

Master thesis

**Master's degree in Energy Engineering
(MUEE)**

**Modeling and analysis of an electrolyser for
power to gas applications**

REPORT

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ABSTRACT

Year after year the installed capacity of renewable sources (such as photovoltaics or wind turbines) is growing, but this increase must be accompanied by new storage systems to make the most of the generation and respond to the load demand even when the generation isn't possible.

One of the options that is under development and has a very promising future as a complement to renewable energy systems is hydrogen electrolyser, which by applying electricity splits water into oxygen and hydrogen. The produced hydrogen can be used as an energy carrier, stored and converted back into electricity when needed by using fuel cells. The idea of this study is to derive a mathematical model of an electrolyser, capable of capturing the most important dynamics of hydrogen production process.

Among different electrolyser technologies, Polymer Electrolyte Membrane (PEM) seem to be the ideal option for this case, due to the maturity of the technology, better working conditions, fast response and availability in the market.

After a comprehensive literature review on the modelling techniques for PEM electrolysers, the next step followed is the study of all chemical and electrical phenomena that take place. The mathematical model is divided in four modules (anode, cathode, membrane and voltage) that are modelled in Matlab Simulink, to study their dynamics. The results generated are compared with current literature for validation. Once the model is validated, different values of stack's pressures and temperatures are tested to obtain the optimal operation conditions (60°C and 1 Bar).

PEM electrolyser response time is less than 1 s, but the start up procedure may take 10 s. Another fact to consider is that at high current conditions, the electrolyser has losses that are translated in heat (between a 20-10 % of the total power), which could be used in other processes to make the overall efficiency higher.

This project aims to present electrolysers as a great storage system for using the surpluses of the grid, because they have a fast response and could be great for improving the efficiency.

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1. GLOSSARY

<i>A</i>	Cell area, m^2	<i>n</i>	Number of cells
<i>a</i>	Water activity	<i>n_d</i>	Electroosmotic drag coefficient
<i>A_{ext}</i>	External area of the electrolyser, m^2	<i>P</i>	Pressure, Pa
<i>C_p</i>	Heat capacity, $J\ mol^{-1}\ K^{-1}$	<i>Pr</i>	Prandtl number
<i>C_w</i>	Concentration of water, $mol\ m^{-3}$	<i>Q</i>	Heat, W
<i>D_w</i>	Membrane diffusion coefficient, $m^2\ s^{-1}$	<i>Re</i>	Reynolds number
<i>ε</i>	Emittance of the material	<i>R_{ohm}</i>	Membrane resistance, Ω
<i>E</i>	Open circuit voltage, V	<i>R_u</i>	Universal gas constant, $8.314\ J\ mol^{-1}\ K^{-1}$
<i>EW</i>	Equivalent weight	<i>T</i>	Electrolyser temperature, K
<i>F</i>	Faraday constant, $96485\ C\ mol^{-1}$	<i>t_{me}</i>	Thickness of the electrolyser, m
<i>h</i>	Enthalpy, $J\ kg^{-1}$	<i>V</i>	Volume, m^3
<i>h_c</i>	Conductive heat transfer coefficient, $W\ m^{-2}\ K^{-1}$	<i>V</i>	Volume m^3
<i>h_r</i>	Radiative heat transfer coefficient, $W\ m^{-2}\ K^{-1}$	<i>W</i>	Electrical work applied, W
<i>I</i>	Current, A	<i>y</i>	Molar fraction
<i>i</i>	Current density, $A\ m^{-2}$	<i>z</i>	Compressibility factor
<i>i₀</i>	Exchange current density, $A\ m^{-2}$	<i>η_{el}</i>	Electrolyser efficiency
<i>k_{ao}</i>	Anode outlet flow coefficient, $mol\ s^{-1}\ Pa^{-1}$	<i>η_F</i>	Faraday efficiency
<i>k_{ca}</i>	Cathode outlet flow coefficient, $mol\ s^{-1}\ Pa^{-1}$	<i>ΔH</i>	Enthalpy of formation, $J\ mol^{-1}$
<i>k_m</i>	Thermal conductivity of air, $W\ m^{-1}\ K^{-1}$	<i>ΔG</i>	Gibbs free energy of formation, $J\ mol^{-1}$
<i>L</i>	Electrolyser length, m	<i>σ_m</i>	Membrane conductivity, $S\ cm^{-1}$
<i>M</i>	Molar weight, $g\ mol^{-1}$	<i>α</i>	Charge transfer coefficient
<i>m</i>	Mass Flow, $kg\ s^{-1}$	<i>λ</i>	Membrane water content
<i>N</i>	Molar flow rate, $mol\ s^{-1}$	<i>ρ</i>	Density, $kg\ m^{-3}$
<i>N_u</i>	Nusselt number	<i>σ</i>	Boltzmann constant, $5.67 \cdot 10^{-8}\ W\ m^{-2}\ K^{-4}$

2. PREFACE

The energy engineering sector has been evolving since the beginning of electrical production, but nowadays it is facing one of the most important and promising challenges, which is transitioning to a model with the lowest environmental impact possible.

The increasing price of fossil fuels and its contamination have open the door to other substitutes such as hydrogen, which isn't contaminant and could be used in the same processes: transport, heating or electricity generation. This element is very abundant in the earth, despite that it isn't available in a pure way, so it has to be processed. Electrolysers are one of the most interesting options to obtain hydrogen without damaging the environment.

In order to play our part in this transition, the aim of this report is to understand how electrolysers work and their possibilities as storage systems. With the collaboration of Oriol Gomis-Bellmunt and Saman Dadjo Tavakoli which are part of the CITCEA (research UPC group specialized in power electronics and its applications), we are going to study and develop a dynamic model in Matlab Simulink to study the possibilities of this technology.

3. INTRODUCTION

Nowadays climate change is an increasingly reality, both the scientific community and the vast majority of countries recognize this phenomenon and have set different objectives to avoid global warming and the changes that this may entail.

Avoiding the climate catastrophe and making the transition to a carbon neutral world is one of the greatest challenges that today's society must face in the coming years, that's why the European Union has set a zero-emission objective for 2050. The energy system must change drastically and one of the solutions is the introduction of renewable energy [5].

In the specific case of Spain in 2020, the generation of electricity from renewable sources, according to REE (Red Eléctrica de España), accounted for 43.6 % a value never achieved before. By 2030 the goal is to generate the 74 %, so there is a lot of work for the coming years, the installed power must increase considerably and the efficiency of the grid has to improve [9].

One of the disadvantages of renewable energy is the dependence on the environmental conditions, so to achieve a zero emissions system there must be also an investment on storage installations, to use as much as possible the renewable sources and compensate the demand even when the conditions do not allow production [20]. Today there are different systems that can be the perfect complement to renewables.

The pumped-storage hydroelectric plants are one of the most mature technologies, they are very efficient but there are few places where these facilities can be established, the capital costs are high and also the environmental impact. Batteries are as well a very developed technology, but when it comes to storing large quantities of energy, they are not the most efficient option, the used materials, their lifetime and the hard recycling process, make them a valid technology but not the most attractive [2].

There are more technologies for storage, but electrolysers are one of the most promising technologies because they allow to transform the electricity into hydrogen, a gas that can be stored, used as a substitute for fossil fuels (transportation), or converted back into electricity by using fuel cells [1].

The following paper aims to study the world of hydrogen to see if it could be a useful tool to accelerate the transition to a zero emissions system. The focus will be put on obtaining a representative model of an electrolyser, for understanding its operation and see if they could be a great complement to transform the surpluses of the grid.

3.1. Project objectives

The principal objectives must be defined to know exactly which is going to be the direction:

1. Discover the world of hydrogen, know where the technology is now, the different types and which are the future directions.
2. Understand the difference between electrolysers, fuel cells and reversible fuel cells. The different types available in the market, applications and working conditions.
3. Select the type and characteristics of the electrolyser that suits the project conditions in the best way.
4. Study the different electrical and chemical phenomena that happen in the anode, cathode, membrane and voltage modules. Once the mathematical expressions are known, create a dynamic model with the help of Matlab Simulink.
5. Present the energy balance of the electrolyser, studying the heat gains and losses and adding a heat exchanger to assess the necessity of heating or cooling depending on the conditions.
6. Compare the results provided by the model with literature and select the best operating pressure and temperature.
7. Study the performance of the system at the selected conditions, determine the storage tank volumes and working limitations.

3.2. Hydrogen





It is one of the candidate energy sources for replacing fossil fuels, there are a lot of expectations and its presence in our society has been increasing during the last years. What makes it really interesting is that it can be used as fuel at combustion reactions (to generate heat) or at fuel cells (to generate electricity) and in both cases water is generated as product, avoiding the emissions of contaminant gases such as CO_2 [3]. Also, it has a higher energy density, so produces a greater amount of energy per unit of volume than any other fuel [5].

Despite being a very abundant element on the planet it is practically impossible to find it at pure state, so it must be produced from elements with a good concentration of hydrogen such as water or hydrocarbons. It is considered as a source of energy like electricity because more energy is needed to produce it than what can provide. Currently the major part of H_2 is not used for energy purposes, is destined to other processes such as the synthesis of pharmaceutical and chemical products like ammonia [2].

Approximately the 95% of produced H_2 comes from fossil resources and the most common processes are reforming or partial oxidation of fuels (such as methane or coal), in which polluting compounds like carbon dioxide are obtained. There are cleaner ways of producing it and the International Renewable Energy Agency (IRENA) considers the following types of hydrogen, depending on the production process [3]:

- **Grey:** It is produced from methane or coal and as by-products of the process (apart from H_2) polluting gases such as carbon dioxide or carbon monoxide are produced, which are released into the environment.
- **Blue:** Natural gases or coal are used, but in this case the contaminant products generated are captured by Carbon Capture Systems (CCS). It allows the reduction of emissions (between 85-95 %), but it is still not a neutral system, the CCS technology is still under development and very energy consuming.
- **Turquoise:** Generally methane is subjected to a pyrolysis process and hydrogen and carbon are obtained, the later is in solid state avoiding the production of CO_2 . It's in between green and blue, produced with heat and electricity.
- **Green:** Basically, all hydrogen that does not come from fossil fuels and its production do not generate carbon emissions is classified as green. The most widely used and mature technology is the electrolysis of water, using renewable energy sources such as solar or wind.

Figure 1 shows these 4 types of hydrogen, despite that new ways of production (pink or yellow) have appeared in the last years, but are still under development

Color	GREY HYDROGEN	BLUE HYDROGEN	TURQUOISE HYDROGEN*	GREEN HYDROGEN
Process	SMR or gasification	SMR or gasification with carbon capture (85-95%)	Pyrolysis	Electrolysis
Source	Methane or coal 	Methane or coal 	Methane 	Renewable electricity 

Note: SMR = steam methane reforming.

* Turquoise hydrogen is an emerging decarbonisation option.

Figure 1: Colours of Hydrogen according to IRENA classification [3]

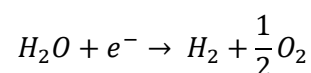
Currently, the production of green H_2 is insignificant and there are only few projects; however, an increase is expected for the next few years. *Iberdrola* for example opened this May at Spain the biggest plant in Europe, with an electrolysis capacity of 20 MW, that will use the gas for producing fertilizers [5].

Today the production of hydrogen for power generation isn't competitive if it's compared with other energy sources but, according to European *Hydrogen Roadmap* [5], they state that it could be profitable if the surpluses of renewable energy were used. The truth is that nowadays only the energy that is going to be consumed is produced, this means that sometimes renewable sources have to be limited while their generation could be higher, losing as a consequence an energy that could be used.

When it comes to consuming or obtaining green hydrogen, two types of devices stand out. In one hand there are the electrolyzers, whose objective is to produce H_2 (from water and electricity) and in the other the fuel cells, which are responsible for transforming the fuel into electricity and heat. Currently there are devices that allow both processes to be carried out, it is important to know the reactions that occur, the types and how each one works, that's why they are going to be studied in the following sections.

3.3. Electrolyzers

They base their operation on the electrolysis of water, an electrochemical process that consists on separating the H_2O into hydrogen and oxygen, through the application of electricity. The overall reaction could be written as:



This general one is the result of two intermediate reactions:

- **Oxidation:** is where the oxygen is generated and it happens at the anode.
- **Reduction:** it occurs in the cathode and is where the hydrogen appears.

These two interactions depend on the characteristics of the electrolyser and the most determining and important components are [6]:

- **Electrodes:** Two are needed, the anode and the cathode. In each one the reaction that takes place is different, both are connected to a current source and in contact with the electrolyte.
- **Electrolyte:** It could be liquid or a solid solution, its main objective is decreasing the current resistance and facilitate the ions and electrons circulation between electrodes.
- **Separation membrane:** It is in charge of avoiding the mixing between the products (O_2 and H_2) and allowing the circulation of the ions between electrodes.

A source of electricity (where the electrodes are connected) is also indispensable to carry out the process, but it does not determine the behaviour of the system.

Table 1: Alkaline and PEM electrolyser indicators from 2020 and in 2050 according to IRENA [18]

	2020		2050	
	Alkaline	PEM	Alkaline	PEM
Cell Pressure (Bar)	< 30	<70	>70	>70
Energy required vs Hydrogen generation ratio (kWh/KgH₂)	50-78	50-83	<45	<45
Lifetime (thousand hours)	60	50-80	100	100-120
CAPEX for stacks >1MW (USD/kW_{el})	270	400	<100	<100

Currently the most mature technologies are the alkaline and PEM electrolysers, *Table 1* reflects how both where in 2020 and the expected improvements for the coming years. Now PEM are much more expensive, but a reduction is expected for 2050, the system efficiency is more or less the same and both technologies are supposed to reduce the energy consumption. Alkaline have a slightly lower lifetime and work at lower pressure, despite that both types are going to be studied in the following sections to decide which suits better the

study case.

3.3.1. Alkaline electrolyzers

This is one of the most used techniques in the chemical industry, due to its simplicity and state of development, the basic components of alkaline electrolyser are shown at *Figure 2*. Normally both the anode and the cathode are made of the same material (Nickel-coated iron or Nickel-derived metal) and must be quite porous to maximize the surface in contact with the solution. For the electrolyte, an aqueous solution of NaOH or KOH is generally used and in the case of the separation membrane the most common are polymers or porous ceramic materials (in the past asbestos) [6].

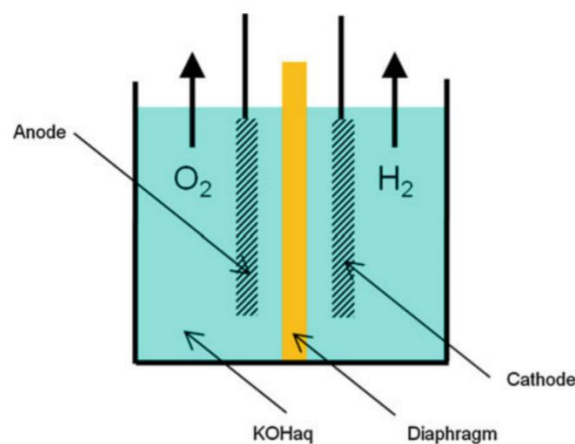
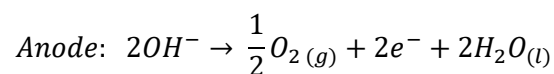
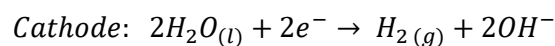


Figure 2: Alkaline electrolyser schema

When applying current, two are the intermediate reactions that take place:



In this way hydrogen is obtained at the cathode and oxygen at the anode. As we have a basic solution, the hydroxide ion (OH^-) is the one that crosses the separation membrane and is responsible for transferring the charge from one electrode to other.

Alkaline electrolyzers are the cheapest of the market and it is a very mature technology, however they have certain limitations. Their energy efficiency is low, they only work at low pressures and at limited current densities. This last factor is the one that rules out this technology for the combination with intermittent energy sources (such as renewables) due to its operation is not flexible [2].

However, the new trends in AWE are focused on the development of new structures and

materials for the electrolyte, to work in wider current ranges and higher pressures, but this is still under development.

3.3.2. Polymer electrolyte membrane electrolysis

As an alternative in 1966, proton exchange membrane electrolyzers (PEM) were proposed, which allow working at high pressures, have low gas permeability and very good proton conductivity [8].

This is one of the best options for converting renewable energy into green hydrogen due to the compact design, high current density, energy efficiency, its rapid response time, the low operating temperature range (5-90 °C) and the purity of the hydrogen obtained [2].

As a difference with the alkaline, the components are displaced in a more compact way, the separation membrane and electrolyte are all in the same block known as the membrane-electrode assembly (MEA). The main parts such as the current collectors (which also function as gas diffusion membranes), the electrodes and the separator plates, are reflected at *Figure 3*.

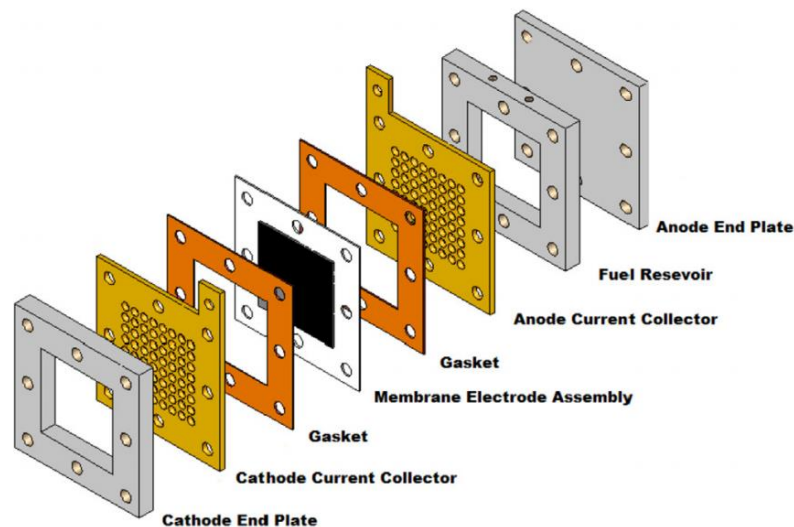


Figure 3: Example of a PEM electrolyser

The MEA is formed by a separation membrane, generally made of Nafion (synthetic polymer with ionic properties, known as ionomers) a durable material that allows working at high current densities, has good proton conduction and mechanical stability. There are also anode and cathode electrocatalysts, with the aim of reducing the activation energy and increasing the speed of reaction, and an ionomer solution to improve ion transport properties [11].

Regarding its operation it is described at *Figure 4*, the water penetrates through the anode and when gets in contact with it the first reaction occurs, obtaining oxygen as a product in

gas state, hydrogen protons and electrons. Next, the H^+ crosses the membrane reaching the cathode and producing the second reaction where hydrogen is obtained in gas state.

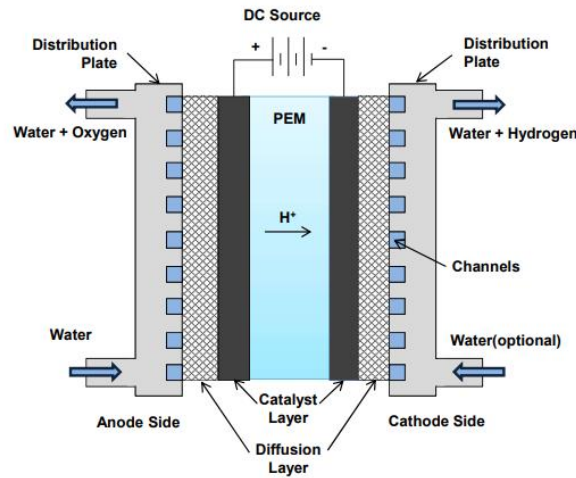
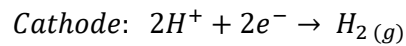
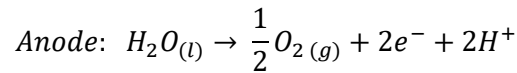


Figure 4: PEM electrolyser operation, flows in and out and components.

The membrane avoids the mixing between the O_2 generated and H_2 and prevent the passage of most of the water. The intermediate reactions can be expressed as:



Despite being more expensive than alkaline electrolyzers, PEM can operate in a more flexible way. This is a huge advantage when it comes to using the energy excess from the grid, since it allows to manage a large amount of electricity in a short period of time. For these reasons, nowadays the best way to obtain green hydrogen through the surplus energy generated from renewables, is by using PEM-type electrolyzers, which are becoming more and more economical and are already available on the market.

3.4. Fuel Cells

Like batteries, Fuel Cells (FC) intend to produce electricity from an electrochemical reaction, in this case between a fuel and an oxidizing agent (such as O_2), with the advantage that it is not necessary to recharge them since they always generate electricity as long as fuel (usually methane or hydrogen) is injected.

Structurally they are very similar to electrolyzers (as it is shown at *Figure 5*), made up of two electrodes, an anode where the fuel is introduced and a cathode where the oxidizing component enters, separated in between by an electrolyte. The H_2 is injected and when

contacts the anode catalyst, the molecule separates into electrons and hydrogen protons. The electrons travel through an external circuit creating the flow of electricity and the protons move to the cathode through the electrolyte, to obtain water and heat as a by-product [35].

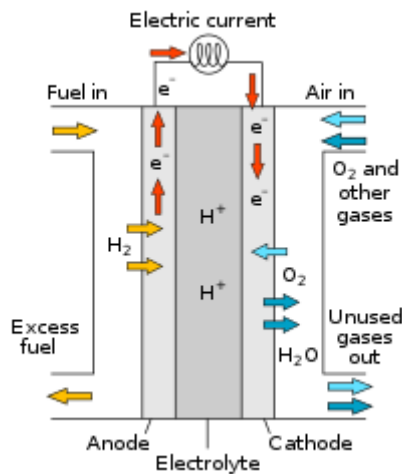


Figure 5: Fuel Cell structure and flows

They have a wide range of possibilities within the energy market where their use can be more beneficial than current options. Stationary cells have the advantage, compared to batteries, that they do not self-discharge, their useful life is much longer and they can work at higher temperatures, but they are still more expensive and the overall efficiency of the process is lower. According to IRENA [2], in cases where large amounts of thermal energy and electricity are needed, Fuel Cells are the most interesting option. They are also an option to replace diesel generators that require more maintenance and pollute much more.

Depending on their application FC can be more manageable, like the ones installed in vehicles, or more robust and stationary, which are usually destined to supply buildings such as hospitals or industries.

Table 2: Comparison between Fuel Cell technologies [35]

FC TYPE	PEMFC	AFC	PAFC	MCFC	SOFC
Name	Polymer Electrolyte Membrane	Alkaline	Phosphoric acid	Molten carbonate	Solid Oxide
Working T (°C)	<120	<100	150-200	600-700	500-1000
Applications	Vehicles Portable power Backup power	Space Backup power Transportation	CHP scenarios Electrical generation	CHP scenarios Electrical generation + turbine	CHP scenarios Electrical generation + turbine
Electrical Efficiency	60% H_2 40% other fuels	60%	40%	50%	60%

*CHP: Combined Heat and Power

Nowadays they are classified according to the used electrolyte, since it determines factors such as the electrochemical reactions, the type of catalyst, the operating temperature

range, the fuel, etc. There are already a wide variety of possibilities for Fuel Cells on the market as it is shown at *Figure 6* and the most relevant types are listed at *Table 2* [35].



Figure 6: Commercially available and types of FC

3.4.1. Polymer electrolyte membrane fuel cells (PEMFC)

They use a solid polymer with special electronic characteristics (ionomer) as electrolyte and the electrodes are usually made of porous carbon covered with a noble metal, usually platinum, which acts as a catalyst. For their operation they only need oxygen from the air, water and hydrogen, which must be pure to avoid poisoning the catalyst. The also known as proton exchange membrane fuel cell, works at a relatively low temperature what makes the heating time short, a fast start-up and avoids the necessity of resistant materials [35].

Its fast start-up procedure and the power-to-weight ratio (among other characteristics) make the PEMFC the most used for the automotive sector, such as cars and buses, and an attractive option for certain stationary applications where a fast start-up is essential. The only drawback of this type of cell is that the platinum catalyst are expensive and sensitive to carbon monoxide, what means that it has to work with a very pure hydrogen to avoid poisoning. When the fuel is derived from hydrocarbons, must be processed before entering the FC to eliminate the carbon monoxide.

3.4.2. Alkaline fuel cells (AFC)

AFC'S were one of the first technologies to appear in the world of fuel cells. They use a basic solution of potassium hydroxide as electrolyte and for the catalysts (both the cathode and the anode) have a wide range of possibilities and non-precious materials, a fact that reduces their cost.

They stand out for their low price, their long experience and efficiency, but they have a drawback that rules them out compared to other options. The biggest problem with these cells is that they are extremely sensitive to carbon dioxide and a minimal concentration

(such as that presents in the air) can reduce their durability and production, due to the formation of carbonate.

Its operation is very similar to conventional PEMFC with the difference that they have an acidic environment and the alkaline ones are basic. To be competitive with current technologies, alkaline fuel cells must improve in factors such as sensitivity to CO_2 , higher operating temperatures, improve power density, conductivity and durability of the membrane.

3.4.3. Phosphoric acid fuel cells (PAFC)

The electrolyte used is made from phosphoric acid, the electrodes are from porous carbon and they use platinum as a catalyst. PACF'S are considered the first generation of modern fuel cells, what makes them one of the most mature technologies and has led them to be among the first available on the market.

One of the advantages is that they are more tolerant to the presence of carbon dioxide, so the catalysts are not so easily poisoned. With regard to efficiency, in cogeneration mode where heat and electricity are used they can reach values higher than 85 %, but if we use them only to generate electricity, efficiencies drop to 37-42 % [6], similar values to conventional generation plants which usually are around 33 % [35].

They are generally used for stationary applications, due to their weight and width, where the energy needs are both heat and electricity, such as a hospital. Its main drawback is the high price, because of the amount of platinum, and also the low starting speed, due to they generally work at high temperatures and take a long time to heat up.

3.4.4. Molten carbonate fuel cells (MCFC)

MCFCs use a molten carbon salt suspended in a ceramic matrix as electrolyte. The main characteristic of these FCs is its working temperature, which is usually close to 650 °C [35], a fact that determines the materials used and the efficiency. As by-product high-temperature vapor is obtained, which can be used to generate electricity through a turbine and allows to reach electrical efficiencies close to 65 %. In addition, if the residual heat is also used the efficiency can be greater than 85 %. They are generally used for stationary applications with high energy demands, where heat and electricity are needed, and in situations where the start-up time is not a.

When working at such high temperatures, an external reactor is not necessary to convert the biogas or natural gas into hydrogen, since reforming reactions take place automatically inside the cell, what reduces the cost and the possibility of poisoning. At the same time the main disadvantage is the high working temperatures, which reduces the lifetime because accelerates processes such as corrosion or the wear of materials. Work is currently under

way on this front to increase the useful life beyond 5 years.

3.4.5. Solid oxide fuel cells (SOFC)

As the previous type, the working temperatures are high reaching up to 1000 °C and also a non-porous ceramic compound is used as the electrolyte. Its electrical efficiency is round 60 % and in situations where residual heat is also used, can reach 85 % [35]. When working at such high temperatures, catalysts are not necessary (which reduces the cost) and the reforming process is carried out internally, what allows to work with a wide range of fuels and makes them very resistant to the presence of sulphur.

As in MCFCs, the high temperatures are at the same time a disadvantage, because they make the start-up slow, the rate of degradation of materials increases and has to be very well insulated (to avoid energy losses and damage), what makes them robust and heavy. SOFCs stand out for their high efficiency, for having a wide range of possible fuels and for their economic price, which makes them a good option for stationary applications. Despite its slow start-up and the rapid degradation of materials, are disadvantages to consider.

3.5. Reversible fuel cells

These types of cells can carry out both processes, generating electricity and hydrogen with the same device, depending on the necessities.

They could be the ideal complement for renewable energy sources, such as wind or solar, since they allow to convert the excess electricity into hydrogen, in such a way that when the distribution network requires it and we do not have resources, can be transformed into electricity [5]. Despite of this promising future, the RFCS are still under development and there are only demonstration projects in aeronautical applications or similar, where the cost is not one of the most relevant factors.

They can be classified into two types [6]:

- **Discrete Reversible Fuel Cells (DRFC's):** The electrolyser (EL) and the fuel cell (FC) are two different components that work independently, but are part of the same system. This allows to generate electricity and hydrogen simultaneously and that the EL and the FC are designed to optimize their individual operation and cost. They are generally accompanied by three storage systems for water, oxygen and hydrogen. The main disadvantage is the big volume that the system occupies and its complexity, it can only be used in applications where space is not a problem.
- **Unified Reversible Fuel Cells (URFC's):** Both the electrolyser and the fuel cell are the same element, they are made up of the same parts. In this case, they are fully reversible fuel cells, in electrolyser mode the electrochemical reaction goes in one

direction and in cell mode in the opposite, in such a way that only one of the processes can be carried out. The advantages of this system is its size and its lower price compared to DRFC'S, which makes it very attractive for space applications.

3.6. Conclusions

Electrolysers and Fuel Cells are a very attractive option to manage the power surplus of the grid, the former allows to transform and store this energy in the form of hydrogen, that can be used when needed. Reversible fuel cells are a great concept but there aren't actually many real projects and the technology is still under development.

Fuel cells have been available in the market for a few years, there is a great variety and their presence has increased lately in places such as hospitals, cars, datacentres, etc. However, such increase must be accompanied with the production of green hydrogen and a reduction in its cost, which at present is still not competitive (economically speaking) with other fuels. Nowadays FC normally run with natural gas or other hydrocarbons derivatives.

4. MATHEMATICAL MODEL

According to the literature electrolyser models are generally divided in four modules anode, cathode, membrane and voltage, where the principal phenomena take place. In this case the model is going to be similar to the ones proposed by [29] [32] [34]. *Figure 7* shows a simple schema of a conventional PEM electrolysis plant.

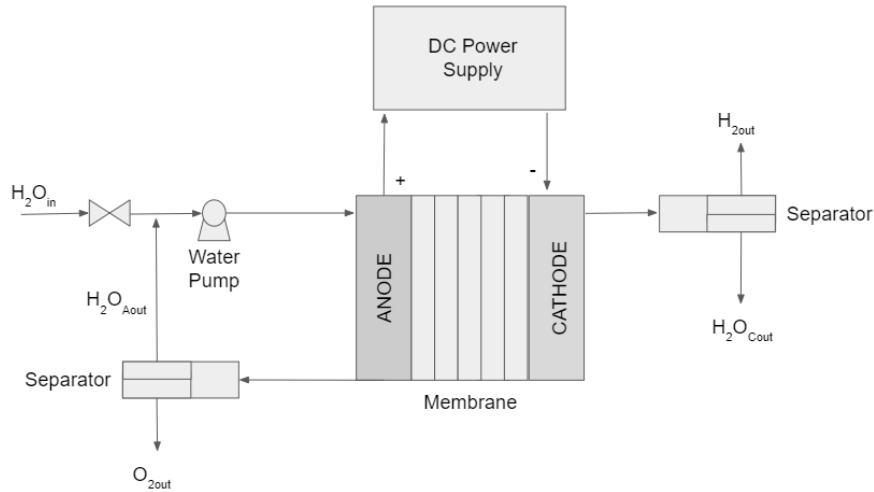


Figure 7: PEM electrolyser schema

Figure 8 reflects approximately how the modules are interconnected together to make an overall model of PEM stack. The Matlab Simulink files can be found at the *Appendix I, II* and *III*.

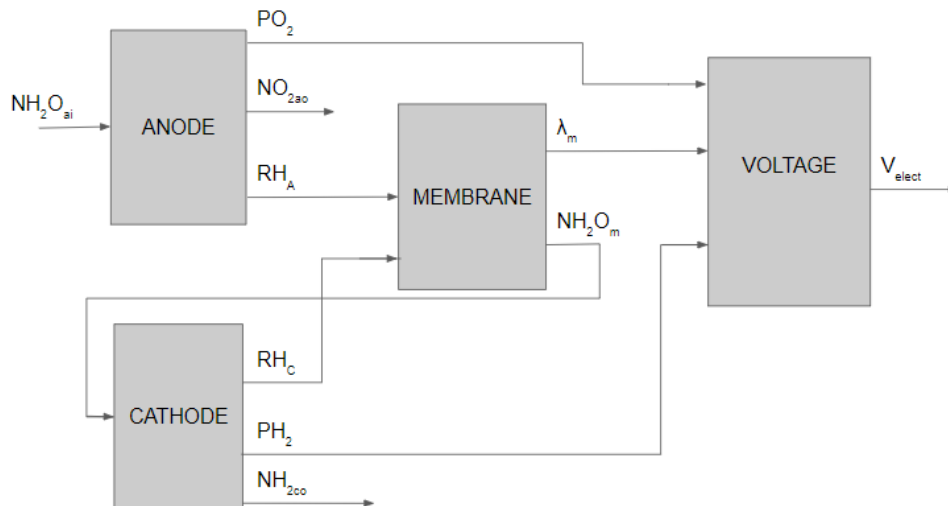
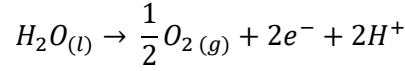


Figure 8: Distribution of the modules at Simulink

4.1. Anode

The water is injected into the electrolyser and once it gets in contact with the anode starts the reaction, obtaining as products oxygen in gas state, electrons and hydrogen ions. The reaction is represented as:



The O_2 and the excess H_2O go out of the anode to their respective storage tanks, the H^+ travel through the membrane to the cathode and the electrons go to the power supply via the external circuit.

Two are the main mass balances:

- **Water:** Equal to the water flow that goes inside the anode, subtracted by the one that exits it and the amount that is dragged to the cathode as a consequence of the diffusion and the electro-osmotic drag phenomena. The differential equation would be represented as:

$$\frac{dNH_2O_{an}}{dt} = \dot{N}H_2O_{ai} - \dot{N}H_2O_{ao} - \dot{N}H_2O_{eod} - \dot{N}H_2O_{diff} \quad [mol/s] \quad (1)$$

The $\dot{N}H_2O_{ai}$ is given and constant during the time and $\dot{N}H_2O_{ao}$ must be calculated. $\dot{N}H_2O_{eod}$ and $\dot{N}H_2O_{diff}$, as they are phenomena that occur at the membrane, will be explained and calculated at that module.

- **Oxygen:** The molar flow is given as the quantity that goes inside the anode, plus the generated and subtracted by the flow that goes out.

$$\frac{dNO_2}{dt} = \dot{N}O_{2ai} + \dot{N}O_{2gen} - \dot{N}O_{2ao} \quad [mol/s] \quad (2)$$

As we consider that the only flow that goes in is water, $\dot{N}O_{2ai}$ is equal to 0 and we could rewrite the equation as:

$$\frac{dNO_2}{dt} = \dot{N}O_{2gen} - \dot{N}O_{2ao} \quad [mol/s] \quad (3)$$

The oxygen generated is calculated from *Faraday's* equation where n is the number of electrolyser cells, I the current, F the Faraday's constant and η_F the Faraday efficiency.

$$\dot{N}O_{2gen} = \frac{n \cdot I}{4 \cdot F} \cdot \eta_F \quad [mol/s] \quad (4)$$

To obtain the Faraday's efficiency we use (5), where i is the current density (which is equal to I divided by the active Area) and i_{loss} represents the internal loss considered as a 1% of the current density [29].

$$\eta_F = \frac{i - i_{loss}}{i} \quad (5)$$

Another important parameter that must be considered is the pressure (P). The two main elements in the anode are the O_2 and H_2O , so the total pressure is equal to the sum of their partial pressures. To know the P of each species it is used the *Ideal Gas Law* [29].

$$PO_2 = \frac{NO_2 \cdot R_u \cdot T}{V_{an}} \quad [Pa] \quad (6)$$

$$PH_2O_{an} = \frac{NH_2O_{an} \cdot R_u \cdot T}{V_{an}} \quad [Pa] \quad (7)$$

$$P_{an} = PO_2 + PH_2O_{an} \quad [Pa] \quad (8)$$

Once PO_2 and PH_2O_{an} are known the molar fractions (y) can be obtained using the *Dalton Law* [33].

$$yO_2 = \frac{PO_2}{P_{an}} \quad (9)$$

$$yH_2O_{an} = \frac{PH_2O_{an}}{P_{an}} \quad (10)$$

The anode total outlet flow (\dot{N}_{ao}) is calculated using (11), where P_{el} represents the working pressure of the electrolyser and k_{ao} is the outlet flow coefficient of the anode, which is equal to 0.95 ($mol/s \cdot Pa$) [29].

$$\dot{N}_{ao} = k_{ao} \cdot (P_{an} - P_{el}) \quad [mol/s] \quad (11)$$

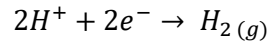
With the total outlet molar flow (\dot{N}_{ao}) and the molar fractions, it can be calculated the flow of oxygen and water that exits the anode.

$$\dot{N}_{O_{2ao}} = \dot{N}_{ao} \cdot y_{O_2} \quad [mol/s] \quad (12)$$

$$\dot{N}_{H_2O_{ao}} = \dot{N}_{ao} \cdot y_{H_2O_{an}} \quad [mol/s] \quad (13)$$

4.2. Cathode

The ions that have passed through the membrane recombine with the electrons to generate H_2 in gas state. The reaction that takes part could be represented as:



In terms of the molar flows we consider two, as in the anode:

- **Water:** In this case we do not have a direct injection of H_2O , the flow is consequence of two phenomena that happen in the membrane:

$$\frac{dNH_2O_{2ca}}{dt} = \dot{N}_{H_2O_{ci}} - \dot{N}_{H_2O_{co}} + \dot{N}_{H_2O_{eod}} + \dot{N}_{H_2O_{diff}} \quad [mol/s] \quad (14)$$

$\dot{N}_{H_2O_{ci}}$ could be neglected, so the equation would be:

$$\frac{dNH_2O_{2ca}}{dt} = \dot{N}_{H_2O_{eod}} + \dot{N}_{H_2O_{diff}} - \dot{N}_{H_2O_{co}} \quad [mol/s] \quad (15)$$

- **Hydrogen:** The flow of H_2 is equal to the amount generated subtracted by the quantity that exists the cathode. The general equation could be written as:

$$\frac{dNH_2}{dt} = \dot{N}_{H_{2ci}} + \dot{N}_{H_{2gen}} - \dot{N}_{H_{2co}} \quad [mol/s] \quad (16)$$

As at the inlet there isn't any flow of hydrogen $\dot{N}H_{2ci}$ is equal to 0, so the equation would be:

$$\frac{dNH_2}{dt} = \dot{N}H_{2gen} - \dot{N}H_{2co} \quad [mol/s] \quad (17)$$

If the electrolyser works at a higher pressure than atmospheric, the hydrogen will not exit the cathode till the desired pressure is achieved. To calculate the generation of H_2 in real time we use *Faraday's* equation:

$$\dot{N}H_{2gen} = \frac{n \cdot I}{2 \cdot F} \cdot \eta_F \quad [mol/s] \quad (18)$$

As in the previous case the *Ideal gas law* is used to calculate the partial pressures which are essential to determine the flows at the outlet:

$$PH_2 = \frac{NH_2 \cdot R_u \cdot T}{V_{ca}} \quad [Pa] \quad (19)$$

$$PH_2O_{ca} = \frac{NH_2O_{ca} \cdot R_u \cdot T}{V_{ca}} \quad [Pa] \quad (20)$$

$$P_{ca} = PH_2 + PH_2O_{ca} \quad [Pa] \quad (21)$$

With these three values the molar fractions are calculated:

$$y_{H_2O_{ca}} = \frac{PH_2O_{ca}}{P_{ca}} \quad (22)$$

$$y_{H_2} = \frac{PH_2}{P_{ca}} \quad (23)$$

Then the molar flow that goes out of the cathode (\dot{N}_{co}) is obtained basing on the flow coefficient ($k_{co} = 0.45 \text{ mol/s}\cdot Pa$), the pressure at cathode (P_{ca}) and desired working pressure (P_{el}).

$$\dot{N}_{co} = k_{co} \cdot (P_{ca} - P_{el}) \quad [mol/s] \quad (24)$$

Once \dot{N}_{co} is known, multiplying it by the molar fractions we can calculate the quantity of hydrogen (\dot{N}_{H_2co}) and water (\dot{N}_{H_2Oco}) that exits the cathode.

$$\dot{N}_{H_2Oco} = \dot{N}_{co} \cdot y_{H_2Oca} \quad [mol/s] \quad (25)$$

$$\dot{N}_{H_2co} = \dot{N}_{co} \cdot y_{H_2} \quad [mol/s] \quad (26)$$

4.3. Membrane

It is important to know what happens in this module, that is responsible of the H^+ transference between the anode and the cathode. Through the membrane there is also a flow of water ($\dot{N}_{H_2O_m}$) from one side to the other caused by diffusion ($\dot{N}_{H_2O_{diff}}$) and electro-osmotic ($\dot{N}_{H_2O_{eod}}$) phenomena, which are influenced by the water content in the membrane.

$$\dot{N}_{H_2O_m} = \dot{N}_{H_2O_{eod}} + \dot{N}_{H_2O_{diff}} \quad [mol/s] \quad (27)$$

- **Electro-osmotic drag:** It represents the water that travels through the membrane attracted to the H^+ . According to [32] round 3 to 4 molecules of H_2O are attached to a proton of hydrogen while it travels between electrodes and this transportation phenomena is estimated with the following expression:

$$\dot{N}_{H_2O_{eod}} = \frac{n_d \cdot i \cdot M_{H_2O} \cdot A}{F} \quad [mol/s] \quad (28)$$

Where F represents the Faraday Constant, M_{H_2O} the molecular weight of water, A the cell active area and n_d the Electroosmotic drag coefficient, that can be calculated as:

$$n_d = 0.0029 \cdot \lambda_m^2 + 0.05 \cdot \lambda_m - 3.4 \cdot 10^{-19} \quad (29)$$

In this case λ represents the membrane water content and λ_m is the mean of anode and cathode. This parameter depends on the water activities (a_{an} and a_{ca}) of each electrode which can be calculated knowing the water saturation pressure (P_{sat}) at

the given conditions, the pressure of water at anode (PH_2O_{an}) and at cathode (PH_2O_{ca}), calculated at previous sections.

$$a_{an} = \frac{PH_2O_{an}}{P_{sat}} \quad (30)$$

$$a_{ca} = \frac{PH_2O_{ca}}{P_{sat}} \quad (31)$$

$$P_{sat} (T \text{ } ^\circ C) = -2846.4 + 411.24 \cdot T - 10.554 \cdot T^2 + 0.16636 \cdot T^3 \quad [Pa] \quad (32)$$

It is considered that the behaviour of the gases mixture is ideal, that's why the expression for the water activities is the same as the relative humidity. Once a_{an} and a_{ca} are known λ_{an} and λ_{ca} can be calculated in both cases using (33).

$$\begin{aligned} \lambda_i &= 0.43 + 17.18 \cdot a_i - 39.85 \cdot a_i^2 + 36 \cdot a_i^3 & 0 < a_i \leq 1 \\ \lambda_i &= 14 + 1.4 \cdot (a_i - 1) & 1 < a_i \leq 3 \end{aligned} \quad (33)$$

Then the membrane water content (λ_m) is equal to:

$$\lambda_m = \frac{\lambda_{an} + \lambda_{ca}}{2} \quad (34)$$

- **Diffusion:** The particles of H_2O are injected at the anode and they tend to travel to a place where the concentration is lower (cathode), this kind of processes are represented by *Ficks law*:

$$\dot{N}_{H_2O_{diff}} = D_w \cdot \frac{C_{wc} - C_{wa}}{t_{me}} \cdot A \quad [mol/s] \quad (35)$$

Being C_{wc} and C_{wa} the water concentration of anode and cathode, t_{me} the membrane thickness and D_w the diffusion coefficient.

$$C_{wa} = \frac{\rho_{me}}{EW_{me}} \cdot \lambda_{an} \quad [mol/m^3] \quad (36)$$

$$C_{wc} = \frac{\rho_{me}}{EW_{me}} \cdot \lambda_{ca} \quad [mol/m^3] \quad (37)$$

The water concentration of the membrane in both electrodes is calculated knowing the density of the membrane at dry state (ρ_{me}) [27], the equivalent weight (EW_{me}) [28] and the anode and cathode water content (λ_i).

The diffusion coefficient (D_w) is equal to:

$$D_w = D_\lambda \cdot \exp \left[2416 \cdot \left(\frac{1}{300} - \frac{1}{T} \right) \right] \quad [m^2/s] \quad (38)$$

Where D_λ :

$$\begin{aligned} D_\lambda &= 10^{-10} & \lambda_m &\leq 2 \\ D_\lambda &= 10^{-10} \cdot (1 + 2 \cdot (\lambda_m - 2)) & 2 < \lambda_m &\leq 3 \\ D_\lambda &= 10^{-10} \cdot (3 - 1.76 \cdot (\lambda_m - 3)) & 3 < \lambda_m &\leq 4.5 \\ D_\lambda &= 1.25 \cdot 10^{-10} & 4.5 < \lambda_m & \end{aligned} \quad (39)$$

4.4. Voltage

Most of the commercially available electrolysers work at current mode (despite they can work at I or V mode) and the operating voltage is calculated depending on the open circuit voltage (E) activation (V_{act}), ohmic (V_{ohm}) and mass transfer (V_{mt}) overpotentials.

$$V_{cell} = E + V_{act} + V_{ohm} + V_{mt} \quad [V] \quad (40)$$

In this case we can neglect V_{mt} , because it is significant when the current density applied is higher than $3 A/m^2$ (out of the scope of this study) so the equation would be:

$$V_{cell} = E + V_{act} + V_{ohm} \quad [V] \quad (41)$$

- **Open circuit voltage (E):** Defined by the *Nernst Equation*:

Where R is the gas constant, T the electrolyser temperature, PH_2 and PO_2 the partial pressures, F the Faraday's constant and a_{H_2O} the water activity between anode and electrolyte, considered as 1 in this case [29]. The standard potential (E_0) is calculated from *Gibbs free energy*:

$$E = E_0 + \frac{R \cdot T}{2 \cdot F} \cdot \left[\ln \left(\frac{PH_2 \cdot PO_2^{1/2}}{a_{H_2O}} \right) \right] \quad [V] \quad (42)$$

$$E_0 = \frac{\Delta G}{2 \cdot F} \quad [V] \quad (43)$$

Being the Gibbs free energy of formation (ΔG) for water 236.48 kJ/mol.

- **Activation polarization (V_{act}):** It is equal to the overpotential in the anode plus the cathode.

$$V_{act} = V_{act-an} + V_{act-ca} \quad [V] \quad (44)$$

$$V_{act-an} = \frac{R \cdot T}{2 \cdot \alpha_{an} \cdot F} \cdot \operatorname{arcsinh} \left(\frac{i}{2 \cdot i_{0an}} \right) \quad [V] \quad (45)$$

$$V_{act-ca} = \frac{R \cdot T}{2 \cdot \alpha_{ca} \cdot F} \cdot \operatorname{arcsinh} \left(\frac{i}{2 \cdot i_{0ca}} \right) \quad [V] \quad (46)$$

In this case α is the charge transfer coefficient (2 for anode and 0.5 for cathode), i the current density and i_0 the exchange current density known as $2 \cdot 10^{-7}$ for anode and $2 \cdot 10^{-3}$ at cathode.

- **Ohmic overpotential (V_{ohm}):** Is calculated with the help of *Ohms Law*

$$V_{ohm} = i \cdot R_{ohm} \quad [V] \quad (47)$$

Knowing the thickness (t_{me}) and the conductivity (σ_m) of the membrane we can calculate the resistance R_{ohm} :

$$R_{ohm} = \frac{t_{me}}{\sigma_m} \quad [\Omega] \quad (48)$$

$$\sigma_m = (0.00514 \cdot \lambda_m - 0.00326) \cdot \exp \left[1268 \cdot \left(\frac{1}{303} - \frac{1}{T} \right) \right] \quad [S/cm] \quad (49)$$

Once all the variables are known, the cell efficiency can be calculated:

$$\eta_{el} = \frac{V_{th}}{V_{cell}} \quad (50)$$

Where V_{cell} is the voltage of one cell of the electrolyser and V_{th} corresponds with the minimum voltage required for the electrolysis reaction and can be calculated as:

$$V_{th} = \frac{\Delta H}{2 \cdot F} = 1.481 \quad [V] \quad (51)$$

In this project it has been considered that all the cells behave electrically in the same way, having the same current and voltage, that's why the total stack voltage (V_{stack}) is equal to the V_{cell} multiplied by the number of cells (n).

$$V_{stack} = V_{cell} \cdot n \quad [V] \quad (52)$$

Assuming this, the minimum voltage required for running the stack would be equal to V_{th} per the number of cells (n), so the stack efficiency it's the same as η_{el} .

4.5. Storage ancillary

The hydrogen that exits the cathode is stored at a tank and its pressure can be calculated with the help of the *Ideal Gas Law*:

$$P_{storage} = PH_2 + P_{initial} \quad [Pa] \quad (53)$$

$$P_{storage} = z \cdot \frac{NH_2 \cdot R_u \cdot T_t}{v_t} + P_{initial} \quad [Pa] \quad (54)$$

Where z corresponds to the compressibility factor of the hydrogen (assumed as 1 in this case), $P_{initial}$ is the initial pressure of H_2 in the bottle (assumed to be 0), NH_2 the flow of hydrogen that goes in and T_t and v_t correspond to temperature and volume of the tank.

In the case of the Oxygen storage tank the procedure is the same, with the difference that the tank volume will be smaller due to the production of O_2 is the half of hydrogen:

$$P_{storage} = P_{O_2} + P_{initial} \quad [Pa] \quad (55)$$

$$P_{storage} = z \cdot \frac{NO_2 \cdot R_u \cdot T_t}{v_t} + P_{initial} \quad [Pa] \quad (56)$$

The volume, maximum pressure and temperature of the tank will be determined in the following sections once the operational conditions of the electrolyser are known.

4.6. Temperature control

As mentioned before the commercially available PEM electrolyzers work at a relatively low temperature from 5 to 120 °C. At higher values the MEA loses stability, what can affect the global efficiency, and the durability of the components reduces considerably.

To avoid overheating the temperature must be controlled, because during the operating there are losses and gains that are translated in heat. Building on the *First Law of Thermodynamics*, it has been studied the energy balance of the system to know the heat demand depending on the operational conditions. Assuming that all the cells behave equally and considering the electrolyser as our control volume (CV), the following energy inputs and outputs can be considered:

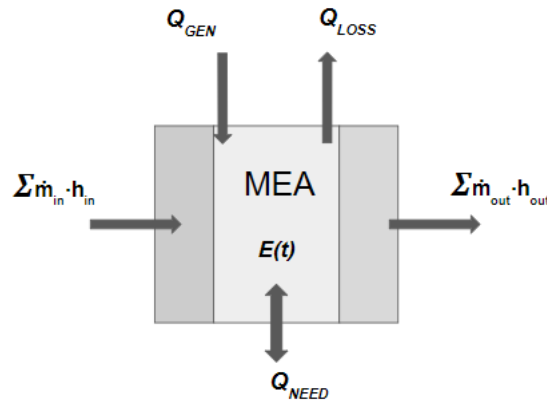


Figure 9: Energy variables related with the system

$$\frac{dE}{dt} = Q_{gen} + \sum (\dot{m}_i \cdot h_i)_{in} - \sum (\dot{m}_i \cdot h_i)_{out} - Q_{loss} + Q_{need} \quad [W] \quad (57)$$

Where:

- $\frac{dE}{dt}$: Represent the energy changes inside the stack and can be calculated as:

$$\frac{dE}{dt} = \frac{d(Cp_i \cdot V_i \cdot \rho_i \cdot T)}{dt} \quad [W] \quad (58)$$

The V_i corresponds to electrolyser volume, it is considered that the density and the heat capacity are constant during the proces and as inside the CV the vast majority is occupied by water $Cp_i = Cp_{H_2O}$ and $\rho_i = \rho_{H_2O}$. The final equation would be:

$$\frac{dE}{dt} = Cp_{H_2O} \cdot V \cdot \rho_{H_2O} \cdot \frac{dT}{dt} \quad [W] \quad (59)$$

- Q_{gen} : Not all the electricity applied is converted into hydrogen and its assumed that the residual energy is translated in heat, represented by this variable.

$$Q_{gen} = W \cdot (1 - \eta_{el}) \quad [W] \quad (60)$$

Where W is the electrical work provided to the system and η_{el} the electrolyzer efficiency. As mentioned above, in this project it is considered that the cells behave equally so the voltage and current are the same for each one. The total power provided could be represented as the equation bellow, considering that n is the number of cells.

$$W = I \cdot V_{cell} \cdot n \quad [W] \quad (61)$$

- $\sum(\dot{m}_i \cdot h_i)_{in}$: Corresponds to the energy provided by the flows that go inside the Control Volume, in this case is composed by H_2O that comes from an external storage (recirculated) at working temperature.

$$\sum(\dot{m}_i \cdot h_i)_{in} = \dot{m}_{H_2O_{ain}} \cdot h_{H_2O_{ain}} \quad [W] \quad (62)$$

- $\sum(\dot{m}_i \cdot h_i)_{out}$: Represents the energy of the flows that go outside the CV, they are composed mainly by H_2O , but there is also H_2 and O_2 .

$$\sum (\dot{m}_i \cdot h_i)_{out} = \dot{m}_{H_2O_{cout}} \cdot h_{H_2O_{cout}} + \dot{m}_{H_2_{cout}} \cdot h_{H_2_{cout}} + \dot{m}_{O_{2_{cout}}} \cdot h_{O_{2_{cout}}} [W] \quad (63)$$

- **Q_{need}** : Stands for the heat needed to control the system at a given temperature. We have considered a water heat ex-changer that depends on the desired (T_{ref}) and electrolyser temperature (T), that can be represented as:

$$Q_{need} = \dot{m}_{H_2O_{HT}} \cdot C_{pH_2O} \cdot (T_{ref} - T) [W] \quad (64)$$

- **Q_{loss}** : To make the control system as real as possible it must be taken into account the heat dissipated to the environment due to convection and radiation, supposing that the electrolyser isn't isolated.

$$Q_{loss} = Q_{conv} + Q_{rad} = (h_c + h_r) \cdot A_{ext} \cdot (T - T_{env}) [W] \quad (65)$$

The A_{ext} corresponds to the external area of the electrolyser (equal to 8.25 m^2), T is the temperature of the electrolyser, T_{env} is equivalent to the environment temperature ($25 \text{ }^\circ\text{C}$) and h_c and h_r correspond to the conductive and radiative heat transfer coefficients that are calculated depending on the characteristics of the system.

- **h_c** : It can be calculated knowing the *Nusselt Number*, the thermal conductivity (for air $k_m = 0.026 \frac{W}{m \cdot K}$) and the electrolyser length (L).

$$h_c = \frac{Nu \cdot k_m}{L} \left(\frac{W}{m^2 \cdot K} \right) \quad (66)$$

Considering that the electrolyser is a rectangle, with a slow-moving air ($0.2 \frac{m}{s}$) and assuming a $Re = 5000$ and $Pr = 0.7$, we can calculate Nu :

$$Nu = 0.66 \cdot Re^{0.675} \cdot Pr^{1/3} \quad (67)$$

- **h_r** : This parameter can be estimated knowing the emittance of the material ($\epsilon = 0.6$ for rough stainless steel), the *Boltzmann* constant ($\sigma = 5.67 \cdot 10^{-8} \frac{W}{m^2 K^4}$) and the average temperature between stack and environment (T_m):

$$h_r = 4 \cdot \epsilon \cdot \sigma \cdot T_m^3 \quad \left(\frac{W}{m^2 \cdot K} \right) \quad (68)$$

5. DYNAMIC STUDY OF THE MODEL

In this section we are going to study the behaviour and dynamics of the model at Matlab Simulink and all the scripts generated can be find at the *Appendix I, II and III*.

5.1. Ensure the proper functioning

Once the model has been developed in Simulink (a detailed description can be found at *Annex I*), the first step is to test it with the same conditions and characteristics as in other papers. In this case we have compared the system with the experiments made at [32], where it is studied the response of the voltage and the hydrogen generation depending on the current.

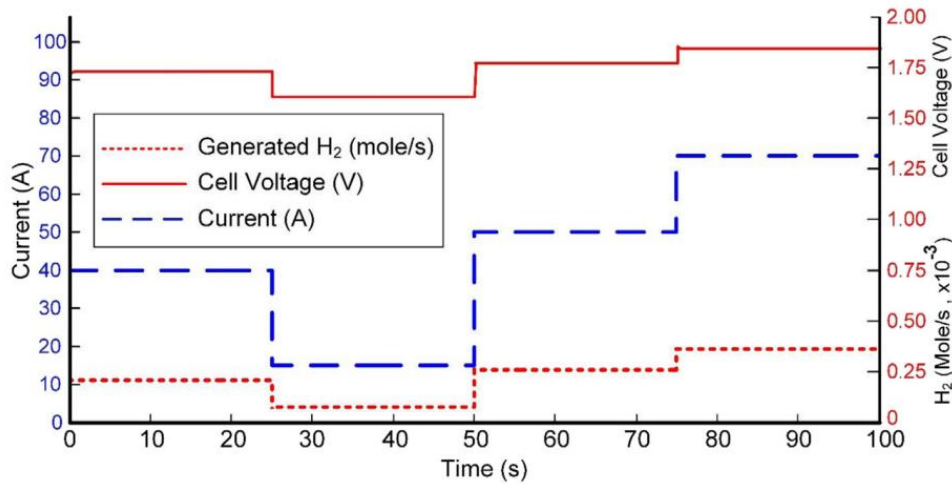


Figure 10: Results from the model proposed by [32]

Figure 10 shows how their system works at cell level, the total stack voltage and H_2 generation would be equal to these values multiplied by 5, that corresponds to the number of cells. To replicate this simulation the same current changes have been applied to the model created and the Figure 11 shows the results obtained.

The cell voltage and hydrogen generation react equal or very similar to the test realised by [32]. At 15 A the model generates round $0.75 \cdot 10^{-4}$ (mol H_2 /s) and 1.6 V and at higher currents (like 70 A) $3.7 \cdot 10^{-4}$ (mol H_2 /s) and 1.8 V. These values are approximately the same as the ones reported in the study, that's why it can be concluded that the system works correctly and the implementation has been satisfactory.

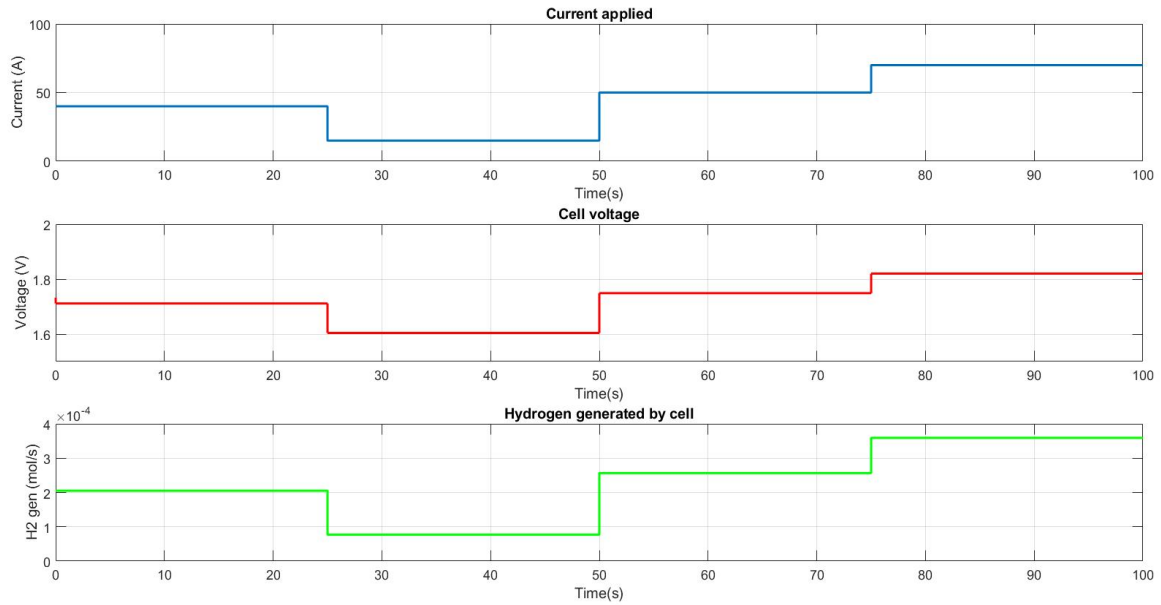


Figure 11: Influence of the current on cell voltage and hydrogen production

5.2. Converting the model into a high power one

The vast majority of models published are focused on small electrolysers with low electrical capacities, as the ones proposed by [32], [29] or [17]. The aim of this project is to study the

Table 3: Allagash 1 MW PEM electrolyser Data Specifications

Allagash Stack Technical Specifications				
Specification	Units	Illustrative H ₂ Flow Rates		
Hydrogen Flow Rate	Nm ³ /h	50	100	200
Oxygen Flow Rate	Nm ³ /h	25	50	100
Operating Pressure	barg	← 1 - 40 →		
Voltage*	V	64.4	130.9	259.8
Current	A	← 375 - 3750 →		
Operating Temperature	°C	← 5 - 60 →		
Deionized Water Flow	l/m	240	488	968
Number of Cells	--	32	65	129
Dimensions (W x D x H)	cm	81.3 X 106.6 X 131.6	81.3 X 106.6 X 141.0	81.3 X 106.6 X 173.6

*BoL, 60°C

behaviour of an electrolyser connected to the grid and for that reason the idea is to work with a large-scale one.

After proving that the results generated by the system are coherent with the bibliography

[32] [29] [16], the next step is converting our model into a 1 MW PEM electrolyser. Building on the data specifications of an electrolyser [25] manufactured by *Giner ELX* we are able to transform the initial into a bigger one.

As it is reflected at the Data Specifications (*Table 3*) there are some limitations regarding variables such as the pressure (P), temperature (T) or current (I), so before starting the simulations with the grid we should decide the optimal working conditions.

In the model the current is a parameter provided by the grid, so it is important to take into account for the DC-DC converter that the operational limitations will be from 375 A to 3750 A. Regarding the P and T it has been studied which are the best values for making the system as efficient as possible.

5.3. Optimal working temperature

This is a determinant value with a deep influence on the stack dynamics and for finding the optimal working conditions, the system has been tested at 3 different temperatures 20 °C, 40 °C and 60 °C (Maximum). For the simulations it has been considered a constant water inlet flow ($\dot{N}H_2O_{ai}$) of 968 l/min, atmospheric pressure (1 Bar) and for the I some steps have been applied, to study the performance at the maximum (3720 A) and minimum (375 A) values recommended by the manufacturer.

Figure 12 and *13* reflect that as higher is the T better is the electrolyser performance,

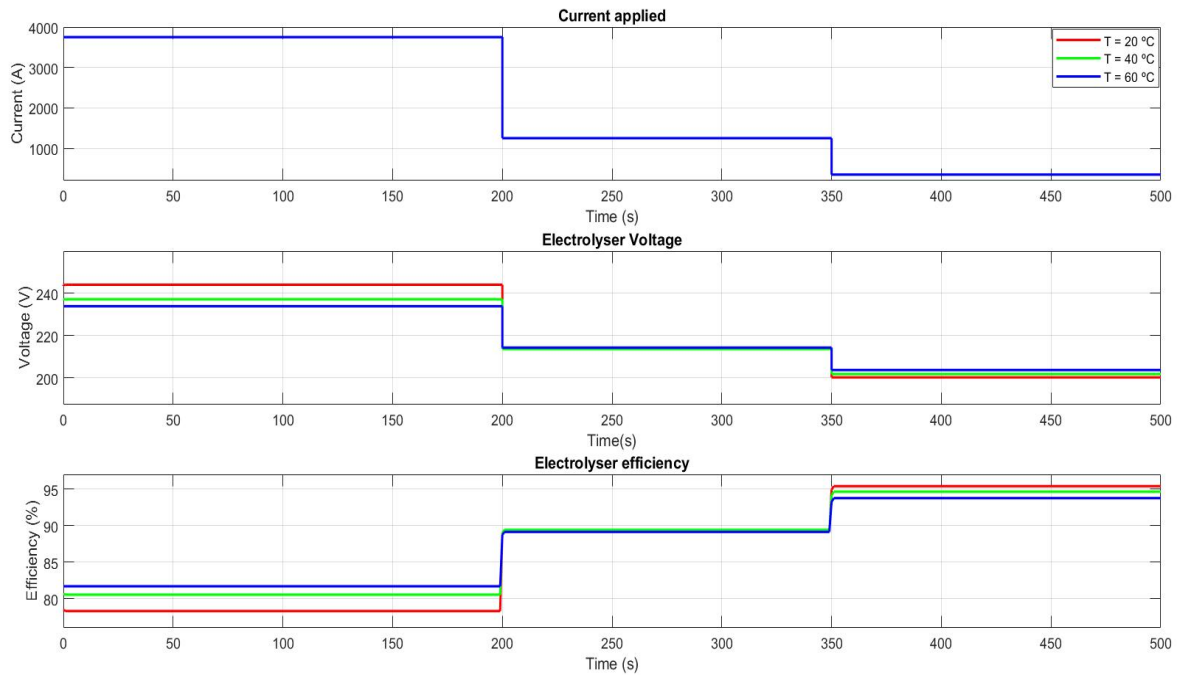


Figure 12: Stack voltage and efficiency depending on working temperature and current steps

reaching at maximum current (3750 A) and 60 °C a value of 82 %.

As lower the current, better is the performance of the electrolyser and the differences between scenarios decrease. Close to 375 A the efficiency is slightly bigger at 20 °C (but the deviation between cases is very small) and at high-medium currents, working at maximum temperature makes the system more efficient.

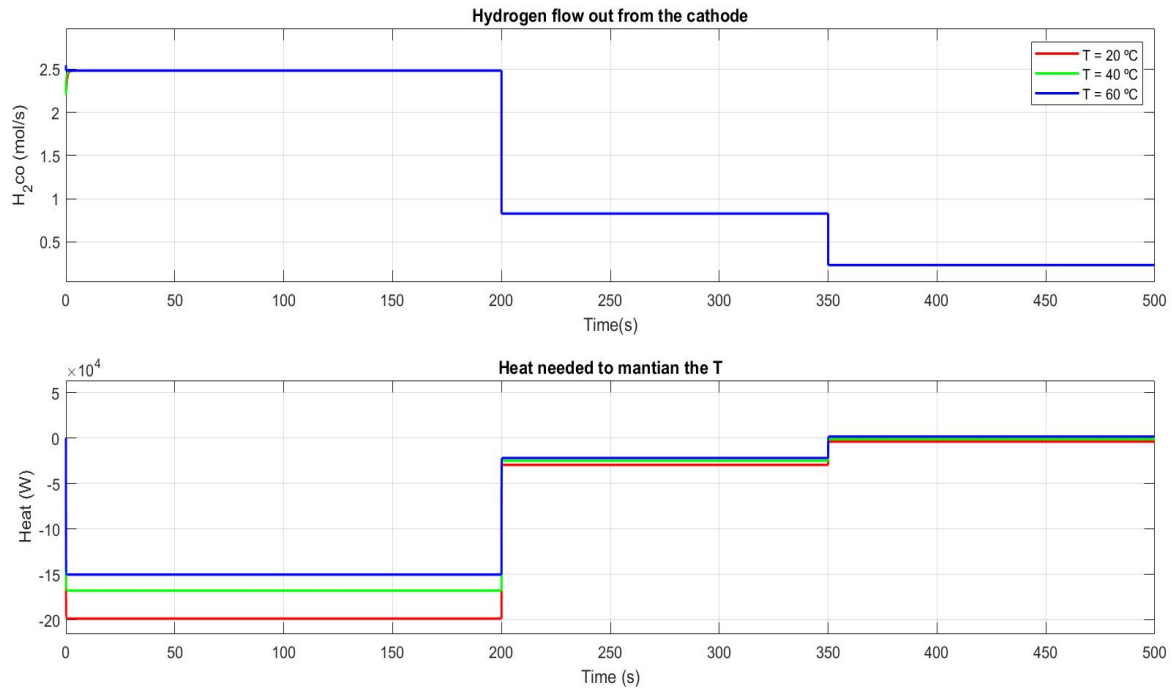


Figure 13: Hydrogen out of the cathode and heat necessities depending on working temperature and current steps

Figure 13 shows that the production of H_2 is directly proportional to the current and is the same at the 3 different temperatures, the unique difference is that at lower values the system is slower. It is worth to mention that as greater is the working T lower heat must be extracted from the MEA.

Figure 14 shows one of the most characteristic representations of electrolyser performance, Cell voltage and Efficiency versus Current density. At lower current densities the differences between scenarios are low and at higher I , working at 60 °C seem to be much more efficient.

The ohmic loses are directly proportional to the i and the R (Eq. 47), so as higher is the current density (i) higher V_{ohm} . In the case of the membrane resistance of (R), decreases as higher is the temperature what explains the better efficiency at 60 °C.

At low i , V_{ohm} is not as relevant for the cell voltage as E and V_{act} , which are directly proportional to the Temperature and hat explains why under $0.1f A/cm^2$ the cell voltage is a little bit higher at 60 °C.

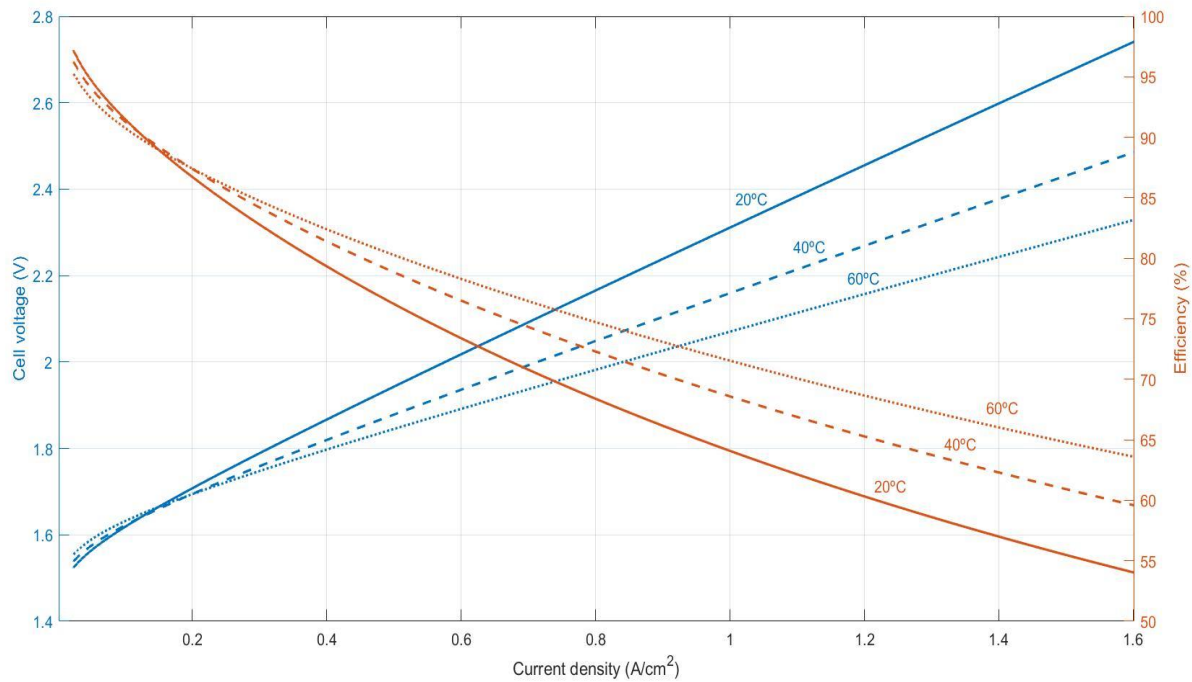


Figure 14: Cell voltage and efficiency depending on current density and temperature

As *Figure 14* reflects, at 60 °C the energy needed to break the H_2O particles is less than in other scenarios, bringing as a consequence a lower stack voltage and higher efficiency. The conductivity of the membrane is higher at this temperature, which decreases the ohmic losses and consequently the cell voltage. The cooling necessities also are lower so that's why for this case the optimal operation temperature corresponds with the maximum recommended by the manufacturer.

5.4. Optimal working pressure

Once the optimal temperature is known it is time to study with different pressures, following the same procedure as in the previous case. Here the T is constant (60 °C) and different values of pressure are applied (1, 10 and 20 Bar).

At maximum current the 1 Bar simulation provides the highest efficiency (aprox. 82 %) and at 20 Bar is where the lowest is obtained. As it can be seen from *Figure 15* the same happens at lower I values, where working at atmospheric pressure is more efficient. As mentioned before, the relation between efficiency and voltage is inversely proportional, the lowest the stack voltage better is the efficiency.

The model is designed in a way that till the internal pressure of the anode and cathode are equal to the operational pressure, the valves at both modules are closed to avoid the exit of products. As a consequence of operating at higher pressures, more time is needed till

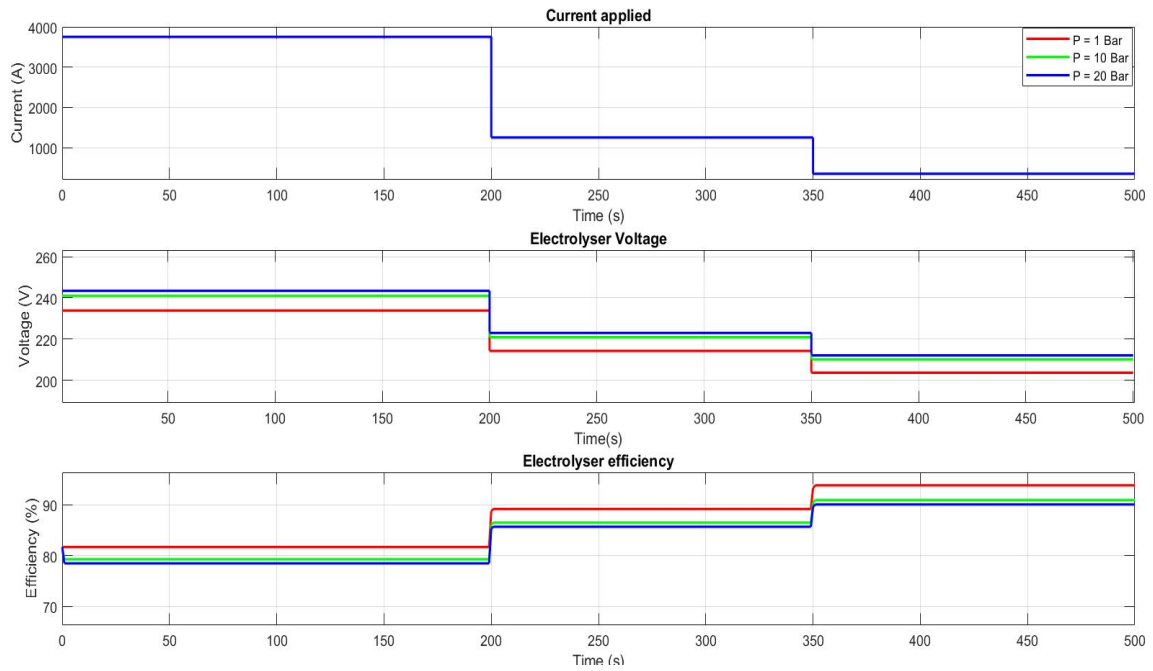


Figure 15: Stack voltage and efficiency depending on working pressure and current steps

the valves open and flows exit the electrolyser. That explains why at scenarios where the operational pressure is higher, there is a small delay (1 to 5 s) to reach a stable regime.

Regarding the H_2 production as it is shown at *Figure 16*, it is not influenced by the change in pressure, the unique benefits of working at high P values, as reported by [38] is that improves the dynamic properties of the cell. The gas bubbles generated are smaller and

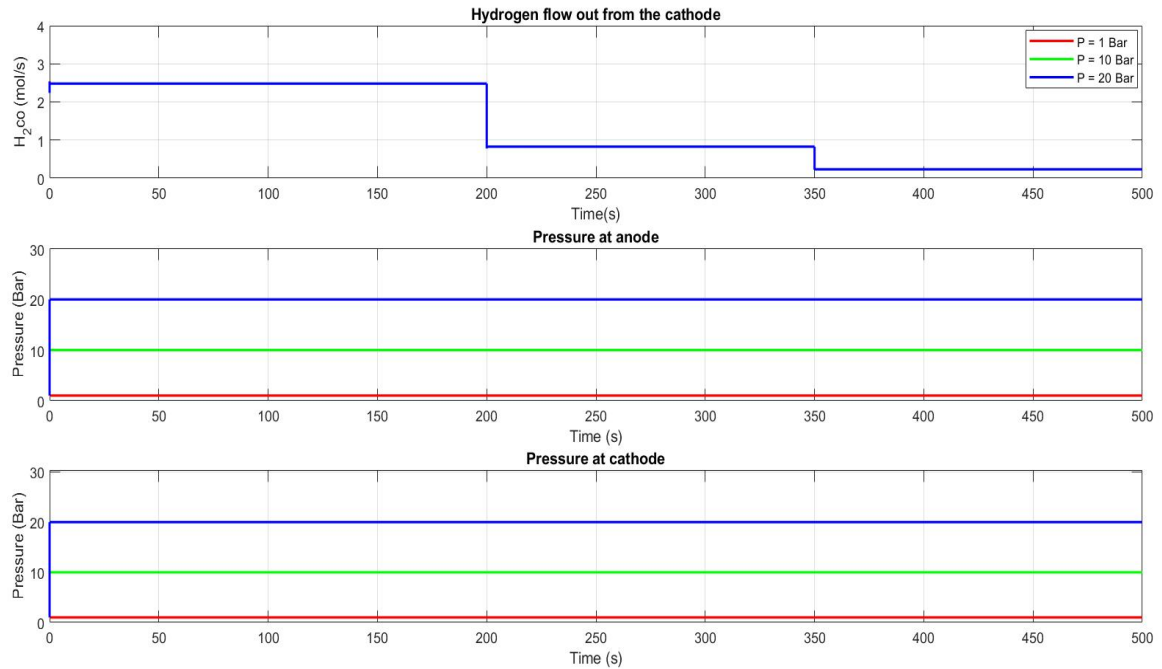


Figure 16: Hydrogen out of the cathode and pressures depending on working pressure and current steps

the energy required for injecting the gases at their storage tanks is lower.

Looking at *Figure 17* it can be confirmed that when the electrolyser works at lower pressures the efficiency is slightly better, that's why in this project we are going to consider as optimal a P equal to 1 Bar. Also the majority of studies [32][17][30] recommend for systems with intermittent load (where there is a big variability of the power provided), to work at ambient pressure for the durability of the electrolyser, the faster response and the higher efficiency.

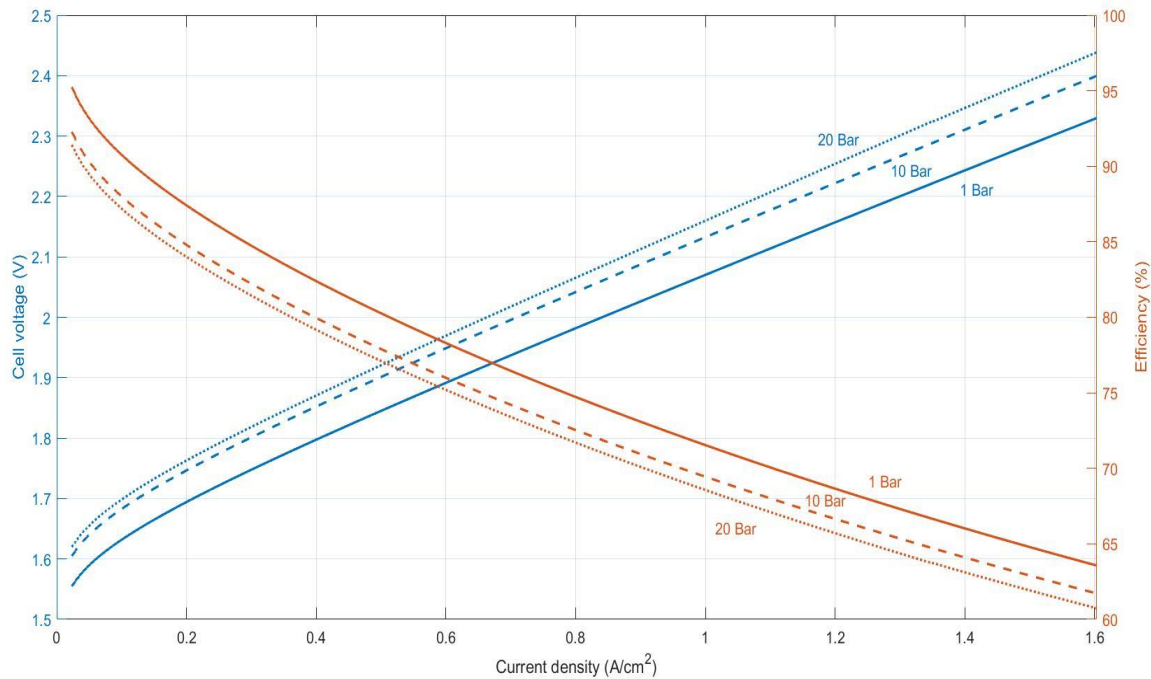


Figure 17: Cell voltage and efficiency depending on current density and pressure

5.5. Storage tank volume

Today there isn't still a pipeline distribution network of H_2 or O_2 (as it happens with Natural gas), so when they exit the electrolyser must be stored at tanks. At production plants these two gases are generally stored in pressurized vessels that can reach between 50-60 Bar [36] [37]. For this model it has been assumed that there must be enough storage for approximately 3 days, so knowing the maximum production of both elements we can estimate the volume needed.

- Hydrogen tank:** According to the model the maximum production of H_2 (reached at 3750 A) is equal to $2.48 \frac{mol}{s}$ and the outlet temperature is $60^\circ C$. Considering that the maximum tank pressure is 60 Bar and with the help of the *Ideal Gas equation*, it is obtained that the maximum volume occupied per day is equal to $98.9 \frac{m^3}{day}$ what makes approximately a total needed volume of $300 m^3$ for the 3 days.

$$V_{H_2} = \frac{\dot{N}_{H_{2co}} \cdot R \cdot T_{out}}{P_{tank}} = 98.87 \quad [m^3/day] \quad (62)$$

- **Oxygen tank:** The maximum production of O_2 is equal to $1.24 \frac{mol}{s}$ and following the same procedure we obtain a volume of $49.47 \frac{m^3}{day}$. For the 3 days will be needed a $150 m^3$ tank.

$$V_{O_2} = \frac{\dot{N}_{O_{2ao}} \cdot R \cdot T_{out}}{P_{tank}} = 49.47 \quad [m^3/day] \quad (62)$$

5.6. Performance of the electrolyser at optimal conditions

Once that are known the tanks volume, the optimal P (1 Bar) and the T (60 °C), we can study the performance of the system. As mentioned before the manufacturer limits the current between 375 and 3750 A, what is translated into a current density (i) of 0.043 and $0.43 A/cm^2$. At *Figure 18* we can see the relations between current density, efficiency and

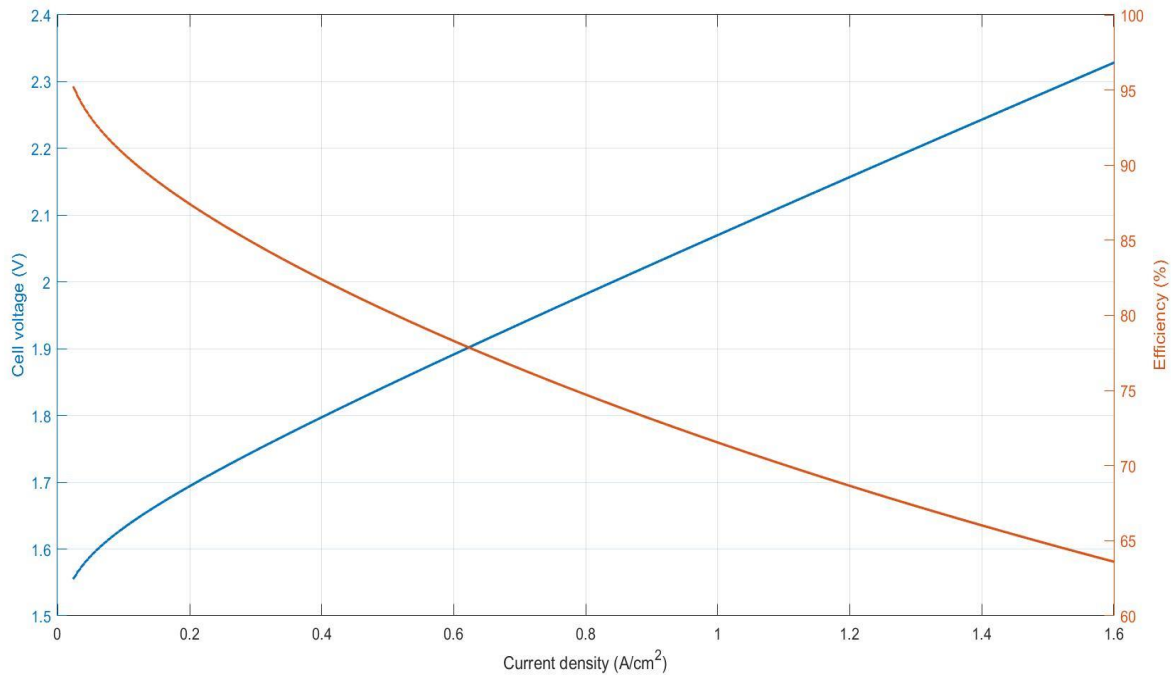


Figure 18: Cell voltage and efficiency versus current density at optimal conditions

cell voltage, which are proportional. As i increases, higher are the losses caused by the ohmic and activation overpotentials, increasing the cell voltage and decreasing the system efficiency. According to the *Giner ELX* specifications the maximum current density is $0.43 A/cm^2$, where the cell voltage arrives to the maximum value and the efficiency the lowest

(81.7 %).

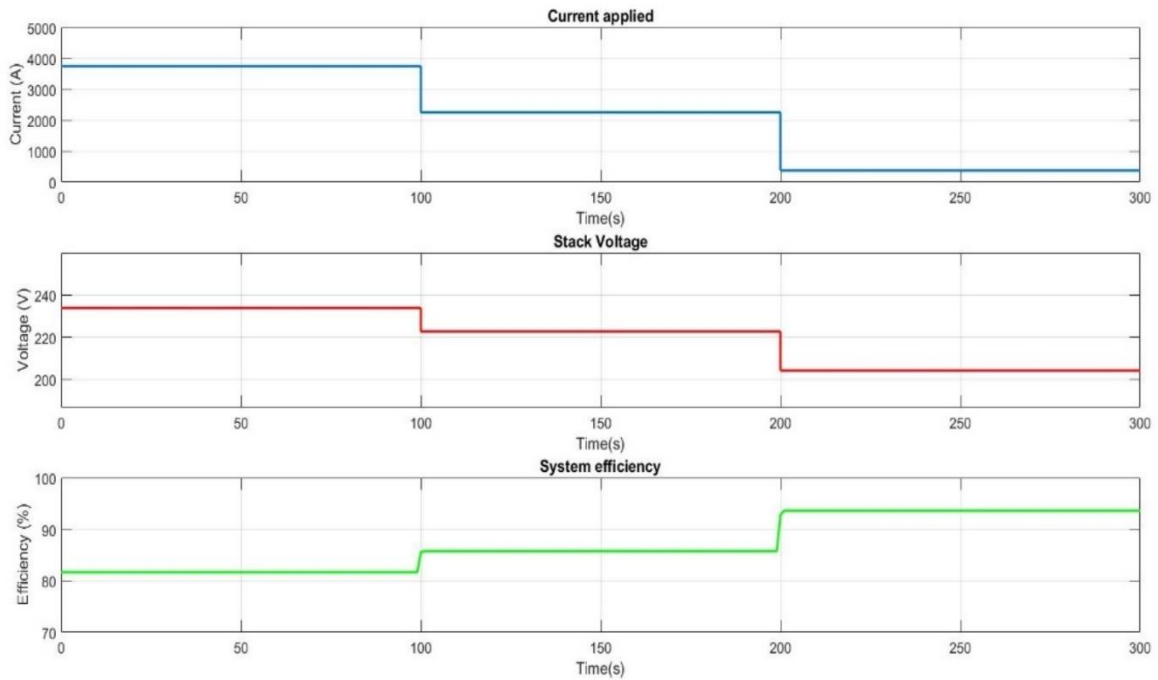


Figure 19: Voltage and efficiency depending on current values at optimal conditions

To see how the stack works and the dynamic response along the current operating range, the system has been submitted into different current scenarios (shown at *Figure 19*), as in

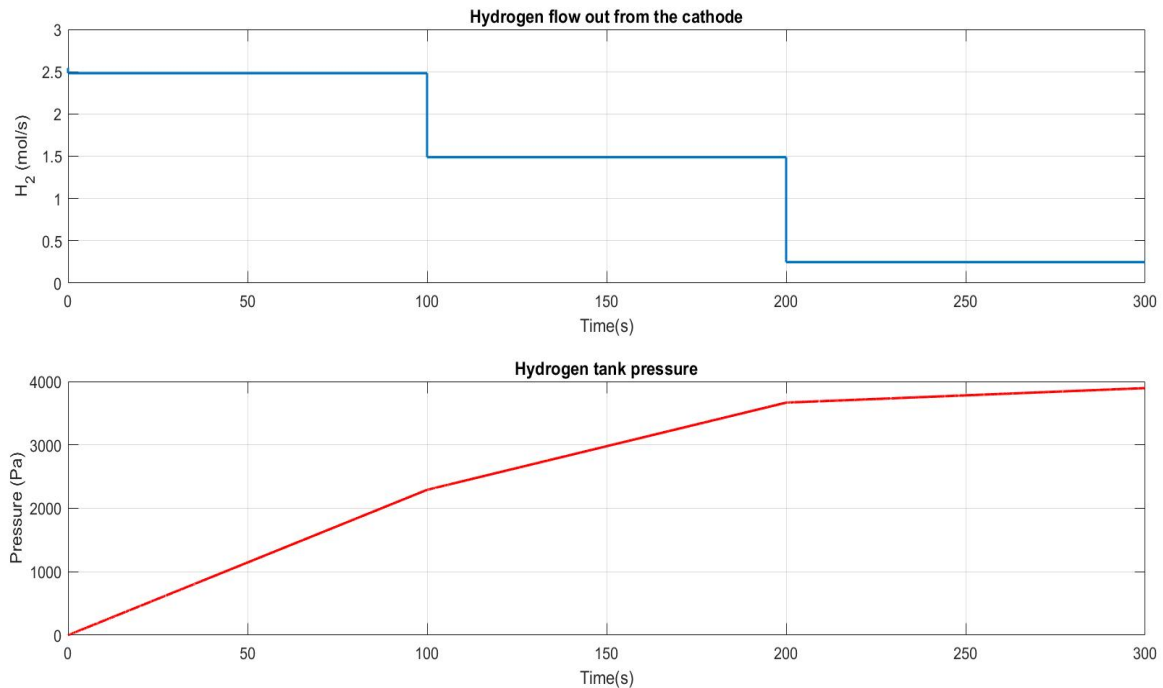


Figure 20: Hydrogen out of the cathode and tank pressure depending on current values

the previous sections. The reaction of the voltage module and the hydrogen generation are very fast and adapt to the change in less than 1 second, as *Figure 19* and *20* reflect. As mentioned before the system is more efficient at lower currents (reaching as maximum 93.6 % at 375 A) and the stack voltage (at operational conditions between 200-240 V) is directly proportional to the I .

The state of the hydrogen tank appears at *Figure 20* and shows how the pressure evolves with the time (maximum 60 Bar). The hydrogen production is directly proportional to the current, so as higher the current better for the generation.

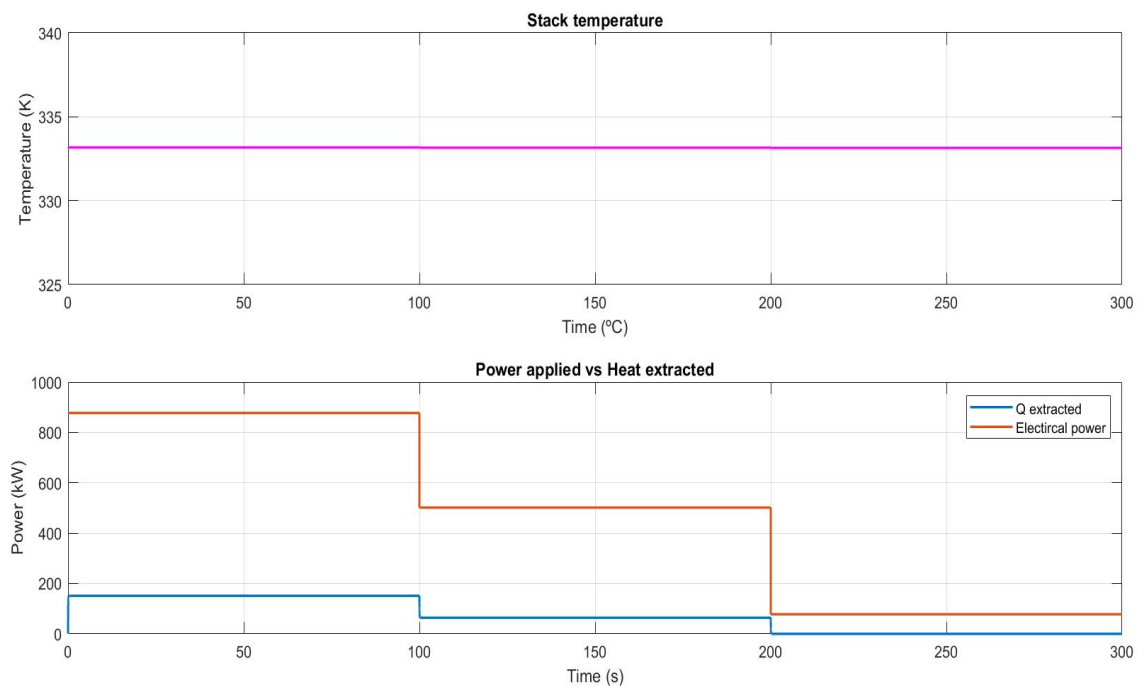


Figure 21: Temperature and heat necessities depending on the I at operational conditions

Regarding the temperature constraints it has been assumed that the MEA is at optimal temperature ($T_0 = 60\text{ }^{\circ}\text{C}$) when starts working and the plot reflects that changes in I barely affect the working T . In fact, depending on the current we have to cool or heat the system to maintain it at 333.15 K. *Figure 21* shows that at 3750 A, as the system is less efficient there is a big generation of heat that has to be extracted from the stack, but at 375 A (where the system has an efficiency of 91%) the cooling necessities are close to 0. The inlet flow of H_2O is considered to be also at $60\text{ }^{\circ}\text{C}$, because the excess water is recirculated to the system and as reported by [22] this gives more stability to the electrolyser.

The pressure, as the temperature, remains constant in both electrodes and isn't influenced by current changes, as it reflected by *Figure 22*.

Comparing this dynamic analysis with data provided by the manufacturer and other studies

such as [25] [22] it could be said that the system works correctly. Values such as the production rates of O_2 and H_2 are coincident with the one exposed at the data sheet and also, the dynamic response is considerably good needing as maximum 5 s to reach the steady state.

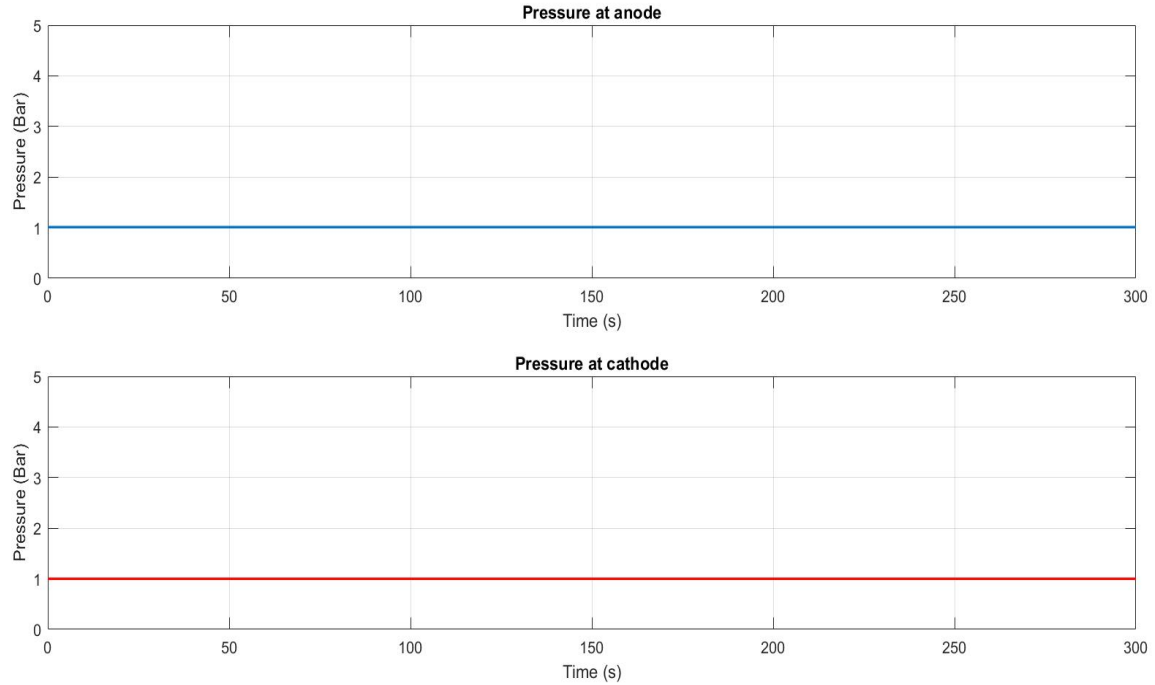


Figure 22: Pressure depending on the current at operational conditions

Regarding the operational conditions it should be mentioned that at lower current densities, electrolysers are more efficient, what is translated in less cooling necessities. The generation is directly proportional to the I , so the highest hydrogen production will be provided at maximum current.

6. CONCLUSIONS

The world of hydrogen has been improving a lot during the last decades, we already have a lot of ways of producing it and there is a lot of expectation of this technology for the coming years. Nevertheless, the reality is that the vast majority of hydrogen produced is not used for energy purposes and comes from processes that are contaminant, such as the reforming of methane or coal.

It is clear that if we want to introduce this gas as a substitute of fossil fuels, the ways of production have to change and must invest in greener ways of production such as electrolysers. This project has aimed to understand their behaviour and their possibilities to be connected to the grid to use the surpluses and make it more efficient.

For these kind of purposes PEM electrolysers are the most adequate technology due to the fast response, more flexible operation and durability. Regarding the working conditions it is important to remark that higher temperatures bring better efficiencies, because the conductivity of the membrane increases what reduces the ohmic losses. For the pressure we have confirmed that 1 Bar is the most interesting scenario because it brings the highest efficiency, as it is reported by current literature.

The hydrogen and oxygen production are directly proportional to the current (the higher the better) and parameters such as temperature and pressure do not affect the generation directly. Apart from the temperature and pressure, the stack voltage is also dependent on the stack current and at high values the cells have more losses, what is translated in a lower efficiency.

The energy loss in the process is converted in heat so, at low currents (where efficiency is high) the cooling necessities are very small, but as I increases (the efficiency decreases) the heat generated is higher and we have to cool more the system.

As it has been confirmed in this project, electrolysers are ready to be connected to the grid and convert the surpluses into hydrogen. The global generation of green hydrogen must increase, if we want to substitute part of the fossil fuels with it, and this technology will be a determinant tool in the coming years to achieve this transition.

7. APPENDIX

7.1. Simulink Model

7.1.1. General overview

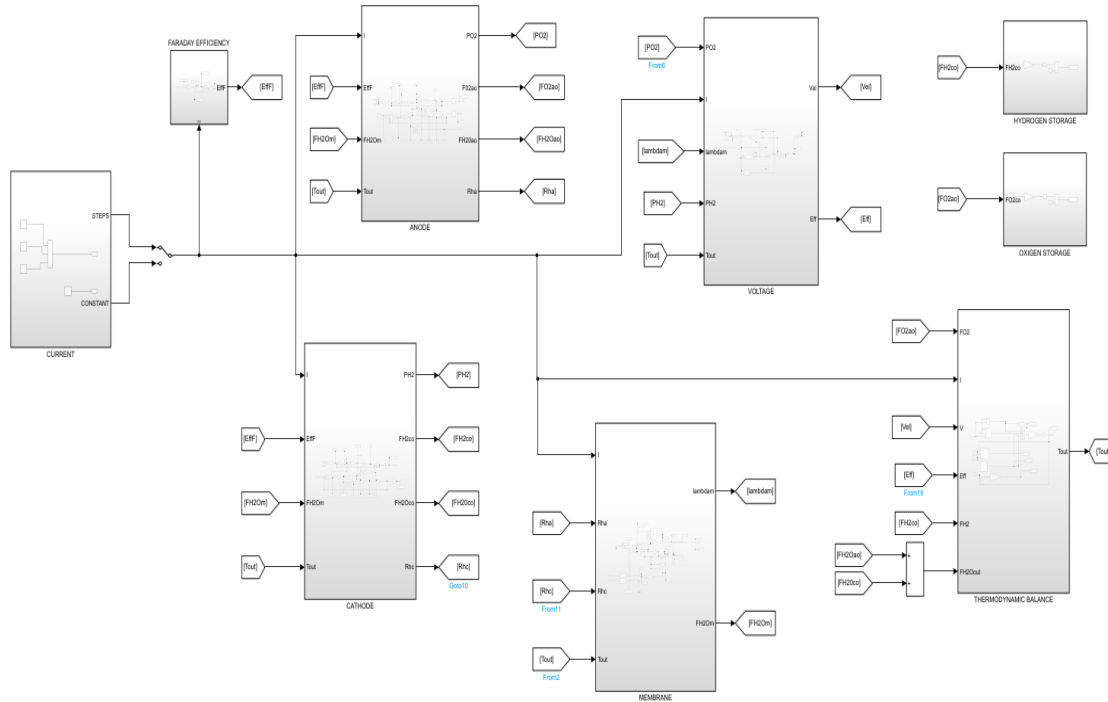


Figure 23: General Simulink diagram

7.1.2. Faraday Efficiency

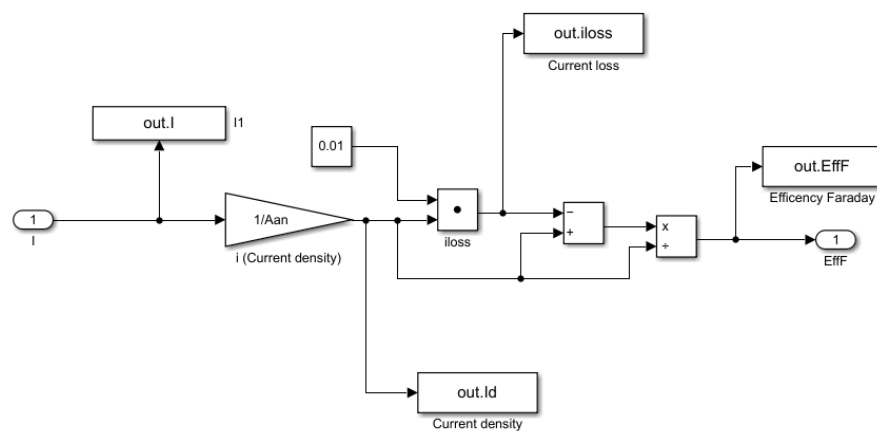


Figure 24: Faraday efficiency calculations

7.1.3. Anode

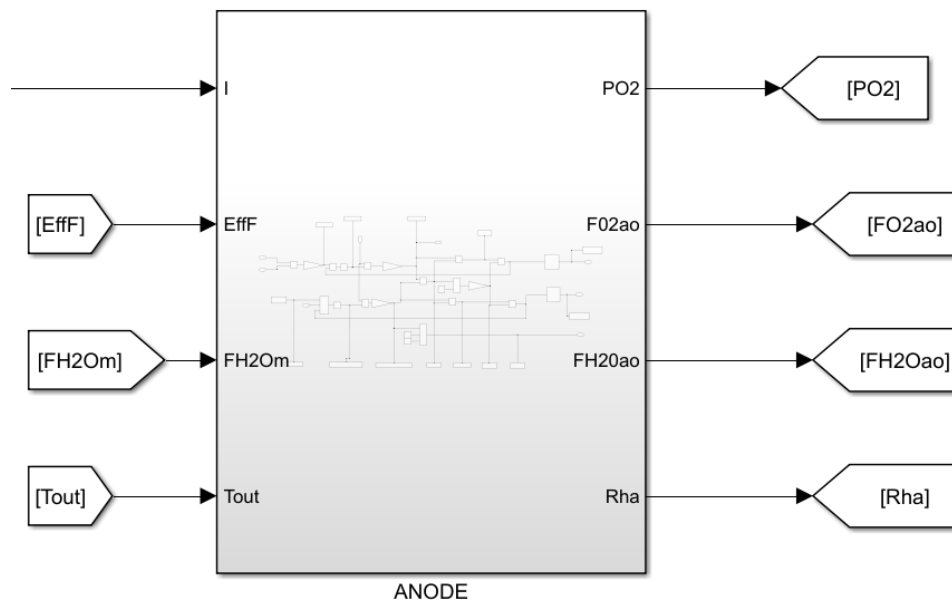


Figure 25: Anode inlets and outlets at the model

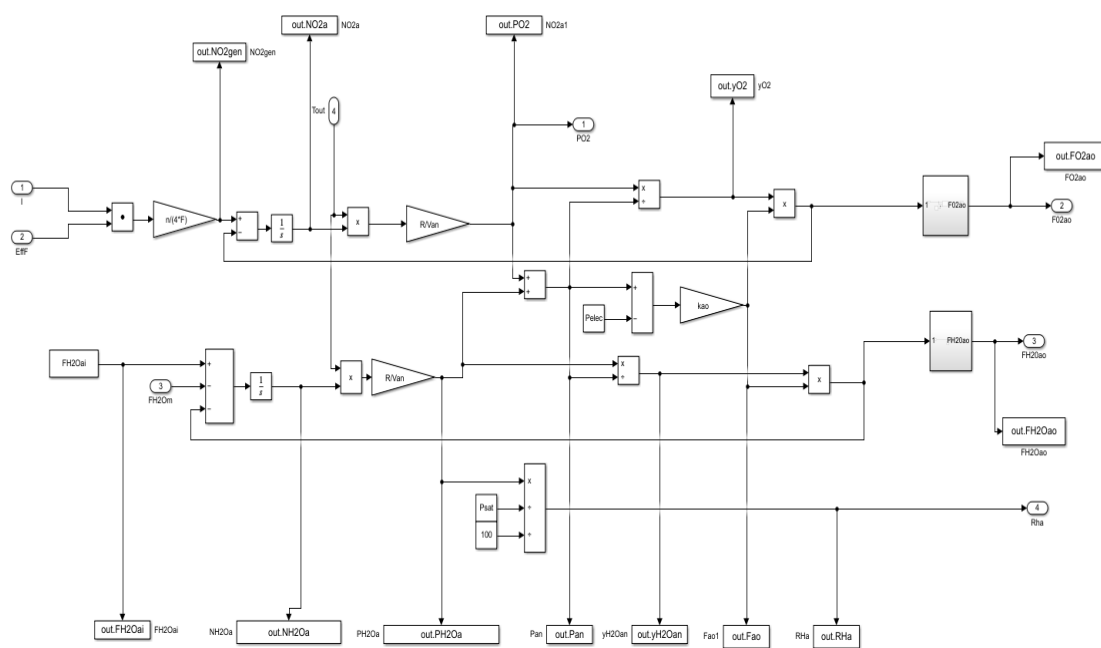


Figure 26: Anode calculations and variables

7.1.4. Cathode

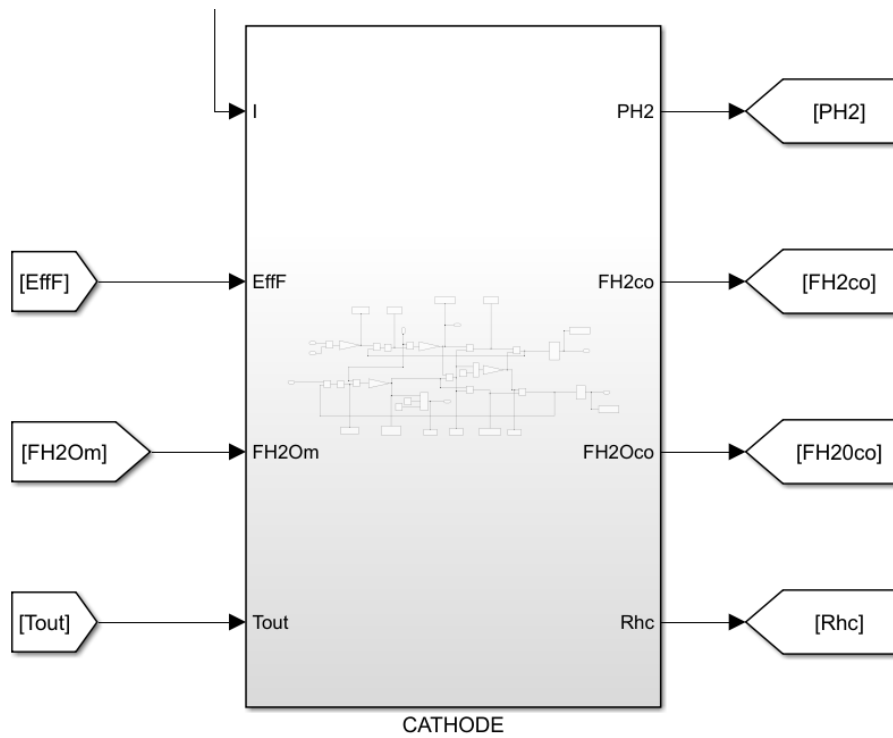


Figure 27: Cathode inlets and outlets at the Model

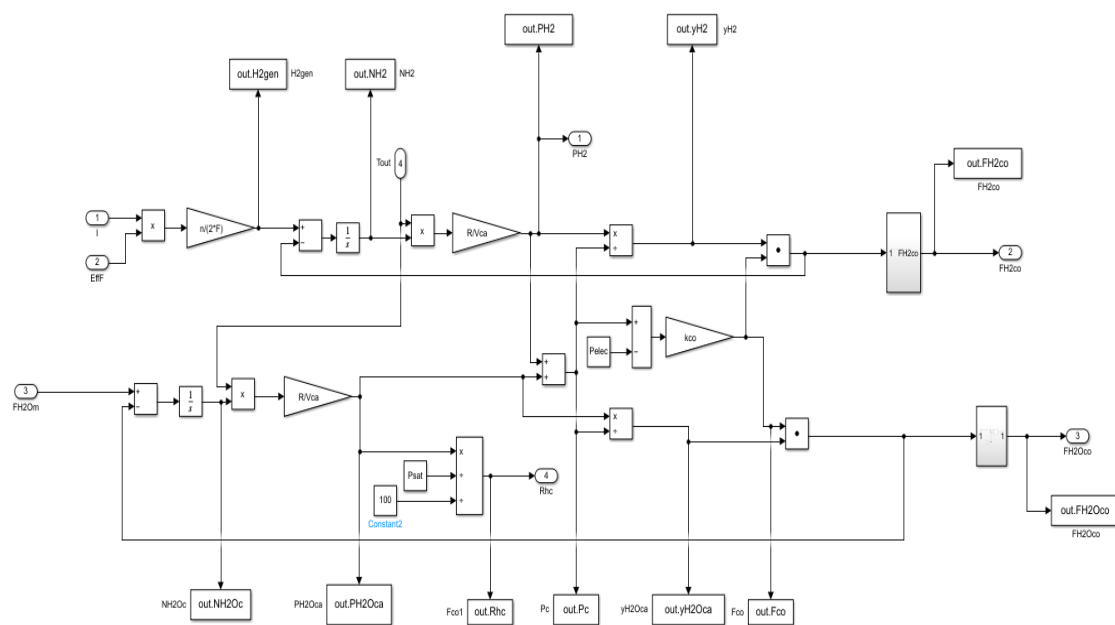


Figure 28: Cathode calculations and variables

7.1.5. Membrane

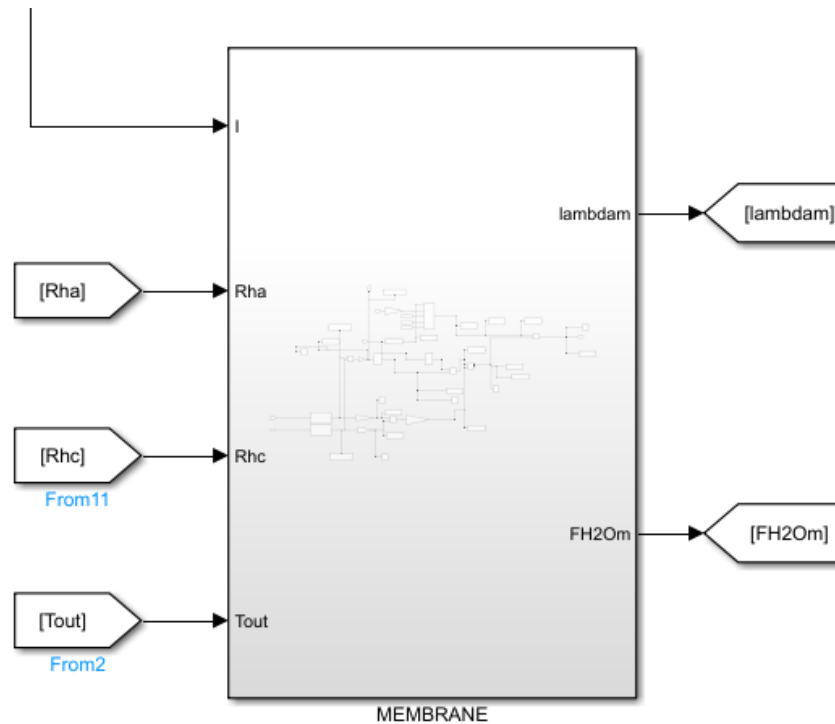


Figure 29: Membrane inlets and outlets at the Model

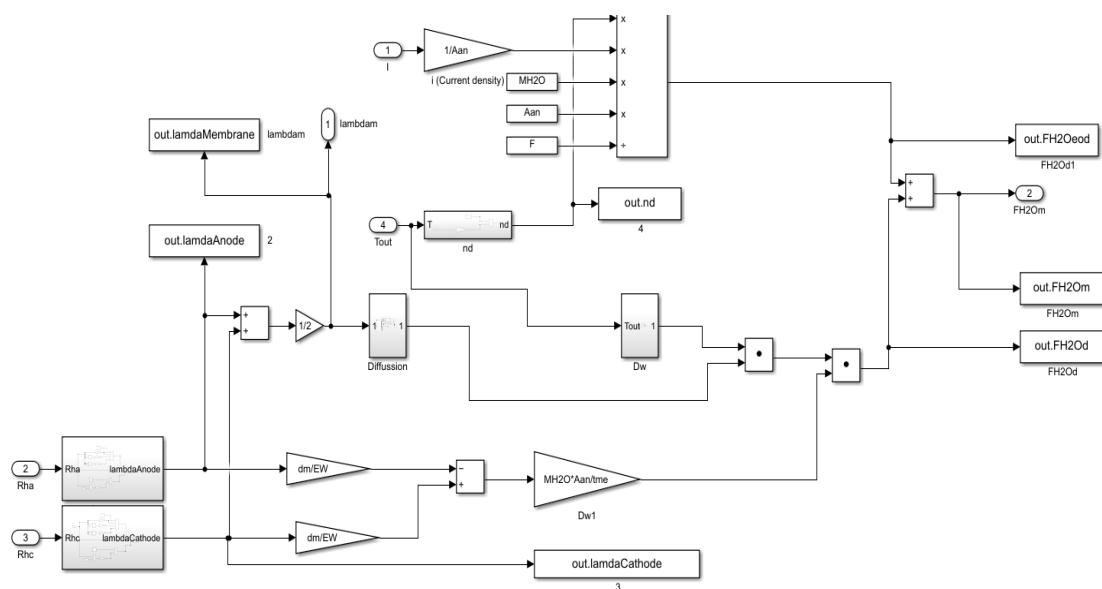


Figure 30: Membrane calculations and variables

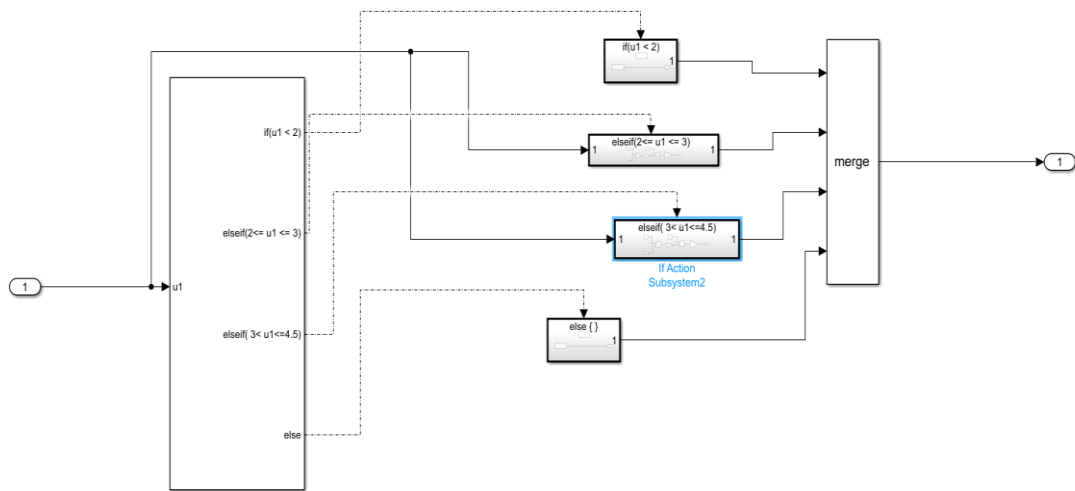


Figure 31: Membrane calculations for D_λ

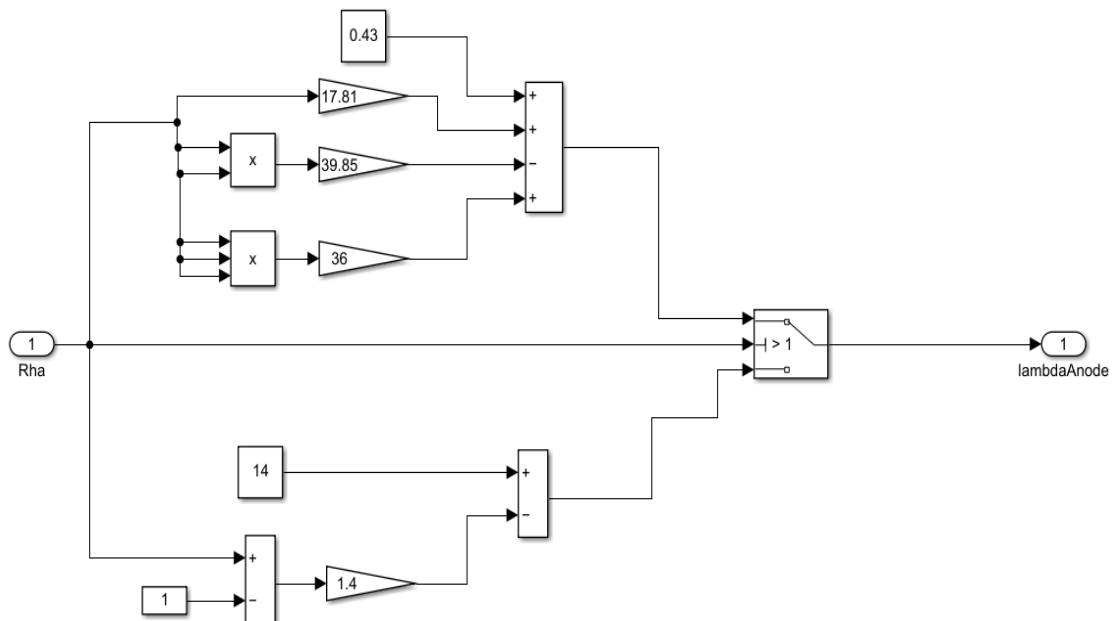


Figure 32: Membrane calculations for the water uptake (λ) at anode and cathode

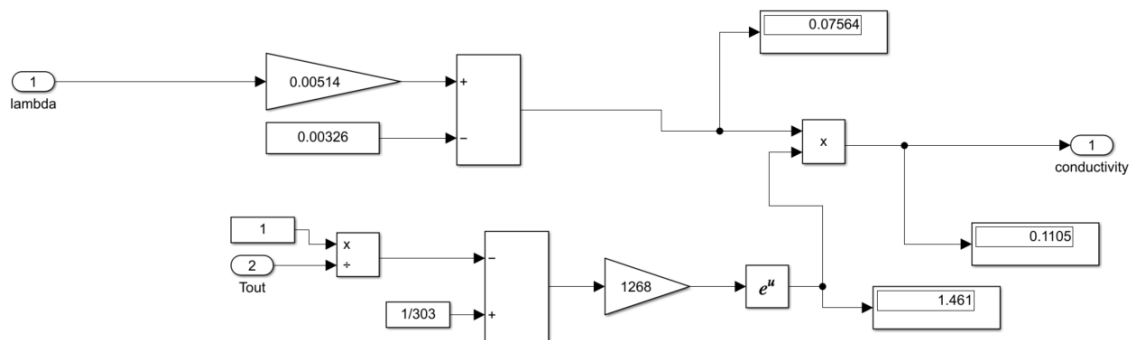


Figure 35: Voltage calculations, membrane conductivity (σ) calculations

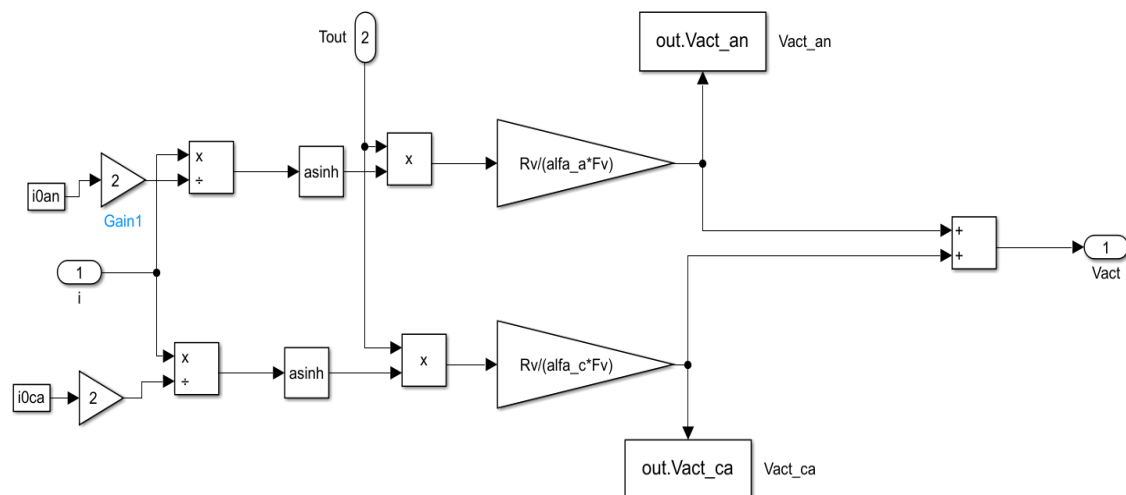


Figure 36: Activation overpotentials of the anode and cathode

7.1.7. Temperature control

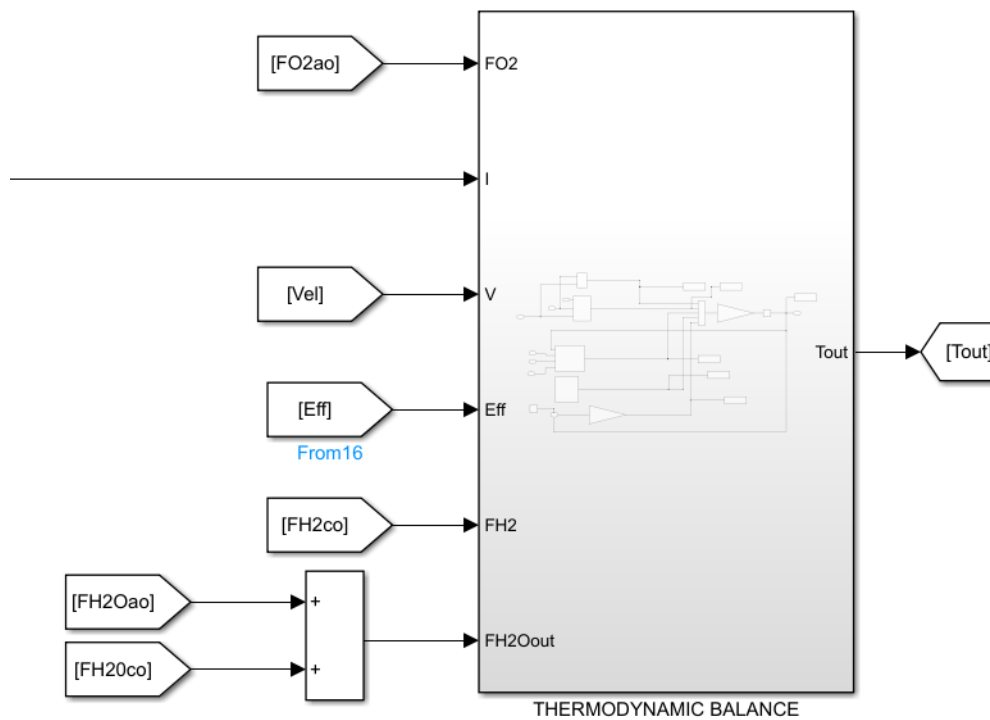


Figure 37: Temperature inlets and outlets

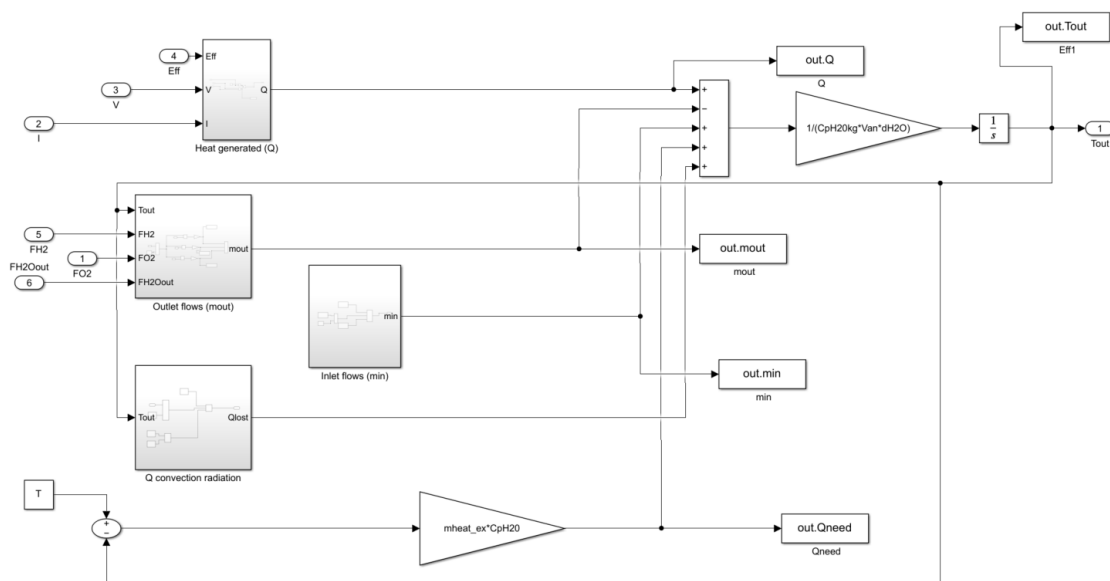


Figure 38: Temperature module calculations and variables

7.1.8. Storage tanks

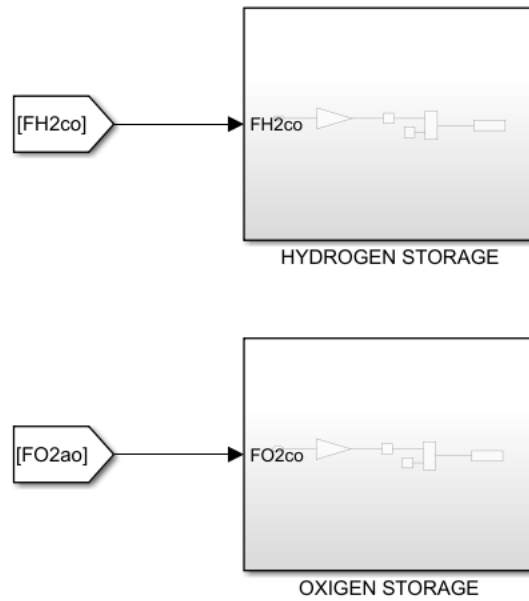


Figure 39: Hydrogen and Oxygen storage tanks inlets and outlets

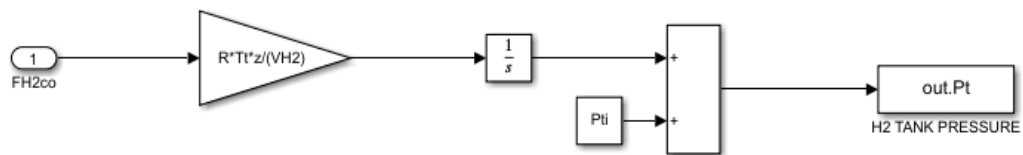


Figure 40: Calculations and variables at Hydrogen storage tank

7.2. Matlab I: General data

```
% Name: PEM_elctrolyzer_data_1MW.m

% This script contains the simulation constant variables

%% CHANGING VARIABLES:
I = 3750; %A
n = 129; %Number of cells
FH2Oai = 893.6; %mol/s
Tin = 25+273.15; %°C
TC = 60; %°C
Aan = 81.3*106.6/10000; % Active area (m2) 81.3 x 106.6 cm2
tme = 0.45/1000 ; %Thickness (m) 0.5 mm0.5 3
Pelec = 1*10^5; % Electrolizer pressure Pa (1-40 Bar)

%% ANODE CONSTRAINS:

F = 96485.3329; %Faraday constant s·A/mol
R = 8.314;%Ideal Gases constant m3·Pa/K·mol
Pelec0 = 1; %Electrolizer initial pressure Pa
T = TC+273.15; %K overall temperature
Psat = -2846.4+411.24*TC-10.554*TC^(2)+0.16636*TC^(3); %Saturation Pressure (Pa)
Van = Aan*tme*n; %Anode Volume (m3)
kao = 0.95; %Anode outlet flow coefficient

%% CATHODE CONTRAINS:
Acn = Aan; % Active area (m2)
Vca = Van; %Cathode Volume (m3)
kco = 0.45; %Anode outlet flow coefficient

%% MEMBRANE CONSTRAINS:
EW = 960; %Equivalent weight of the membrane (kg water/kg nafion)
dm = 1.96; %Density of dry membrane (Kg/m3)
MH2O = 18; % Water molar weight (kg/kmol)

%% VOLTAGE CONSTRAINS:
INC_GIBBS = 236.483; %Kj/mol for H2O liq
Fv = 96.48533212; %J/mol·V
Rv = 0.0083447; % 8.314 J/mol·K
E0 = INC_GIBBS/(2*Fv); %V
aH2O = 1; %Water activity
i0an = 2* 10^(-7); %Exchange current density andode A/cm2
i0ca = 2 * 10^(-3); %Exchange current density cathode A/cm2
alfa_a = 3; %Charge transfer coefficient for anode
alfa_c = 2; %Charge transfer coefficient for cathode
Vth = 1.481; %Thermoneutral voltage V

%% STORAGE CONSTRAINS:
z = 1; %compressibility factor for Hydrogen
MV = 1; %Hydrogen tank volume (kg)
dH2 = 0.0771; % Hydrogen gas density kg/m3 at 60°C
MH2 = 2; % Hydrogen Molar Mass (kg/kmol)
VH2 = 300; % Hydrogen tank volume (m3)
VO2 = 159; % Oxygen tank volume (m3)
Tt = 333.15; % Tank temperature (K)
Pti = 0.101325; % Tank initial pressure (Pa)
```

zO2 = 0.304; %compressibility factor for Hydrogen

%% HEAT MANAGEMENT:

CpH2O = 75.4; %J/mol·K Heat capacity of H2O

CpH2 = 28.63; %J/mol·K Heat capacity of H2

CpO2 = 29.248; %J/mol·K Heat capacity of O2

dH2O = 997000; %g/m3

CpH2Okg = 4.18; %J/g·K Heat capacity of H2O

mheat_ex = 100000; %mol/s

% Radiation and Convection losses

hc = 15; %Convective heat transmission coefficient for solid-air (W/m2K)

hr = 4.5; %Radiative heat transmission coefficient (W/m2K)

Aext = (81.3*173.6*2+81.3*106.6*2+173.6*106.6*2)/10000; %External area (m2)

Toutside = 298.15; %Outlet temperature 25°C (K)

7.3. Matlab II: Running the Simulink and plotting the results

```
% The objective of this script is to run the Simulink and generate the plot
% Name: run_electrolyzer_simulink_PEM_1MW.m
% (C) 2022 Andrés Bernabeu Santisteban
```

```
clc
clear all
close all
```

```
%% Read data file
PEM_elctrolyzer_data_1MW;
```

```
%% Steps and simulation information
tmax = 300;
t_step1 = 0;
I_step1 = 3750;
t_step2 = 100;
I_step2 = -1500;
t_step3 = 200;
I_step3 = -1875;
```

```
%% Run Simulink from Matlab
opciones.AbsTol='1e-8';
opciones.RelTol='1e-8';
opciones.StopTime=num2str(tmax);
opciones.Refine='10';
opciones.solver='ode15s';
salidas=sim('PEM_1MW_TEMPERATURE.slx',opciones);
```

```
%% Extracting the results from Simulink
Pt = salidas.get('Pt'); %Tank Pressure
Eff = salidas.get('Eff'); %Efficiency
NO2gen = salidas.get('NO2gen'); %Oxigen generated
FH2co = salidas.get('FH2co'); %Hydrogen flow out of the cathode
FO2ao = salidas.get('FO2ao'); %Oxigen flow out of the anode
FH2Oao = salidas.get('FH2Oao'); %Water flow out of the anode
FH2Oco = salidas.get('FH2Oco'); %Water flow out of the cathode
FH2Om = salidas.get('FH2Om'); %Water flow out of the membrane
FH2Oain = salidas.get('FH2Oai'); %Water flow out of the membrane
H2gen = salidas.get('H2gen'); %Hydrogen generation
Is = salidas.get('I'); %Cell current
Vel = salidas.get('Vel'); %Cell voltage
Id = salidas.get('Id'); %Current density
Rha = salidas.get('RHa'); %Humedad relativa ánodo
Rhc = salidas.get('Rhc'); %Humedad relativa cátodo
Pan = salidas.get('Pan'); %Humedad relativa ánodo
Pca = salidas.get('Pc'); %Humedad relativa cátodo
Tout = salidas.get('Tout'); %Temperatura electrolizador (K)
W = salidas.get('W'); %Electrical power applied (W)
Q = salidas.get('Q'); %Heat losses from de system (W)
mout = salidas.get('mout'); %Power from the outlet flows (W)
min = salidas.get('min'); %Power from the inlet flows (W)
Qneed = salidas.get('Qneed'); %Heat needed to maintain the system at T(W)
```

```

%% Representation of the results
% CURRENT, VOLTAGE, EFFICIENCY
figure (1)
subplot(3,1,1)
plot(Is.time,Is.signals.values,'LineWidth',1.5)
title('Current applied')
xlabel('Time(s)')
ylabel('Current (A)')
ylim([0 5000])
grid on

hold on
subplot(3,1,2)
plot(Vel.time,Vel.signals.values,'r','LineWidth',1.5)
title('Stack Voltage')
xlabel('Time(s)')
ylabel('Voltage (V)')
ylim([100 300])
grid on
hold on

subplot(3,1,3)
plot(Eff.time,Eff.signals.values*100,'g','LineWidth',1.5)
title('System efficiency')
xlabel('Time(s)')
ylabel('Efficiency (%)')
ylim([70 100])
grid on

% H2 FLOW OUT THE CATHODE AND TANK PRESSURE
figure (2)
subplot(2,1,1)
plot(FH2co.time,FH2co.signals.values,'LineWidth',1.5)
title('Hydrogen flow out from the cathode')
xlabel('Time(s)')
ylabel('H_2 (mol/s)')
ylim([0 3])
grid on

subplot(2,1,2)
plot(Pt.time,Pt.signals.values,'r','LineWidth',1.5)
title('Hydrogen tank pressure')
xlabel('Time(s)')
ylabel('Pressure (Pa)')
grid on

% TEMPERATURE AND HEAT NECESSITIES
figure (3)
subplot(2,1,1)
plot(Tout.time,Tout.signals.values,'m','LineWidth',1.5)
xlabel('Time (°C)')
ylabel('Temperature (K)')
title('Stack temperature')
ylim([325 340])
grid on

subplot(2,1,2)

```

```
plot(Qneed.time, -Qneed.signals.values/1000, 'LineWidth', 1.5)
hold on
plot(W.time, W.signals.values/1000, 'LineWidth', 1.5)
xlabel ('Time (s)')
ylabel ('Power (kW)')
legend('Q extracted', 'Electircal power')
title('Power applied vs Heat extracted')
grid on

% PRESSURE AT ANODE AND CATHODE
figure (4)
subplot (2,1,1)
plot(Pan.time, Pan.signals.values/100000, 'LineWidth', 1.5)
xlabel ('Time (s)')
ylabel ('Pressure (Bar)')
title('Pressure at anode')
ylim([0 5])
grid on

subplot (2,1,2)
plot(Pca.time, Pca.signals.values/100000, 'r', 'LineWidth', 1.5)
xlabel ('Time (s)')
ylabel ('Pressure (Bar)')
title('Pressure cathode')
ylim([0 5])
grid on
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8. REFERENCES

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