i u_i = F \sum |z_i| c_i \left(\frac{|z_i| q}{6\pi \mu r_{ion}} \right) \tag{4-40}$$

This equation shows that the conductivity reflects the charge and mobility of all ions present in the solution, and their concentrations.

4.2.4 Ionic Conductivity of Polymer Electrolytes

A good conductor polymer is a polymer that has a fixed number of charge sites and open space. Charged sites have the opposite charge of moving ions and provide a temporary resisting place for the ion. The more charged sites the higher ionic conductivity, but if there are an excessive number of charged side chains, the stability of the polymer would be degraded.

Ions have a good mobility in polymers due to polymers usually have a certain amount of free volume. Ions are also transported through the polymer membrane by hitching onto water molecules that move through the membrane. Nafion is a high conductivity polymer and is currently the most popular membrane used in PEMFCs and DMFCs. Nafion has a similar structure to Teflon, but includes sulfonic acid groups ($SO_3^- H^+$) that provide sites for proton transport.

Nafion has to be fully hydrated with water in order to have high conductivity, becoming as conductor as liquid electrolytes. To hydrate Nafion is not difficult because it can hold significant amounts of water. Since conductivity and hydration of the membrane are correlated, determining the water content correlates with determining conductivity of the membrane. The membrane water content at the electrode/membrane interface is determined by the activity of water vapor assuming equilibrium. The water vapor activity can be defined by:

$$\sigma_{water\_vap} = \frac{p_w}{p_{sat}} \tag{4-41}$$

Where p_w is the partial pressure of water vapor in the system and p_{sat} is the saturation water vapor pressure for the system at temperature of operation.

The conductivity of a membrane depends on its structure and water content. The amount of water uptake in the membrane also depends upon the membrane properties and pretreatment. The following equation describes the relationship between water activity on the faces of the membrane and water content:

$$\lambda = 0{,}043 + 17{,}17\, a_{water\_vap} - 39{,}85 \left(a_{water\_vap}\right)^2 + 36 \left(a_{water\_vap}\right)^3 \tag{4-42}$$

Where a_{water_vap} varies between 0 and 1. The main reason for the variation of water content in Nafion is because protons normally have one or more water molecules associated with them. This phenomenon is known as electroosmotic drag (n_{drag}), which is the number of water molecules accompanying the movement of each proton:

$$n_{drag} = n_{drag}^{Sat} \frac{\lambda}{22} \tag{4-43}$$

The electroosmotic drag (n_{drag}^{Sat}) for a fully hydrated membrane is in the range from 2,3 to 2,7, in equilibrium with liquid water at 30ºC to 50ºC. The water content (λ) is in the range from 0 to 22 water molecules per sulfonate group. The water drag flux from the anode to the cathode with a net current flux is:

$$J_{H_2O,drag} = 2\, n_{drag} \frac{i}{2F} \tag{4-44}$$

Where $J_{H2O,drag}$ is the molar flux of water due to the electroosmotic drag (mol/scm^2). The electroosmotic drag moves water from tha anode to the cathode but some water travels back through the membrane once the cathode has been reached. This is called back diffusion and it usually happens because there is more water in the cathode than in the anode:

$$J_{H_2O,\,bdiff} = \frac{\rho_{dry}}{M_n} D_\lambda \frac{d\lambda}{dz} \tag{4-45}$$

Where ρ_{dry} is the dry density of Nafion, M_n is the Nafion equivalent weight (kg/mol), D_λ is the water diffusivity and z is the direction through the membrane thickness. The net water flux in the membrane is a combination of the electroosmotic drag and back diffusion:

$$J_{H_2O,bdiff} = 2n_{drag}^{Sat} \frac{i}{2F} \frac{\lambda}{22} - \frac{\rho_{dry}}{M_n} D_\lambda(\lambda) \frac{d\lambda}{dz} \tag{4-46}$$

Water uptake results in the membrane swelling and changes its dimensions and conductivity, which is a significant factor for a fuel cell design. When the water profile in the membrane has been determined, the membrane conductivity, resistance and potential drop across it can be calculated. The ionic conductivity (S/cm) can be correlated with water content and temperature:

$$\sigma = \left(0{,}005139\,\lambda - 0{,}00326\right) e^{\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right]} \tag{4-47}$$

The total resistance of a membrane (R_m) can be found by integrating the local resistance over the membrane thickness:

$$R_m = \int_0^{t_m} \frac{dz}{\sigma\left[\lambda(z)\right]} \tag{4-48}$$

Where t_m is the membrane thickness and λ is the water content.

4.2.5 Ionic Conductivity of Ceramic Electrolytes

As it has been exposed in section 2.7, some high temperature fuel cells use yttria stabilized zirconia (YSZ) as a ceramic electrolyte. Using this material introduces oxygen vacancies, which enables YSZ to have high ionic conductivity.

Vacancies are considered charge carriers because of the need for ions to move within the ceramic. Increasing the yttria content results in increased oxygen vacancies, but doping an amount of 8%

molar yttria concentration for YSZ at maximum. Mobility is directly related to the diffusion coefficient (D) by Einstein's equation:

$$u_i = \frac{z_i D}{k T} \tag{4-49}$$

Where k is the Boltzmann constant. Substituting this equation into equation (4-32) it gives:

$$\sigma_i = \frac{|z_i|^2 c_i D}{k T} \tag{4-50}$$

For thermally-generated ionic defects, the concentration and diffusion are activated processes:

$$c \propto e^{\left(-\frac{q_1}{k T}\right)} \qquad D \propto e^{\left(-\frac{q_2}{k T}\right)} \tag{4-51}$$

Conductivity also has the same form:

$$\sigma = \sigma_0 \, e^{\left(-\frac{E}{k T}\right)} \tag{4-52}$$

Where $E=q_1+q_2$ is the activation energy for conduction.

4.3 Fuel Cell Mass Transport

The study of mass transfer of uncharged species is important because the fuel cell performance is directly related with it. In fact, the reactant and product concentrations within the catalyst layer determine the fuel cell performance. Optimizing the mass transport in the fuel cell electrodes and flow structures leads to the minimization of concentration losses. In this section, the mass transport will be studied in fuel cell electrodes and flow structures.

The mass transport in fuel cell flow structures is dominated by convection and fluid dynamic laws since the flow channels are macroscale. Conversely, the mass transport of fuel cell electrodes occurs on a microscale and is dominated by diffusion.

The convective forces that dominate mass transfer in the flow channels are primarily imposed by the fuel, while the oxidant flow rates are imposed by the user. High flow rates may ensure a good distribution of reactants but may cause some problems such as high pressures or fuel cell membrane rupture.

The diffusive forces that occur in the electrode/catalyst layer are shielded from the convective forces in the flow channels. The speed of the reactants tends to slow down near the gas diffusion/catalyst layers where the diffusion regime of the reactants begins.

4.3.1 Convective mass Transport from Flow Channels to Electrode

As shown in the next picture, the reactant is supplied to the flow channel at a concentration C_0, and is transported from the flow channel to the electrode surface at a concentration C_s through convection.

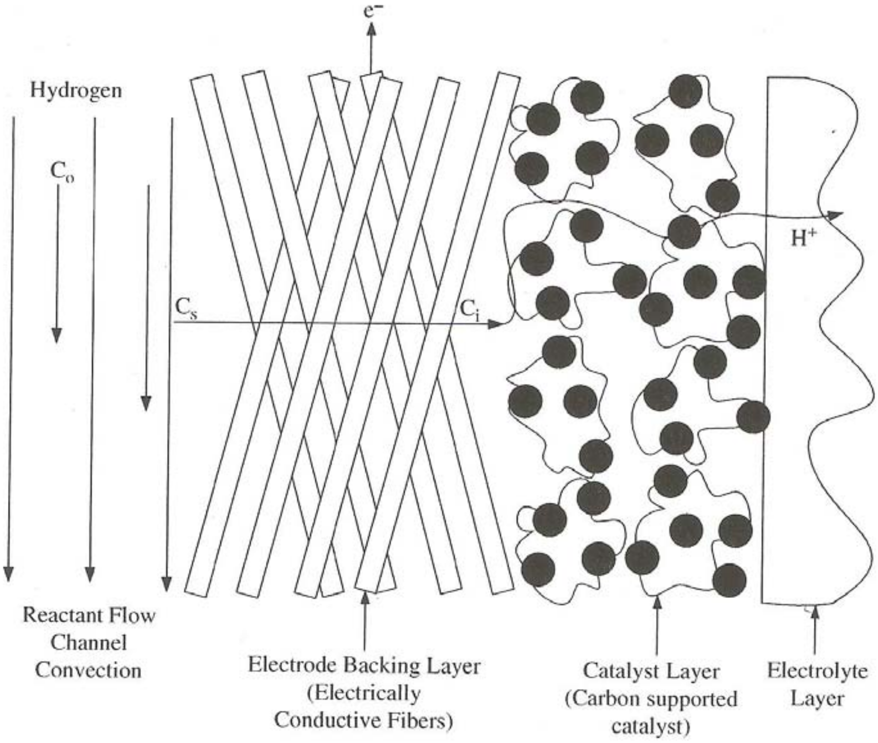

Figure 7 – Convective and diffusive mass transport within a fuel cell

The rate of mass transfer is:

$$\dot{m} = A_{elec} h_m (C_0 - C_s) \tag{4-53}$$

Where A_{elec} is the electrode surface area and h_m is the mass transfer coefficient. The value of h_m is dependent upon the channel geometry, the physical properties of species i and j, and the wall conditions. The term h_m can be found from the Sherwood number:

$$h_m = Sh \frac{D_{i,j}}{D_h} \tag{4-54}$$

Where Sh is the Sherwood number, D_h is the hydraulic diameter and D_{ij} is the binary diffusion coefficient for species i and j. The Sherwood number depends upon channel geometry:

$$Sh = \frac{h_H D_h}{k} \tag{4-55}$$

Where Sh=5,39 for uniform surface mass flux and Sh=4,86 for uniform surface concentration.

The binary diffusion coefficients can be found in tables at T_{ref} and can be calculated using the following expression:

$$D_{i,j}(T) = D_{i,j}(T_{ref}) * \left(\frac{T}{T_{ref}} \right)^{\frac{3}{2}} \tag{4-56}$$

If the fuel cell working temperature (T) is different from T_{ref}.

4.3.2 Diffusive Mass Transport in Fuel Cell Electrodes

As shown previously, the diffusive flow occurs at the electrode backing and catalyst layer. The electrochemical reaction in the catalyst layer can lead to reactant reduction, which can affect fuel cell performance. To determine the concentration loss, first must be found the amount the catalyst layer reactant and product concentrations differ from the bulk values.

The rate of mass transfer by diffusion of the reactants to the catalyst layer ($\dot{m}$) can be calculated as:

$$\dot{m} = -D \frac{dC}{dx} \tag{4-57}$$

Where D is the bulk diffusion coefficient and C is the reactants concentration. Thus, the diffusive transport through the electrode backing layer at steady-state is:

$$\dot{m} = A_{elec} D^{eff} \frac{C_s - C_i}{\delta} \tag{4-58}$$

Where C_i is the reactant concentration at the backing layer/catalyst interface, δ is the electrode-backing layer thickness and D^{eff} is the effective diffusion coefficient for the porous electrode backing layer. Assuming uniform pore size, the backing layer is free form flooding of water or liquid electrolyte, and D^{eff} can be defined as:

$$D^{eff} = D\phi^{3/2} \tag{4-59}$$

Where ϕ is the electrode porosity. Combining equations (4-53) and (4-55), the total resistance to the transport of the reactant to the reaction sites is found:

$$\dot{m} = \frac{C_0 - C_i}{\left(\frac{1}{h_m A_{elec}} + \frac{\delta}{D^{eff} A_{elec}} \right)} \tag{4-60}$$

The denominator terms represent the convective and diffusive mass transfer resistances, respectively. When the fuel cell is producing electricity, the reactant and product concentrations are constant. Nevertheless, as soon as the fuel cell starts producing current, the electrochemical reaction leads to the consumption of reactants at the catalyst layer. The next equation describes the flux of reactants and products matching the consumption rate of reactants and products at the catalyst layer:

$$i = \frac{nF\dot{m}}{A_{elec}} \tag{4-61}$$

Substituting equation (4-60) into (4-61) it gives:

$$i = -nF\,\frac{C_0 - C_i}{\left(\frac{1}{h_m} + \frac{\delta}{D^{eff}}\right)} \tag{4-62}$$

The reactant concentration in the backing layer/catalyst interface is less than the reactant concentration supplied to the flow channels, which depends upon i, δ and D^{eff}. The higher the current density, the worse the concentration losses will be. These losses can be improved by reducing the diffusion layer thickness or increasing the effective diffusivity.

The reactant concentration can drop to zero if the current density is high enough. When this phenomenon happens, this current density value is called limiting current density (i_L) and can be expressed as:

$$i_L = -nF\,\frac{C_0}{\left(\frac{1}{h_m} + \frac{\delta}{D^{eff}}\right)} \tag{4-63}$$

The limiting current density can be increased by ensuring that C_0 is high (good flow structures to evenly distribute the reactants must be designed), and ensuring that D^{eff} is large and δ is small. The typical limiting current density is 1 to 10 A/cm^2. The fuel cell performance is affected by the reactant concentration through the Nernst equation:

$$E = E_r - \frac{RT}{nF}\ln\left(\frac{\prod \alpha_{prod}^{v_i}}{\prod \alpha_{react}^{v_i}}\right) \tag{4-64}$$

The incremental voltage loss due to reactant consumption in the catalyst layer is calculated in the following equations:

$$v_{conc} = E_{r,Nernst} - E_{Nernst} \tag{4-65}$$

$$v_{conc} = \left(E_r - \frac{RT}{nF} \ln \frac{1}{C_0} \right) - \left(E_r - \frac{RT}{nF} \ln \frac{1}{C_i} \right) \tag{4-66}$$

$$v_{conc} = \frac{RT}{nF} \ln \frac{C_0}{C_i} \tag{4-67}$$

The term $E_{r,Nernst}$ used in equation (4-65) represents the Nernst voltage using C_0 values and the term E_{Nernst} is the Nernst voltage using C_i values. Combining equations (4-62) and (4-63):

$$\frac{i}{i_L} = 1 - \frac{C_i}{C_0} \tag{4-68}$$

This equation also can be written as:

$$\frac{C_0}{C_i} = \frac{i_L}{i_L - i} \tag{4-69}$$

Combining equations (4-67) and (4-69) yields:

$$v_{conc} = \frac{RT}{nF} \ln \left(\frac{i_L}{i_L - i} \right) \tag{4-70}$$

This is the equation for concentration polarization loss. Obviously, it is only valid for $i < i_L$. Concentration also affects fuel cell performance through reaction kinetics. The reaction kinetics are dependent upon the reactant and product concentrations at the reaction sites. As explained in section 4.1.1, the Butler-Volmer equation is:

$$i = i_0 \left(\frac{C_i}{C_0} e^{\left(\frac{-\alpha nF(E-E_r)}{RT} \right)} - \frac{C_j}{C_n} e^{\left(\frac{-(1-\alpha)nF(E-E_r)}{RT} \right)} \right) \tag{4-71}$$

Where C_i and C_j are arbitrary concentrations and i_0 is measured as the reference reactant and product concentrations values C_0 and C_n. In the high current-density region the expression becomes:

$$i = i_0 \frac{C_i}{C_0} e^{\left(\frac{-\alpha nF(E-E_r)}{RT}\right)} \tag{4-72}$$

In terms of activation overvoltage:

$$v_{conc} = \frac{RT}{\alpha nF} \frac{C_0}{C_i} \tag{4-73}$$

Combining this equation with (4-69) results:

$$v_{conc} = \frac{RT}{\alpha nF} \frac{i_L}{i_L - i} \tag{4-74}$$

This equation describes the fuel cell concentration loss (or mass transport loss).

4.3.3 Convective Mass Transport in Flow Structures

Fuel cell flow structures are designed to distribute reactants equally across the fuel cell, and to keep mass transport losses to minimum. This section presents some equations for modeling the mass transport in the flow structures.

MASS TRANSPORT IN FLOW CHANNELS

In order to modeling the mass transport in flow channels, a control volume is used for reactant flow from the flow channel to the electrode layer:

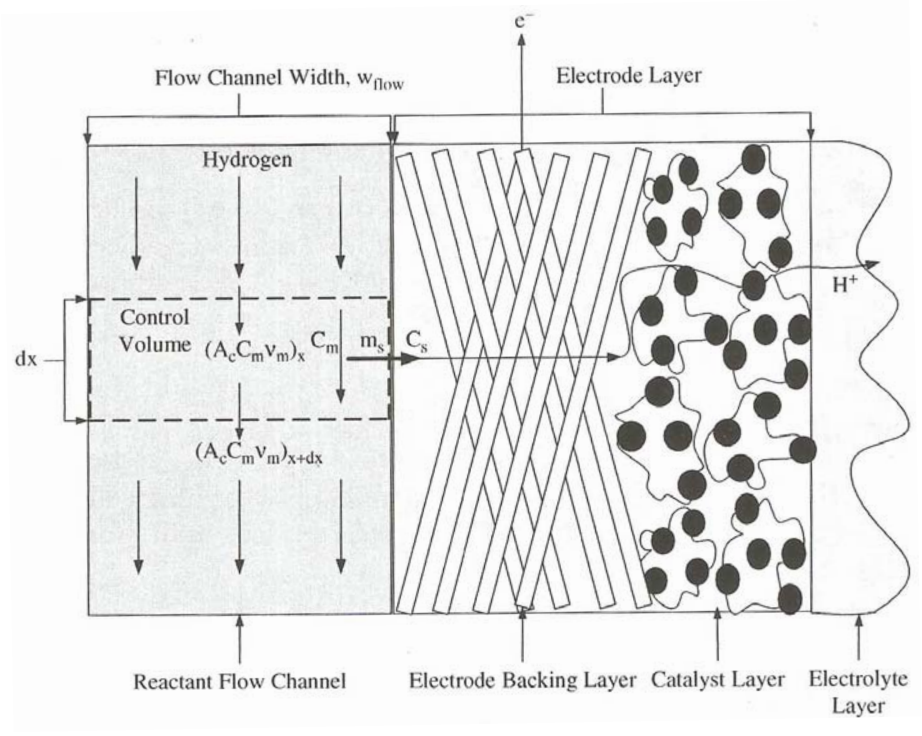

Figure 8 – Control volume for reactant flow in the flow channel

The following equation represents the rate of convective mass transfer at the electrode surface:

$$\dot{m}_s = h_m (C_m - C_s) \tag{4-75}$$

Where C_m is the mean concentration of the reactant in the flow channel, and C_s is the concentration at the electrode surface. The molar flow rate can be expressed as:

$$\frac{d}{dx}(A_c C_m v_m) = -\dot{m}_s\, w_{elec} \tag{4-76}$$

Where A_c is the channel cross-sectional area, v_m is the mean flow velocity in the flow channel and w_{elec} is the electrode surface width. The velocity and concentration are constant if assuming the flow to be steady:

$$\frac{d}{dx} C_m = \frac{-\dot{m}_s}{v_m w_{flow}} \tag{4-77}$$

If $i<0{,}5 \cdot i_L$, the current density can be assumed constant. Integrating equation (4-77) using Faraday's law ($\dot{m}_s = i/nF$) it gives:

$$C_m(x) = C_{m,in} - \frac{\left(\frac{i}{nF}\right)}{v_m w_{flow}} x \tag{4-78}$$

Where $C_{m,in}$ is the mean concentration at the flow channel inlet. On the other hand, if the current density is high ($i>0{,}5 i_L$) then the concentration at the electrode surface (C_s) is assumed to be constant:

$$\frac{d}{dx}(C_m - C_s) = \frac{-h_m}{v_m w_{flow}} (C_m - C_s) \tag{4-79}$$

Integrating this equation, yields:

$$C_m - C_s = (C_m - C_s)_{in}\, e^{\frac{-h_m}{v_m w_{flow}} x} \tag{4-80}$$

A simple expression can be found if the entire flow channel is assumed to be the control volume:

$$\dot{m}_s = v_m w_{flow} w_{elec} \left(\Delta C_{in} - \Delta C_{out} \right) \quad (4\text{-}81)$$

If C_s is constant:

$$\dot{m}_s = A h_m \Delta C_{lm} \quad (4\text{-}82)$$

Where ΔC_{lm} is the logarithmic mean concentration. The local current density corresponding to the rate of mass transfer is:

$$i(x) = nFh_m (C_m - C_s) e^{-\frac{h_m}{v_m w_{flow}} x} \quad (4\text{-}83)$$

Finally, the current density averaged over the electrode surface is:

$$\bar{i} = nFh_m \Delta C_{lm} \quad (4\text{-}84)$$

PRESSURE DROP IN FLOW CHANNELS

The flow fields are usually a number of parallel flow channels where the gas moves from one end to the other at a mean velocity. The fluid flow is driven by the pressure difference between the inlet and outlet. By increasing the pressure drop between the outlet and inlet, the velocity is increased. The flow through bipolar plate channels is typically laminar, and is proportional to the flow rate. The pressure drop can be approximated by:

$$\Delta P = f \frac{L_{chan}}{D_H} \rho \frac{\bar{v}^2}{2} + \sum K_L \rho \frac{\bar{v}^2}{2} \quad (4\text{-}85)$$

Where f is the friction factor, L_{chan} is the channel length (m), D_H is the hydraulic diameter (m), ρ is the fluid density (kg/m^3), $\bar{v}$ is the average velocity (m/s) and K_L is the local resistance. The hydraulic diameter is defined by:

$$D = \frac{4 A_c}{P_{cs}} \quad (4\text{-}86)$$

Where A_c is the cross-sectional area and P_{cs} is the perimeter. For a rectangular flow field, the hydraulic diameter can be written as:

$$D = \frac{2w_c d_c}{w_c + d_c} \tag{4-87}$$

Where w_c is the channel width and d_c is the depth. The channel length can be defined as:

$$L_{chan} = \frac{A_{cell}}{N_{ch}(w_c + w_L)} \tag{4-88}$$

Where A_{cell} is the cell active area, N_{ch} is the number of parallel channels and w_L is the space between channels (m). The friction factor is defined by:

$$f = \frac{56}{Re} \tag{4-89}$$

The velocity at the fuel cell entrance is:

$$v = \frac{Q_{stack}}{N_{cell} N_{ch} A_{ch}} \tag{4-90}$$

Where v is the velocity in the channel (m/s), Q_{stack} is the air flow rate at the stack entrance (m^3/s), N_{cell} is the number of cells in the stack, N_{ch} is the number of parallel channels in each cell and A_{ch} is the cross-sectional area of the channel. The total flow rate at the stack entrance in a PEMFC is:

$$Q_{stack} = \frac{I}{4F} \frac{S_{O_2}}{x_{O_2}} \frac{RT_{in}}{P_{in} - \phi P_{sat}} N_{cell} \tag{4-91}$$

Where I is the stack current, S_{O2} is the oxygen stoichiometric ratio, x_{O2} is the oxygen content in the air, T_{in} is the stack inlet temperature, P_{in} is the pressure at the stack inlet, ϕ is the relative humidity and P_{sat} is the saturation pressure at the given inlet temperature. By combining equations (4-88), (4-90) and (4-91), the velocity at the stack inlet is:

$$v = \frac{I}{4F} \frac{S_{O_2}}{x_{O_2}} \frac{RT_{in}}{P_{in} - \phi P_{sat}} \frac{(w_c + w_L) L_{chan}}{w_c d_c} \tag{4-92}$$

To approximate the pressure drop in the flow channels, the Reynolds number must be calculated first:

$$\mathrm{Re} = \frac{\rho \mathrm{v_m} \mathrm{D_{ch}}}{\mu} = \frac{\mathrm{v_m} \mathrm{D_{ch}}}{\upsilon} \tag{4-93}$$

For rectangular channels, D_{ch} must be de hydraulic diameter, as shown in equation (4-86). For PEMFC, the Reynolds number can be calculated by:

$$\mathrm{Re} = \frac{\rho \mathrm{v} \mathrm{D_H}}{\mu} = \frac{1}{\mu} \frac{\mathrm{i}}{2\mathrm{F}} \frac{\mathrm{S_{O_2}}}{\mathrm{x_{O_2}}} \frac{(\mathrm{w_c} + \mathrm{w_L})\mathrm{L_{chan}}}{\mathrm{w_c} + \mathrm{d_c}} \mathrm{M_{air}} + \mathrm{M_{H_2O}} \frac{\phi \mathrm{P_{sat(T_{in})}}}{\mathrm{P_{in}} - \phi \mathrm{P_{sat(T_{in})}}} \tag{4-94}$$

The flow rate at the stack outlet is usually different than the inlet. If it is assumed that the outlet flow is saturated with water vapor, for PEMFCs the flow rate is:

$$\mathrm{Q_{stack}} = \frac{\mathrm{I}}{4\mathrm{F}} \left(\frac{\mathrm{S_{O_2}}}{\mathrm{x_{O_2}}} - 1 \right) \frac{\mathrm{RT_{out}}}{\mathrm{P_{in}} - \Delta \mathrm{P} - \phi \mathrm{P_{sat}}} \mathrm{N_{cell}} \tag{4-95}$$

Where ΔP is the pressure drop in the stack. The variation in viscosity varies with temperature. For dilute gases, the temperature dependence of viscosity can be estimated using a simple power law:

$$\frac{\mu}{\mu_0} \approx \left(\frac{\mathrm{T}}{\mathrm{T_0}} \right)^{\mathrm{n}} \tag{4-96}$$

Usually, fuel cells gas streams are gas mixtures. The following expression provides a good estimate for the viscosity of a gas mixture:

$$\mu_{\mathrm{mix}} = \sum_{i=1}^{N} \frac{\mathrm{x_i} \mu_i}{\sum_{i=1}^{N} \mathrm{x_j} \Phi_{ij}} \tag{4-97}$$

Where Φ_{ij} is a dimensionless number obtained from:

$$\Phi_{ij} = \frac{1}{\sqrt{8}} \left(1 + \frac{\mathrm{M_i}}{\mathrm{M_j}} \right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{\mathrm{M_i}}{\mathrm{M_j}} \right)^{1/4} \right]^2 \tag{4-98}$$

Where N is the total number of species in the mixture, x_i and x_j are the mol fractions of species i and j, and M_i and M_j are the molecular weight (kg/mol) of species i and j. For porous flow fields, the pressure drop is determined by Darcy’s Law:

$$\Delta P = \mu \frac{Q_{cell}}{k\,A_c} L_{chan} \tag{4-99}$$

Where Q_{cell} is the geometric flow rate through the cell (m^3/s) and k is the permeability (m^2).

If the equations in this section are used, the results will differ from the actual values because some assumptions have been made [1].

4.4 Heat Transfer

Temperature and heat distribution are critical parameters when predicting temperature-dependent parameters as well as rates of reaction and species transport. Therefore, both variables must be determined accurately. Two different types of heat transfer take place in a fuel cell:

- Convective: it occurs between the solid surface and the gas streams.
- Conductive: it occurs in the solid and porous structures.

Heat transfer depends basically of the reactants, products and electricity generated. In this section, the basic heat transfer equations will be described in order to accurately modeling the fuel cell performance.

4.4.1 Fuel Cell Energy Balance

GENERAL ENERGY BALANCE PROCEDURE

The first step to design accurately a fuel cell system is to account the energy that flows into and out of each process unit in order to determine the overall energy requirements for the process. An energy balance usually determines the cell exit temperature knowing the reactant composition, the temperatures, H_2 and O_2 utilization, the power produced and the percent of heat loss.

The energy balance procedure begins with a flowchart, which must include the enough information in order to calculate the specific enthalpy of each stream component. The next figure shows a detailed flowchart:

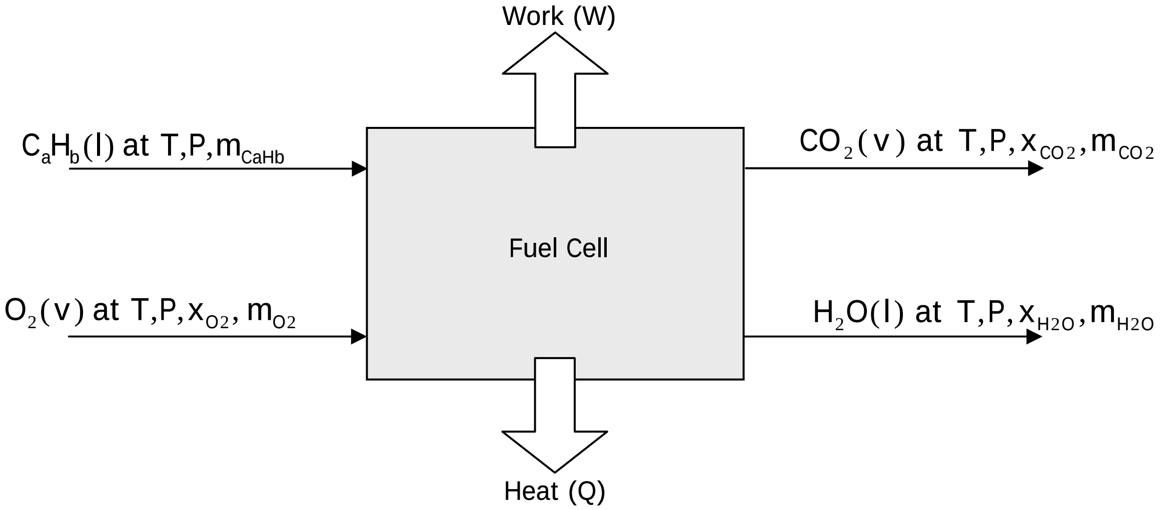

Figure 9 – Detailed flowchart of a fuel cell system

The reaction that takes places within the fuel cell can be expressed as:

$$C_aH_b + \left(a + \frac{b}{4}\right)O_2 \longrightarrow aCO_2 + \frac{b}{2}H_2O$$

As shown in figure 8, W is the work generated and Q is the heat leaving the fuel cell. The energy balance for this fuel cell is:

$$\frac{W}{m_{fuel}} + \frac{Q}{m_{fuel}} = h_{fuel} + \left(a + \frac{b}{4}\right)h_{O2} - ah_{CO2} - \frac{b}{2}h_{H2O} \qquad (4\text{-}100)$$

ENERGY BALANCE OF FUEL CELL STACK

The energy balance on the fuel cell stack is the sum of the energy inputs equals the sum the sum of the energy outputs:

$$\sum Q_{in} - \sum Q_{out} = W_{el} + Q_{dis} + Q_c \qquad (4\text{-}101)$$

Where Q_{in} is the enthalpy of the reactant gases in, Q_{out} is the enthalpy of the unused reactants and heat produced by the products, W_{el} is the electricity produced, Q_{dis} the heat dissipated to the surrounding and Q_c is the heat taken away from the stack by active cooling. The heat generation in the fuel cell is associated with voltage losses. Most of the heat is created in the catalyst layers, but there is also generation in the membrane and in the electrically conductive parts of the fuel cell due to ohmic losses.

A good estimate for the fuel cell stack balance can be obtained by equating the energy of the fuel reacted to the heat and electricity generated:

$$\frac{I}{nF}H_{HHV}\, n_{cell} = Q_{gen} + I\, V_{cell}\, n_{cell} \qquad (4\text{-}102)$$

When the entire water product leaves the stack as a liquid at room temperature, the heat generated in a fuel cell stack is:

$$Q_{gen} = (1{,}482 - V_{cell})I\, n_{cell} \qquad (4\text{-}103)$$

Where Q_{gen} is the heat generated from the stack (W), n_{cell} is the number of cells and V_{cell} is the cell voltage. Conversely, if all of the product water leaves the stack as vapor, the following equation can be used instead:

$$Q_{gen} = (1{,}254 - V_{cell}) I\, n_{cell} \quad (4\text{-}104)$$

Equations (4-103) and (4-104) are approximations and do not take into account the heat or enthalpy brought to the stack.

GENERAL ENERGY BALANCE FOR FUEL CELL

The fuel cell energy balance is the sum of all the energy inputs ant outputs:

$$\sum (h_i)_{in} = W_{el} + \sum (h_i)_{out} + Q \quad (4\text{-}105)$$

This equation represents a general balance of a fuel cell, as shown in Figure 8. The enthalpy (J/s) for each dry gas or mixture of dry gases is:

$$h = \dot{m} c_p T \quad (4\text{-}106)$$

Where c_p is the specific heat (J/g*K). If the gas has a high heating value, its enthalpy is:

$$h = \dot{m}\left(c_p T + h^0_{HHV}\right) \quad (4\text{-}107)$$

Where h^0_{HHV} is the higher heating value of that gas (J/g) at 0ºC. The enthalpy for vapor is:

$$h = \dot{m}_{H2O(g)}\, c_{p,H2O(g)} T + h^0_{fg} \quad (4\text{-}108)$$

The enthalpy of liquid water is:

$$h = \dot{m}_{H2O(l)}\, c_{p,H2O(l)} T \quad (4\text{-}109)$$

ENERGY BALANCE FOR FUEL CELL COMPONENTS AND GASES

The overall energy balance for the electrolyte and porous layers can be written as:

$$Q_s = Q_c + h_f A_f \left(T_e - T_{f,av}\right) + h_a A_a \left(T_e - T_{a,av}\right) \quad (4\text{-}110)$$

Where Q_c is the heat conduction in the solid structure, Q_s is the heat source to account for the electrochemical heat generation and h is the convective heat transfer coefficient.

- Energy balance in the gaseous phase: It is commonly assumed that gradients of temperature in the gas flows depend only on convection due to mass and heat transfer from the channel walls to the gases:

$$\sum_i n_i c_p \frac{\partial T_g}{\partial x} + \sum_i c_p \frac{\partial n_i}{\partial x}\left(T_g - T_s\right) + h_g B_g \frac{1}{a}\left(T_g - T_s\right) = 0 \tag{4-111}$$

Where B_g is the ratio between the gas-solid heat exchange area to the cell area, c_p is the specific heat at the constant pressure of species i, T_g is the solid temperature and h_g is the heat transfer coefficient calculated from:

$$h_g = Nu \frac{k}{D_h} \tag{4-112}$$

The Nusselt number (Nu) depends upon the channel geometry, the Reynolds number and the Prandtl number for laminar flow.

- Energy balance of a solid structure: The energy balance of the solid structures of the stack describes the unsteady heat conduction. The convective heat, transferred from the gas flow to the solid, is related to the reaction enthalpies in the following equation:

$$\frac{1}{s}\sum_g h_g B_g \left(T_g - T_s\right) - \frac{1}{s}\left(\frac{\Delta H}{n_e F} + V\right) I + K_x \frac{\partial^2 T_s}{\partial x^2} = 0 \tag{4-113}$$

Where K_x is the effective thermal conductivity of the solid structure, accounting for the parallel heat conduction through the parallel layers:

$$K_x = \frac{\sum_h K_h \delta_h}{\sum_h \delta_h} \tag{4-114}$$

4.4.2 Heat Generation and Flux in Fuel Cell Layers

Heat generated by the electrochemical reaction in the anode catalyst layer can be expressed as:

$$q_{ACL} = i\left(\eta_a - \frac{\Delta H_a - \Delta G_a}{nF}\right) \tag{4-115}$$

Where ΔH_a is the anodic reaction enthalpy and ΔG_a is the anodic Gibbs free energy. The heat flux can be related to the temperature gradient across the membrane as:

$$q_{ACL} = -\lambda_{mem} \frac{dT}{dx} \tag{4-116}$$

Where λ_{mem} is the effective thermal conductivity of the membrane.

4.4.3 Heat Conduction

In a homogeneous substance, a temperature gradient results in an energy transfer through the medium. The rate of heat transfer in the x-direction through a finite cross-sectional area, A, is:

$$q_x = -kA \frac{dT}{dx} \tag{4-117}$$

Where k is the thermal conductivity (W/m·K). The steady-state heat conduction is governed by the equation:

$$\frac{d^2T}{dx^2} = 0 \tag{4-118}$$

When heat conducted through two adjacent materials with different thermal conductivities, the third boundary condition comes from a requirement that the temperature at the interface is the same for both materials:

$$q = h_{tc} A \Delta T \tag{4-119}$$

Where h_{tc} is the convective heat transfer coefficient (W/m^2K), A is the area normal to the direction of the heat flux and ΔT is the temperature difference between the solid surface and the fluid. Internal fuel cell heat generation is described by the Poisson equation:

$$\frac{d^2T}{dx^2} + \frac{q_{int}}{k} = 0 \tag{4-120}$$

Where q_{int} is the rate of heat generation per unit volume (W/m^3).

4.4.4 Heat Dissipation through Natural Convection and Radiation

The heat lost by the stack through natural convection and radiation to the surroundings is:

$$Q_{dis} = \frac{T_s - T_0}{R_{th}} \tag{4-121}$$

Where T_s is the stack surface temperature, T_0 is the temperature of the surrounding walls and R_{th} is the thermal resistance. This resistance can be written as:

$$R_{th} = \frac{1}{\frac{1}{R_c} + \frac{1}{R_R}} \tag{4-122}$$

Where R_c is the convective thermal resistance:

$$R_c = \frac{1}{h A_s} \tag{4-123}$$

Where $h = \left(k/L\right) Nu_L$ and R_R is the radioactive thermal resistance:

$$R_R = \frac{1}{\sigma F A_s \left(T_s + T_0\right)\left(T_s^2 + T_0^2\right)} \tag{4-124}$$

Where σ is Stefan-Boltzmann constant, F is the shape factor and A_s is the stack exposed surface area. For small stacks or single cell stacks, the surface area is large and the heat dissipation is greater than the heat generation. Sometimes, small stacks are heated to maintain a certain operating temperature.

4.4.5 Fuel Cell Heat Management

As seen on section 2, every type of fuel cell has its own operating temperature range. In order to achieve a high efficiency, temperature must be controlled accurately. According to this issue, most fuel cells have a cooling system, so temperature cannot exceed operating values.

HEAT EXCHANGER MODEL

The fuel cell can be assumed as a heat exchanger with internal heat generation. The heat transferred to the cooling fluid is:

$$\frac{dQ_c}{dA_c} = h\left(T_s - T_c\right) \tag{4-125}$$

Where A_c is the entire heat exchange surface. Similar to the heat exchanger:

$$Q_c = UA_c\,LMTD \tag{4-126}$$

Where U is the overall heat transfer coefficient and LMTD is the Log Mean Temperature Difference [8]. Depending upon the stack design, the temperature difference between the stack body and the cooling fluid can be constant or it can vary. The heat must be absorbed by the cooling fluid and brought to the outside of the stack:

$$Q_c = mc_p\left(T_{c,out} - T_{c,in}\right) \tag{4-127}$$

The temperature difference is a design parameter that needs to be optimized depending upon the amount of heat generated and the water that needs to be evaporated.

AIR COOLING

Fuel cells can be cooled with air if cooling channels are put into the bipolar plates. The flow rate can be found from a simple heat balance. The heat transferred into the air is:

$$Q = m_{coolant}\, c_p\left(T_{coolant,out} - T_{coolant,in}\right) \tag{4-128}$$

Using this equation, the exit temperature of the coolant can be calculated. A heat transfer coefficient may be used to estimate the maximum temperature of the channel wall. The Nusselt number is:

$$Nu = \frac{hD_h}{k} \tag{4-129}$$

For channels that have a constant heat flux at the boundary, with a high aspect ratio and laminar flow, the Nusselt number can be assumed with a value of 8,23 [8]. For a circular channel, the Reynolds number must be less than 2300 to insure laminar flow through the channel. The Reynolds number for the coolant can be expressed as:

$$\mathrm{Re} = \frac{4m_{coolant}}{\mu_{gas} P_{cs}} \tag{4-130}$$

The Nusselt number is calculated by the following empirical equation [8]:

$$\mathrm{Nu} = 0{,}664\,\mathrm{Re}^{1/2}\,\mathrm{Pr}^{1/3} \tag{4-131}$$

As the coolant travels along the channel it heats up. Therefore, there is a temperature difference between the inlet and outlet of the flow channel:

$$Q = L_{plate}\,P_{cs}\,h\left(T_{surface} - T_{gas}\right) \tag{4-132}$$

The relationship between the surface temperature and cell edge is:

$$Q = L_{plate}\,P_{cs}\,k_{solid}\,\frac{\left(T_{edge} - T_{surface}\right)}{t_{bc}} \tag{4-133}$$

Where t_{bc} is the thickness of bipolar plate, cathode, anode and electrolyte.

EDGE COOLING

Heat can also be removed from the sides of the cell instead of between the cells. The following equation describes the one-dimensional heat transfer in a flat plate with generation:

$$\frac{d^2T}{dx^2} + \frac{Q}{k\,A\,d_{BP}^{eff}} = 0 \tag{4-134}$$

Where Q is the heat generated in the cell (W), k is the bipolar plate thermal conductivity, A is the cell active area and d_{BP}^{eff} is the average thickness of the bipolar plate in active area. The solution for equation (4-134) for symmetrical cooling on both sides (T(0)=T(L)=0) is:

$$T - T_0 = \frac{Q}{k\,A\,d_{BP}^{eff}}\frac{L^2}{2}\left[\frac{x}{L} - \left(\frac{x}{L}\right)^2\right] \tag{4-135}$$

Where T_0 is the temperature at the edges of the active area and L is the active area width. The maximum temperature difference between the center and the edge is:

$$\Delta T_{max} = \frac{Q}{k\,A\,d_{BP}^{eff}}\frac{L^2}{8} \tag{4-136}$$

The total temperature difference between the center and the edge of the plate is:

$$\Delta T_{max} = \frac{Q}{kA} L \left(\frac{L}{8 d_{BP}^{eff}} + \frac{b}{2 d_{BP}} \right) \quad (4\text{-}137)$$

Where d_{BP} is the thickness of the plate at the border.

4.5 Fuel Cell Modeling

The last four sections described the basic phenomenon occurring in fuel cells. This last section exposes the basic equations used in modeling a device like a fuel cell. Fuel cell modeling can lead to design improvements and more efficient fuel cells.

4.5.1 Conservation of Mass

Every process inside a fuel cell that involves mass transport is governed by the following equation:

$$\frac{\partial \rho}{\partial t} + \nabla(\rho v) = S_M \quad (4\text{-}138)$$

Where v is the velocity vector (m/s) and S_M represents the additional mass sources.

4.5.2 Conservation of Momentum

In order to model the fluid velocity and species partial pressures, the Navier-Stokes equation is required:

$$\frac{\partial(\rho v)}{\partial t} + \nabla(\rho v) = -\nabla p + \nabla(\mu_{mix} \nabla v) + S_M \quad (4\text{-}139)$$

Where p is the fluid pressure, μ_{mix} is the mixture average viscosity and S_M is the external body forces. For different parts of the fuel cell, the S_M term is different [1].

4.5.3 Conservation of Energy

The conservation of energy equation for a fuel cell is:

$$(\rho c_p)_{eff} \frac{\partial T}{\partial t} + (\rho c_p)_{eff} (v \nabla T) = \nabla (k_{eff} \nabla T) + S_e \quad (4\text{-}140)$$

The energy source term (S_e) includes the heat from reactions, ohmic heating and heat associated with a phase change. $(\rho c_p)_{eff}$ and k_{eff} can be solved using the following equations:

$$(\rho c_p)_{eff} = (1-\varepsilon)\rho_s c_{p,s} + \varepsilon \rho c_p \quad (4\text{-}141)$$

$$k_{eff} = -2k_s + \left[\frac{\varepsilon}{2k_s + k} + \frac{1-\varepsilon}{3k_s} \right]^{-1} \tag{4-142}$$

Where ρ_s, $c_{p,s}$, k_s represent density, specific heat capacity and thermal conductivity of the solid matrix. The following equations describe the energy source term in the gas diffusion layers, in the catalyst layers and in the membrane:

$$S_e = \frac{i^2}{\kappa_s^{eff}} - \sigma A_{fg} \left(x_{sat} - x_{H2O(g)} \right) \left(\Delta h_{fg} \right) \tag{4-143}$$

Where i is the current density (A/m^2) and κ_s^{eff} is the effective electric conductivity of the gas diffusion layer (S/cm).

$$S_e = |i| \left[|\Delta V_{act}| - \frac{T\Delta S}{nF} \right] + \left(\frac{i_m^2}{\kappa_m^{eff}} + \frac{i_e^2}{\kappa_s^{eff}} \right) - \sigma A_{fg} \left(x_{sat} - x_{H2O(g)} \right) \left(\Delta h_{fg} \right) \tag{4-144}$$

Where i is the transfer current density (A/cm^3), ΔV_{act} is the activation overpotential (V), i_m is the ionic current density (A/cm^2) and κ_m^{eff} is the effective ionic conductivity of ionomer phase in the catalyst layer (A/cm).

$$S_e = \frac{i_m^2}{\kappa_m} \tag{4-145}$$

4.5.4 Conservation of Species

For the gas phase, species conservation equation is:

$$\frac{\partial(\varepsilon \rho x_i)}{\partial t} + \nabla(v \varepsilon \rho x_i) = \left(\nabla \cdot \rho D_i^{eff} \nabla x_i \right) + S_{s,i} \tag{4-146}$$

Where x_i is the mass fraction of gas species, D^{eff} is a function of porosity and $S_{s,I}$ represents additional species sources. This last term is equal to zero everywhere except in the catalyst layers:

$$S_{s,H2} = -i_a \frac{M_{H2}}{2F} \tag{4-147}$$

$$S_{s,O2} = -i_c \frac{M_{O2}}{4F} \tag{4-148}$$

4.5.5 Conservation of Charge

Current transport is described by a governing equation for the conservation of charge for electrical current and for ionic current:

$$\nabla \cdot \left(\kappa_s^{eff} \nabla \phi_s\right) = S_{\phi s} \tag{4-149}$$

$$\nabla \cdot \left(\kappa_m^{eff} \nabla \phi_m\right) = S_{ms} \tag{4-150}$$

Where κ_s^{eff} is the electrical conductivity in the solid phase (S/cm), κ_m^{eff} is the electrical conductivity in the electrolyte phase, ϕ_s is the solid phase potential (V), ϕ_m is the electrolytic phase potential and S_ϕ is the source term representing volumetric transfer current.

4.5.6 The Electrodes

The electrochemical reaction takes place in the electrodes. The electrode performance depends upon the properties and composition of the materials, thickness and bonding to the adjacent layers. Therefore, mathematical modeling is helpful in optimizing and characterizing these parameters.

MASS TRANSPORT

In order to solve the species balance equation, the mass flux must be determined. The concentration losses are incorporated into a model as the reversible potential decreases due to a decrease in the reactant's partial pressure. There are three basic approaches for determining N:

1. The simplest diffusion model is Fick's law. The binary component form of Fick's law is:

$$N_i = -cD_{i,j} \nabla X_i \tag{4-151}$$

   Where c is the total molar concentration. This diffusion model is used to describe diffusion processes involving two gas species.

2. The Stefan-Maxwell model is more rigorous and more commonly used in multicomponent species systems. It may be used to define the gradient in the mole fraction components:

$$\nabla y_i = RT \sum \frac{y_i N_j - y_j N_i}{p D_{ij}^{eff}} \tag{4-152}$$

Where y_i is the gas phase mol fraction of species i, N_i is the superficial gas phase flux of species i averaged over a differential volume element:

$$D_{ij}^{eff} = \frac{a}{p}\left(\frac{T}{\sqrt{T_{c,i}\,T_{c,j}}}\right)^{b}\left(p_{c,i}\,p_{c,j}\right)^{1/3}\left(T_{c,i}\,T_{c,j}\right)^{5/12}\left(\frac{1}{M_i}+\frac{1}{M_j}\right)^{1/2}\varepsilon^{3/2} \qquad (4\text{-}153)$$

Where T_c and p_c are the critical temperature and pressure, M is the molecular weight of species, a=0,0002745 for diatomic gases and a=0,000364 for water vapor, and b=1,832 for diatomic gases and b=2,334 for water vapor.

3. The Dusty Gas Model is also commonly used and looks similar to the Stefan-Maxwell equation except that it also takes into account Knudsen diffusion:

$$-\nabla X_i = \frac{N_i}{D_{i,k}} + \sum_{j=1,\, j\neq 1}^{n} \frac{X_j N_i - X_i N_j}{c\,D_{i,j}} \qquad (4\text{-}154)$$

ELECTROCHEMICAL BEHAVIOR

The electrochemical reactions in the electrodes create the potential and electrical currents in fuel cells. The Nernst equation can be used to determine the potential for hydrogen electrochemically reacting with oxygen:

$$E = \frac{\Delta G}{2F} + RT\ln\frac{P_{H2}P_{O2}^{1/2}}{P_{H2O}} \qquad (4\text{-}155)$$

The mass flux is related to the electric current through Faraday's law and the kinetics can be described by the Butler-Volmer Equation (section 4.1.1).

ION/ELECTRON TRANSPORT

The main governing equations for the charge transport processes have been explained in section 4.5.5. However, two important equations must be described in order to modeling the electrodes and the electrolyte. These equations are the electronic and ionic currents generated:

$$i_{el} = -\kappa_s^{eff}\,\nabla\phi_s \qquad (4\text{-}156)$$

$$i_{io} = -\kappa_m^{eff}\,\nabla\phi_m \qquad (4\text{-}157)$$

4.5.7 The Electrolyte

The electrolyte cannot be modeled accurately if the transport of both charge and energy are not included in the model. Equations (4-149), (4-150), (4-156) and (4-157) must be solved in the electrolyte for ion transport.

For a PEMFC or a DMFC, the two important fluxes are the proton flux and the water flux as described in sections 4.2 and 4.3.

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