ChE-203 TP-6
Review of a fuel cell

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1 Theory

1.1 Hydrogen

Fossil fuels such as coal, oil and natural gas are primary sources of energy for humanity, but their supply is limited. It is for this reason that we must look for alternatives that would allow us to continue to use energy at the same speed. The required sustainable system must be based on renewable energy sources, although this option cannot be applied to all areas. For example, in the automotive industry, it is not feasible to use solar panels or wind turbines as the sole source of energy for vehicles. Taking this example into account, hydrogen and fuel cells are an alternative in the field of transport, but also self-sufficient houses, stationary energy production and even space missions.

Hydrogen has been used for many years in the chemical and petrochemical industries, it is used for the treatment and refining of fossil fuels, as well as in the synthesis of ammonia. Hydrogen is also used m various applications, for example as a hydrogenation agent in the food industry, for the production of several acids, the reduction of metals and shielding gases for welding.

From a technical point of view, it is interesting to mention that hydrogen is used for the cooling of electric generators (because of its high thermal conductivity), as well as in cryogenic research and superconductivity. In addition, its isotopes have unlimited applications.

Although hydrogen is the most abundant element in the universe, it is not found in pure form on Earth, and energy is needed to obtain it. Thus, hydrogen is not considered as a source of energy, but an energetic carrier.

The characteristics of hydrogen, compared with other common fuels, are described in the table below. We can observe that hydrogen has a higher heat of combustion per unit of mass than other fuels (one gram of hydrogen contains more than twice the energy of the same amount of natural gas). However, this property is limited by its low density per unit volume, i.e. one cubic meter of hydrogen contains less energy than other gaseous fuels. Compared to the liquid state, one liter of hydrogen contains less than 10% of the energy contained in one liter of gasoline.

	Unit	Hydrogen	Gasoline	Propane
Low calorific value	KJ/g	120	43	46
Density of the gas	Kg/Nm^3	0.09	-	2.01
Energy density of gas	mJ/Nm^3	10.8	-	92.5
Density of the liquid	Kg/L	0.071	0.733	-
Energy density of the liquid	mJ/L	10.8	31.5	-
Flammability limits	%	4.0-75	1.0-7.6	2.1-9.5
Detonation limits	%	18.03.59	1.1-3.3	0.3.01.07
Minimum activation energy	mJ	0.02	0.24	0.26
Spontaneous combustion temperature	K	858	501-744	760
Emissions	mg_{CO2}/KJ	0	80	65
Visibility of the flame		No	Yes	Yes
Toxicity (flames / emissions)		No/No	Yes/Yes	Yes/Yes

Comparison of hydrogen characteristics with other common fuels

Among the advantages of hydrogen, we can mention that the CO_2 emissions associated with its combustion are zero (only water is produced during combustion) and that the hydrogen is highly volatile. Therefore, it is a very safe fuel in open spaces. Apart from its low density, hydrogen has a low activation energy, that is to say that very little energy is required for its combustion to be activated. This property may be, according to our objectives, an advantage or a disadvantage. The main industrial sources are:

- Electrolysis
- Catalytic reforming

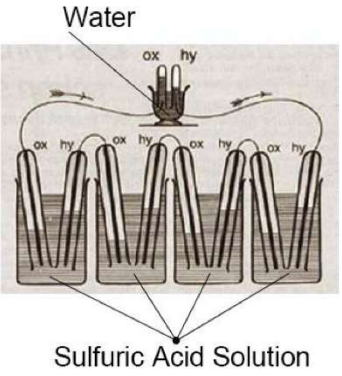
If hydrogen can be produced from solar energy, such as photoelectrolysis, or another renewable energy source, then a completely sustainable energy cycle can be realized. An obstacle to this is the storage and transport of hydrogen.

1.2 Storage of hydrogen in a metal hydride

Loading hydrogen into a metal hydride material is a safe method for storing hydrogen. This method is reliable, but can be very expensive. It is based on the fact that some metals and alloys have the property of forming reversible covalent bonds when they react with hydrogen to form what is called a metal hydride. These bonds decompose when heated and release hydrogen. In practice, a hydride is formed by subjecting a certain metal to a high hydrogen pressure. The hydrogen diffuses inside and reacts with the metal, and finally reaches an equilibrium concentration in the metal, depending on the metal and the pressure. The external pressure is decreased so that the metal can release the hydrogen. This process can be accelerated by increasing the temperature. When fully charged, a metal hydride has a proportion of hydrogen up to 7% of its weight. In metals such as titanium, the concentration of hydrogen per unit volume is higher than in liquid hydrogen.

1.3 Origins of the fuel cell

The fuel cell is an electrochemical device that directly converts the energy contained in a fuel into electrical energy. This method of obtaining electricity, in the form of direct current, is carried out without the necessity of a combustion process, since the oxidation of the fuel and the reduction of the oxidizing agent are produced in different physical locations. The electrochemical conversion achieved in a fuel cell guarantees a high efficiency in the process of energy transformation, superior to the efficiency obtained from thermal machines, due to the limitation imposed on them by the Carnot cycle.



The operating principles of a fuel cell were already known even before the first internal combustion engine appeared. Around the year 1838, some experiments suggested the possibility of establishing an electric current between two electrodes separated by a suitable medium and using catalyst. In 1939, the English, Sir William Robert Grove, lawyer and professor of physics, had an original idea. That same year, he published a document in which he describes a fuel cell consisting of a pair of platinum electrodes immersed in acid. In his experiment, Grove discovered that a weak electric current between the electrodes of the cell was generated. It was the reverse process of electrolysis previously used by fellow countryman Anthony Carlisle to break water into hydrogen and oxygen by means of an electric current.

Grove's Experience

Grove named his invention "gas cell", but was renamed "fuel cell" sometime later. The fuel cell has been studied for many years after its invention. For example, it was Nernst who deduced the thermodynamics that is the basis of the principles of fuel cell operation. However, because of the difficulty in obtaining reliable, inexpensive electrodes and with good characteristics, the fuel cell has fallen into oblivion. On the other hand, power generation devices, such as steam turbines and internal combustion engines, have begun to be developed rapidly. They were inexpensive to manufacture and reliable. Moreover, around 1860, the storage of electrical energy in lead batteries was developed, and these batteries were sufficient to cover the energy needs of that time.

It was not until more than a century after the discovery of Grove that Francis Thomas Bacon assembled a stacked structure (membrane-electrode assembly) with a current density sufficient to produce usable energy.

Bacon's cell was the space vehicle energy production system, which allowed the first man to walk on the moon in 1969.

The fuel crisis of the 1970s and the Gulf War in the 1990s prompted some governments to consider the use of electrochemical generators for automobiles and for stationary energy production. This meant significant momentum in the funding of many fuel cell research and development projects for different uses. At present, the use of fuel cells is applied both in the automotive industry and in low power stationary applications.

The use of electrochemical generators could triple the efficiency of current engines, which would mean a drastic reduction in the consumption of fossil fuels.

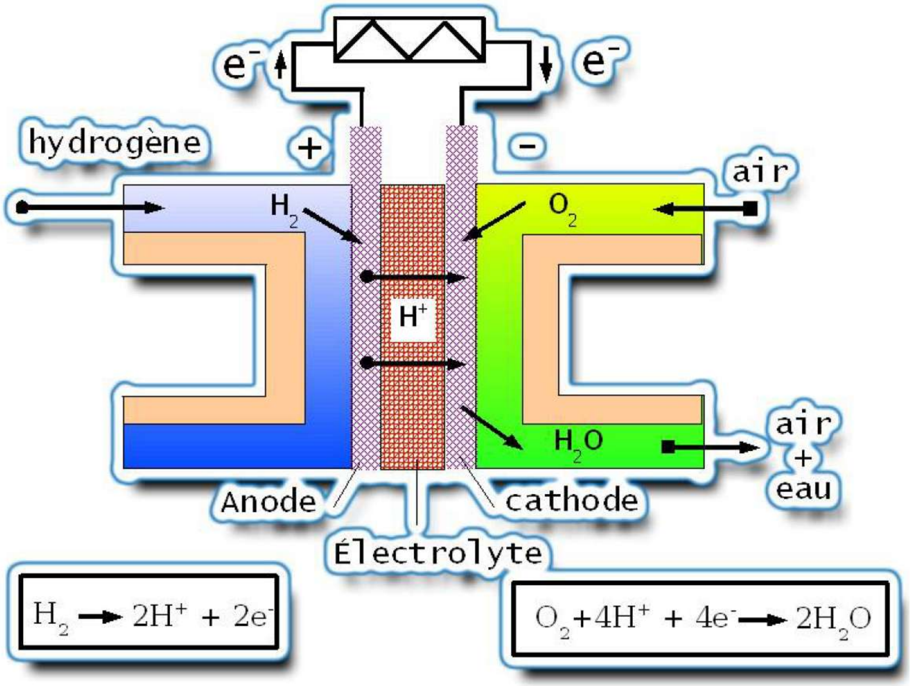
Automakers have discovered that low-temperature fuel cells with a polymer membrane fueled by methanol or hydrogen are an alternative to the internal combustion engine, the price of which tends to increase gradually.

1.4 Principle of operation of a fuel cell

A fuel cell is an electrochemical device that converts the chemical energy of a reaction directly into electrical energy. For example, electricity can be produced by the combination of electrochemical hydrogen and oxygen without any combustion. These cells do not discharge like a battery, and do not need to be recharged, because they produce energy in the form of electricity and heat as long as they are supplied with fuel. In practice, corrosion and degradation of materials and components of the cell can limit their life.

These cells operate through an electrochemical cell that is composed of two electrodes, an anode and a cathode, separated by an electrolyte. Oxygen from the air passes through one electrode and hydrogen gas passes through the other.

Hydrogen oxidizes and loses an electron during ionization at the anode. When this occurs, the oxidized hydrogen (now in the form of a proton) and the electron take different paths, migrating to the second electrode called cathode. The proton moves through the electrolyte, while the electron moves through an external material (charge). At the end of their displacement, they meet again in the cathode, where the reduction reaction, i.e. the formation of water. Thus, this process generates 100% pure water, an electric current as well as electric heat, i.e. thermal energy.



Operating principle of a fuel cell

Unlike a combustion engine, whose efficiency is governed by the Carnot cycle and is limited by temperature, the theoretical efficiency of fuel cells is given by Faraday's laws. These laws connect the current produced in an electrochemical reaction to the amount of reactive material, i.e., the amount of fuel.

The biggest advantage of fuel cells is that they are not limited by temperature, which gives them the advantage of achieving high efficiencies. Thus, in theory, each molecule of hydrogen gas will generate two free electrons, which will react with an oxygen atom to produce a molecule of water. Such an electrochemical reaction is exothermic, so that the heat produced can be used and, as a result, the energy efficiency of the cells is increased.

Features such as power generation with high efficiency and the advantage of producing no polluting emissions when the fuel is hydrogen, make fuel cells the best candidate for electric power generation.

On the other hand, they also offer the possibility of using any fuel containing hydrogen. Although hydrocarbons such as natural gas, methanol, ethanol, biogas and propane, as well as diesel and gasoline, are the ones that have attracted more attention for practical reasons.

1.5 Types of fuel cells

Phosphoric acid fuel cells (PAFCs) operate at temperatures of 150 to 200 ° C, contain phosphoric acid as the electrolyte and porous carbon electrodes containing a platinum catalyst.

The molten carbonate fuel cells (MCFC) contain molten carbonate electrolyte (usually sodium or lithium), are suitable for large scale cogeneration, and operate with hydrocarbons, including: natural gas, biogas, synthesis gas, methane and propane.

Solid Oxide Fuel Cells (SOFC) are composed of a hard, non-porous ceramic electrolyte. Since the electrolyte is a solid, the cells need not necessarily be plate-shaped in the same way as other types of fuel cells. They operate at very high temperatures (around 1000 ° C). High temperature operation eliminates the need for a catalyst from precious metals, reducing the cost.

Alkaline fuel cells (AFCs) are one of the first developed fuel cell technologies, consisting of an electrolyte solution of potassium hydroxide in water and a variety of non-precious metals is used as a fuel cell. as catalyst at the anode and at the cathode. At high temperatures the AFC can operate at temperatures between 100 ° C and 250 ° C. However, the new AFC models operate at temperatures in the range of 23 ° C to 70 ° C.

Solid polymer fuel cell or proton exchange membrane (PEM) fuel cell These cells consist of an electrolyte formed of a proton-conducting polymer membrane. The membrane is located between two porous electrodes impregnated on one side by an electrocatalyst (generally Pt) and on the other side a hydrophobic material. They operate at relatively low temperatures (around 80 ° C) and at a high power density. They can change their production quickly to respond to changes in electricity demand. So, they are suitable for applications in which a high initial demand is needed. The only liquid in the PEM is water, so the damage from corrosion is minimal.

Modern technologies make it possible to manufacture cells in a compact way. They can be as thick as one sheet of paper and can generate several mA of current per square centimeter, i.e., higher current densities than other types of cells.

Recent developments avoid the need to pressurize the fuel to increase the efficiency of the system and allow the water to be controlled to prevent "flooding" of the porous electrodes, while at the same time maintaining the degree of humidity wanted in the membrane so as to allow the conduction of the positive charges that come from the anode.

PEM fuel cell

Operating pressures are normally about 30 psi. However, suitable current collectors and support frames can lead to PEM cells reaching pressures up to 3000 psi. This makes it possible to increase the voltage of the cell and the current density.

In general, the performance of PEM batteries is very varied, as it depends, among other things, on the pressure, the temperature and the quality of the gas.

The current best performance of PEM batteries is held by the Los Alamos National Laboratory, USA, with 0.78 V per cell and currents of 200mA / cm 2 at pressures of 3 atm H_2 and 5 atm of air, using charges of 0.4 mg / cm 2 of Pt. This type of cell generates useful heat that cannot be used in cogeneration for electricity, but can be used in heating systems and hot water, for example in homes and offices.

Much of the success achieved by this cell is due to the progress of materials with physico-chemical properties, more adapted to this system. Other additional improvements are also expected in the field of materials. Research is mainly focused on electrolysers, replacing them with cheaper ones and improving porous electrode design to reduce the cost of the electrocatalyst. Other components, such as current collectors, which also act as gas distributors and the final plates of the cell, are subjects of research in academic institutions. They have become the main contributors and providers of technological developments for cell manufacturers. PEM cells are the main candidates for light vehicles. Other minor applications and potential markets for PEM cells, besides residential applications, are rechargeable batteries for video cameras and cordless phones.

1.6 Operation of Proton Exchange Membrane (PEM) Fuel Cells

The PEM type fuel cell is conceptually one of the least complicated batteries. The anode is supplied with hydrogen gas and the cathode with pure oxygen or oxygen from the air.

A PEM fuel cell is an elementary unit divided into several elements among which we find an electrolyte layer, two electrodes (anode and cathode), a catalyst, bipolar plates and a gas diffusion layer. Its operation starts at the moment when the hydrogen is supplied to the anode and the oxygen at the cathode. The two gases penetrate along the channels of the bipolar plates of their respective electrodes. Then they are distributed over the entire surface through the gas diffusion layers.

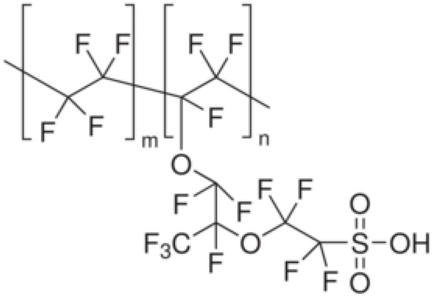
Once the reactive gases have passed through the diffusion layer, the catalyst is reached. In PEM fuel cells, the catalyst is a platinum-based metal alloy. This layer containing the catalyst is located between the gas diffusion layer and the electrolyte. The function of the anode is to dissociate the molecule of hydrogen into protons and electrons.

When the fuel molecule has been dissociated, the protons pass through the polymer membrane to the cathode, while the electrons move along an external electrical circuit to the load to be fed.

The catalyst placed between the polymer membrane and the cathode combines the H^+ ions from the electrolyte with the oxygen from the air and the electrons into the external circuit to give water. The most important feature of the catalyst is its contact surface with the reactive gases, not its thickness or weight.

1.6.1 Proton exchange membrane. Electrolyte

The electrolyte in the PEM, unlike other cells, is a polymer membrane of 75 and 150 microns. It is called in the trade Nafion, a derivative of Teflon (PTFE). The structure is as follows:



Nafion is a material with high mechanical and chemical resistance. It can absorb a lot of water, allowing the protons to move inside with a certain amount of freedom. On the other hand, the ionic conductivity of Nafion increases as the relative humidity increases, but without temperature rise because it is unable to retain water at temperatures above 80 °C.

1.6.2 Catalysts

In PEM cells, the reaction between hydrogen and oxygen occurs very slowly. Therefore, it is necessary to speed up the process so that the device can operate and produce electrical power. This is done using a platinum catalyst. Once the fuel (hydrogen) passes through the diffusion layer of the cell and arrives at the platinum-based electrolyte layer, the dissociation of the fuel molecule is catalyzed into two bound hydrogen atoms to two platinum atoms. At this moment, each hydrogen atom releases an electron to form a hydrogen ion H^+ according to the following reactions:

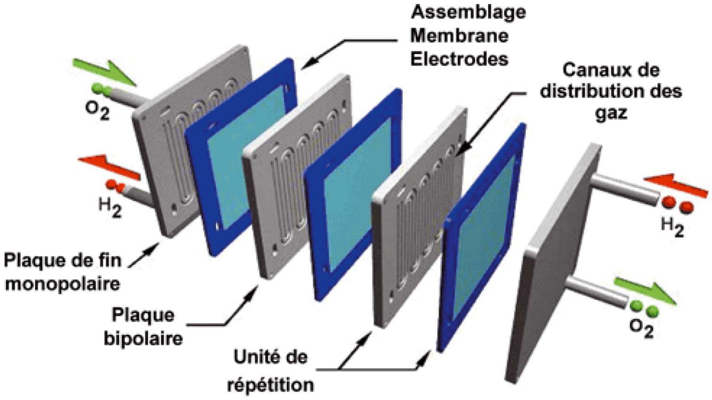
$$H_2 + 2Pt \rightarrow 2Pt - H$$

$$2Pt - H \rightarrow 2Pt + 2H^+ + 2e^-$$

1.6.3 Stacking of elementary cells

The elementary cells operate at a yield of less than 100%: the output voltage of an elementary cell is about 0.7 V, and its efficiency is not much higher than 60%. Since the vast majority of applications require much higher voltages, the required voltage is obtained by connecting the elementary cells in series and thus forming a stack called a fuel cell.

The elementary cells are interconnected by bipolar plates, so that only one plate with a double channel between each of the active surfaces is present, as shown in the following figure:



Stacking of elementary cells using bipolar plates

The power supplied by the cell is equal to the cell voltage multiplied by the intensity of the current flowing through it.

$$W_{pc} = V_{Apl} * I$$

However, it is quite common to use the term current density instead of current in fuel cell design:

$$I = i * A_{\text{cell}}$$

where: i is the current density (A/cm^2) and A_{cell} the surface of each cell (cm^2). On the other hand, the potential of each cell and the electric current are connected by the polarization curve of the cell:

$$V_{cell} = f(i)$$

The number of cells in a stack is determined based on the required maximum voltage. The total potential of the stack is the sum of the contributions of each cell:

$$V_{Apl} = \sum_{i=1}^{N_{cell}} V_i = V_{cell} * N_{cell}$$

where: V_{apl} is the voltage of the cell (V), V_{cell} is the voltage of each cell (V) and N_{cell} is the total number of cells.

1.7 Thermodynamics of fuel cells

1.7.1 Thermodynamic considerations

A PEM cell transforms the energy contained in the fuel into electricity. The total intrinsic energy of a fuel (or any other substance) can be quantified through a property called internal energy (U). This energy is associated with the movement and interactions of particles of a compound at the molecular level.

For a proton exchange membrane cell, part of the internal energy contained in the hydrogen is converted into electricity. Energy conversions are limited by the first and second principles of thermodynamics.

First principle of thermodynamics

The first principle of thermodynamics, also known as the principle of conservation of energy, states that energy is neither destroyed nor produced, but is transformed.

$$d\,(Energy)_{Total} = d\,(Energy)_{System} + d\,(Energy)_{Environment}$$

Energy can be transferred in two ways from the closed system to its environment: through heat (Q), or work (W). This allows us to deduce the first principle of thermodynamics in a general way:

$$dU = dQ - dW$$

Second principle of thermodynamics

The second principle of thermodynamics introduces the notion of entropy.

This term is determined by the number of possible micro-states accessible to the system, i.e. the different possible ways of configuring a system. It is also defined as a measure of the part of the internal energy that cannot be used to produce work. In other words, it is the degree of disorder of the molecules that make up a body, or the degree of irreversibility reached after completing a process that involves an energy transformation.

For an isolated system, it is represented by the following equation:

$$S = k * \log \Omega$$

where: S is the total entropy of the system, k is the Boltzmann constant and Ω is the number of possible states of the system.

Potential of fuel cells

For a constant pressure process, the maximum amount of energy that can be extracted from a fuel depends on the reaction enthalpy of the fuel used. If the enthalpy is expressed as a function of the internal energy mentioned above, we obtain the following equation:

$$dH = T\,dS = dU + dW$$

From this expression, we can deduce that the heat developed in a reaction is due to changes in the internal energy of the system, which is generated by the changes and reconfigurations of the different chemical bonds that compose it.

The overall reaction of water formation is identical to the combustion reaction of hydrogen. It is therefore a strongly exothermic reaction, which means that energy is released during the process.

As a result, water contains less internal energy than separated hydrogen and oxygen.

$$H_2 + 1/2O_2 \rightarrow H_2O + chaleur$$

The enthalpy of reaction of a chemical reaction is the difference between the heat of formation of the products and that of the reagents. So that if the heat of formation of water is -286 kJ / mol, at 25 ° C, and the heat of formation of hydrogen and oxygen are, by definition, equal to 0, then following expression for the formation of water:

$$\Delta_{\mathrm{r}}H = \left(h_f\right)_{H_2O} - \left(h_f\right)_{H_2} - \frac{1}{2}\left(h_f\right)_{O_2} = -286\ kJ.mol^{-1} - 0 - 0 = -286\ kJ.mol^{-1}$$

The enthalpy variation associated with a combustion reaction is called Combustion Heat, although in the case of the heat of combustion of hydrogen, this notion is called the calorific value of hydrogen.

This heat represents the minimum amount of energy that can be extracted from the combustion of one mole of hydrogen. In addition, depending on the conditions under which this reaction is given, we can speak of higher or lower calorific value.

The heating value (PCS) has an approximate value of -286 kJ / mol, while the low heating value (PCI) is about -241 kJ / mol. The difference between the two is called the evaporation heat of water (45 kJ / mol at 25 ° C). For fuel cells, the PCS is almost always used to calculate the yield.

According to the second principle of thermodynamics, a certain amount of entropy is generated in each chemical reaction, implying that part of the PCS of the hydrogen is not converted into electricity.

The portion of energy contained in the fuel that can be converted into electricity is determined by the Gibbs free energy equation:

$$\Delta_{\mathrm{r}}G = \Delta_{\mathrm{r}}H - T\Delta_{\mathrm{r}}S$$

Apart from determining the amount of useful work that is extracted during a reaction, the Gibbs free energy also makes it possible to determine the spontaneity of such a process. If ΔG is equal to zero, no work can be extracted from the reaction, if this variation of energy is positive, energy must be added to the process, and if it is negative, we can speak of a reaction energetically favorable (the reaction occurs spontaneously by producing energy). Nevertheless, many reactions, which are considered spontaneous, are not generated immediately because of certain energy barriers that must be overcome.

As the equation of enthalpy represents the difference between the heats of formation of reactants and products, during the combustion of hydrogen, $\Delta_{\mathrm{r}}S$ represents the entropic difference between the products and the reagents:

$$\Delta_r S = \left(S_f\right)_{H_2O} - \left(S_f\right)_{H_2} - \frac{1}{2}\left(S_f\right)_{O_2}$$

Enthalpy values and entropy of products and reagents in a PEM cell are shown in the following table

	H_f (kJ/mol)	S_f (kJ/mol)
H_2	0	0.13066
O_2	0	0.20517
Liquid water H_2O(PCS)	-286.03	0.06996
Water vapor H_2O(PCI)	-241.98	0.18884

From the Gibbs free energy equation, we can deduce the amount of energy we have available to obtain electricity from an electrochemical energy generator:

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

$$\Delta_r G = \left(\left(h_f\right)_{H_2O(l)} - \left(\left(h_f\right)_{H_2} + \frac{1}{2}\left(h_f\right)_{O_2}\right)\right) - T\left(\left(S_f\right)_{H_2O(l)} - \left(\left(S_f\right)_{H_2} + \frac{1}{2}\left(S_f\right)_{O_2}\right)\right)$$

$$\Delta_r G = \left(-286.02 - (0 - 0)\right) - 298.15 * \left(0.006996 - \left(0.13066 + \frac{1}{2} * 0.20517\right)\right)$$

$$\Delta_r G = -237.34\ kJ.mol^{-1}$$

Therefore, from 286.02 kJ / mol of available energy, and at 25 ° C, only 237.34 kJ / mol can be used to produce energy, while the remaining 48.68 kJ / mol are transformed into heat. In general, electrical work can be defined as the product of the load multiplied by the potential:

$$W_{el} = qE$$

where: W_{el} is the molar electric work (J/mol), q is the molar electric charge (C/mol) and E is the electric potential (V). For a PEM cell, the total amount of electric charge transferred per mole of hydrogen consumed is determined by the following relationship:

$$q = n * N_{Avg} * q_{\mathrm{el}}$$

where: n represents the number of electrons per molecule of hydrogen, N_{Avg} is the Avogadro constant (6.023×10^{23} molecules/mol), q_{el} is the charge of an electron (1.3052×10^{-19} C/electron).

When fuel cells, or any other device that involves an electrochemical process, are studied, the expression nF is often found. Such an expression links thermodynamics to electricity.

In fact, the expression nF represents one of the main parameters of electrochemistry: the quantity of electrons transferred into the electric current flowing between the reactive chemical species.

In each electrochemical reaction, there is a relationship between the amount of chemical species that reacts and the electrons transferred. In this way, in a PEM cell two electrons are transferred per mole of hydrogen that reacts, so that n = 2 for the equation of the transferred electric charge.

To transform this quantity into a molar electric charge, "n" must be multiplied by the Avogadro constant, N_{avg}, and by the charge of an electron:

$$q = n * N_{Avg} * q_{\mathrm{el}} = nF$$

The term F is the Faraday constant and its value is F = 96485 C/mol. Having a high Faraday constant means that a relatively large amount of electricity can be obtained from a small chemical reaction. This makes fuel cells usable in technological applications.

Therefore, the expression of electrical work is:

$$W_{el} = n\,FE$$

From what we have seen so far, we know that the maximum amount of electrical energy obtained from a fuel cell is given by Gibbs' free energy equation:

$$W_{el} = -\Delta_r G$$

The electric potential of the fuel cell is therefore as follows:

$$E = -\frac{\Delta_r G}{nF} = \frac{237.04\ kJ.mol^{-1}}{2 * 96485\ C.mol^{-1}} = 1.229\ V$$

1.7.2 Thermodynamic efficiency of the fuel cell

We have seen previously that the term $T\Delta_r S$ affects the theoretical maximum potential of a fuel cell. The value of E = 1.229V corresponds to the maximum voltage that can be obtained from a cell if Gibbs free energy is completely transformed into electricity (i.e. in the ideal case of a reversible process). The thermodynamic efficiency of a fuel cell is based on the enthalpy of the liquid water formed. This is obtained using the following relationship, which leads to the conclusion (using the voltage values deduced above) that the maximum efficiency of a PEM fuel cell is 83% at 298K. The difference of this value to 100% corresponds to the losses induced by the non-reversibility of the system.

$$\eta_{th} = \frac{\Delta_r G}{\Delta_r H} = \frac{-237.34\ kJ.mol^{-1}}{-286\ kJ.mol^{-1}} = 0.83$$

It is important to mention that the value $\Delta_r G$, and thus the calculated efficiency, vary according to the temperature at which the apparatus operates. For example, for a hydrogen/oxygen cell that operates above 100 ° C, the enthalpy and entropy values that must be taken to calculate the Gibbs free energy will be those of the water vapor (This gives a thermodynamic efficiency of 95%). Below 100 °C, these values correspond to those of liquid water.

1.7.3 Energy balance

In order to determine the energy balance, we consider that the sum of the input energy is the same as the sum of the output energy.

$$\sum Q_{in} - \sum Q_{out} = W_{el} + Q_{dis} + Q_c$$

where: Q_{in} is the enthalpy (heat) of the incoming elements, Q_{out} is the enthalpy (heat) of the outgoing elements, Q_{dis} is the heat dissipated by convection/radiation in the environment, W_{el} is the electrical work obtained and Q_c is the heat extracted by a coolant flow.

Some of the heat produced inside the cell is dissipated by convection and radiation into the environment, however the rest must be evacuated by more complex cooling systems. The heat generation in a fuel cell is directly associated with the loss of voltage. This heat is generated especially in the catalyst layers, although considerable losses are also generated in the polymer membrane and in the external electricity circuit.

A good estimate of the energy balance can be established by matching the enthalpy of reaction to the sum of heat and electricity produced:

$$\Delta_r H * N_{cell} = Q_{gen} + nF * V_{cell} N_{cell}$$

When the water from the cathode is liquid, the higher heating value is used, so that the heat generated by the fuel cell is as follows:

$$Q_{gen} = (1.482 - V_{cell}) * nF * N_{cell}$$

On the other hand, if it passes through the cathode as a gas, the lower heating value is used, so that the heat generated by the fuel cell is as follows:

$$Q_{gen} = (1.254 - V_{cell}) * nF * N_{cell}$$

1.8 Kinetics of fuel cells

When an electric current passes through the fuel cell, kinetic phenomena come into play. Although the theoretical thermodynamic efficiency is 83%, the activation and diffusion processes render this value unattainable in practice. Indeed, the real voltage obtained at the terminals of a stack is given by:

$$E_{réel} = E_{th} - \eta_{act} - \eta_{conc} - \eta_{ohm}$$

where E_{th} is the electromotive force of the cell, given by thermodynamics (1.229V in our case, see previous paragraph), η_{act} is the activation polarization, η_{conc} is the polarization of concentration and η_{ohm} is the ohmic polarization.

1.8.1 Activation polarization

For an electrochemical reaction to take place, the reagents must have sufficient energy to exceed the activation energy of the reaction. The Butler-Volmer equation allows to evaluate the losses due to this activation. Normally, the losses due to the oxidation reaction of hydrogen at the anode and those due to the reduction of oxygen at the cathode should be taken into account. However, the oxidation reaction of hydrogen is much faster, and thus the voltage loss is here dominated by the oxygen reduction reaction. This loss is then given by:

$$\eta_{act} = \frac{RT}{\alpha_a nF} * \ln\left(\frac{i}{i_{0,O_2}}\right)$$

where α_a is the anodic charge transfer coefficient, n is the number of electrons involved in the reaction, i is the anode current, and $i_{0,\,O2}$ is the exchange current (i.e. the current obtained at E = E_{th} and in the absence of electrochemical reaction). This loss becomes less important with an increase in temperature and pressure.

1.8.2 Polarization of concentration (or mass transfer)

If the concentration of reagents at the electrodes is not constant during the use of the fuel cell, a concentration gradient is created. This is mainly due to diffusion problems of the gaseous reactants up to the electrode/electrolyte interface, or the fact that at high current density the hydrogen supply is not done quickly enough (hydrogen is consumed faster than it is sent to the anode). When this last case occurs, the current reaches a limit value, defined by the incoming flow of hydrogen. This is the diffusion limit current i_L. The corresponding losses at the anode and at the cathode are given by Fick's law:

$$\eta_{conc,a} = \frac{RT}{nF}\ln\left(\frac{C_{O_2}^S}{C_{O_2}}\right)$$

$$\eta_{conc,c} = \frac{RT}{nF}\ln\left(\frac{C_{H_2}^S}{C_{H_2}}\right)$$

where C_X are the concentrations at the cell inlet and $C^S{}_X$ are the concentrations at the surface of the electrode.

On the other hand, Faraday's law gives the relation between concentration of the reactive species and electric current, we obtain:

$$\eta_{conc\ (BV),a} = \frac{RT}{\alpha_a nF}\ln\left(\frac{i_{L,a}}{i_{L,a} - i}\right)$$

$$\eta_{conc\ (BV),c} = \frac{RT}{\alpha_c nF}\ln\left(\frac{i_{L,c}}{i_{L,c} - i}\right)$$

where i corresponds to the current flowing through the cell and the currents $i_{l,\,x}$ corresponds to the limit currents at the electrodes.

the polarization of total is the sum of two parts as following:

$$\eta_{conc} = \eta_{conc\ (Fick)} + \eta_{conc\ (BV)}$$

Or

$$\eta_{conc,a} = \frac{RT}{nF}\left(1 + \frac{1}{\alpha_a}\right)\ln\left(\frac{i_{L,a}}{i_{L,a} - i}\right)$$

$$\eta_{conc,c} = \frac{RT}{nF}\left(1 + \frac{1}{\alpha_c}\right)\ln\left(\frac{i_{L,c}}{i_{L,c} - i}\right)$$

1.8.3 Ohmic polarization

As in any electrical system, an ohmic loss occurs through the fuel cell. They are mainly due to the limited conductivity of the electrolyte. These losses are simply given by Ohm's law:

$$\eta_{ohm} = ir$$

where i is the current flowing through the stack and r the resistance of the system.

1.8.4 Polarization curve and electrical efficiency

We thus obtain the expression of the real voltage produced by the fuel cell:

$$E_{réel} = E_{th} - \frac{RT}{\alpha_a nF} * \ln\left(\frac{i}{i_{0,O_2}}\right) - \frac{RT}{nF}\left(1 + \frac{1}{\alpha_a}\right)\ln\left(\frac{i_{L,a}}{i_{L,a} - i}\right) - \frac{RT}{nF}\left(1 + \frac{1}{\alpha_c}\right)\ln\left(\frac{i_{L,c}}{i_{L,c} - i}\right) - ir$$

Thus when the current through the fuel cell increases, the voltage produced at its terminals decreases. This is illustrated by plotting the polarization curve i-E of the stack. The electrical efficiency of the fuel cell, which corresponds to the ratio of the voltage measured at the terminals of the fuel cell to the electromotive force of the fuel cell, is further defined:

$$\eta_{élec} = \frac{E_{réel}}{E_{th}} = \frac{E_{réel}}{1.229}$$

1.9 Hydrogen flow control

The rate of supply of reagent gases supplied to the cell must be equal to or greater than the rate at which they are consumed. Hydrogen and oxygen are supplied to the cell at a rate that depends on the current density. Thus, a system of pressurized tanks or pumps is used because they provide the reactive gases in a fixed or variable stoichiometric ratio. This stoichiometric ratio is a way of measuring the amount of reagent supplied to the fuel cell. It reflects the rate at which gases feed the cell according to the speed at which they are consumed. The stoichiometric ratio can be expressed as a function of the total mass or the molecular weight:

$$S = \frac{N_{real}}{N_{cons}} = \frac{m_{real}}{m_{cons}}$$

where: N_{real}, m_{real} are the actual quantities of reagents supplied (molecular weight and mass, respectively), N_{cons}, m_{cons} are the gas consumptions in the cell (molecular weight and mass, respectively). So, for example, S = 2 means that the cell is fed with a quantity of reagents twice the amount it really needs. If the stoichiometric number is too high, fuel is unnecessarily used and internal currents generated, resulting in losses. And if the stoichiometric number is too low, it may happen that the gases are not supplied quickly enough to allow the cell to respond to peak demand for energy. As a general rule, a stoichiometric number of about 1.2-1.5 in hydrogen is used to feed the PEM fuel cells.

Moreover, the flow of the reagents depends on the size of the cell and the stack in general, since the larger the cells, the more a large quantity of reagent will be required, and the more complicated their diet becomes.

Basically, the mass balance of the fuel cell requires that the sum of the mass of the incoming species be equal to the sum of the mass of the outgoing species. In a proton exchange membrane fuel cell, the incoming species are hydrogen, oxygen and water vapor present in these gases. On the other hand, the outgoing species are the quantities of unused fuel and oxidant, as well as water in the liquid or gaseous state. If hydrogen comes from the recombination of any other type of fuel, then other types of substances can be found in the electrochemical process of the internal reaction of the cell, and must be considered when performing the energy balance. These substances may be small traces of CH 4, CO 2 or CO. They must be taken into account to adjust the inflow of gas, so that there is just enough hydrogen to produce the required power.

2 Instructions, Warnings and Precautions

2.1 Warnings and main precautions

- Hydrogen metal hydride cartridges should be kept away from fire, source of heat or at temperatures above 40 ° C during activation, refilling, storage and use.

- Do not carry the hydrogen cartridge with the connected pressure regulator.

Make sure that the cartridge cover is always correctly positioned.

- This unit uses hydrogen as fuel. Hydrogen is not toxic, but it can act as an asphyxiating gas because it displaces oxygen from the air.

So when working with the device in a closed room:

- Make sure that the ventilation system is not obstructed during the operation.
- Always operate within the indicated temperature limits.
- The cell should always be handled in a well-ventilated area to avoid potential excess hydrogen.
- The mixture of air and hydrogen is potentially flammable and explosive and may ignite by a spark or heat source. For this reason, all sources of inflammation, such as smoking, are prohibited in the vicinity of the unit.

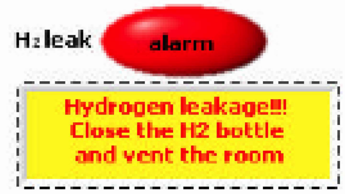
When the cell is running, there is a potential electrical hazard as it can cause burns or electric shocks:

- Avoid touching the plates of the fuel cell or any other electrical element.
- Do not wear metal jewelry (rings, bracelets, necklaces, etc.) When using the fuel cell.
- Minimize conductivity, avoid touching surfaces that are in contact with water or gas, and avoid working or keeping the unit in humid conditions.

2.2 Security devices installed in the unit

1. A hydrogen detector installed on the upper side of the unit.

When it detects a leak, a message such as the one below is sent to the user via the software:



Hydrogen leakage!!!
Close the H2 bottle
and vent the room

As soon as this message appears, the metal hydride cartridge must be closed so that it stops releasing hydrogen and the room must be ventilated.

2. Overheating protection: When the cell temperature sensor (ST-1) is above 65 ° C, AVS-1 is closed and the hydrogen input to the cell is cut off (three beeps are emitted).

3. Overcurrent and Low Voltage Protection: When a current greater than 12A or a voltage below 12V is detected, the AVS-1 supply valve is shut down and the load is disconnected, emitting 3 beeps.

4. Due to the importance of correctly purging the water that has been formed and the remaining hydrogen in these systems, the AVS-2 purge valve opens automatically. When the cell starts, it is open for 3 to 4 seconds, then it opens cyclically for about half a second every 15 seconds.

2.3 Operating considerations

As a result of proper operation of these fuel cells, it is necessary to purge the remaining hydrogen and the generated steam. This purge is programmed to be performed every three seconds. When this occurs, the cell, at the same time as the purge is performed, during this half-second, absorbs hydrogen, generating large increases in momentary flow. These "peak" flows are not taken into account during the practical exercises.

In addition, the ball of the flowmeter can lock on the upper side. If this happens, gently pat the plastic covering until the ball falls.

3 Experimental procedure

1. Please read section 2.1 (warnings and precautions) before starting the exercise.

2. Turn on the interface, set the multimeter on the left on V (volt) and the one on the right on A (ampere) to and start the UC5C program on the computer. Take knowledge of different sensors and actuators. The stack is composed of 24 PEM cells.

3. Open the hydride cartridge slowly counter-clockwise. Press and keep on **Start for 5 seconds** and then check that the pressure at the input of the cell (read through the SP-1 with the software) is less than 0.6 bar (it should be between 0.5 and 0.6).

4. The purge valve opens for a half-second initially and then every three seconds to expel remaining hydrogen and water vapor.

5. Check that shortly after the introduction of hydrogen into the cell, the electrical energy starts to be generated. Current (SW1-A), voltage (SW1-V), and generated electrical power can be measured (SW-1).

6. The output power demand can be varied by changing the load value, and to a lesser extent the flow rate and inlet pressure by adjusting the flowmeter valve. It is necessary to arrange to have a flow of hydrogen giving a pressure lower than 1 bar, while being high enough to be read by the sensor.

4 Report

A plant located near a methane steam reforming site decides to take advantage of it to fuel part of its installation with fuel cells.

Your company produces proton exchange membrane fuel cells, and you are contacted by this factory. You must provide them with the characteristics of your product.

1. From the notions of thermodynamic operation of the stack given in the theoretical part, express the theoretical maximum power provided by a cell powered with a mass flow of H_2 of 1kg/h. Same question with a volume flow of 1 Nm^3/h.

Note: Standardized unit Nm^3 corresponds to a standard volume measurement at a pressure of 1 bar and a temperature of 0 ^{o}C.

2. Give the expression of the efficiency of the cell. Express the efficiency with parameters that can be directly measured or are tabulated.

3. Calculate the efficiency of the cell under these conditions. It can be one specific value, or an average/median value, a plot with the efficiency as a function of a parameter… The important is to justify your choice.

4. Plot the voltage curve as a function of the output current of the cell (V-I curve). Take values across the range of accessible current.

5. Determine three distinct regions on this curve and assign the predominant kinetic effect in each of these regions. What should be the value of the voltage at zero current?

6. Draw the P-I curve (power - intensity) of the cell.

7. Considering the P-I curve obtained, what using conditions would you recommend to the company?

8. The company tells you that it wants to generate 500W of electricity per fuel cell. How many cells will it need, assuming they work under the conditions set out in question 6? In reality, it will require additional cells. Why?

Additional remark: Students are expected to prepare for the laboratory session before attending. Preparing for the TP involves more than just a quick read-through. Students should take the time to understand how the devices they will be using operate (for example, learning about fuel cells), and answer the questions that can be addressed ahead of time (such as Q1 and Q2).