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Zaragoza

## Trabajo Fin de Grado

Estudio del efecto de CO<sub>2</sub> y temperatura en la eficiencia de un compresor electroquímico de hidrógeno

A study of the effect of CO<sub>2</sub> and temperature in the efficiency of an electrochemical hydrogen compressor

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## Abstract

Hydrogen is seen as the energy carrier for the future and is currently produced via steam reforming of natural gas for large scale production. Afterwards, contaminants have to be removed from the stream, as the time hydrogen is pressurized. Traditionally, these processes take place separately, but the Electrochemical Hydrogen Compressor (EHC) is appearing as a promising technique that combines both purification and pressurization.

In this work,  $\text{CO}_2$  is studied as main contaminant in the gas mixture obtained from steam methane reforming and water gas shift processes. After analyzing operating conditions of the compressor with pure  $\text{H}_2$ , the effect of the  $\text{H}_2$ - $\text{CO}_2$  mixture is explained in detail. Firstly, considering literature, different possible ways of polluting the catalyst are taken into account, from which Reverse Water Gas Shift (RWGS) is concluded to be the most influential one. Recovery methods are also evaluated, being air bleeding the most convenient because of its effectivity and velocity. For ending this part, different working conditions are imposed to the compressor in order to analyze its behavior. These experiments lead to conclude faster catalyst inhibition for lower  $\text{H}_2$  concentrations and lower voltages supplied.

It is also briefly explained the effect of temperature in the EHC behavior. For all inlet mixtures studied, an increase of temperature has a positive effect in the efficiency of the compressor. The case of  $\text{CO}_2$  is studied separately, due to the fact that higher temperatures mean faster pollution of the catalyst, and consequently faster decreasing of the efficiency. In these experiments it is also analyzed the different permeation mechanisms of the contaminants across the membrane. For instance, helium mechanism consists simply in permeating across the membrane, whereas  $\text{CO}_2$  crossover is due to its solubility in water.

Finally, some changes are implemented to a previous Matlab<sup>®</sup> model, in order to obtain a validation for different temperatures. For doing so, mass transfer coefficient depending on temperature is implemented, as well as some parameters of the compressor are adjusted to fit better with the experimental results. The graphics obtained show a good validation of the model.

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# Chapter 1

## Introduction and aim of the work

World's use of energy is changing rapidly due to the need of using other sources of energy that will reduce the drawbacks provoked by fossil fuels. In this way, they are appearing new forms of energy to supply these traditional ones. One of those, the Hydrogen-based energy, is the one that will matter for the development of this work.

This last century, the incredible dependence on fossil fuels (mainly petroleum, natural gas and coal) is undeniable. For instance, in 2013 almost 80% of the energy used worldwide came from them.[1]. However, these sources of energy have important weaknesses. Their main one is the contribution to greenhouse effect by the production of CO<sub>2</sub>, due to the fact that fossil fuels are the main producers of this harmful gas.

Because of all these issues, nowadays it is clear the requirement of renewable energies, to reduce CO<sub>2</sub> emissions. In this way, new policies are being implemented by the governments. For instance, EU is supporting the programme "Horizon 2020", in which there are highlighted some priorities to be reached by 2020:

- Achieving an energy efficient Europe.
- Building a truly-pan European integrated market.
- Empowering consumers and achieving the highest level of safety and security.
- Extending Europe's leadership in energy technology and innovation.
- Strengthening the external dimension of the EU energy market.

Figure 1 illustrates recent evolution of the renewable energies used in Europe, showing an increasing trend. Moreover, the share of energy from renewable sources in gross final energy consumption has almost doubled in the last years, from around 8.5 % in 2004 up to 17.0 % in 2016. [2].

As it is known, renewable energies are highly dependent on season, moment of the day or other conditions that are uncontrollable for humans. Because of that, if we want to be completely dependent on renewable energy, it is necessary to find the solution to store the energy for when these resources are not enough to cover the all energy demands.

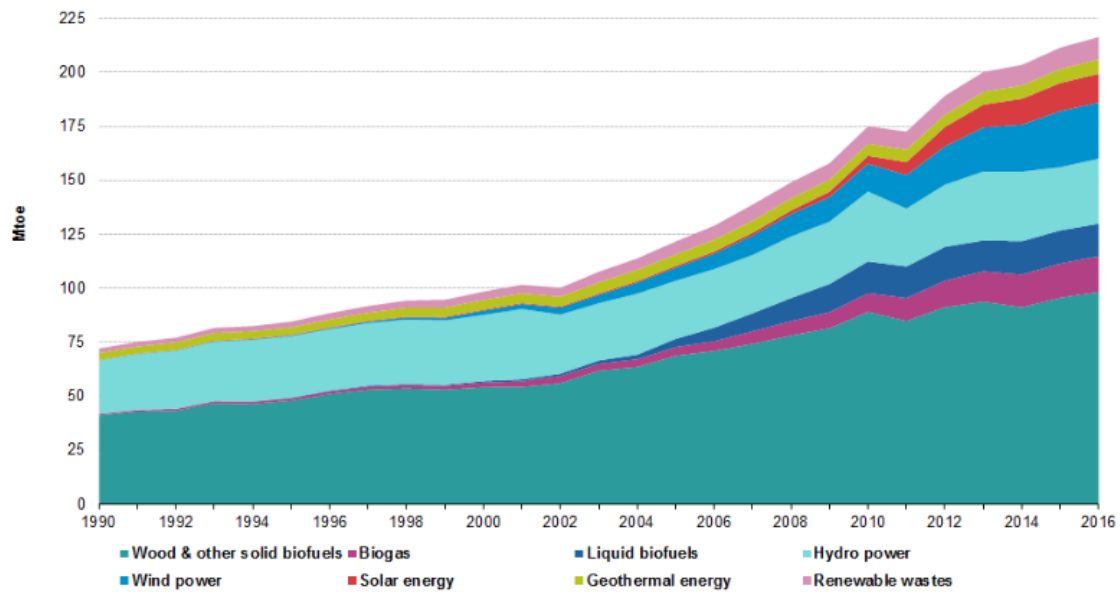


Figure 1. Gross inland consumption of renewables, EU-28, 1990-2016 (Mtoe).

Traditionally, water pumping has been the most extended way of energy storage, due to its simplicity, but also air compressed or heat storage were used. However, this method has reached a limit, and in order to go further other techniques were developed. [3].

Last decades, the use of batteries has exponentially increased. Many companies are focusing their efforts to investigate and produce new kinds, such as Lithium-ion batteries. These ones have been greatly developed, but they still have the same problems as ancient batteries, such as fast discharge and not very high capacities.

In the last years, this clean energy demand has arrived even to the field of cars and ways of transport. Important automotive companies are developing new car models based in hybrid, electrical or hydrogen energy, so that reducing both the noise and the pollution generated.

In this scenario, hydrogen is finding his place, as a non-polluting source of energy.

## 1.1 Conventional technologies

Before analyzing the EHC it is given some information about the hydrogen and the plants used for its production, purification and compression.

### 1.1.1 Hydrogen

Hydrogen is a fuel with a very high specific energy density and equal to 120MJ/kg. It is a zero emission fuel and the main product from its reaction with oxygen is water.

It can be directly burned in combustion engines or it can also be converted in Fuel Cell producing electricity, as thermodynamic limits and pollutants as  $\text{NO}_x$  are avoided. Another advantage is the use of  $\text{H}_2$  in an electrical motor, which efficiency is higher

than traditional internal combustion engines. The efficiency of an electrical motor is around 90%, which combined with the efficiency of the Fuel Cell (around 60%) it is obtained an overall efficiency of 54%, contrary to the 25% yield that internal combustion engines have. [4]

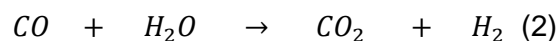
It is important to clarify in this point that hydrogen is not an energy source itself but an energy vector, and nowadays it can be produced by many different ways: gasification, electrolysis of water, using nuclear energy or reforming of natural gas.

Among all these possibilities, reforming of natural gas is the most used process because of its high efficiency. This makes that around 95% of world's hydrogen production comes from this process, while electrolysis account for about 4%. [4].

This last process is one of the most promising one since it can be coupled with renewable technologies such as solar or wind power. Furthermore, this process is a small-scale system that can be placed near the users in order to decrease transport and storage costs. However, its main drawback is the efficiency, with overall values of the process of 15% when combining electrolysis with wind or solar power.

Although it is trying to be developed this technique as very environmentally friendly, methane reforming is nowadays the most used. Combined with Water Gas Shift reaction, it is the main way of H<sub>2</sub> production, due to the feasibility to take natural gas for make this process going on, with an efficiency around 70%, value considerably higher than for the case of electrolysis. However, it is a high-scale process that has to be made in specific plants, with the disadvantages of H<sub>2</sub> transport and storage.

However, it is not only H<sub>2</sub> formed, but also CO<sub>2</sub> and CO according to the reactions shown in equations (1) and (2). This leads to problems in future process, due to the presence of these compounds as contaminants.



In the first reaction, most of the H<sub>2</sub> is produced. This reaction is an endothermic catalytic reaction, with high temperatures that can go from 500°C to 800°C, and 20 bar of pressure. Catalyst used can change depending on the conditions established. For instance, Ni and Rh on La<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub>–ZrO<sub>2</sub> are used for 500°C because it was found that they were very active and coke resistance.[5].

The reaction written in equation (2) is Water Gas Shift Reaction. From this one, carbon monoxide is converted in carbon dioxide and more hydrogen is produced. It is an exothermic reaction, and fixed bed reactors are used. Temperatures decreased until values around 200-300°C, in order to obtain better conversions of CO.

### 1.1.2 Conventional storage and purification

The hydrogen produced can be stored in many different ways. The volume specific energy of hydrogen is always low and represents one of the biggest problems of dealing with hydrogen as energy vector. That is why, in order to maximize its volume



specific energy, the storage in all the different physical states of hydrogen is experimented.

There are three main types of storage varying the pressure and temperature of hydrogen. The first one uses gaseous hydrogen at ambient temperature and pressures around 350-700 bar, where the vessel is made of aluminum wound in carbon fiber compound. The second type is using liquid hydrogen, which is kept at temperatures around 20-30 K and pressures of 6 bar. These vessels are made of stainless steel surrounded by a vacuum insulator and an outer metallic vacuum jacket. The last possibility is absorption of hydrogen into solid state compounds, like metal hydrides, but this method is still in early development.

Moving into purification of hydrogen, Pressure Swing Adsorption (PSA) appears as the main method developed. It consists in increasing the pressure of the gas mixture in a chamber, where there is an adsorbent that selectively holds the contaminants that should be removed. While this happens, the hydrogen is allowed to escape from the upper part, with very low concentrations of contaminants. The regeneration of the adsorbent takes place when reducing the pressure, allowing desorption of the contaminant. Because of this, it is necessary to have several chambers connected in parallel, to make this process continuous.

Another important point to consider is hydrogen pressurization. The main compressors available in the market are reciprocating mechanical compressors. The reciprocating compressor has a very low efficiency compared to the rotating. Anyway for large scale, it is very suitable, but when working in low power applications it shows a lower efficiency.

The Electrochemical Hydrogen Compressor can find a place in this scenario, combining both hydrogen storage and purification, as using a small-scale structure instead of traditional ones. The compressor tested is provided by High Yield Energy Technologies (HyET®) Group. The compressor itself is poorly studied in literature, so that makes more important its study to get a better understanding of its behaviour.

### **1.2 Work structure**

This work is mainly focused on the study of the CO<sub>2</sub> problem, as main contaminant of steam methane reforming. The first task is to try to understand the influence of a mixture H<sub>2</sub>-CO<sub>2</sub> on the performances of the electrochemical compressor. Later on, the compressor is tested under the same mixture and different conditions of voltage and H<sub>2</sub> concentration, to see the effect of these variables in the results.

Later on, experiments changing the temperature are performed. The main task is to study the influence of this variable on the polarization curves for an inlet of pure H<sub>2</sub>, a mixture of hydrogen and an inert gas for the compressor, such as N<sub>2</sub>, and finally a mixture H<sub>2</sub>-CO<sub>2</sub>. The last experiment is performed for a better understanding of the effect of temperature on catalyst inhibition. Finally, it is checked the mechanism of permeation used by CO<sub>2</sub> and He to go through the membrane.

The thesis has been structured as follows:

Chapter one contains a brief introduction of the hydrogen as energy source and possible applications of the electrochemical hydrogen compressor in comparison with the available solutions for hydrogen separation. It is also included the main scheme followed.

Chapter two, is a description of the electrochemical hydrogen compressor's working principle.

The third chapter describes the experimental setup. It shows the pipes and instruments diagram (P&ID) with an explanation of all its components. The experimental procedure is detailed for the different experiments performing, establishing the parameters varied and the range in which they are changed.

The fourth chapter reports the data and results obtained for the different experiments performed. Explanations and comments of the physical phenomena are reported according to literature.

The fifth chapter implements a model in Matlab<sup>®</sup>. Considering a previous model developed, it has been added the mass transfer coefficient in the anode side in order to take into account the mass transfer limitation.

Chapter 6 contains the conclusions and the main considerations of all the performed. There are also described future recommendations for continuing the research of this study.

# Chapter 2

## Electrochemical Hydrogen Compressor

Electrochemical Hydrogen Compression (EHC) is a known technology since the precursors of the first Nafion® membrane was developed in 1960s to be used in fuel cell devices because of increasing use of hydrogen as source of energy, the EHC is also getting more attention from industries and researches, that see in this technology a very promising way to substitute mechanical compression.[6].

In the following chapter it is firstly analyzed briefly the actual situation of hydrogen as a source of energy. An overview of the technology has been described in order to indicate its strengths and weaknesses, for a completely understanding of the device.

### 2.1 State of art of EHC

In literature there are many works about PEMFC but there is still not much material about the EHC. It is here shortly reported some of the researches related to the analysis that will be performed in this work.

First of all it is important to notice that the EHC could have many applications such as recirculation of hydrogen from the fuel cell exhaust as reported by Barbiret al. [7] or it can be used to separate the hydrogen stored in the methane pipelines as reported by Ibeh et al. [8]

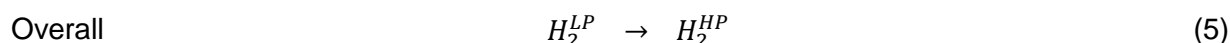
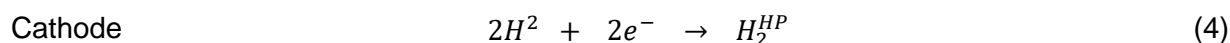
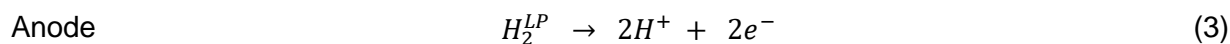
Ströbelet. al.[9] shown the possibility to reach high cathode pressures and analyzed the back diffusion loss. Dale et. al.[10] compared the EHC with respect to a traditional compressor at different outlet pressure for storage purpose. Nguyen et al. [11] characterized the EHC performances in different operating conditions, highlighting low performances at low inlet hydrogen concentrations. The influence of CO<sub>2</sub> was poorly analyzed and it has been shown in some works but mostly together with the CO, analyzing also possible recovery methods.[12].

The present work can find a place in the literature increasing the available data to characterize the negative effect of a H<sub>2</sub>-CO<sub>2</sub> mixture on the EHC performance. Temperature dependence is also briefly studied in literature. In the end, it is considered a Matlab® model to compare the experimental results obtained with the theoretical ones.

### 2.2 EHC Technology introduction

The Electrochemical Hydrogen Compressor is a device that allows purification and compression of hydrogen following an electrochemical reaction. Its structure is similar to a Fuel Cell: there is

a membrane, such as Nafion® membrane, like in this work, that separates the compressor in two electrodes, anode and cathode. At the anode takes place the oxidation of hydrogen molecule in protons and electrons as described in equation (3). The protons go through the membrane while the electrons follow an external electrical circuit due to the application of the total voltage. For finishing the process, protons and electrons are recombined again in the cathode, where hydrogen molecule is formed but at higher pressure, according to equation (4).



The overall result of the process, as said, is the compression of hydrogen, from low pressure to high pressure side. Furthermore, the hydrogen obtained in the cathode outlet is purified from other contaminant gases that could be present at the anode inlet, thanks to the selectivity of the membrane that allows only the passage of protons.

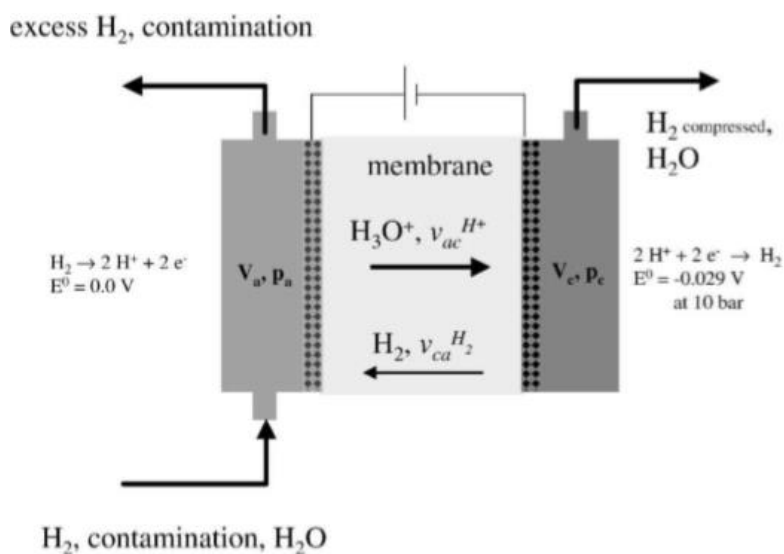


Figure 2. Electrochemical Hydrogen Compressor

A scheme of the EHC is shown in Figure 2. The black points that are at both sides of the membrane represent the Catalyst Layer (CL), that connects the electrodes and the membrane. The gas stream enters to the anode, where the hydrogen is oxidized, and it is clearly seen the path followed by the protons and the electrons for reaching the cathode. There, it takes place the reverse reaction, forming again the hydrogen, but pressurized. The overall potential necessary to perform the reactions is applied in the external circuit represented on the top of the figure.

### 2.2.1 Advantages and disadvantages of EHC

The EHC has many advantages comparing to traditional technologies. They have been highlighted:

- High purities obtained, due to the high selectivity of the Nafion® membrane.
- No movable parts, which leads to less losses due to friction, and less required maintenance.
- Also because of the lack of movable parts, there is no noise produced, making this technology suitable for applications where acoustical emissions are a constraint.
- Use of single units connected electrically in parallel and in series for large-scale operation. With their high efficiencies, can replace traditional hydrogen purification techniques even for industrial applications.

Unfortunately, the EHC has some drawbacks that are similar to the disadvantages of the Fuel Cells, that still needs some improvement to be implemented in the market.

- The high cost of the materials used, especially the cost of the platinum as catalyst. It is the responsible of making the process going on with good efficiencies, and also it is good for stabilizing its functioning performances.
- Related to the previous one, the catalyst is easily inhibited. CO is the compound that causes this phenomena, but also CO<sub>2</sub> can formed carbon monoxide and provoke catalyst pollution.
- Adequate performance at high temperatures is very difficult to achieve. Even though the performance improves, perfect humidification is quite complex to achieve, leading easily to dehydration issues.

### 2.2.2 Nernst potential and overpotentials

The theoretical voltage necessary to have the overall reaction could be computed by the Nernst potential at equilibrium, as shown in equation (6). [13]

$$E_r = E_0 + \frac{RT}{n_e F} \ln \frac{P_c}{P_a} \quad (6)$$

Where  $E_0$  is the potential required in standard conditions, and  $P_c$  and  $P_a$  are the hydrogen partial pressures in the cathode and anode respectively. This is only the theoretical potential that is needed to pump the hydrogen, and it is only valid theoretically at equilibrium. The real potential is the Nernst potential plus the contributions of all the losses presented in non-equilibrium conditions. It has to be also considered the proton resistance across the membrane.

The main equation to represent the non-equilibrium characteristics of the EHC is the Butler-Volmer represented in equation (7), where  $i_0$  is the exchange current density and  $\alpha_{Rd}$  and  $\alpha_{Ox}$  are the transfer coefficients for both reduction and oxidation. Their typical value for reactions on a metallic surface is 0.5.

$$i = i_0 \left( e^{\frac{-\alpha_{Rd} F(E-E_r)}{RT}} - e^{\frac{-\alpha_{x} F(E-E_r)}{RT}} \right) \quad (7)$$

$$i_0 = i_0^{ref} a_c L_C \left( \frac{P_r}{P_r^{ref}} \right)^\gamma \exp \left[ -\frac{E_a}{RT} \left( 1 - \frac{T}{T_{ref}} \right) \right] \quad (8)$$

The exchange current density  $i_0$ , has been calculated as written in equation (8), where  $i_0^{ref}$  refers to reference exchange current density per unit catalyst surface area,  $a_c$  is catalyst specific area,  $L_C$  is catalyst loading,  $P_r^{ref}$  is the reference pressure of the component considered,  $\gamma$  is the pressure dependency coefficient (always between 0.5 and 1), and  $E_a$  is the activation energy.

Furthermore, the total voltage applied to the compressor  $E$  is always bigger than the Nernst potential, since there are some losses which have to be taken into account. The total voltage is described in equation (9):

$$E = E_r + E_{act} + E_{ohmic} + E_{conc} \quad (9)$$

$E_{act}$  refers to the activation polarization losses. Some of the supplied potential is necessary to make the electrochemical reaction on going. These losses are noticeable only when working at low voltage. In equation (10) it is shown how to calculate this losses in the anode side. For the cathode is the same, but the transfer coefficient it would be related to the cathode side.

$$E_{act} = \frac{RT}{2\alpha_a F} \ln \left( \frac{i}{i_0} \right) \quad (10)$$

$E_{ohmic}$  are the ohmic losses which describe the resistance that the membrane offers to the flow of ions and the resistance of the electrical circuit to the pass of electrons. The equation can be written as in equation (11), where the resistance of the membrane is expressed as function of the thickness of the membrane  $\delta$  and its proton conductivity  $\sigma$ .

$$E_{ohmic} = \frac{\delta}{\sigma} i \quad (11)$$

Related to mass transfer limitation it appear the concentration polarization losses  $E_{conc}$ . This phenomena is presented in the Gas Diffusion Layer (GDL) and in the Catalyst Layer (CL), as can be clearly seen in Figure 3. The hydrogen flows in the anode and, at certain point, it passes through the GDL when mass transfer limitation problems start. Until the gases don't reach the electrolyte, this phenomena will happen. However, it will be in a different way in GDL and CL, due to different characteristics (pore radius, presence of catalyst in CL...).

It is also known that the main mechanism of mass transfer is diffusion. As regards the flow in the channels it has a non-negligible velocity and a convective mass transfer takes place, but not in a considerable way as it happens with diffusion. Equation (12) describes the hydrogen flux taking into account the change in concentration between the bulk and the surface of the anode side due to mass transfer limitation.

$$N_{H_2} = Ah_m(C_0 - C_s) \quad (12)$$

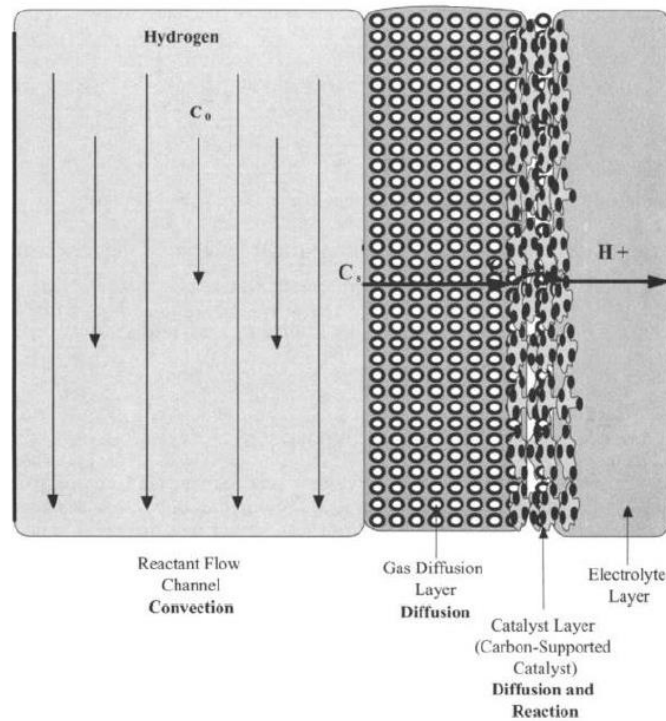


Figure 3. Mass transport phenomena in an electrode

## 2.3 Real operating conditions

Once considered the main contributions which affect the EHC behavior, it is worth to mention other possible phenomena that can have an influence on its efficiency. In this way, it is possible to get an overall overview.

### 2.3.1 Diffusivity

This mechanism has been mentioned before as the main way of mass transport phenomena. As expressed in equation (12),  $h_m$  is referred to mass transfer coefficient. For calculating the mass transfer coefficient, the binary diffusivity should be known. One of the most accredited ways for its calculation is through the Fuller equation, where the diffusion coefficient is calculated depending on temperature and pressure for different binary mixtures of gases. This diffusivity can be corrected with the values of porosity ( $\varepsilon$ ) and tortuosity ( $\tau$ ), taking into account the friction due to the porous matrix of the GDL. These relations are shown in equations (13) and (14).

$$D_{i,j} = \frac{0.00143T^{1.75}}{\frac{P}{100000}MM_{AB}^{\frac{1}{2}}\left(K_i^{\frac{1}{3}}+K_j^{\frac{1}{3}}\right)^2} \quad (13)$$

$$D_{i,j}^{eff} = \frac{\varepsilon}{\tau}D_{i,j} \quad (14)$$

Many other formulations are available, as Knudsen diffusivity. In the end it is important to highlight that the choice of the diffusivity can have a relevant impact on the model, and should be chosen according to experimental results.

### 2.3.2 Back diffusion

Another discrepancy from the ideal case is due to this phenomena, which happens by a difference in the partial pressure of hydrogen between electrodes. It is an important characteristic of the EHC to study, since one of the objectives of this device consist in obtaining a more pressurized current. This diffusion rate can be expressed by Fick's Law as in equation (15).

$$N_i = -D_i \frac{\Delta C_i}{\Delta x} \quad (15)$$

This diffusion coefficient can be calculated by measuring the electrical compensation current, which is the necessary value to maintain the pressure difference without having hydrogen flow.

Back diffusion is an important parameter, since it limits the maximum pressure difference. Furthermore, it decreases the efficiency of the compressor and for this reason it should be lowered, for example, by increasing the membrane thickness.

### 2.3.3 Water management

This is an important aspect for the EHC since the proton conductivity of the membrane is determined by its water content. The membrane has to be perfectly hydrated, so that means no dehydration or water clogging should appear.

Contrary to Fuel Cell, water is not produced, so the only water inside the compressor is the one that enters with the inlet stream. Water injection can be done in different ways such as vapor injection or direct liquid water injection.

Water can go across the membrane in many different ways, which are briefly explained: electro-osmotic drag, diffusion and hydraulic permeation. The first one is provoked by proton transfer, which carries along water molecules while flowing through the membrane. Diffusion happens, as in case studied in back diffusion, due to a concentration gradient between electrodes [14].

There is a high risk of dehydration in the anode, but mostly in the cathode, where the amount of water is related with the flow of water that passes due to the two mechanisms previously mentioned. For achieving a better hydration in the membrane, it is a good solution to push back this water that reaches the cathode by increasing its pressure, causing a flow of hydrogen to the anode side. This phenomena is the called hydraulic permeation.

Ideally, the sum of the three mechanisms should be zero, getting a perfect hydration in the membrane. It is also important to mention that these processes are under research in order to have a better and more complete understanding of the problem.



### 2.3.4 Proton conductivity

The proton conductivity of the membrane is one of the most important characteristic of the EHC and it should be carefully evaluated. It was already said that it is a function of the temperature and water content.

Nafion<sup>®</sup> membranes are polytetrafluorethylene membrane (PTFE). Its structure has a sulfonic acid group ( $\text{SO}_3\text{H}^+$ ), which are highly hydrophilic. This makes the membrane become hydrated when feeding the mixture of gases humidified. When hydrogen reaches the ducts, they are mixed in the surface of  $\text{SO}_3^-$ , forming hydronium that is able to pass through the membrane.

### 2.3.5 Contaminant crossover

This aspect is related with the importance of the EHC in purifying hydrogen from pollutants. The membrane allows only the passage of protons and water. However the selectivity is not infinite, and small percentages of contaminants can reach the cathode side. For defining this crossover, it has been analyzed the hydrogen purity at the outlet stream.

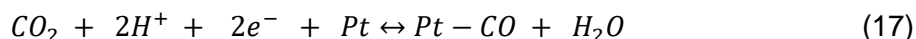
Purity is defined as the percentage of hydrogen presented in the outlet of the compressor related to the total flow measured. The crossover of contaminant will definitely decrease the purity obtained.

### 2.3.6 Carbon dioxide poisoning

It is well-known from literature regarding the Fuel Cells that the  $\text{CO}_2$  poisons the catalyst reducing its performance when it is fed with hydrogen. However, the reasons and description of this phenomena are still controversial. Despite this, they mostly agree that the contaminant is not the  $\text{CO}_2$  itself, but the CO formed because of different reactions which involve the carbon dioxide.

The main problem when dealing with CO is that, contrary to the case of  $\text{CO}_2$ , carbon monoxide strongly adsorbs in the catalyst, decreasing the active surface area. Because of that, the efficiency of the compressor decreases substantially.

Then, it is important to study the  $\text{CO}_2$  poisoning in order to understand how the CO is formed and how it is possible to regenerate the catalyst. As explained from many authors, CO can be formed mainly because of two reactions: Reverse Water Gas Shift (RWGS), reported in equation (16), and the electrochemical reduction reaction, shown in equation (17). [15] [16].

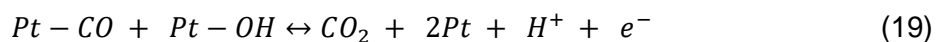
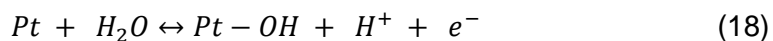


Most of the papers state that RWGS is the most probable reaction. This is a slightly endothermic reaction, so that means is less likely to happen at lower temperatures. Because of that, even though considerable amounts of  $\text{H}_2$  and  $\text{CO}_2$  are fed to the compressor, few ppm of CO are formed. Because of this pollution, it is also important to study how the efficiency can be

recovered. Many methods are proposed from literature, but the most important one is to perform air bleeding, where it is sent a small amount of air to the anode inlet, so that CO adsorbed and oxygen will react, forming the CO<sub>2</sub> that is easily removed.[17].

It is also possible to feed a normal mixture of gases and the catalyst is recovered too, although more time is spent. The mechanism that makes this possible to happen is the desorption. However, because of strong adsorption of CO and the low temperatures used, desorption requires long time in order to recover completely the catalyst.

Other method proposed was the reaction of hydroxyl ions of water with the CO adsorbed to form CO<sub>2</sub>, according to equations (18) and (19).[18].



# Chapter 3

## Materials and methods

In this chapter the instrumentations, the setup and the methodology applied to characterize and test the Electrochemical Hydrogen Compressor are described. Firstly, it is important to analyze each of the components in detail, paying special attention to the EHC as main component of the setup. After that, it is described the experiments that are following explained and analyzed to completely understand the behavior of the compressor. An appropriate setup construction is of high importance in order to assure a correct functioning when performing the experiments.

### 3.1 Electrochemical Hydrogen Compressor technical characteristics

The Electrochemical Hydrogen Compressor was manufactured by HyET<sup>®</sup> Group. The compressor is a single cell composed of a 50 cm<sup>2</sup> area Nafion<sup>®</sup> membrane with an equivalent resistance, when feeding pure hydrogen and a perfect humidification, equal to 6.2m $\Omega$ . The anode channel is in a flow-through configuration while at the cathode side it is not present an inlet flow but only an outlet flow regulated at the desired pressure. All the channels are made of steel and separated from the membrane by a Gas Diffusion Layer (GDL).

The catalyst is made of Platinum and it is deposited on the Nafion<sup>®</sup> membrane forming the Membrane Electrode Assembly (MEA). The catalyst loading is 0.46mgPt/cm<sup>2</sup> which is, according to the company, lower compare to values from fuel cells. Also specific area is provided, with a value of 800cm<sup>2</sup>/mg. Unfortunately, most of the internal structure of the EHC was not given because of the confidentiality agreement taken with HyET<sup>®</sup> Group according to the European project of which this work is taking part. The remaining data known about the compressor are summarized in Table 1.

Table 1. Electrochemical Hydrogen Compressor Data from HyET<sup>®</sup> Group

Parameters	Value	Unit
<b><math>I_{o,ref}</math> = Reference exchange current density</b>	0.103	microA/cm <sup>2</sup> @ 25°C 1 atm
<b><math>\gamma</math> = Pressure dependency coefficient</b>	0.77	-
<b>Activation energy anode</b>	75	kJ/mol
<b><math>I_{max}</math> = Maximum current</b>	60	A
<b><math>V_{max}</math> = Maximum voltage</b>	0.9	V

A general scheme of the EHC is shown in Figure 4. The compressor which has been studied, probably it has a different configuration, since not all the characteristics were provided, but it has been depicted in order to give an approximate overview of the system.

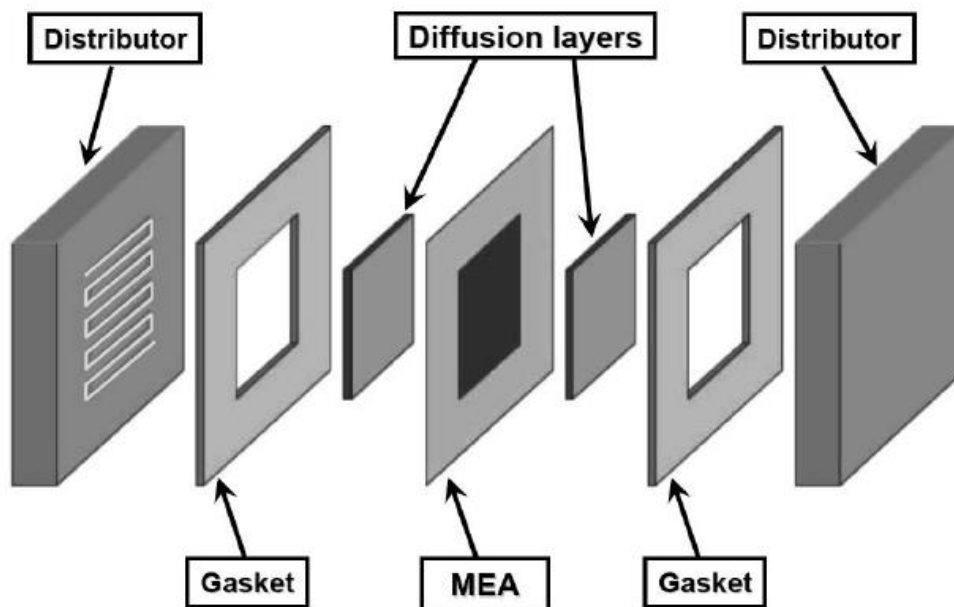


Figure 4. Components of EHC

### 3.2 Experimental setup

In Figure 5 it is described the proposed setup for the experimental tests performed in this work. Depending on the type of experiment performed, the gases could be sent to the micro GC or to the flow meter depending if the composition of the cathode side need to be studied.

The gases considered are methane, nitrogen, hydrogen, helium and carbon dioxide. The nitrogen can be supplied before the anode, as a contaminant fed with the  $H_2$  to analyze its influence in the behavior of the compressor, or as a mixture gas sent directly to the cathode outlet stream, for the analysis with the Gas Chromatograph (GC). The flows of this gases are governed by an electronic valve which receives as input the flow measured by EL-Flow Prestige mass flow controller from Bronkhorst which has a standart accuracy of  $\pm 0.5\% Rd + 0.1\% FS$  and a maximum volume flow rate of 10l/min for  $H_2$  and  $N_2$ , and 2l/min for  $CO_2$  and  $CH_4$ . The mass flow controllers are calibrated with a linear interpolation of the theoretical values given by the flow controller respect to the values measured with the flowmeter. This regression always give values of  $R^2$  equal to 1, proving the accuracy of the calibration.



From the bottle to the compressor, two tracing lines ThermocoaxlsopadGmbH IS-SP, have been used with a length equal to 1.5m for the first one and 0.5m for the second. They require respectively a power consumption of 220 W and 50 W, and a maximum reachable temperature of 450°C controlled by a laboratory regulator series KM-RX1003 of Mohr & Co. with a maximum temperature of 1200°C and a maximum power supply of 2300W. The temperature imposed in these lines is again slightly higher than the one in the bottle, to avoid any condensation.

Air is also used for recovering the activity of the catalyst. It is sent to the compressor through an external line connected directly to the inlet of the compressor. In this case, it is used a Smart Mass Flow 5850S as mass flow controller. It is provided by Brooks® with a standard accuracy of  $\pm 1\% \text{ Rd} + 0.2\% \text{ FS}$  and a maximum volume flow rate of 2 l/min.

The outlet of the cathode side is sent to a condenser, where it is cooled with ice in order to remove the water presented in the gases, avoiding condensation in both the flow meter and in particular in the micro GC, which could not stand liquid water.

At the condenser, the pressure is regulated by a manual back pressure regulator produced by Parker. The pressure is detected using a digital pressure gauge, from EmvoTechniek, which has a ceramic sensor that can measure from 0 to 16 bar with an accuracy equal to  $\pm 0.25\% \text{ FSO BFLS}$ . This pressure is usually kept at 1.3bar, which is the pressure needed by the micro GC to analyze the samples.

Thermocouples have been used to monitor the temperature of the compressor and the bottle. All of them are type K, with an accuracy of  $\pm 2.2^\circ\text{C}$  or  $\pm 0.75\% \text{ RD}$ .

The compressor temperature is controlled by a forced cooling fluid which flows inside the EHC. The fluid is first cooled by the Lauda MC250 till  $15^\circ\text{C}$  and after heated by C6 CP Lauda thermostats which is able to reach the required temperature with a higher stability and an accuracy of  $\pm 0.05^\circ\text{C}$ .

The power is supplied by the SM 30-100D from Elektronikawhich could range from 0 to 30V and from 0 to 100A with an accuracy of  $\pm 0.5\%$  in the measure of the voltage and current in potentiostatic mode.

All the values of the different parameters (temperature, pressure, voltage, current and power supply) are monitored and recorded via Intouch software of Wonderware. The data is collected by an Input/Output box that is connected to an automation controller also called PLC (Programmable Logic Controller) which permits the sharing of data with the computer via Ethernet cable. The voltage imposed sends the value of the setpoint to the power supply which, with a control loop, reaches the imposed value. The system shows the value of voltage provided by the compressor, and the values of the different variables studied.

The  $\text{H}_2$  flow rate through the membrane was measured with a manual volume flow meter, Horiba VP3, which covers a range between 20ml/min and 1000ml/min.

### 3.3 Micro Gas Chromatograph (GC)

This device has been studied in depth due to its importance in analyzing the results obtained from the compressor. It is used the 490 Micro-GC from Agilent Technologies with detection limits equal to 10 ppm for Micropacked columns (Carboxene) and 2 ppm for PLOT columns (Molsieve 5A) which are the first and second column used in this GC.

Each column corresponds to one channel read by screen. The first one is 1m Cox column with heated injector using Helium and a method with 100°C of injection and column temperature, 100ms of injection time, 8s of backflush time, initial pressure equal to 110kPa, sampling frequency of 100Hz and a run time of 180s is used. The second column is 10m MS5A heated injector with Argon and uses a different method with 80°C of injection and column temperature, 100ms of injection time, 10s of backflush time, initial pressure 170kPa, sampling frequency of 100Hz and a run time of 180s.

All parameters are founded from literature, but not the backflush time. It consists in the time the carrier gas is inverted in the column to clean it in order to remove the gases which could mainly make the micro GC dirty: CH<sub>4</sub> and CO<sub>2</sub>. What it is done is to create many methods with different backflush time and it is chosen the value that gives the highest peak.

#### 3.3.1 Calibration

In order to be able to measure the correct volume flow rates, a calibration of the micro GC is necessary. For doing so, it is determined the Relative Response Factor (RRF) for the different gases used. This task is performed sending different concentrations of the mixture of gases considered: for calculating the RRF of N<sub>2</sub>, helium is used as carrier gas, but for the rest of the gases it is used N<sub>2</sub>. Knowing the peaks of the gases obtained and the fluxes sent, it is possible to determine the RRF as expressed in equation (20):

$$\dot{n}_i = \frac{Area_i}{Area_{carrier}} \cdot \frac{1}{RRF_i} \cdot \dot{n}_{carrier} \quad (20)$$

The results obtained are reported in Table 2, where it is shown the RRF obtained for the different contaminants including the error and uncertainty of the measurements. With the micro GC has been checked that the value of RRF doesn't have an important dependence on the concentration of the gas sent, so it is considered as a constant value. This doesn't happen for the case of H<sub>2</sub>, where the RRF changes a lot. So it has been decided to measure the flow of H<sub>2</sub> directly with the value of current, once known its value and the relationship between this two parameters is directly proportional and expressed by Faraday's Law.

Table 2. RRF, errors and uncertainty for the gases used.

Gas	RRF <sub>i</sub>	Average measurement deviation (%)	Relative standard deviation RRF (%)	Average absolute error (± %)
CO <sub>2</sub>	1.19	1.36	1.5	1.02
N <sub>2</sub>	0.48	0.17	1.38	1.03
CH <sub>4</sub>	0.81	0.73	1.24	1.04

### 3.4 Experimental procedure

The aim of this work is to explain the negative effect of CO<sub>2</sub>-H<sub>2</sub> mixture on the performances of the EHC. Moreover a second interesting task is to study the influence of temperature in presence of CO<sub>2</sub> problem and when feeding inert gases with H<sub>2</sub>.

The first part consists in understanding the behavior of the compressor with pure H<sub>2</sub> for comparing later this data with the case of using CO<sub>2</sub> as contaminant. After verifying the negative effect of CO<sub>2</sub> in the performance of the compressor, it has been studied the reason of this issues and a possible solution in order to recover it efficiently. Experiments have been performed changing the concentration of H<sub>2</sub> and the voltage supplied to the compressor, to study how the CO<sub>2</sub> could affect the performances of the compressor.

The next step was to analyze the way in which temperature is affecting the current and the hydrogen permeation through the membrane. Firstly it is analyzed the case of pure H<sub>2</sub> and later on a mixture of H<sub>2</sub> with a contaminant different to CO<sub>2</sub>, that work as inert gas. After this, it was explained CO<sub>2</sub> problem with the temperature when inhibiting the catalyst.

#### 3.4.1 Parameters and experiments

The tests are performed varying different variables. The main ones can be explained following:

- Hydrogen concentration: varying from 30% to 80%.
- Contaminant: CO<sub>2</sub> mainly, but it is also used N<sub>2</sub> or CH<sub>4</sub> in particular cases.
- Temperature: from 19°C to 30°C.

This range of used temperature is because, for keeping the perfect hydration, it is necessary to get very similar temperatures in the bottle and in the compressor. By heating a glass bottle with the heating plate used, is possible to achieve values of temperature of 130°C with a relevant gradient of temperatures between the top and bottom part of the bottle which could explode. Because of that, it has been chosen to work with a maximum temperature of 30°C.

It is used all the time the same total flow rate fed to the compressor with the same amount of water in the bottle. This is due to the fact that perfect hydration is very difficult to reach, and slightly changes in these parameters lead to a non-adequate hydration of the membrane. Once verified the membrane was perfectly humidified, these variables were kept constant.



As explained before, the micro GC was used to measure the concentration of the contaminants in the outlet stream. Depending on the time of the experiment, it was run a 7-runs sequence or an infinite sequence. The infinite one is used to see the trend of the flows of the different gases within a long period of time, while the shorter sequence has been used mainly for measuring the purity. In this case, the values considered are the 3 last ones, regarding the average value of them. It is of highly importance to check that the flows recorded are constant or with the expected trend.

The micro GC was cleaned periodically to avoid possible pollution of the samples sent to analyze, especially with CO<sub>2</sub> that remains inside with more ease. As checked, its calibration doesn't change so much, so there are neglected the small variations caused due to this.

The purity of the hydrogen has been checked for a better understanding of the CO<sub>2</sub> effect on the compressor.

Before data analysis, it has to be computed the uncertainty of the performed measurements to understand the validity and confidence interval of the results obtained. For the different devices described in the setup, their uncertainties are shown in Table 3:

Table 3. Instruments used and related uncertainties

Measured Variable	Manufacturer	Model	Range of measurement	Uncertainty (u)
H <sub>2</sub> anode inlet volume flow rate	Bronkhorst	EL-Flow Select	0-2000 ml/min	± (0.5 % RD + 0.1 % FS)
Contaminant anode inlet volume flow rate	Bronkhorst	EL-Flow Select	0-10000 ml/min	± (0.5 % RD + 0.1 % FS)
Cathode outlet volume flow rate	HoribaStec	VP-3	20-1000 ml/min	±0.5% RD
Voltage	Elektronika	SM 30-100D	0-30 V	± 0.5% RD
Current	Elektronika	SM 30-100D	0-100 A	± 0.5% RD
Cathode outlet concentrations	Agilent Technologies	Agilent 490 Micro Gas Chromatograph	10 ppm – 100%	± 2.3% RD

Furthermore, the repeatability of the measurements was not very easy to get, due to unstable behavior of the compressor and the difficulties encountered to reach stable operating conditions in the compressor. Despite that, the validity of the results was checked with the literature, getting expected results.

## Chapter 4

# Experimental results and data analysis

In this chapter the experimental results are described, in order to understand in depth the behavior of the Electrochemical Hydrogen Compressor (EHC). Firstly, it is explained the effect of the  $\text{CO}_2$ .  $\text{CO}_2$  and  $\text{H}_2$ , has been fed in the electrochemical hydrogen compressor while the applied voltage and the hydrogen concentration in the inlet stream were changed to see the influence on the catalyst pollution. By analyzing these experiments it is possible to study the purity obtained.

It is also highlighted the influence of temperature in the results. Considering the possible error of the experiments, it is possible to explain the range of validity of the obtained results.

### 4.1 Pure Hydrogen

Before starting analyzing the results of the  $\text{CO}_2$ , it is worth to highlight the behavior of the EHC in case of pure hydrogen. For this reason, the electrochemical compressor has been tested feeding 1 l/min of  $\text{H}_2$ . The polarization curve obtained is shown in Figure 6.

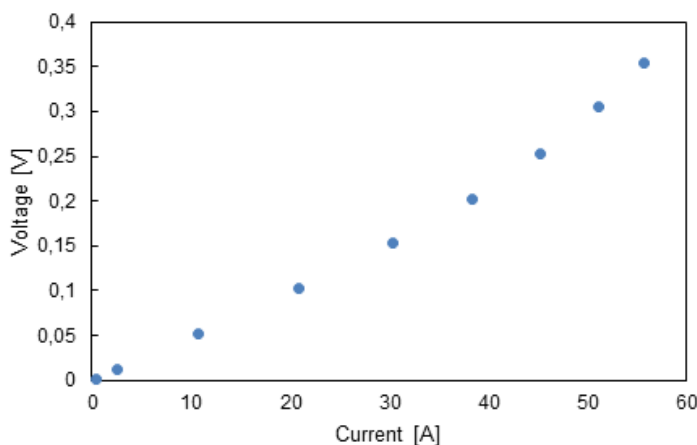


Figure 6. Complete polarization curve for 1 l/min  $\text{H}_2$ , 19°C

According to the results shown, two main considerations are made. Firstly, the fact that activation losses are not visible since there is only a linear trend in the range of low voltages. This means that the electrochemical reactions of oxidation and reduction of the hydrogen which take place on the catalyst are very fast. Because of this, at the beginning ohmic losses are dominant.

From Figure 6 it can also be calculated the resistance of the membrane. According to equation (21), current and voltage are directly proportional, so the slope of the straight line is equal to the resistance. Considering ohmic losses are predominant until 0.3 V, the value of resistance obtained was 5.2mΩ for room temperature.

Later on, the plot of the polarization curve for different flows of H<sub>2</sub> has been depicted. The temperature is kept constant at 19°C, and the imposed voltage is changed. The results are shown in Figure 7. It is possible to notice the difference between the polarization curves at different total volume flow rate is not really remarkable. It is good to highlight the increasing of the mass transfer limitation in case of lower volume flow rate for a voltage higher than 0.3 V. In the polarization curve from 0.3 V, the trend is not linear due to the concentration polarization losses which describe more in details the mass transfer limitation occurring in the electrochemical compressor. For this reason, the difference between the polarization curves for inlet different volumen flow rate of hydrogen become more important for higher voltages.

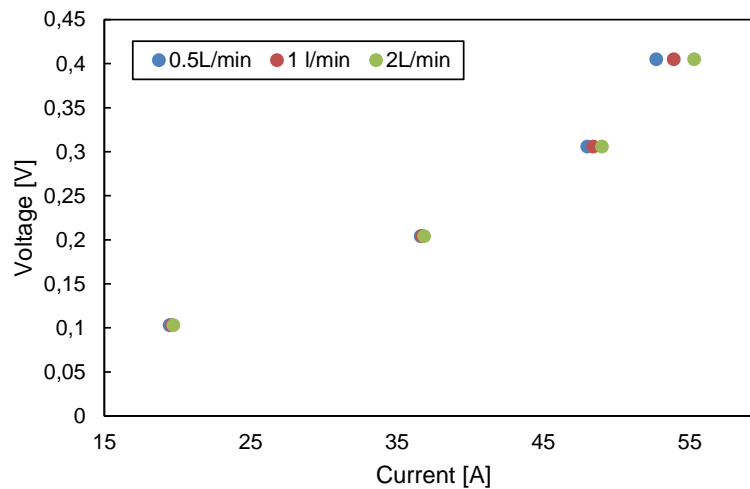


Figure 7. Polarization curves for pure H<sub>2</sub> changing the flow

In Figure 8 it has been plotted the current and the hydrogen volumen flow rate at the cathode side with the voltage. It is possible to notice the directly proportional relationship between the current of the compressor and the flow of H<sub>2</sub> that permeates into the membrane as stated in the Faraday equation(21).

$$\frac{\dot{V}}{I} = \frac{RT \cdot 60 \cdot 10^6}{P \cdot n_e \cdot F} = 7.6 \frac{ml}{min \cdot A} \quad (21)$$

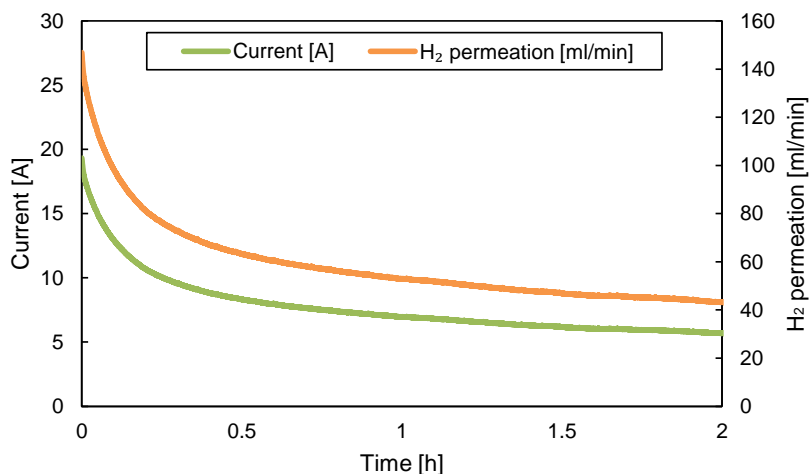


Figure 8. Relation between current and flow of H<sub>2</sub> in the cathode side.

## 4.2 Carbon dioxide effect

The effect of the mixture H<sub>2</sub>-CO<sub>2</sub> in the EHC has been studied more in details. It is interesting to study the effect of the pollution in order to understand the mechanism and find a possible solution. From literature, there is not an intensive study on the EHC, but it is possible to use Polymer Electrolyte Membrane Fuel Cell (PEMFC) literature as reference thanks to its similarity to the EHC. Despite this, there is also little information founded regarding the effect of H<sub>2</sub>-CO<sub>2</sub> on PEMFC.

### 4.2.1 Catalyst inhibition

First of all, it is important to underline the important decrease in the efficiency of the EHC when feeding CO<sub>2</sub> and H<sub>2</sub>. Other gases, such as methane, helium or nitrogen, can be considered as inert, but not carbon dioxide.

In order to show the negative effect of H<sub>2</sub>-CO<sub>2</sub> mixture on the electrochemical hydrogen compressor, the results obtained from this mixture have been compared with the one in which H<sub>2</sub>-N<sub>2</sub> has been fed. In Figure 9 the results are shown. At the beginning the inlet consists in 1 l/min of 50% N<sub>2</sub> and 50% H<sub>2</sub> and the applied voltage was equal to 0.1 V. After that, the N<sub>2</sub> was substituted with the CO<sub>2</sub> in the point on the Figure 9, highlighted with an arrow. After verifying the current value was constant, it was fed 50% of CO<sub>2</sub>, keeping the same volume flow rate of H<sub>2</sub>. According to the results, it is clearly occurring from the beginning a strong decrease in the value of the current. After certain time, it is fed again the N<sub>2</sub> in the mixture with H<sub>2</sub> in order to show the value of the current has decreased remarkably while using CO<sub>2</sub>.

During the experiments, the temperature was always kept constant at 19°C while the applied voltage was 0.1 V and the pressure was 1.3 bar in both anode and cathode. This inhibition is not directly caused because of the CO<sub>2</sub>, since its adsorption is not strong. The main problem is the CO, produced because of the reaction occurring between both H<sub>2</sub> and CO<sub>2</sub>. This aspect will be commented in details later.

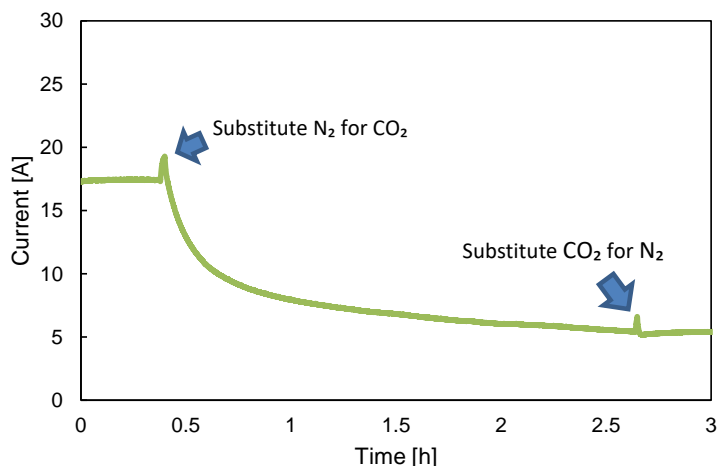


Figure 9. Current trend when putting CO<sub>2</sub>

Since it is already known the decreasing trend of the hydrogen permeance when H<sub>2</sub>-CO<sub>2</sub> is fed, because it is proportional to the current depicted in Figure 8. In Figure 10, CO<sub>2</sub> volumetric flow rate which permeates the membrane is shown versus time in comparison with the hydrogen volumetric flow rate at the cathode side. For doing so, considering longer experiments will help in understanding better the results since the flow of CO<sub>2</sub> that is permeating the membrane is very low in comparison with the H<sub>2</sub> flow, so that makes more complex to notice the changes.

The conditions in which the experiments are performed are the same as the one explained before.

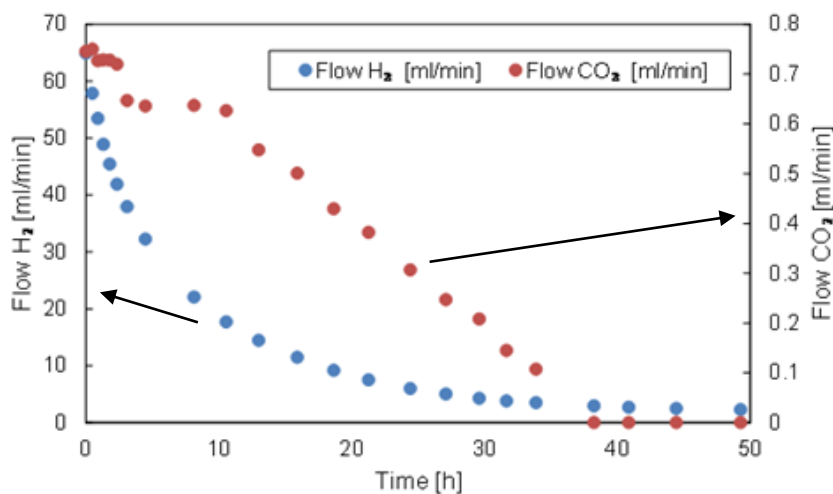


Figure 10. Trend of flows of CO<sub>2</sub> and H<sub>2</sub> in the outlet stream

First thing to consider from this plot is that the trend of the flow of  $H_2$  tends to 0 following a negative exponential curve. As the current is directly proportional to the  $H_2$  flow, it would reach zero in a longer experiments.

It is possible to notice from the results the important decrease of the carbon dioxide in the cathode side during the time. At the beginning, the value of the flow of  $CO_2$  remains constant in 0.6ml/min, if it is not considered the initial trend caused by the pollution in the GC. The mechanism which allows the carbon dioxide to permeate the membrane, is the solubility of this gas in water, which will be explained later. At some point, the flow of  $CO_2$  starts to decrease considerably until reaching 0. The main explanation is that, the less  $H_2$  permeating, the less water will go through the membrane, so less  $CO_2$  will be able to overpass the membrane since water solubility is the permeation mechanism of  $CO_2$ , as will be explained later.

Maybe the value of the crossover of  $CO_2$  is not completely 0, but with the accuracy of the GC we cannot measure it. Since this value will be lower than 0.1ml/min in the best of the cases, we can neglect it.

### 4.2.2 Inhibited catalyst recovery

After inhibiting the catalyst in the experiments with  $CO_2$ , it is necessary to know the possible ways to recover the catalyst. In this work it will be studied the recovery with two different methods: by doing the air bleeding in both anode and cathode in order to burn the carbon monoxide, and the other one sending directly the humidified mixture of  $N_2/H_2$  to the compressor for desorbing the CO on the catalyst.

#### 4.2.2.1 Air bleeding

Firstly, feeding air, the oxygen react with CO forming  $CO_2$  that is easily removed from the EHC. The experiments performed are shown in Figure 11. For doing the air bleeding, low flows of air are sent to the compressor. After certain time, using the same mixture of  $N_2/H_2$  as before, it can be checked that the value obtained is the same as at the beginning of the experiment, meaning the catalyst has been completely recovered.

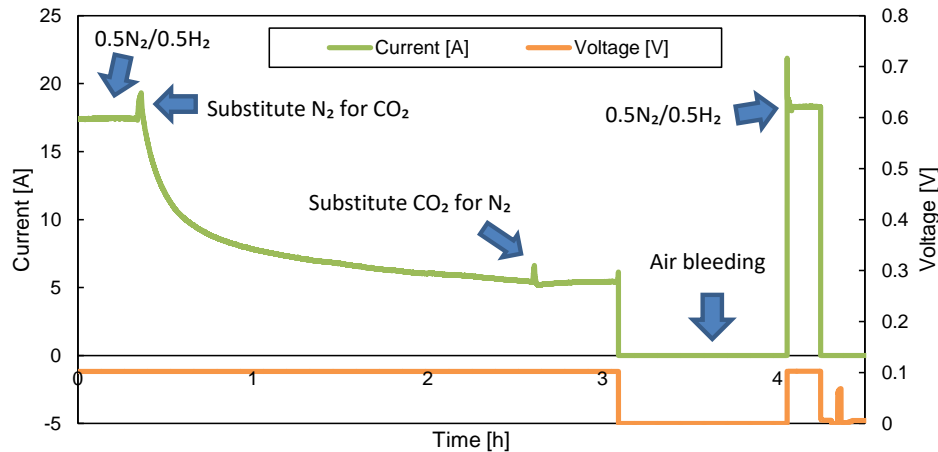


Figure 11. Recovery of the catalyst with air bleeding

Although in the graphic it is seen that the time for air bleeding lasts for 1 hour, this process is almost instantaneous. However, its drawback is the possible behavior of the EHC as a Fuel Cell, due to the possible presence of a residue of hydrogen. Since the hydrogen molecule is very small, it is very difficult to achieve a complete removal, so that when feeding the oxygen they can both react, as happens in a Fuel Cell. It means an increase in the voltage, and can cause problems to the compressor when achieving values over the voltage limit.

Furthermore, the inhibition of the catalyst can happen in both anode and cathode. As explained in Figure 12, it is checked the pollution of the catalyst and just after that, it is performed air bleeding in the anode. The value obtained of the current just when feeding again N<sub>2</sub>/H<sub>2</sub> is almost the same as before polluting the catalyst, but it is still possible to recover the complete efficiency. This is due to the little crossover of CO<sub>2</sub>, that pollutes the catalyst of the cathode side. However, as can be checked, the surface of catalyst inhibited is negligible in comparison with the anode, since the value of the current after air bleeding in the anode was 17.2A and the value after the air bleeding in the cathode 17.8A.

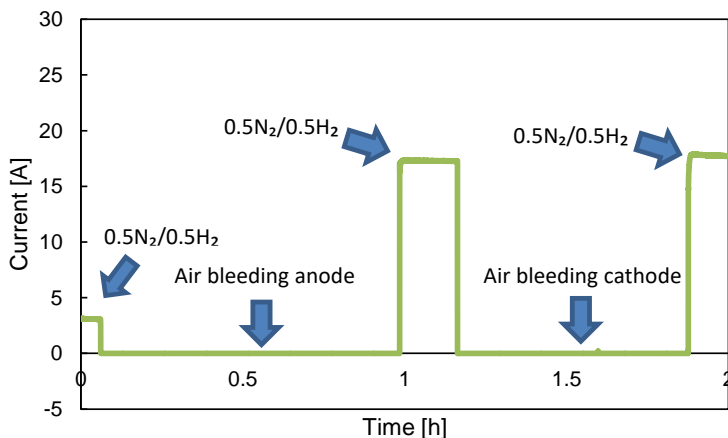


Figure 12. Recovery of catalyst in both electrodes

#### 4.2.2.2 Without air bleeding

Despite the high efficiency of the previous process, it is going to be checked another method of catalyst recovery in which it is used a mixture of  $H_2$ - $N_2$  to remove the CO adsorbed.

In Figure 13 can be clearly seen the trend. Initially a mixture of hydrogen-nitrogen was fed in order to verify the current. Later on, the  $N_2$  had been substituted by the  $CO_2$ . After the pollution had occurred, it was removed the  $CO_2$  and fed again  $N_2$  to the compressor in the mixture with  $H_2$ . In this point, it was supplied the initial mixture of  $N_2/H_2$  for a long time in order to understand if it could have been possible to recover the catalyst. The increasing trend of the current is clear, meaning the catalyst could be completely recovered through desorption.

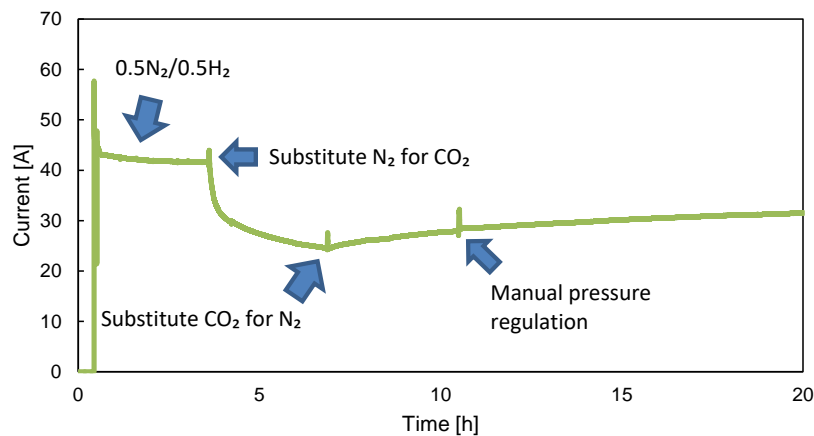


Figure 13. Recovery of the catalyst without air bleeding

However, the great inconvenience of this method consists in its slowness. A comparison is shown in Table 4, even though this method has been applied for 15 hours instead the 2 seconds that air bleeding needs to be done to completely recover the catalyst.



Table 4. Comparison of catalyst recovery with and without air bleeding

	Current before CO <sub>2</sub> [A]	Current after CO <sub>2</sub> [A]	Current recovery after method [A]	% Recovery
Without air bleeding	41.5	24.4	32	43.17%
With air bleeding	17.4	5.4	18.2	107%

### 4.2.3 Catalyst inhibition reactions

After demonstrating the negative effect of CO<sub>2</sub> on the EHC, it is of high importance to explain the reason for which it takes place. As explained before, the main effect is not caused by the CO<sub>2</sub> itself, but by the CO. The adsorption of carbon monoxide, as founded in literature, is much stronger than the CO<sub>2</sub>. It is relevant to understand the type of reaction which occurs in the electrochemical compressor to form CO.

Two possible reactions could be the reason for CO formation: Reverse Water Gas Shift reaction (RWGS) or the electrochemical reduction of CO<sub>2</sub>. It is going to be explained more in details in order to get a proper understanding of the catalyst inhibition by CO<sub>2</sub>.

#### 4.2.3.1 Reverse Water Gas Shift

The reaction of reverse water gas shift is explained in equation (16). As said, it is an endothermic reaction, so that means that in the range of temperatures in which we are using the compressor (between 20-30°C) should not have a remarkable effect. Even with few ppm of CO formed, it is possible to inhibit the catalyst considerably.

Experiments performed are shown in Figure 14. The initial mixture sent to the compressor was 1l/min of 50%N<sub>2</sub> and 50%H<sub>2</sub>, for an imposed voltage of 0.1V. After reaching stable conditions, it was removed the N<sub>2</sub> to put the CO<sub>2</sub> while the voltage was switched off. After certain time, when turning back to the same conditions as the beginning of the experiments, it had checked that the stable value obtained was decrease. The temperature was always kept constant in 19°C.

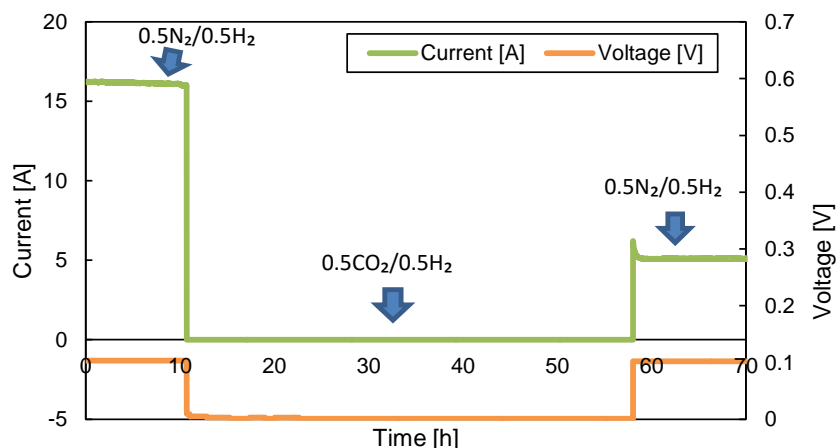


Figure 14. Demonstration of the presence of RWGS

The key point of this experiment is in the voltage. When switching it off, electrochemical reactions cannot take place. Because of that, the only possible reaction to pollute the catalyst is the RWGS. As explained before, the decrease of the current without any imposed voltage, confirms the assumption that this reaction is taking place.

Furthermore, it is demonstrated the formation of CO in the catalyst. For doing so, the catalyst has been inhibited completely. After that, it has been sent 100 ml/min of  $N_2$  to the compressor meanwhile both the anode and the cathode side were connected to the micro GC. The purpose of this experiment consisted in checking if it could be possible to measure any CO peak, meaning the RWGS had occurred. It was necessary to increase the temperature of the compressor until  $70^\circ\text{C}$ , since the desorption of CO from the catalyst is more likely to happen at higher temperature.

For CO formation, RWGS can happen in many different ways. Although the reaction is endothermic and at lower temperatures few ppm of CO are formed, they cannot be neglected due to the fact that small amounts of CO can easily inhibit the catalyst. For checking this small formation of carbon monoxide, a mixture of  $CO_2$  and  $H_2$  is sent directly to the micro GC. Indeed, even though the micro GC has a high accuracy, no peaks of CO were detected, meaning this very small CO formation.

Furthermore, it is clear that Platinum catalyst stimulates the CO formation in different ways. This reaction can happen with the  $CO_2$  adsorbed in the catalyst or not, and the CO formed will compete with the  $H_2$  to reach the catalyst surface.

#### 4.2.3.2 Electrochemical reduction reaction

Once demonstrated the presence of the RWGS reaction, the effect of the electrochemical reduction is studied. This reaction needs voltage to carry on, but as already explained, once  $H_2$ - $CO_2$  is fed, on the catalyst the RWGS reaction will occur. The task is to understand if the electrochemical reduction of  $CO_2$  could take place in a relevant way and contribute to have

more CO. So the experiment to demonstrate if it is occurring consists in comparing different experiments.

At the beginning, a mixture of 50% H<sub>2</sub>- 50% CO<sub>2</sub> was fed to the compressor, after verifying the current in presence of H<sub>2</sub>-N<sub>2</sub> was stable. The supplied voltage was 0.1 V. The results are reported in Figure 15.

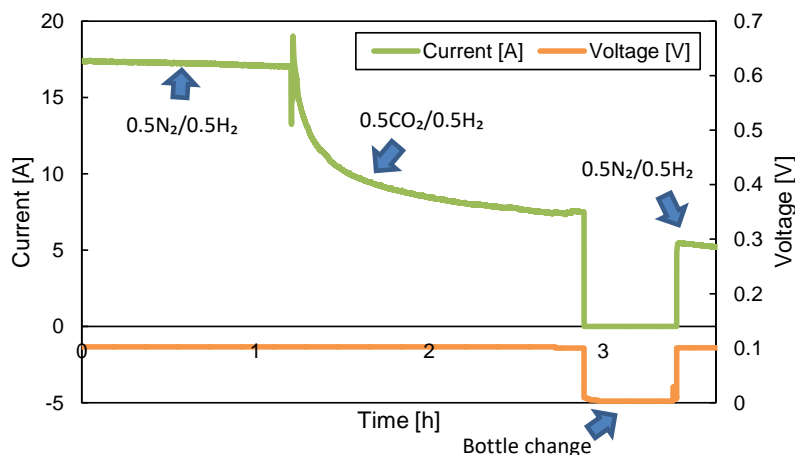


Figure 15. Experiment with voltage for demonstrating electrochemical reduction

Later on, it was performed the same experiment but without supplying voltage in presence of CO<sub>2</sub>. The experiment performed with and without voltages had the same operating conditions. The task is to compare the results obtained from these two experiments because in absence of voltage only reverse water gas shift could take place.

When the voltage was applied, hydrogen could permeate through the membrane and the hydrogen concentration in the anode side was different from the experiment in which no voltage was applied. For that reason, the flow of H<sub>2</sub> supplied in the experiment without voltage, had been changed continuously taking into account the flow of H<sub>2</sub> that permeated in the previous experiment. The idea is to keep the same hydrogen molar fraction in order to verify if any possible difference between the experiment with and without voltage, could be found in different hydrogen concentration in the anode side. If reproducing the same hydrogen molar fraction with and without voltage, it is possible to obtain similar results, it could be stated the main reaction is the reverse water gas shift. If it is possible to get the same amount of H<sub>2</sub> in the anode side, it is possible to have the same stoichiometric amount of H<sub>2</sub> available to react with the CO<sub>2</sub> in both the experiments with and without voltage. The results are shown in Figure 16.

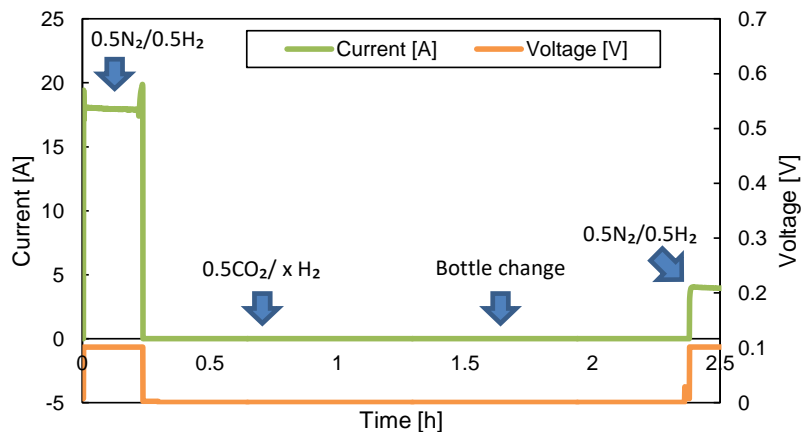


Figure 16. Experiment without voltage for demonstrating electrochemical reduction

In Table 5 the results obtained from the comparison between the experiments described, have been plotted. It is found similar pollution rate in the two experiments performed. Because of that, it can be concluded that the electrochemical reduction is not happening in a very considerable way, so it is possible to neglect it in comparison with RWGS.

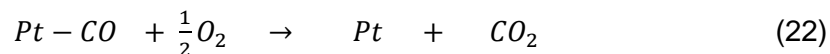
Table 5. Comparison of the pollution for experiments with and without voltage

	Before CO <sub>2</sub>	After CO <sub>2</sub>	Pollution [%]
<b>With voltage</b>	17	5.3	68.82
<b>Without voltage</b>	17.9	4	77.65

#### 4.2.4 Processes happening when recovering the catalyst

Once inhibited the catalyst, it is of high importance, explaining the possible processes to recover it. As said before, the catalyst recovery can be performed with or without air bleeding.

The use of air implies the reaction of the CO adsorbed with the oxygen presented in the air, forming the CO<sub>2</sub> which is easily removed from the compressor. Equation (22) shows this reaction:



On the other hand, other methods could be applied in order to regenerate the catalyst. From literature, it has been founded two options apart from air bleeding, which are described below.

##### 4.2.4.1 Desorption

When having a molecule adsorbed in a catalyst, the easiest way to desorb it is to feed a gas. In the case proposed in Figure 17, the catalyst was polluted in a previous experiment. A mixture of 0.5l/min of N<sub>2</sub> and 0.5l/min of H<sub>2</sub>, was fed in order to see the value of current obtained after the

pollution. At certain point, the voltage was switched off, to assure that no electrochemical reaction can take place. The  $H_2-N_2$  mixture was fed during all the time in which the catalyst was switched off. After two hours the voltage was switched on and when the membrane was re-hydrate properly, the current had increased of almost 3 A. Since there is no other option of recovering the catalyst than desorption, the increase of current when supplying again the voltage means that some CO has been removed by desorption.

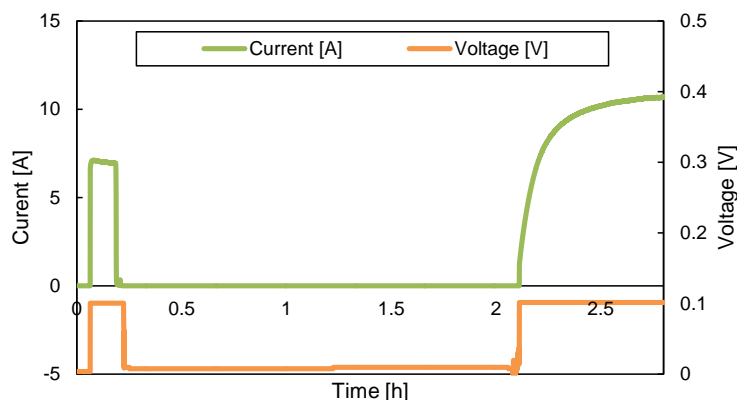


Figure 17. Demonstration of the presence of CO desorption

#### 4.2.4.2 Electrochemical reduction reaction of CO adsorbed

Another possible study shows the electrochemical reaction of the CO adsorbed. The mechanism proposed for this reaction is based on the dissociation and adsorption of water in the catalyst, allowing the reaction between the adsorbed water and the CO. The reactions were previously written in equations (18) and (19).

After trying different ways of checking this phenomena, it is not obtained any concluding results, due to decreasing of current because of dehydration. This leads to be imposible to check the presence or not of this mechanism of CO removal.

#### 4.2.5 Compressor behavior in different conditions

It is of high importance to test how the EHC behaves in different operating conditions. For explaining it, experiments changing the voltage and changing the concentration of  $H_2$  are performed, in order to get a completely understanding of  $CO_2$  issues.

##### 4.2.5.1 Experiments changing the voltage

Firstly it is analyzed the case of different supplied voltages to the compressor. The voltage influence is very clear due to the dependence of electrochemical reactions in this variable, so its study is of great importance.

The experiments are performed in the same way as before. Keeping anode and cathode at 1.3bar of pressure and a temperature of  $19^\circ C$ , it is fed a 1l/min mixture of 50%  $H_2-N_2$ . When

achieving a stable value of current, it is substituted the  $N_2$  with  $CO_2$ , and it is left for 1 hour and 45 min in all cases, when the data is collected. The duration of the experiment does not cover the complete inhibition of the catalyst since it takes several days depending on the operating conditions. The results for all the different voltages are shown in Figure 18, where it is plotted the flow of  $H_2$  at the outlet of the compressor and also the purity obtained, and in Figure 19 where it is possible to check the flow of  $CO_2$ .

The first conclusion is related to the lower hydrogen purity obtained in presence of  $CO_2$  compared to  $N_2$  or  $CH_4$ , when the purity achieved is practically 100%. This is due to the very high solubility of carbon dioxide in water in comparison with these gases.

The little increase in the flow of  $CO_2$  with the voltage, is due to the higher flow rate of  $H_2$  that permeates, which drags the  $CO_2$  to the cathode side. Even with that increase, the value can be considered constant in comparison with the flow of  $H_2$ , which is in a different order of magnitude and increases with higher voltages. Noticing the flow of these two gases, it is possible to evaluate the purity, that increases with the flow of  $H_2$ .

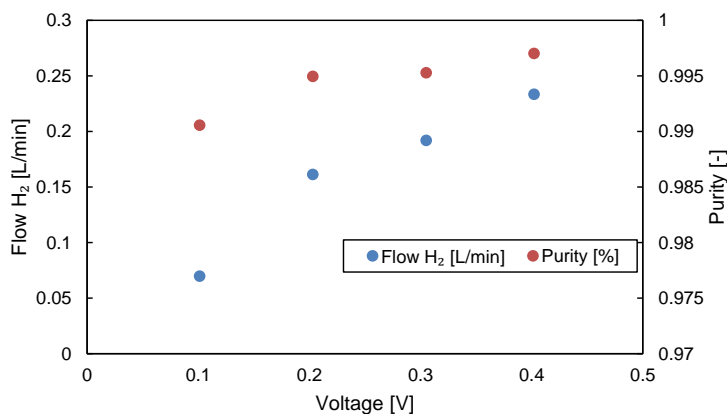


Figure 18. Trend of  $H_2$  flow and purity depending on the voltage supply

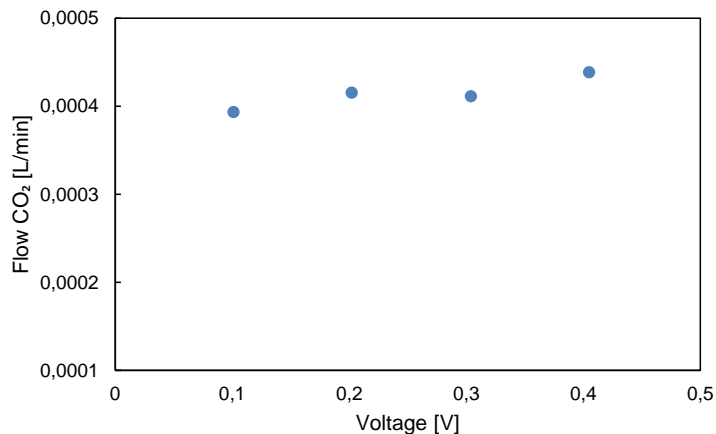


Figure 19. Trend of CO<sub>2</sub> flow depending on the voltage supply

In Figure 20 it is shown the inhibition of the catalyst with the time at different supplied voltages. In the plot, it is seen the lower the voltage, the faster the inhibition. The reason for this is that, in the case of lower voltage, less flow rate of hydrogen permeates through the membrane because less amount of H<sub>2</sub> molecules are splitted in the Platinum. Because of that, more catalyst surface is likely to be polluted by CO, provoking the trend plotted in the picture.

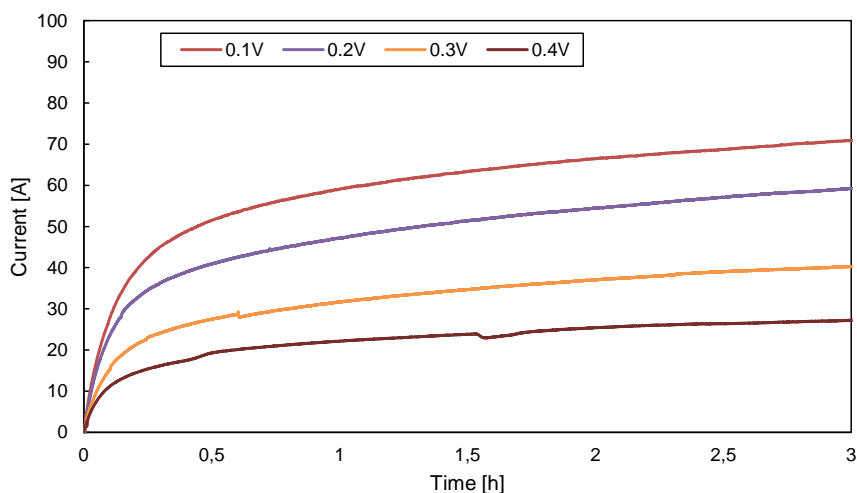


Figure 20. Trend of catalyst inhibition for different voltages

#### 4.2.5.2 Experiments changing the concentration of H<sub>2</sub>

Another different case to consider is when changing the concentration of H<sub>2</sub>. From steam cracking the percentages obtained of the different components can slightly vary because of problems in the process, so it is important to evaluate the behavior of the compressor when this parameter changes.

The experiments were performed in the same way as before, but instead of changing the supplied voltage, it is the concentration of H<sub>2</sub> in the inlet stream that has been varied. The inlet

mixture was always 1l/min, and depending on the hydrogen concentration in the mixture, the initial value of current changed. The experiments were stopped when always at the same value of current even if depending on the conditions, it could have been longer in some cases. The results in Figure 21 show the expected trend, where the increase of H<sub>2</sub> concentration decreases the CO<sub>2</sub> crossover, since there is less CO<sub>2</sub> in the inlet, which leads to higher hydrogen purity.

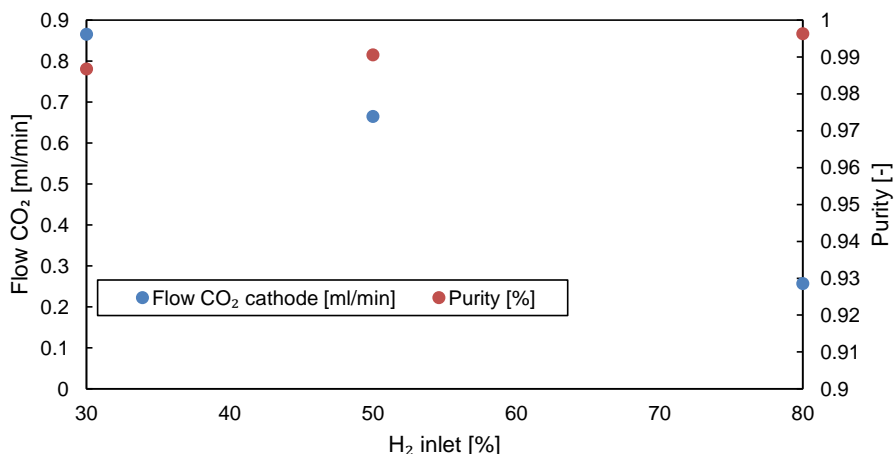


Figure 21. Flow of CO<sub>2</sub> and purity depending on the concentration of H<sub>2</sub>

As before, it is worthwhile to show the evolution of catalyst inhibition for the different cases, so these results are shown in Figure 22. For explaining the trend, it is evaluated the ratio between CO formed and H<sub>2</sub> presented in the anode side.

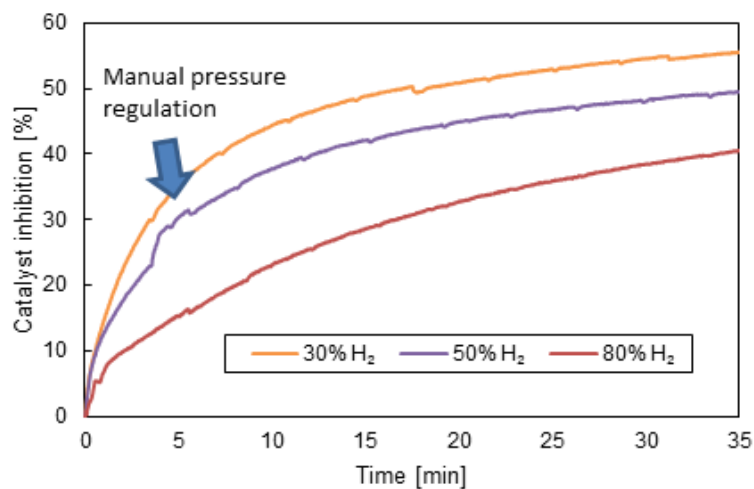


Figure 22. Trend of catalyst inhibition for different concentrations of H<sub>2</sub>

In order to understand the phenomena, CO formed is calculated with Aspen for the different concentrations of H<sub>2</sub>. In the case of lower hydrogen molar fraction in the anode, the CO produced is more likely to reach the catalyst and pollute it. For this reason, in the condition of lower hydrogen concentration in the anode, the pollution of the catalyst takes place faster.



Evaluating the ratio, can be easily concluded that for lower H<sub>2</sub> concentrations there is more amount of CO available to inhibit the catalyst. Results are shown in Table 6.

Table 6. Ratio CO formed/H<sub>2</sub> anode

	CO formed [kmol/h]	CO formed [ml/min]	Current [A]	Flow H <sub>2</sub> permeating [ml/min]	Flow H <sub>2</sub> anode [ml/min]	$\frac{CO\ formed}{H_2\ anode}$
30% H <sub>2</sub>	5.72E-06	1.75	15.5	117.8	182.2	0,00963
50% H <sub>2</sub>	6.95E-06	2.13	18.6	141.36	358.64	0,00595
80% H <sub>2</sub>	5.97E-06	1.83	21	159.6	640.4	0,00286

#### 4.2.6 Considerations on the stability

All the experimental results previously commented were taken into account considering ideal working conditions in the EHC, but this is not always true. The perfect stability of all the parameters related to the process is very difficult to achieve, becoming a great problem to face.

Firstly, when working with the mixture of CO<sub>2</sub>-H<sub>2</sub>, temperature and pressure are very non-stable variables. Room temperature is not always the same, and the performances of the electrochemical hydrogen compressor could suffer considerable changes in different days. Also pressure is very difficult to keep constant. The reason is founded in the use of the micro GC that needs to get a pressure of 1.3 bar in the line but, when taking the sample to its study, this value changes.

However, the problems previously mentioned are not as important as the problem related to the hydration of the membrane. The membrane is assumed to be perfectly hydrated, but this is not always true. The gas fed to the compressor should be saturated of water. However, this can be changed due to the amount of water in the bottle, room temperature and water residence time in the bottle. Also it is important to highlight that, contrary to a Fuel Cell, there is no water production inside the membrane, so the only water available for humidifying the membrane, is the one fed to the compressor with the inlet gases. Non-uniformity of the membrane properties can also lead to different grades of hydration in it. Hydration problems can be caused by an excessive amount of water or a defect of it.

##### 4.2.6.1 Dehydration

The origin of the dehydration issue resides in such a low quantity of water in the bottle that makes more difficult the pass of protons through the membrane. This defect of water in the membrane can be caused because of low amount of water in the bottle, low flow of gases in the inlet mixture or other causes. It is possible to check its appearance as a continuous decrease in the value of the current in the compressor.

### 4.2.6.2 Water clogging

Contrary to previous case, an excessive amount of water in the membrane can also lead to an inappropriate behavior of the EHC. This very high amount of water causes blocking of porous structure and channels in the GDL, which makes a non-stable behavior in the compressor. It just happens in the contrary case as dehydration, with higher amounts of water in the bottle than needed or very high flows in the inlet mixture. The presence of water clogging is possible to notice when getting a thicker line of current, with important changes in the values around the value expected.

### 4.3 Temperature effect

As one of the most influent parameter, it is here analyzed the effect of the temperature on the electrochemical compressor. As it happens to previous cases, it is considered PEMFC literature, due to the lack of information about the EHC.

At the beginning, it was studied the influence of the temperature on the current obtained from the compressor for a fixed applied voltage. For this task, it was sent a mixture of 50% N<sub>2</sub> and 50% H<sub>2</sub> with a total flow rate of 1 l/min. The applied voltage was kept constant at 0.1 V and the pressure in both electrodes was 1.3 bar. The trend of the current with the change of temperature has been depicted in Figure 23.

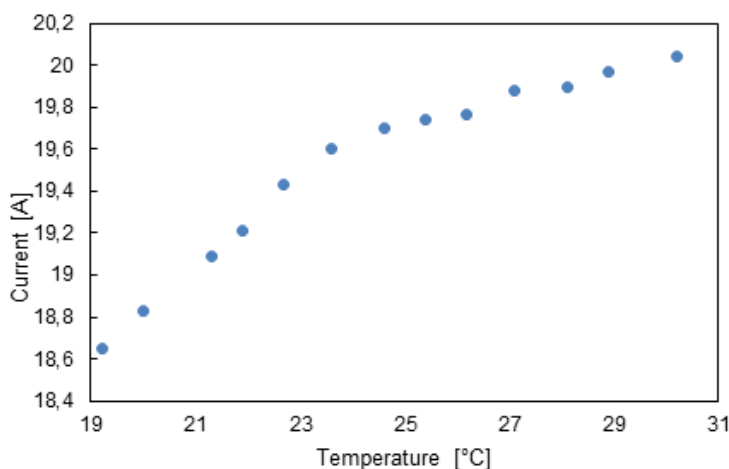


Figure 23. Trend of current depending on temperature

Temperature affects in many ways the behavior of the compressor. For instance, concentration losses decrease with temperature, due to the decrease in the logarithmic part of the equation reported in equation (23). This is caused due to the increase in the limiting current density, which is the maximum value that can be produced by the compressor. This increasing trend can be explained with the increasing of diffusivity with temperature, according to equation (24).[19] [20]

$$E_{conc} = \frac{RT}{nF} \ln \left( \frac{i_L}{i_L - i} \right) \quad (23)$$

$$i_L = \frac{nFDC_B}{\delta} \quad (24)$$

The same happens with activation losses due to increasing rate of electrochemical reactions. Furthermore, membrane resistance decreases with temperature, leading to a decrease in ohmic losses. All these effects make the EHC efficiency increases.

However, the main issue of working at higher temperature, is related to the proper humidification, that is very difficult to achieve when the temperature is increased, reducing this increasing trend. This fact also happen in the experiments performed, as can be checked with lower increase for higher temperatures.

### 4.3.1 Pure Hydrogen

Initially, it is studied the influence of the temperature when case of feeding only H<sub>2</sub> to the compressor. For plotting the corresponding polarization curves, it is proceeded as following: firstly it was taken the data for the polarization curve for the lowest temperature, and from that point the temperature was increased step by step until the highest one.

The total flow rate of H<sub>2</sub> sent to the compressor was of 1 l/min. The polarization curves at different temperatures are represented in Figure 24.

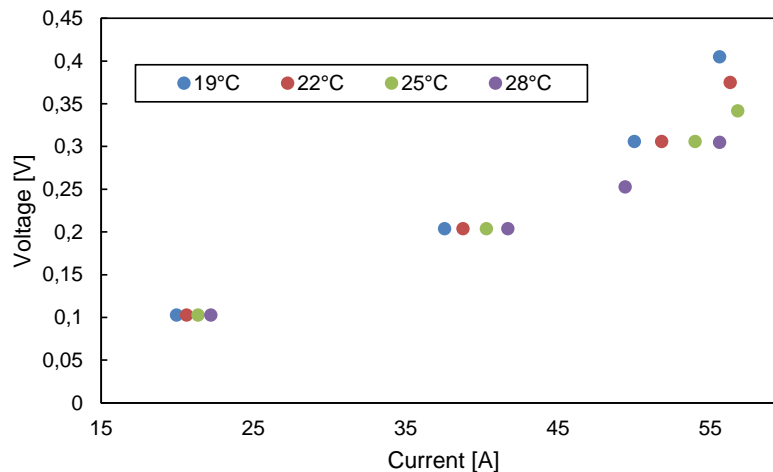


Figure 24. Polarization curves for 1 l/min H<sub>2</sub> changing the temperature

As expected, the higher the temperature of the compressor the higher the current obtained, for the reasons explained previously.

### 4.3.2 Study of Hydrogen with contaminants

Since one of the possible applications of the electrochemical hydrogen compressor is hydrogen separation after steam reforming and water gas shift, it is of interest the study of the  $\text{CO}_2$  as contaminant. Except  $\text{CO}_2$ , all the other gases studied are inert in the process, even if it could appear small changes due to different mechanism of permeation and diffusivity. Because of this, it will be studied the case of one inert gas, and afterwards  $\text{CO}_2$  will be analyzed.

The gas studied as inert contaminant is  $\text{N}_2$ . For this case, it was used a mixture of 1 l/min composed of 50%  $\text{N}_2$  and 50%  $\text{H}_2$ , where the voltage supply was changed in order to get the complete polarization curves. Pressures are kept at 1.3 bar in anode and cathode. The temperature has been changed from 19 to 28 °C. The result obtained is shown in Figure 25.

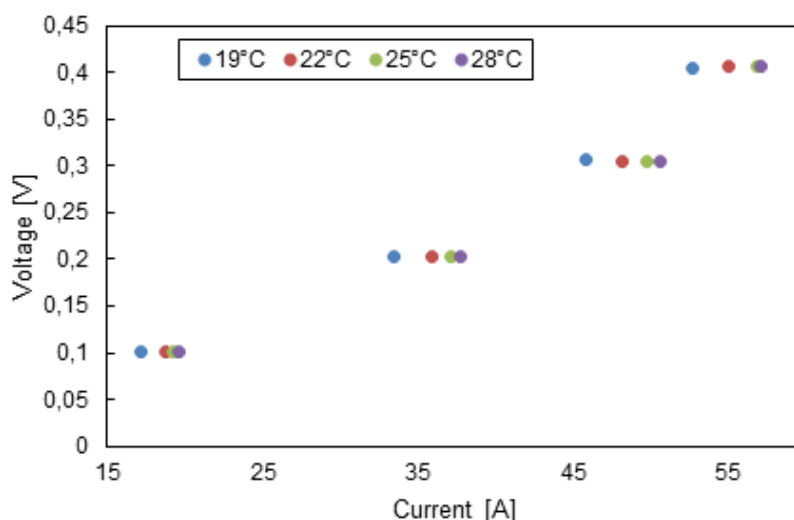


Figure 25. Polarization curves for a mixture of  $\text{N}_2/\text{H}_2$  changing the temperature

As already showed in the experiments performed with pure hydrogen, the same increase of current is possible to be found when the temperature arises. However, the case of  $\text{CO}_2$  is different. As said previously, it inhibits the catalyst when it is fed with  $\text{H}_2$  due to the reverse water gas shift reaction which take place on the catalyst. Since the values obtained of current for each voltage are not constant, it is evaluated the change of inhibited catalyst with time for different temperatures, plotting the results in Figure 26.

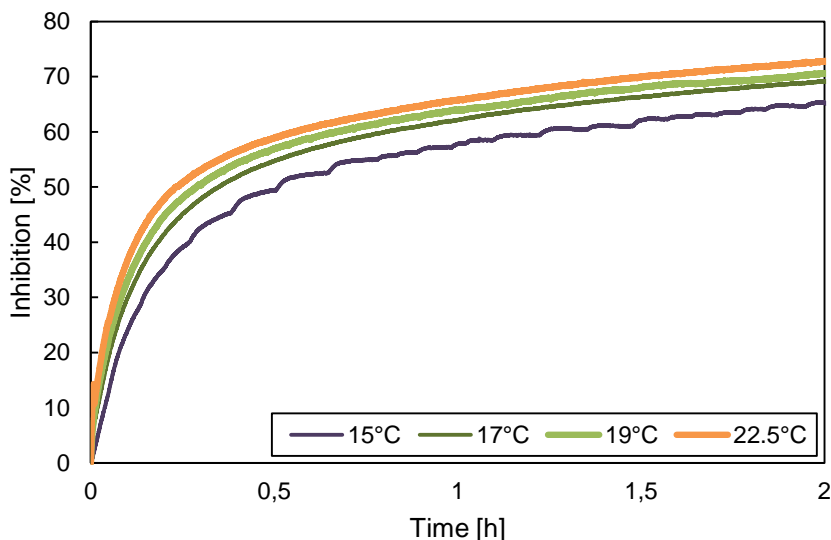


Figure 26. Catalyst inhibition for different temperatures

The increase of temperature leads to an increase in catalyst inhibition. Due to the kinetics, the higher temperature the more CO will be formed, so the ratio  $\frac{CO\ formed}{H_2\ anode}$  increases. This leads to an increase in catalyst pollution.

However, it is important to highlight that the temperature's influence is not always positive. From literature, it has been checked that the compressor efficiency increases with temperature up to a point. [20]. This is explained due to increasing importance of desorption rate, as well as important problems in dehydration due to the high temperatures, that leads to decreasing proton conductivity and increasing Nafion® membrane resistance.

#### 4.3.3 Additional considerations of stability

When dealing with temperature issues, controlling this variable becomes more complex. This problem is directly related with the problem of humidification mentioned before.

For reaching perfect conditions of hydration, as said before, the mixture of gases has to be completely saturated. This means that the value of temperature in the compressor and in the bottle should be the same, or at least similar, so as to assure a perfectly saturation of the gas stream.

The way of heating the gases in the bottle is using the heating plate. Line isolation and tracing lines are used for keeping constant the temperature of the gases when entering in the compressor, assuring no condensation.

As can be checked, the temperatures evaluated are not higher than 30°C. It has been tried to evaluate experiments over this temperatures and the values were not stable. Because of that, for working at higher temperatures, the setup has to be changed, so it is not collected data for higher temperatures in this work.

#### 4.4 Crossover mechanisms of contaminants

Later on, it is studied how the crossover of contaminants takes place. For doing so, it has been evaluated the flow rate of contaminant permeating with temperature in comparison to the theoretical trends of different mechanisms [21].

In the case of the compressor, there are three main mechanisms of crossover. First of all, the solubility, which play a role since the gas could dissolved in the water and permeate through the membrane, making easier for the gas to reach the cathode side.

The second mechanism is the permeability of the gas in the Nafion<sup>®</sup> membrane. The last mechanism depends on the size of the molecule which could pass through pinholes. It is clear the fact that the smaller the molecule of the gas, the more likely will be to permeate. Because of that, it is studied the case of Helium. To check its permeation, it is sent a mixture of 1 l/min 50%He and 50%H<sub>2</sub> to the compressor. It is supplied a voltage of 0.1V, keeping both electrodes at 1.3bar of pressure. The flow of the contaminant is detected at the cathode side with the use of the micro GC. Temperature is changed in order to get the trend shown in Figure 27.

Theoretically, the helium permeation across Nafion<sup>®</sup> should increase with temperature, so that means the experimental results obtained perfectly fit with the trend expected.

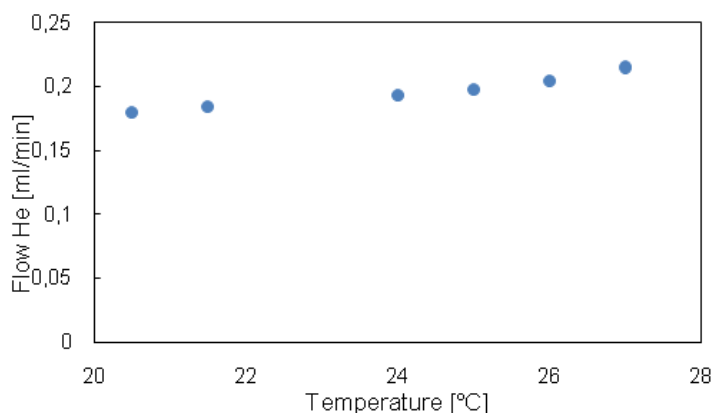
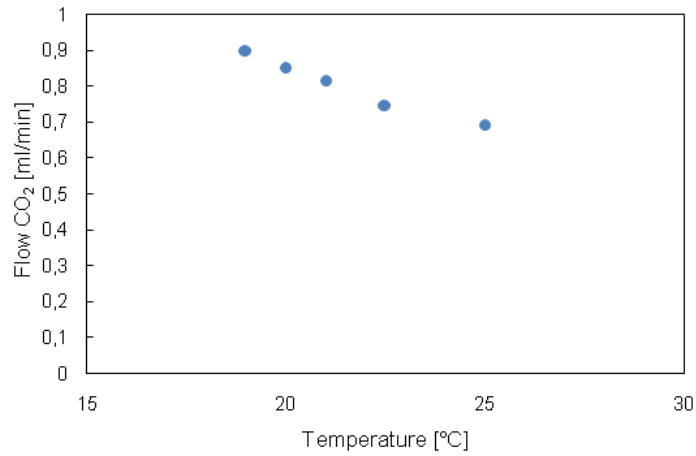


Figure 27. Helium permeation across Nafion<sup>®</sup> membrane

For checking the other mechanism, it is evaluated CO<sub>2</sub>. This gas has the highest solubility in water compared to all the gases analysed, so that makes more possible to measure it and notice its changes. The conditions of the experiments are the same as before, but feeding CO<sub>2</sub> instead of Helium. The result shown in Figure 28, is in line with the CO<sub>2</sub> solubility in water with the temperature.



*Figure 28. CO<sub>2</sub> permeation across Nafion<sup>®</sup> membrane*

In this work it has only been considered these two gases, due to the feasibility of measure them. Other gases, such as N<sub>2</sub> or CH<sub>4</sub>, are more unlikely to permeate, because of their lower solubility, permeability and higher size.

# Chapter 5

## Modeling

After getting a complete understanding of the performances of the electrochemical hydrogen compressor with the experimental results, it is worthwhile to compare it with a model that theoretically represents it. In this way, it is implemented a Matlab<sup>®</sup> model.

For the case of this work, a previous model has been used in order to describe the compressor. Since the proper mass transfer limitation was not implemented in the model, in this work, changes to the model have been performed in order to account for it.

### 5.1 Previous model

Before making the necessary changes in the model, a description of the model used is necessary. To its development, it has been considered literature equations, to make a model that fits with the experimental data. Considering the similarity between the Polymer Electrolyte Membrane [PEM] and the EHC, the equations of the first one are considered for this model [13].

Firstly, the geometry of the compressor considered is explained. Due to simplification reasons, it is assumed a 1D model, with the components flowing only in the x axis, with channels that don't change their area or shape. The different parts of the compressor are shown in Figure 29, with a very simple configuration that separates Gas Diffusion Layer [GDL] and Catalyst Layer [CL].



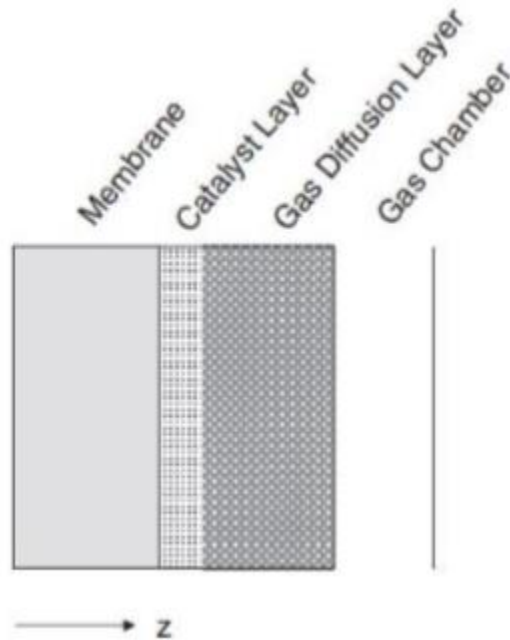


Figure 29. Modeling domain of 1D domain through the membrane model (Bernanrdi-Verbrugge)

It has been made many assumptions to simplify the task. For example, ideal gas and mixture are considered, steady state, constant temperature and contaminant crossover or uniform behavior are some of the main important ones.

For ending this analysis, it is explained the equations used to the development. Even though Tafel equation is accredited in most of the papers for EHC it is not used because it is a simplified case for high values of current, which is not our case. Because of that, the model presented is based in Butler-Volmer equation [10][13].

The starting point is write the Butler-Volmer for the anode and cathode in equations (25) and (26). The subscript "a" refers to anode, while "c" refers to cathode.  $a_{H_2}$  refers to the activity of the hydrogen which is computed using the partial pressure of hydrogen on the catalyst surface assuming negligible pressure drop across the GDL. The current in both cases should be equal.  $E_{Nernst}$  and  $E_{act}$  are the Nernst potential and the activation polarization losses.

$$i_{step} = FK_0 \left[ a_{H_2,a}^{0.5} e^{\frac{\alpha F}{RT}(E_{Nernst,a} + E_{act,a})} - e^{-\frac{\alpha F}{RT}(E_{Nernst,a} + E_{act,a})} \right] \quad (25)$$

$$-i_{step} = FK_r \left[ a_{H_2,c}^{0.5} e^{\frac{\alpha F}{RT}(E_{Nernst,c} + E_{act,c})} - e^{-\frac{\alpha F}{RT}(E_{Nernst,c} + E_{act,c})} \right] \quad (26)$$

Ohmic losses are expressed according to equation (11). Also the imposed voltage that is necessary to supply to the compressor can be derived, as the sum of Nernst potential plus ohmic and activation losses, as written inequation (9).

In order to separate the activation losses from the Nernst potential the latter is written as in equation (27), where  $x_s$  is the surface concentration of hydrogen on the anode catalyst. These

two equations already include the mass transfer loss which is due to the decrease of H<sub>2</sub> concentration at membrane surface with respect to the bulk concentration fed.

$$E_{Nernst} = \frac{RT}{n_e F} \ln \left( \frac{p_c}{x_s p_a} \right) \quad (27)$$

## 5.2 Changes implemented

The goal of this work is, after having analyzed the model explained, try to make it useful to work at different temperatures considered. In the model explained, the value of the mass transfer coefficient has been taken experimentally, so that means is only applicable for the case studied. For this reason, it was one of the task of this work, include the proper correlation for the mass transfer in order to account it for all the possible conditions.

As said before, mass transfer can occur in both Gas Diffusion Layer and Catalyst Layer. Because of that, global mass transfer coefficient for the compressor is equal to the mass transfer coefficient obtained for GDL.

The study of this coefficient is made with dimensionless numbers. The most intuitive relationship for calculating mass transfer coefficients is Sherwood number, whose relation is explained in equation (28), where  $D_h$  is the characteristic length of the GDL and  $D$  is the diffusivity of the mixture of gases considered.

$$Sh = \frac{h \cdot D_h}{D} \quad (28)$$

To calculate Sherwood number, it is founded a correlation valid for cases of low values of Re and Sc, as in our case. In this situation, the value of Sh gets is constant, an equal to 6.18. Because of this, after checking Reynolds and Schmidt, Sherwood is implemented as this value[22].

## 5.3 Validation

The validation of the model is performed with a graphical method.

For doing so, it is considered the case of a mixture of 1 l/min composed of 20% H<sub>2</sub> and 80% N<sub>2</sub>. Temperatures are changed, and the different trends obtained are shown in Figure 31. Lines represent the model, while the marks are the results obtained.

As can be seen, the model seems able to predict the experimental results, despite the experiments performed at 19°C. Due to the fact that only one experiment doesn't fit, with an error around 4%. The difference can be attributed to experimental error, since the conditions of the experiments can change easily. Maybe other possible problem could be related to the assumptions made, that are not completely true. For instance, uniform conditions in the compressor are difficult to get, or the assumption related with the constant temperature in all the surface.

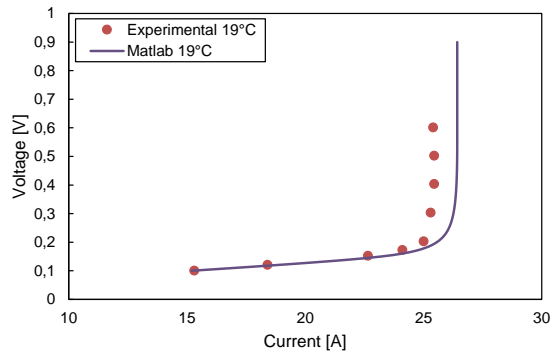


Figure 30. Matlab-experiments comparison for 19 °C

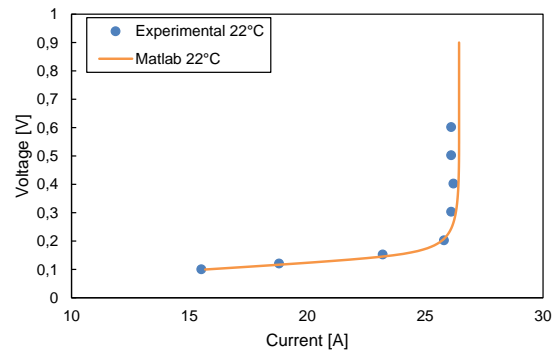


Figure 31. Matlab-experiments comparison for 22 °C

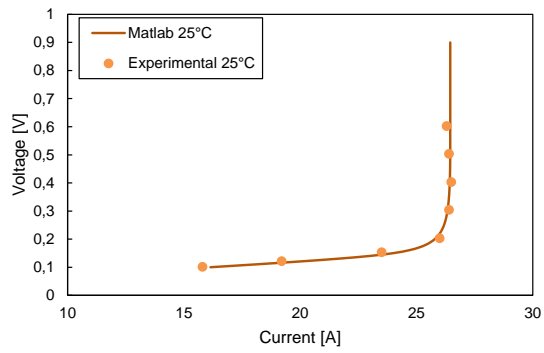


Figure 32. Matlab-experiments comparison for 25 °C

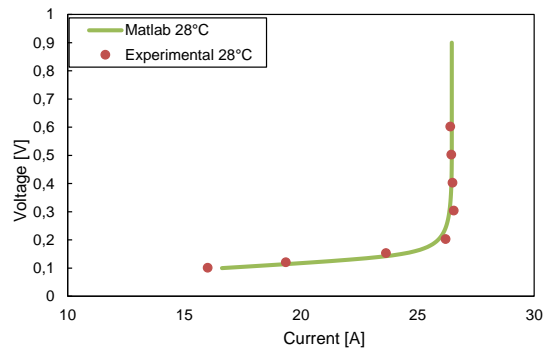


Figure 33. Matlab-experiments comparison for 28 °C

# Chapter 6

## Conclusions and future work

In this work the behavior of the EHC is studied under different operating conditions and compared with a Matlab® model already developed which has been improved. Specifically, CO<sub>2</sub> and temperature influence are studied.

For analyzing the effect of CO<sub>2</sub>, it is firstly analyzed the performances decrease which occurs in case of H<sub>2</sub>-CO<sub>2</sub> mixture. Starting from literature, the Reverse WGS is the most considerable reaction for polluting the catalyst. From the experiments performed, it could be possible to demonstrate the RWGS is actually the main reaction occurring while electrochemical reaction of CO<sub>2</sub> is neglected. For recovering the catalyst, the most promising method is air bleeding, due to the short time required to completely regenerate the catalyst. The influence of voltage and hydrogen concentration has been studied for a proper understanding of the catalyst pollution. The main conclusion is that higher voltages and higher concentrations of hydrogen lead to slower pollution of the catalyst.

For studying the effect of the temperature N<sub>2</sub> as inert gas has been analyzed. For the particular case of carbon dioxide, it is proved the negative influence of temperature in inhibiting the catalyst for low temperatures, due to RWGS reaction which is more likely to occur at higher temperature. Furthermore, permeation mechanisms are evaluated, for the cases of Helium and CO<sub>2</sub>. The results conclude that He goes through the membrane because of its low solubility, while CO<sub>2</sub> permeation is because of its solubility in water.

It is worth to highlight the problem related to hydration of the membrane. This is the most important variable to be controlled when working, and the most susceptible to change. Dehydration is even more likely to happen when working at higher temperatures. All the other variables are easier to control with the setup proposed.

Even though it has to be more developed in this technique, the future of the Electrochemical Hydrogen Compressor seems promising.

The following steps to be made in order to get a better understanding should be related with the temperature. In this work, it has been studied a range of temperatures between 20 and 30°C. However, it is stated by HyET® that the optimum range of working is around 65°C, but with the setup proposed it is very difficult to achieve perfect operating conditions. Because of that, it should be considered making some changes in the setup to make this easier.

Related with CO<sub>2</sub> problems, different catalyst can be tested. For instance, Ruthenium has a positive effect when working with CO<sub>2</sub> at higher temperatures, because it can avoid RWGS in the catalyst, so it can lead to an increase in the efficiency. It can also be considered the case of feeding a small amount of oxygen in the inlet stream that will be able to react with the CO adsorbed in the catalyst. The problem of this change remains in the possibility of reacting H<sub>2</sub> and O<sub>2</sub> electrochemically, making the compressor work as a Fuel Cell, leading to problems related to peaks of voltage.

Despite this last paragraphs, it has been checked that EHC is a promising method when purifying and pressurizing hydrogen. By continuing its development and research, the Electrochemical Hydrogen Compressor will become a competitive technology in a future energy market.

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