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Sviluppo di un sistema di stoccaggio energetico all’idrogeno

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Sviluppo di un sistema di stoccaggio energetico all’idrogeno

Sommario

L'obiettivo di questa tesi è sviluppare e ottimizzare un sistema di accumulo di energia a idrogeno per un centro di ricerca. Il sistema sarà in grado di convertire l'elettricità in idrogeno, immagazzinare l'idrogeno e riconvertirlo in elettricità.

Per raggiungere questo obiettivo, il sistema includerà un innovativo sistema di stoccaggio dell'idrogeno: verrà utilizzato un sistema d’idruri metallici, una tecnologia che consente d’immagazzinare l'idrogeno a basse pressioni ma ad alta densità.

Inoltre, il focus sarà posto anche sullo sviluppo di un sistema di controllo, in grado di gestire in sicurezza non solo il flusso d’idrogeno ma anche l'impianto elettrico, le comunicazioni industriali e la gestione termica. Quest'ultimo argomento è particolarmente rilevante a causa dell'uso d’idruri metallici, che richiede la fornitura e la rimozione di calore per rilasciare e catturare l'idrogeno.

Verrà sviluppato un modello che rappresenta il sistema progettato e sarà utilizzato per eseguire le prove dei sistemi di controllo. Ciò migliorerà i tempi di consegna e fornirà margini di sicurezza più elevati testando diversi scenari.

I risultati di questa tesi forniranno preziose informazioni sul potenziale dell'utilizzo di nuovi sistemi di accumulo di energia a idrogeno per il mercato delle energie rinnovabili in rapida espansione.

Development of a hydrogen-based energy storage system

Summary

The aim of this thesis is to develop and optimize a hydrogen energy storage system for a research center. The system will be able to convert electricity to hydrogen, store the hydrogen, and convert it back into electricity.

To achieve this, the system will include an innovative hydrogen storage system: a metal hydride material will be used, a technology which allows the hydrogen to be stored at low pressures but high densities.

Furthermore, focus will also be placed on the development of a control system, able to safely manage not only the flow of hydrogen but also the electrical system, industrial communication, and thermal management. This last topic is especially relevant due to the usage of metal hydrides, which requires the supply and removal of heat to release and capture the hydrogen.

A model will be developed that represents the projected system and will be used to perform tests of the control systems. This will improve delivery times and provide higher safety margins by testing out multiple scenarios.

The results of this thesis will provide valuable insight into the potential of using novel hydrogen energy storage systems for the rapidly expanding renewable energy market.

Acknowledgements

A la meva família i als meus amics i estimats pel suport inestroncable,
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Table of contents

1 Introduction

There is widespread agreement among scientists that climate change is fundamentally anthropogenic. [1]

A growing global economy, rising population, and an increase of per capita energy needs has entailed a rapid increase in energy consumption. In the past century, this need has been covered mainly by the usage of non-renewable fuel sources, which have in turn caused massive releases of carbon and other pollutants into the atmosphere, which in turn increase the heat absorbed from the rays of the Sun and cause Earth's energy imbalance to increase, ultimately increasing the net heat of the Earth, as seen in Figure 1.

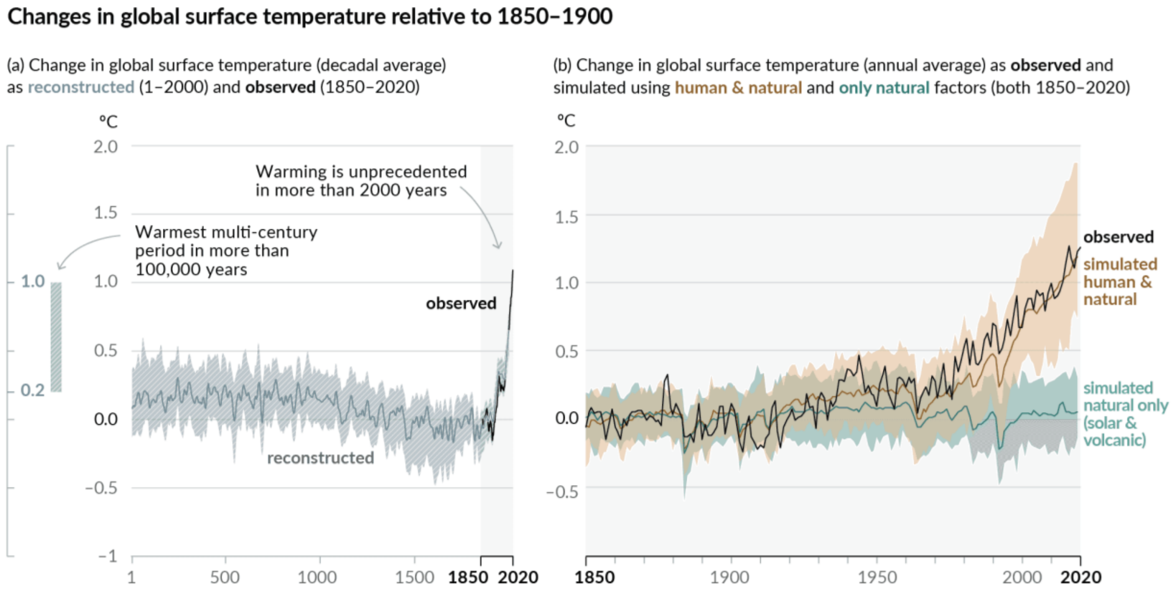


Figure 1. Changes in global surface temperature [2]

The effects of this phenomenon are predicted to cause widespread crises due to an increase in energy costs, political conflict due to resource allocation, and even war. [3]

To reduce and mitigate global warming, humanity must develop new ways to power our technology that will provide a similar quality of life and economic development as fossil fuels have provided, but with a much-reduced polluting effect.

Production of electricity using renewable methods has greatly evolved in the past years. [4] Their main drawback, however, is that generally they cannot provide electricity on demand, so the electricity that they produce must be stored when they are available. Many new technologies have appeared and have increasingly evolved to provide this storage, but they usually lack in economic benefit, scaling, and their life cycle is often not environmentally friendly.

A technology which has been proposed to solve this problem is the so-called hydrogen economy. This element has very interesting properties which mean that it can be created, stored, and used on demand to produce electricity, and with (ideally) zero harmful emissions.

However, there are some drawbacks and challenges that need to be overcome for the hydrogen economy to develop. In this work, the aim is to develop a system that can store electricity with zero emissions during its operation, and which can be a proof of concept for future systems that could potentially shape the future of energy.

1.1 Renewable energy

In the past decades, society has electrified and new, less contaminant ways of converting energy into electricity have been developed thanks to scientific research. Just as importantly, they have also been cheapened, thanks to economy of scale and very significant investment from public and private institutions. Systems such as solar panels and wind power turbines are providing an increasingly higher share of the power that we consume, and their prices have dropped to previously unimaginable amounts. As of today, renewable energy is by far the cheapest and even though they do produce contaminant products during their lifecycle, that impact is negligible compared to the effects of burning fossil fuels.

1.1.1 The storage problem

Unfortunately, everything has its pros and its cons, and these technologies have cons that greatly impact their performance: every day has its night, and thus no sun to produce power; and sometimes there just is not wind. Obviously, in these scenarios electricity is still consumed, so power storage systems are used to store electricity when it's available and to release it into the grid when it is required.

The system most appropriate for each application is highly dependent on factors such as the quantity of energy to be stored the power which is required and even the surroundings of the installation. For example, pumped hydroelectric storage has very reduced polluting effects when compared to other systems and a low operating cost, but it is not suitable for small or medium scale systems.

As electricity production has become increasingly decentralized in recent years, these systems have gained relevance as more medium industries and residential buildings have their own electricity production systems. The most widespread technology in use right now is battery electric storage. This technology offers many benefits: mainly its simplicity, scalability and moderate cost. However, it also comes with many drawbacks: batteries lose their efficiency over time, and they are also very difficult to recycle.

Many alternatives to these systems have been presented. A highly promising one is hydrogen storage, a technology that has existed in theory for many years, but that has found renewed interest in the last decade due to new technological developments and a progressive reduction in costs.

1.2 The hydrogen economy

In 1923, British geneticist JBS Haldane first proposed the concept in his book “Daedalus” [5], in which he described a future England as follows:

> *The country will be covered with rows of metallic windmills working electric motors which in their turn supply current at a very high voltage to great electric mains. At suitable distances, there will be great power stations where during windy weather the surplus power will be used for the electrolytic decomposition of water into oxygen and hydrogen. These gasses will be liquefied, and stored in vast vacuum jacketed reservoirs, probably sunk in the ground. If these reservoirs are sufficiently large, the loss of liquid due to leakage inwards of heat will not be great; thus the proportion evaporating daily from a reservoir 100 yards square by 60 feet deep would not be 1/1000 of that lost from a tank measuring two feet each way. In times of calm, the gasses will be recombined in explosion motors working dynamos which produce electrical energy once more, or more probably in oxidation cells.*

This forecast turned out to be rather clairvoyant, since it details the basic functioning of the hydrogen economy as currently understood.

By using hydrogen as an energy vector, and gradually using it to substitute fossil fuels and other greenhouse gas-producing technologies, emissions can be practically eliminated from the human economy. However, there are some key drawbacks that have yet to be solved.

The main issue is that of the chicken and the egg. The market has no interest in investing in a hydrogen economy because there is no hydrogen economy to participate in to begin with. People don’t buy hydrogen cars because there are barely any hydrogen filling stations, and companies don’t build hydrogen filling stations because there are barely any hydrogen cars.

To solve this issue, institutions are investing very significant amounts of money to kick-start the development of this market and solve its main challenges. [6]

The first is the need for a significant investment in infrastructure. This includes not just the construction of hydrogen filling stations, but also the development of a distribution network to transport hydrogen from production sites to where it is needed.

The second is the need for new hydrogen production technologies. Currently, most hydrogen is produced from natural gas, which results in greenhouse gas emissions. New technologies are needed to produce hydrogen from renewable sources such as wind and solar power.

Finally, the third challenge is the need to develop new storage technologies. Hydrogen is a very energy-dense fuel, but it is also very difficult to store. Current storage technologies are either expensive or have low energy densities. New storage technologies are needed to make hydrogen a practical energy vector.

If these issues are solved, hydrogen can become a key part of a zero-emissions future.

1.3 The hydrogen life cycle

Hydrogen was first identified as a discrete substance by Henry Cavendish in the 18th century, and he also discovered that it produced water when burned, hence its name (hydro -gen means “water former” in Greek). It is the lightest element in the periodic table, with a single proton composing each of the molecules.

This substance finds many uses in industry, mainly in treatment and upgrading of fossil fuels, and is also used as a coolant, due to its high specific heat and thermal conductivity.

Lately, however, hydrogen is increasingly seen as a suitable energy vector for a future cleaner economy. When burned or turned into electricity in a fuel cell, it does not emit any polluting gases, and it can be produced utilizing water electrolysis. This means that it has a completely emission-free energy storage lifecycle.

However, the current methods used to produce and transport hydrogen face significant challenges that make it unsuitable for many applications at its current state. To understand these challenges, and to see how they can be faced, the main methods used in each step of the hydrogen lifecycle will be briefly reviewed.

1.3.1 Hydrogen Production

Production is currently the main limiting factor in hydrogen’s bid to become a clean energy vector. Although many ways to produce it in a nonpolluting manner exist, they are currently economically inviable compared to the more traditional ways of producing the substance in bulk, which are completely dominant in the hydrogen production sector. (

Figure 2) [7].

These methods, which use fossil fuels, produce what is called “gray hydrogen”. When the emissions or part of those emissions are captured and stored (carbon capture and sequestration) “blue hydrogen” is produced. Finally, hydrogen that is produced using renewable energy and through nonpolluting means is called “green hydrogen”.

Both gray and blue hydrogen produce more emissions than burning fossil fuels directly to use their energy and although green hydrogen doesn’t produce greenhouse gases due to its fully renewable energy provenance and its use of electrolysis to produce the hydrogen, it has a much larger cost of production. [8]

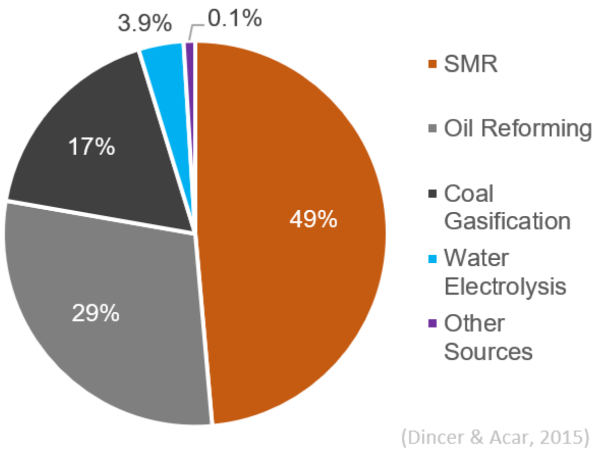


Figure 2. Global hydrogen production by method

1.3.1.1 Steam methane reforming/oil reforming

The share of hydrogen that is produced using fossil fuel-derived methods is 95% of the global amount [9]. The most widespread of these methods is a combination of steam methane reforming (1.1), which uses high-pressure methane and water to obtain hydrogen and carbon monoxide, and water gas shift (1.2), which is used in a second stage of the process to obtain further hydrogen and carbon dioxide.

$$CH_4 + H_2O \rightarrow CO + 3\ H_2 \tag{1.1}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{1.2}$$

From the equations it can be seen that CO and CO2, both very polluting greenhouse gases, are created inevitably during the reaction. Some authors propose carbon capture and sequestration (CC&S), a technique which extracts carbon from the exhaust gases and stores it deep underground, as a way to reduce the emissions from this process [10]. However, this is a complicated and capital-intensive process which hasn't been fully accepted by the scientific community [11].

1.3.1.2 Coal gasification

This process is similar to the one previously described. By combusting the coal at an insufficient oxidation level, a reaction is produced (1.3) which produces hydrogen and carbon monoxide. The water gas shift process (1.2) can then be used to convert the carbon monoxide into carbon dioxide and generate more hydrogen using steam. [12]

$$3C(coal) + O_2 + H_2O \rightarrow H_2 + 3CO \tag{1.3}$$

Again, although the water gas shift process manages to avoid the emission of large amounts of carbon monoxide, there is still a very significant emission of greenhouse gases in the form of carbon dioxide.

1.3.1.3 Electrolysis

The cleanest hydrogen production process is electrolysis. When two electrodes (an anode and a cathode) made of an inert metal are placed in water and an electrical voltage is applied on them, a reaction occurs which generates hydrogen gas on the cathode and oxygen gas on the anode. Due to the composition of water (H_2O) two hydrogen atoms and one oxygen atom is produced from each water molecule.

More particularly, on the anode an oxidation reaction (1.4) occurs which forms oxygen gas and provides electrons to the cathode, which then combines the hydrogen ions and the electrons to form hydrogen gas (1.5).

$$2\ H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1.4}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{1.5}$$

This method of electrolysis, using pure water as the electrolyte (the medium between the two electrodes) is not very efficient due to the low electrical conductivity of pure water [13]. Therefore, different systems have been designed to improve performance, all with different cell designs which have their benefits and drawbacks. These are discussed, together with the fuel cell systems, in the cell technologies (1.4) chapter.

1.3.2 Storage

Hydrogen is a gas which has a very low boiling point. This means that it will remain a gas except under very high pressures and very low temperatures (circa -252ºC) which require a lot of energy. It is also a gas which at certain pressures permeates through many materials, and can even make them become brittle.

Another problem is that in mobile applications, energy density is essential, as both space and weight are limited.

Therefore, care must be taken when selecting a storage solution. For the purposes of this work, only the methods which are viable at a commercial scale will be reviewed, and not research or theoretical projects.

1.3.2.1 Pure hydrogen storage

As seen in Figure 3, storing hydrogen as a pure substance can take one of three forms, all controlled by the pressure and temperature at which the substance is at.

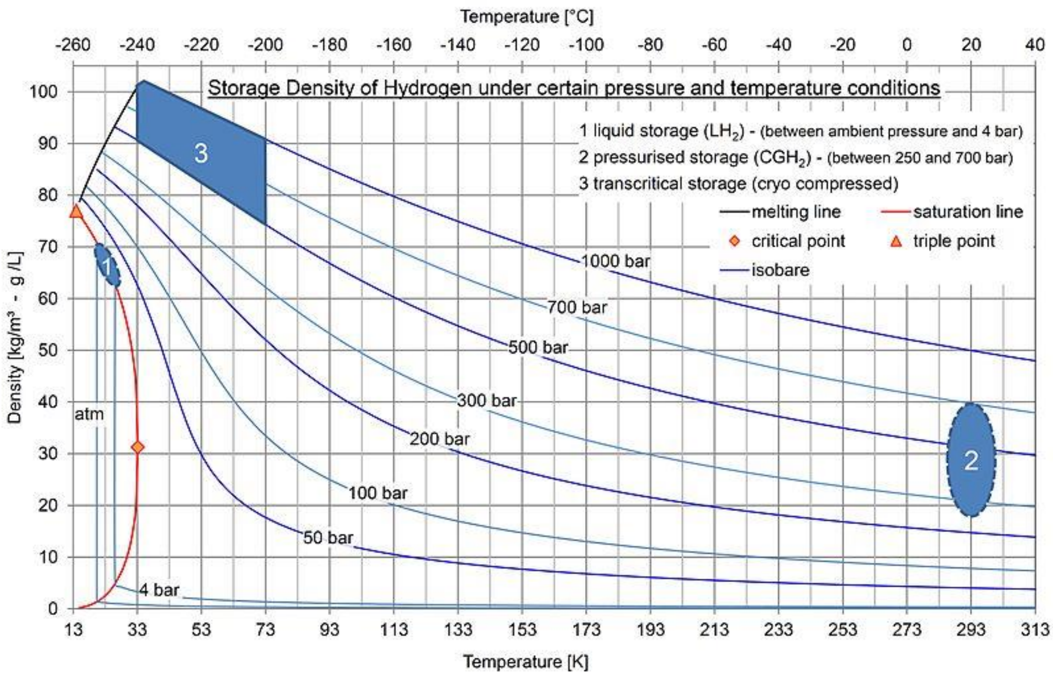


Figure 3. Phase state diagram of hydrogen [14]

Liquid storage can provide high density storage, but requires a large amount of energy to cool it to the very low temperatures required. Furthermore, the hydrogen must be maintained at that temperature, which entails the use of thermally insulated compression vessels. The main benefit is that as with all gases, its liquid form is denser than its gas form, hence being of interest to the developers of automotive and vehicular applications.

Compressed hydrogen storage is the most widespread storage method. In this system, hydrogen is highly compressed to be able to accumulate as much as possible at room temperature. This system is cheap and simple to use, requiring only a high-pressure vessel and the compressor, but is considered dangerous as the gas can reach up to 700 bar, causing an explosion if the container is breached.

Cryo-compressed hydrogen is a combination of the two previous methods, using a high pressure thermally insulated vessel to store low-temperature and very high-pressure hydrogen. This allows for the greatest storage density, but is also difficult to manage. For example, as can be seen in Figure 3, the pressure rises with temperature, so if the storage tank is already at a very high pressure and the temperature is not constantly controlled, the tank will have to vent hydrogen to the outside to avoid reaching unsafe pressures. This has obvious negative implications when considering that many cars are parked in closed indoor spaces. However, some authors [15] propose that with adequate thermal insulation, even during long parking periods the tanks wouldn't need to vent.

1.3.2.2 Chemical methods

To solve the aforementioned drawbacks, several methods have been developed that allow hydrogen to be stored using complex chemical reactions. These reactions, in essence, separate the hydrogen molecules to absorb the gas under certain conditions and release the gas under other conditions.

The leading and most commercially available of these technologies is the one that uses **metal hydrides**. This substance absorbs hydrogen by storing it in the space inside the matrices that the metal lattice forms, hence their alternate name of **interstitial hydrides**. [16]

Although this implies a heavier weight than otherwise empty hydrogen

1.3.3 Electricity Generation

To convert hydrogen back into usable power, it can be burnt for its thermal power, or it can be fed into a fuel cell to generate electricity. The thermal use is finding a lot of interest in the steel industry, since huge quantities of fossil fuels are required to turn iron ore into crude steel using a method known as direct reduction, which theoretically allows for the use of 100% hydrogen fuel [17]. This method is interesting, since as opposed to fuel cells, which will be described in the next section, it doesn't require a very high-quality hydrogen. However, this is not necessarily a good thing since it allows for hydrogen being created by steam methane reduction to be used, therefore negating its benefits for the environment.

The technique which is most relevant are fuel cells. These devices use similar techniques as the electrolysers, but instead of producing hydrogen from water and electricity, they produce water and electricity from hydrogen. This electricity can then be harnessed to power any type of device.

Fuel cells work by passing hydrogen and oxygen over two electrodes and an electrolyte. The hydrogen and oxygen combine to form water, and the electrons that are released as a product of this reaction flow through an external circuit to the oxygen electrode. A fuel cell can have a higher efficiency than an internal combustion engine, and they are often used in conjunction with electric motors. Fuel cells have the potential to be used in a variety of different settings, including in homes, businesses, and even in power plants.

Alkaline fuel cells, the most common in the market, work by the following reaction:

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad (1.6)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1.7)$$

Similarly to the effect seen in electrolysis, the hydrogen combines with the hydroxide in the anode to produce water and electrons, which flow through an external circuit (providing a current) and return to the cathode, where the electrons recombine with the water and the oxygen to produce hydroxide. Since to have stochiometric balance the top equation needs to happen twice, two hydrogen molecules and one oxygen molecule are required for the production of two molecules of water.

1.4 Cell technologies

1.4.1 Electrolysis

Hydrogen electrolysis is fundamentally a simple concept which becomes highly complex when taken to the realm of engineering. In order to provide maximum efficiency and comply with different requirements, a multitude of designs have been developed.

In addition, electrolysers can have a number of different types of electrolyte, which is the medium that carries electrons between the anode and the cathode. The electrolyte is therefore a crucial element of the electrolyser, and each type of electrolyte has its own advantages, disadvantages and limitations.

The membrane that interfaces the oxygen and hydrogen side is also an important part of the system and usually is the most decisive component in the development of the reactions in the cell.

		AEC	**AEM**	**PEM**	**SOE**
Electrode material	*Cathode*	Ni, Co or Fe	Ni, Ni alloys	Pt, Pd	Ni
	Anode	Ni	Fe, Ni, Co oxides	IrO_2, RuO_2	La/Sr/MnO (LSM) La/Sr/FeO (LSCF)
Electrolyte		25-30% KOH in water	1% KOH in water	Fluoropolymer ionomer	ZrO_2 + 8% Y_2O_3
Energy source		Electrical	Electrical	Electrical	25% heat 75% electrical
Current density		Up to 0.5A/cm^2	0.2-1A/cm^2	Up to 3A/cm^2	Up to 0.5A/cm^2
Product		Hydrogen	Hydrogen	Hydrogen	Hydrogen or syngas[1]
Gas outlet pressure		Up to 40 bar	Up to 35 bar	Up to 40 bar	Close to atmospheric
Cell temperature		~80ºC	~60ºC	~60ºC	~750 to 850ºC
Benefits		Durability, Low cost, mature technology	Low cost Less corrosive electrolyte	Compactness Efficiency Good partial loads	Efficiency
Drawbacks		Poor at partial loads Slow response	Low current density Unclear lifetime	Expensive Low durability	Low maturity Low commercialization High temperature required to produce

Table 1. Comparison of electrolysis methods. [18], [19]

[1] Syngas is a mix of hydrogen and carbon monoxide, the direct product of steam methane reforming (paragraph 1.3.1.1)

1.4.1.1 *Alkaline water electrolysis (AWE)*

The most well-established method of producing hydrogen from electrolysis is known as Alkaline water electrolysis (AWE). These systems use an aqueous solution of potassium hydroxide (KOH) as an electrolyte. The two electrodes are separated by a semipermeable membrane called a diaphragm, which allows the ions to pass through but keeps the gases separated, therefore allowing the user to extract each gas independently. [20]

This method is not very efficient, but it is the most widespread one due to its low cost. [18]

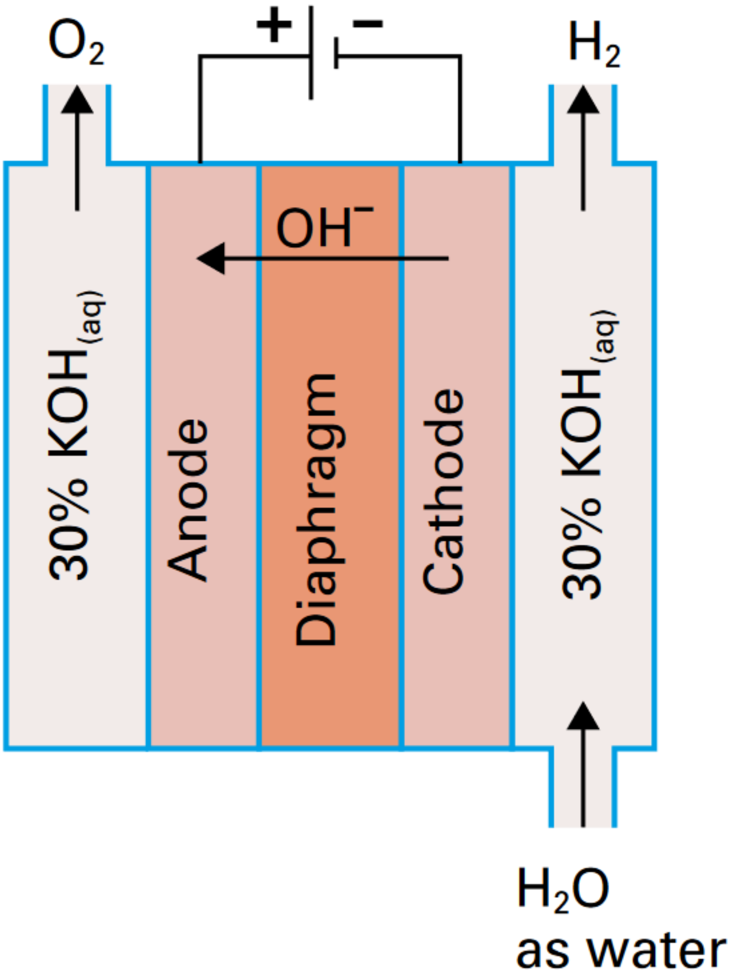


Figure 4. AWE Electrolyser schematic [19]

1.4.1.2 Anion exchange membrane (AEM)

AEM electrolysers have a very similar working principle to AWE electrolysers, but their improved ionomer membrane leads them to be able to operate using a much less corrosive electrolyte. This in turn allows the manufacturer to use less expensive materials than other systems, reducing the cost of the whole system. The internal design of the cell also allows oxygen to be generated at 1 bar as opposed to the 35 bar nominal pressure of the hydrogen side. This keeps oxygen from leaking into the hydrogen side, allowing for a much higher output quality.

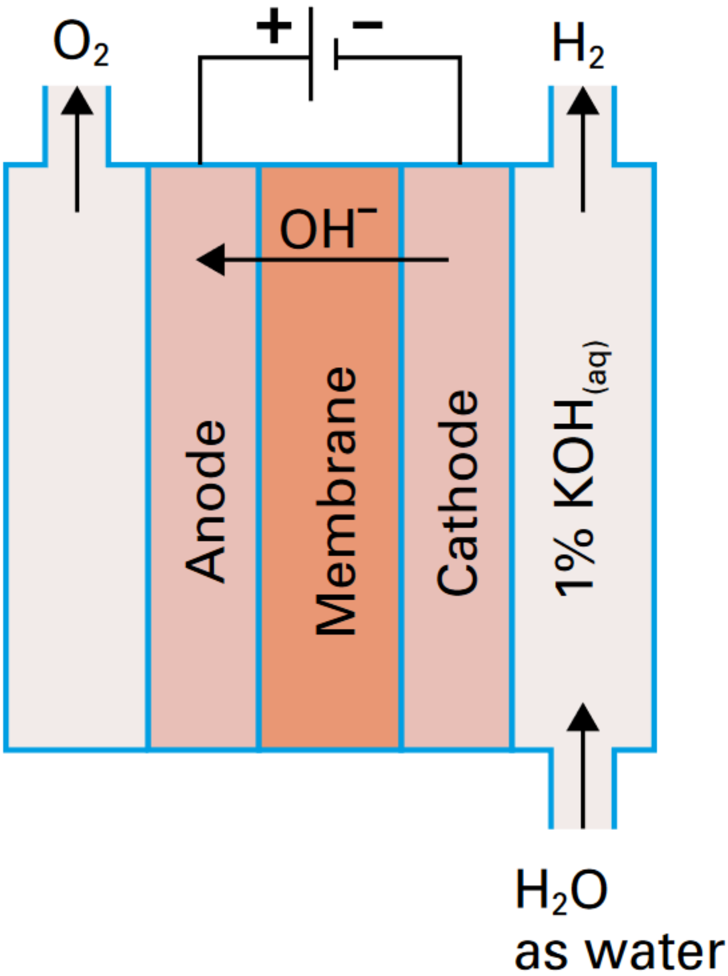


Figure 5. AEM electrolyser schematic [19]

1.4.1.3 *Proton exchange membrane (PEM)*

PEM cells use a solid polymer as electrolyte which, when in contact with water, allows protons to pass through but not electrons or gases as seen below. This method is especially interesting when dealing with the issues of low current density, and low pressure/partial load operation which currently limit the usage of the alkaline water electrolyser. [21]

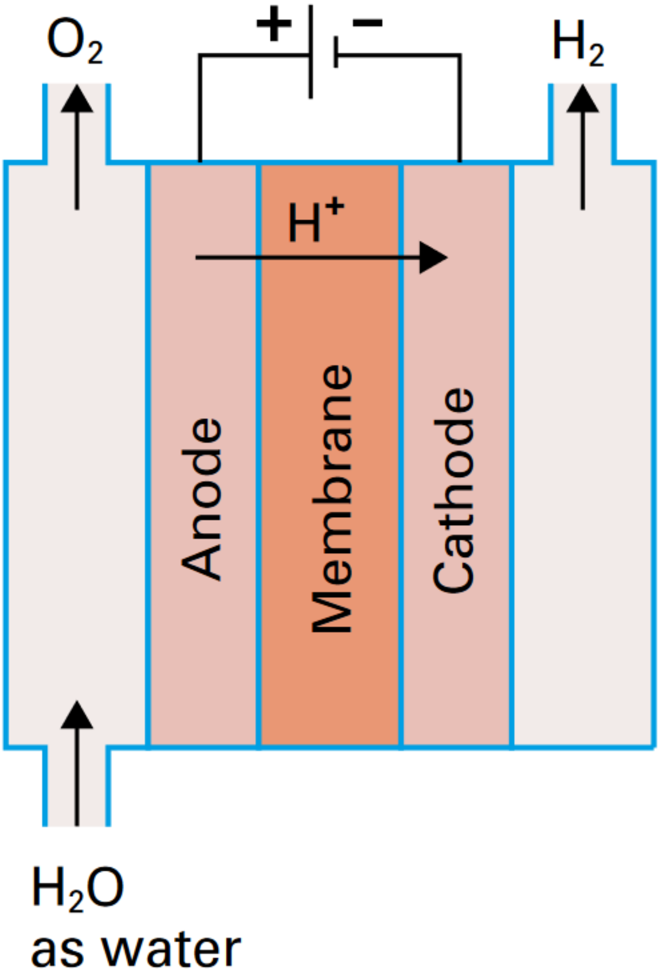


Figure 6. PEM Electrolyser schematic [19]

1.4.1.4 *Solid oxide electrolysis (SOE)*

A method which is recently gaining relevance is known as solid oxide electrolysis (SOE). This system uses a solid oxide electrolyte that allows for high efficiency, but has the drawback of requiring very high temperatures (500-1000ºC) to be able to let the oxygen ions pass from one electrode to another. This method is currently only used in lab settings but it is the most relevant of the new cell designs currently in development [22].

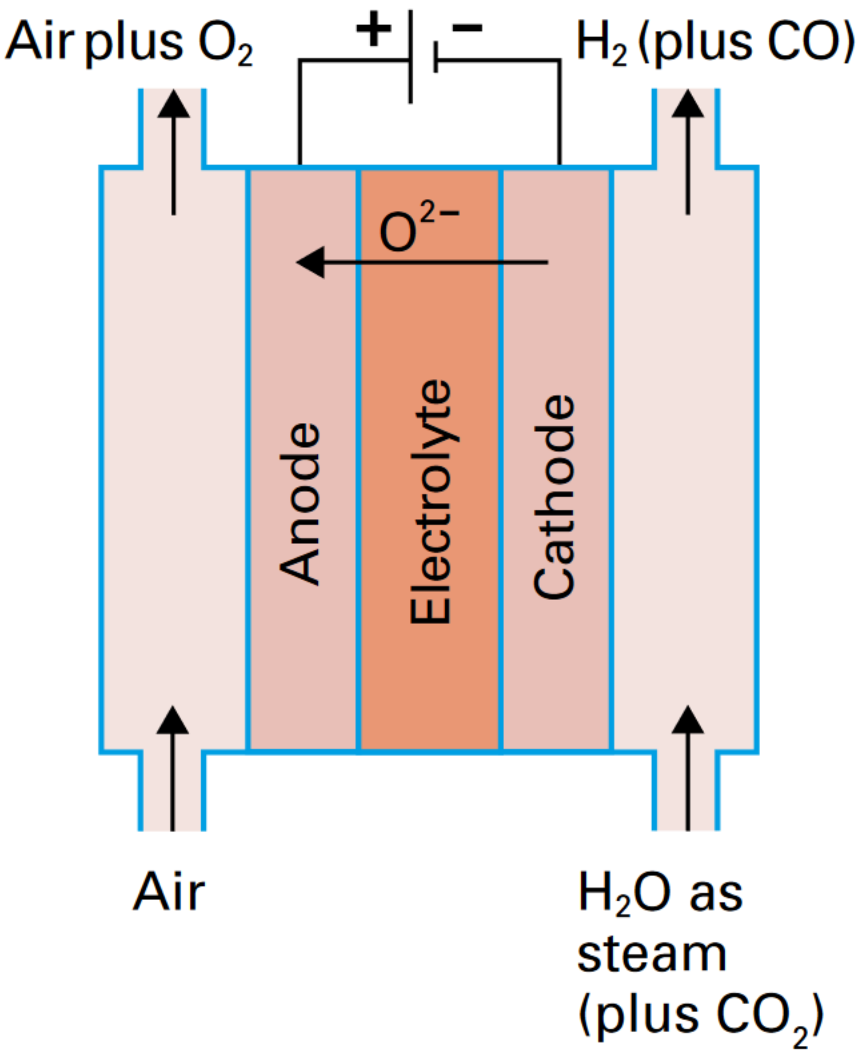


Figure 7. SOE Electrolyser schematic [19]

1.4.2 Fuel cell

Fuel cells and electrolysers are very much alike in that they both contain similar stacks of materials to facilitate the reaction. However, the internal design of the cell usually has some minor changes to facilitate the reaction, which can flow in a different direction.

	AFC	**PEMFC**	**PAFC**	**MCFC**	**SOFC**
Electrolyte	KOH in water	Perfluorosulfonic acid	Phosphoric acid in a porous matrix or polymer	Molten lithium, sodium and/or potassium carbonate	Yttria stabilized zirconia
Typical stack size	1-100kW	<1kW-100kW	5-400 kW (liq. PAFC) <10 kW (polymer PAFC)	300 kW – 3MW	1 kW – 2 MW
Efficiency	60%	60%	40%	50%	60%
Cell temperature	<100ºc	<120ºC	150-200ºC	600-700ºC	500-1000ºC
Benefits	Lower cost Low temperature Quick start-up	Reduced corrosion and management issues due to solid polymer Low temperature Quick start-up Very good load-following	Suitable for CHP[2] Good tolerance to fuel impurities	Suitable for CHP Fuel flexibility Highly efficient	Suitable for CHP Fuel flexibility High efficiency
Drawbacks	Sensitive to CO_2	Expensive catalysts Sensitive to fuel impurities	Expensive catalysts Long start-up Sulfur sensitivity	High temperature corrodes component Long start-up time Low power density	High temperature corrodes component Long start-up time Limited number of shutdowns

Table 2. Comparison of fuel cell types

[2] Combined heating and power. The waste heat produced by these devices is so significant that it can be used for residential, commercial or industrial heating purposes.

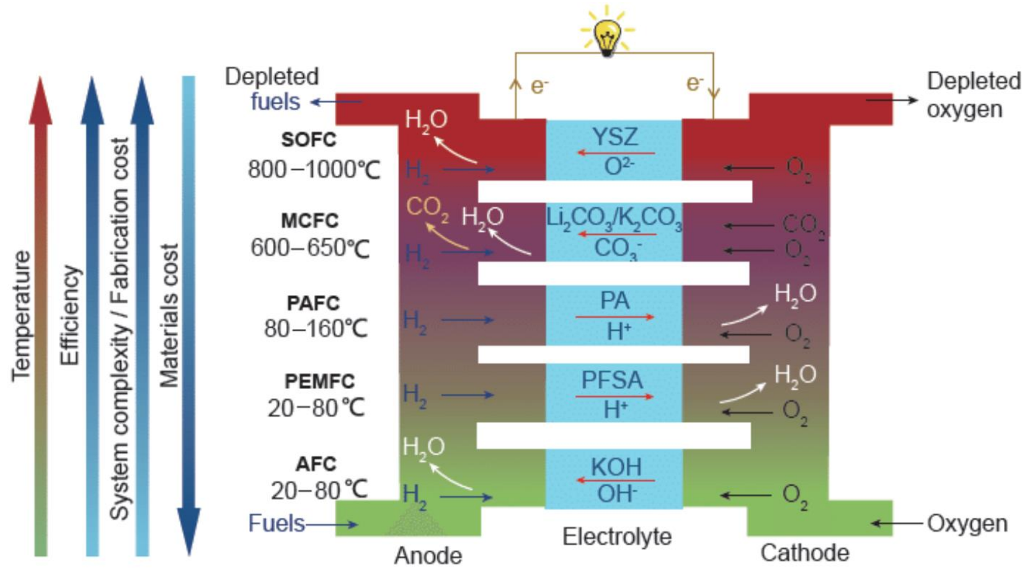


Figure 8. Internal structure of fuel cell designs [23]

1.4.2.1 Alkaline fuel cell (AFC)

AFCs are very similar in design to alkaline water electrolysers. They combine oxygen and hydrogen while using a diaphragm to separate the gases while allowing the passage of the hydroxide, the energy carrier in this case.

1.4.2.2 Proton exchange membrane fuel cell (PEMFC)

This system uses hydrogen ions as the energy carrier. The membrane, made out of a complex assembly of specialized polymers, allows them to pass while electrically insulating the two sides and also blocking gas from crossing over to the other side, which would reduce the efficiency of the reaction.

1.4.2.3 Phosphoric acid fuel cell (PAFC)

Phosphoric acid fuel cells are a type of fuel cell that uses liquid phosphoric acid as an electrolyte. The acid is contained in a Teflon-bonded silicon carbide matrix, and the electrodes are made of porous carbon containing a platinum catalyst. One of the most mature types of fuel cells, PAFCs are considered the "first generation" of modern fuel cells. PAFCs were the first to be used commercially and are typically used for stationary power generation. However, some PAFCs have been used to power large vehicles, such as city buses.

1.4.2.4 Molten carbonate fuel cell (MCFC)

MCFCs use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic lithium aluminum oxide matrix. Because they operate at high temperatures of 650°C (roughly 1,200°F), they can use less-precious metals as catalysts at the anode and cathode, reducing costs.

This high temperature also results in increased efficiency, another cost-saving factor for MCFCs. When coupled with a turbine, MCFCs can reach efficiencies of up to 65%. This is much higher than the 37% to 42% efficiencies of a phosphoric acid fuel cell plant.

1.4.2.5 Solid oxide fuel cells

SOFCs use a hard ceramic electrolyte. These systems, like the electrolyser systems of the same name, require very high temperatures to function, around 1000ºC, meaning that they have a long start up time. However this also has its benefits, as the cell does not require precious catalysts, reducing the cost, and if the waste heat is used for CHP efficiencies can top 85%. [24]

2 Project definition

2.1 Purpose

For the reasons exposed in the introduction, it is of interest to test the performance of the latest technologies as an applied and comprehensive system. The aim of the project is to:

prove the feasibility of a hydrogen-based electricity storage system;

measure and monitor its performance and efficiency;

and analyze and discover improvements that can be made to reduce its cost, improve its efficiency, and reduce its energetic footprint.

2.2 Scope

Therefore, this project aims to design and build a complete energy storage system through hydrogen, including:

a hydrogen generation system using electrolysis;

a hydrogen storage system using metal hydrides;

an electricity generation system using a hydrogen-powered fuel cell;

the required mechatronic interface to control the flows of gases, cooling fluids and electricity;

and the control system required to coordinate the operation of the whole system.

Due to the global supply crisis, some components were not be ready for full integration by the time of the conclusion of this work, in that case an equivalent model was developed which interacts virtually with the rest of the system.

2.3 Collaboration

This system will be developed as a commercial project for the company BluEnergy Revolution, which is engaged in the business of hydrogen system consulting, integration, assembly, and installation.

2.4 System benchmarks

The requirements to be fulfilled by the system are to be able to provide **1kW of power for at least 24 hours**, while reducing energy loss to the greatest extent.

2.5 System description

2.5.1 General overview

To store energy using a hydrogen vector, the electricity needs to be converted to hydrogen, stored, and consumed on demand (Figure 9)

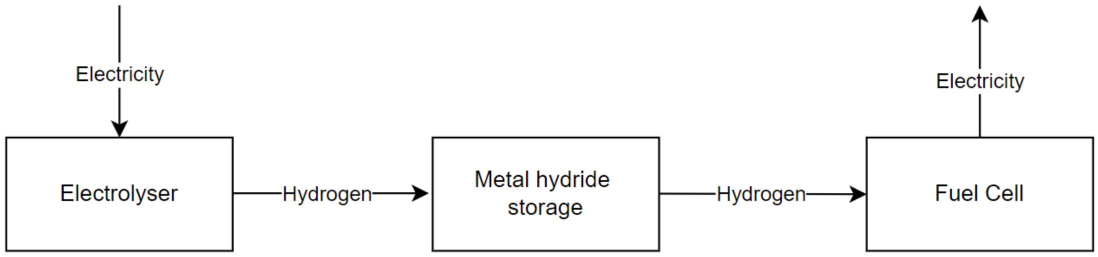


Figure 9. Basic energy flows of a hydrogen electrical storage system

Clearly, this is a very simplified view of the system, which requires the control of thermal, chemical, and electric flows to perform adequately.

To start to define the system in more precise details, the system must be dimensioned according to the specifications set by the project goals.

Since the project requires 1kW to be furnished for 24 hours, the fuel cell needs to be rated at least at 1kW, and the metal hydride storage needs to have a capacity of at least 24 kWh. The electrolyser chosen will have to furnish hydrogen at an adequate rate, so the system can be charged within a reasonable timeframe. Furthermore, the hydride system must be able to both store the required amount of hydrogen and be able to release it with an adequate flow rate to feed the fuel cell.

Since the hydride hydrogen release reaction is endothermic and the hydrogen absorption reaction is exothermic, a thermal management system must be developed which will control the temperature of the system according to the pressure which is required. As detailed in the metal hydride storage section (section Metal hydride storage2.5.3) the system requires less heat than the fuel cell produces during operation. For this reason, if the waste heat is recovered from the fuel cell and managed actively, the need for external energy to heat the hydrides can be eliminated, therefore greatly increasing the efficiency of the system, one of the stated goals of this project.

The thermal power that is not used by the hydrides to release hydrogen will be recovered using a hot water tank with an internal heat exchanger. This stored heat can then be used for building heating, sanitary hot water, or to run a heat pump, uses that fall outside the scope of this project. During hydrogen intake, the hydrides will heat up, and that energy will also be stored inside the water tank.

During protracted operation, the water tank might reach a temperature that is too high and therefore be unable to cool the system. For this purpose, an active thermal control system to dissipate excess heat into the air will also be included. Finally, in certain cold weather conditions the system temperature might be too low to successfully release hydrogen and start the fuel cell; therefore, a heating system will also be included to prime the system before operation if needed.

The nature of the design of fuel cells make them output a direct current of highly variable voltage. To correct this and to be able to supply loads with the adequate voltage, a DC/DC converter will need to be added to the system. Furthermore, to deal with the slow response time of the fuel cell, a small battery bank will be added to act as a buffer, compensating for any voltage shift due to changes in load.

Finally, due to the low throughput of the system, the pure water required for operation will be provided manually and no demineralization system will be included.

With these specifications, the system overview becomes more populated:

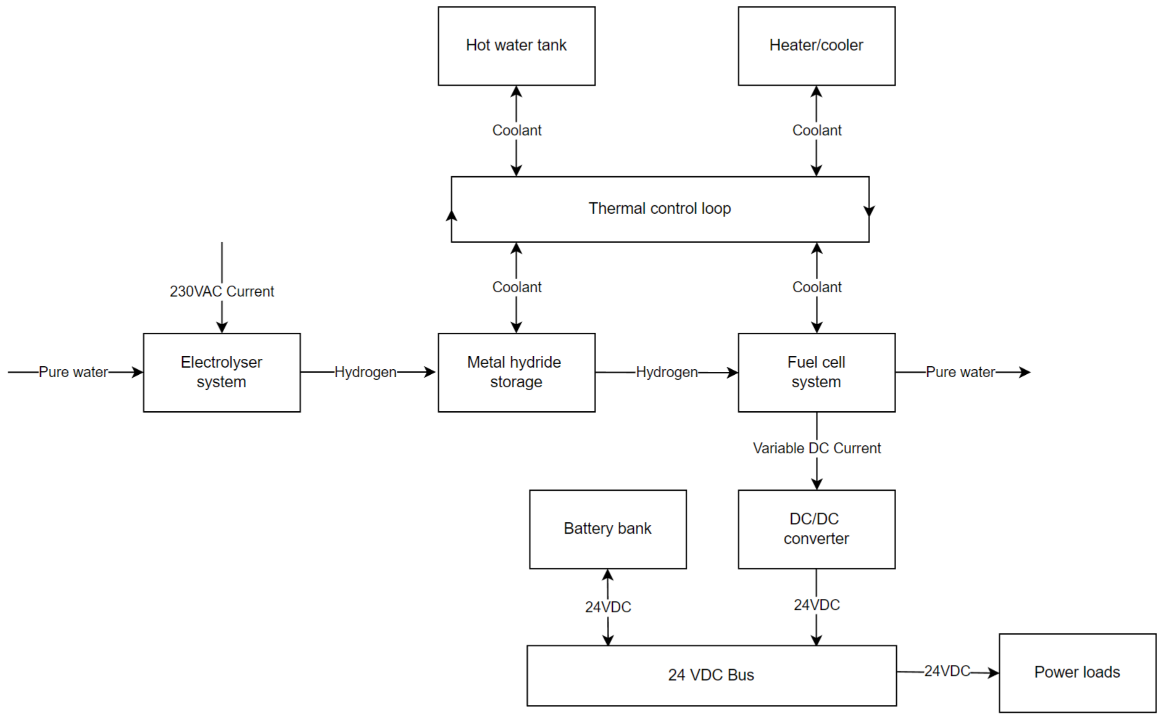


Figure 10. General overview of the substance flows of the system

One of the most important parts will be designing an efficient control system that can control all these subsystems with coordination. To integrate this system into an existing energy management system, a high-level interface will also be developed, to be able to easily control the behavior of the plant.

In the following sections, each subsystem is described in detail.

2.5.2 Electrolyser system

The role of this subsystem is to convert electrical energy into clean hydrogen to be stored in the metal hydride storage. After reviewing several options, the Electrolyser 2.1 system sold by Enapter, seemed to provide the most complete and integrated solution.

This product simplifies the development of the electrolysis subsystem since it provides three discrete devices:

a water tank (Figure 11), which monitors the conductivity of the water to ensure adequate purity and controls the pump to maintain pressure;

the electrolyser (Figure 12), which acts as the central control unit of the rest of the devices and has the necessary controls to allow the user to be able to start, stop and regulate the output in a very simple manner;

and the dryer (Figure 13), which removes the water from the hydrogen output and guarantees the supply of pure hydrogen.

Figure 11. Enapter WT2.1

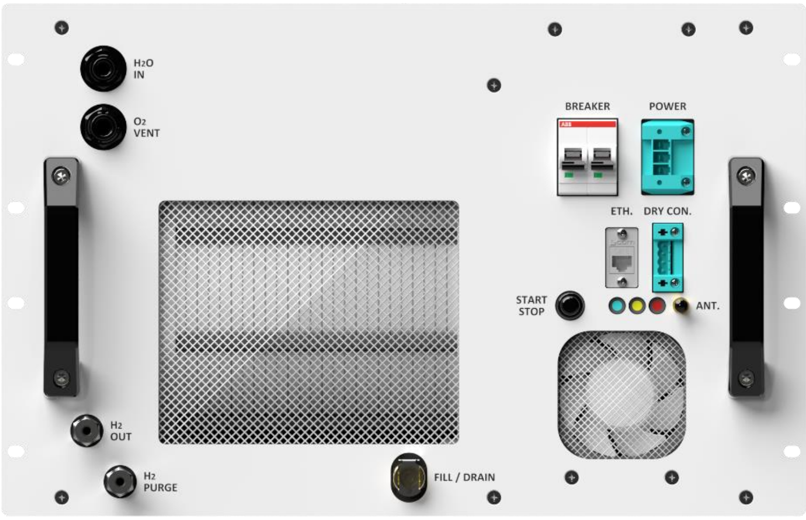


Figure 12. Enapter EL2.1

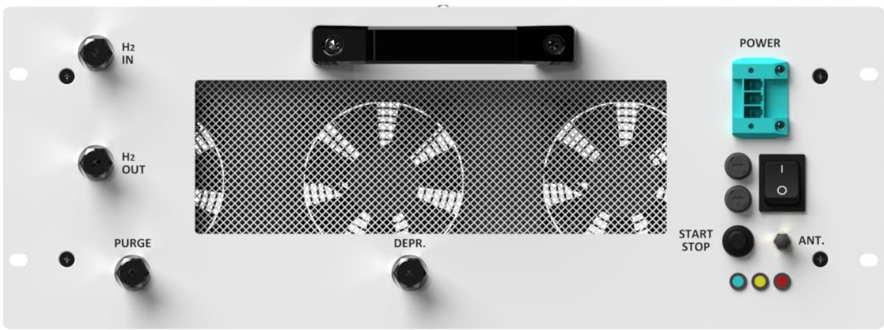


Figure 13. Enapter Dryer

2.5.2.1 Mechanical

The devices are mounted on 19-inch racks to facilitate their set up and scalability. They are designed so that the user can join up to five electrolysers in a single rack using only one water tank and one dryer.

2.5.2.2 Line management

The Enapter system is highly integrated but still has particular requirements to be dealt with, as can be seen in the images of the rack-mounted devices.

The water tank is the simplest one: It only requires a tube to supply water to it, a tube to carry the water to the electrolyser, and a drain tube to guide the water away in case of overfilling.

The electrolyser does have more rigorous requirements.

As expected, there is a water intake and a hydrogen output. The water intake comes from the water tank. The hydrogen output consists of a Swagelok fitting that goes into an AISI 318 alloy tube. As previously described, the ability of hydrogen to permeate metals causes them to become brittle, so this specific alloy must be used as it is rated to minimize the damage cause by this effect.

There are two other lines which are particularly demanding. Both are used to vent unwanted gases during operation of the electrolyser. On one hand, the H2 Purge line vents high pressure hydrogen during ramp-up, ramp-down, and at regular intervals during operation. This is used to clean the electrodes from unwanted water accumulation and causes the whole line to depressurize.

Due to the fact that the electrolyser operates at 35 bar, this depressurization is violent and requires the utmost care to avoid dangerous situations. The manual requires this gas to be vented out of the top of the building.

Another problem is that the vented hydrogen contains a large amount of water. If the hydrogen is to go up, water cannot be allowed to accumulate at the bottom of the pipe since it would block the output and instantly destroy the electrolyser. For this purpose, a device called a water trap, or automatic water discharger, must be placed at the bottom of the line. This device uses an internal flotation system to discharge the liquids that fall on it without allowing the gas to escape: a critical need since gas accumulation outside the system needs to be avoided at all costs.

Similarly, the O2 vent line vents a constant amount of oxygen, an unwanted byproduct of electrolysis. This line also vents water vapor at a low rate, so it also needs to be fitted with a water trap.

An uninformed observer would suggest that to avoid using two costly water traps, one could join the hydrogen and oxygen vent lines and have a single water trap that discharged the water accumulated in both of the lines.

Unfortunately, a mix of pure hydrogen and oxygen gas is extremely explosive and as such the gases must be separated to avoid unexpected disassembly of the system. Therefore, there is a requirement for two separate purging lines, with two separate vents on top of the building that must be separated themselves by at least three meters.

Lastly, the dryer has a similar requirement of an H2 purge line which can be joined directly to the electrolyser's purge line.

2.5.2.3 Power

The electrolyser is directly powered by mains current at 230AC.

2.5.2.4 Control

The electrolyser system provides a graphical user interface through and app and also through a web server that may be accessed when in the same Local Area Network. For integration into a larger system, however, industrial control is necessary, and as such Enapter uncovers a Modbus IP interface which allows PLCs to communicate and operate the devices.

The electrolyser acts as the central control system; therefore, the PLC only connects to it and then it forwards instructions to the other components.

2.5.3 Metal hydride storage

The metal hydride storage system is provided by the company Methydor, an Italian company which produces these systems commercially.

The scope of supply of the system is as follows (Figure 14).

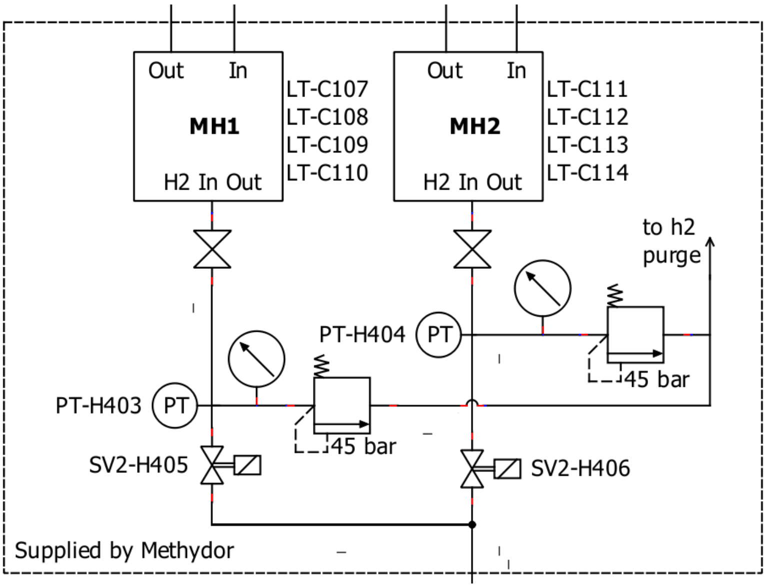


Figure 14. Metal hydrides scope of supply schematic

The system consists of two metal hydride banks. This is to allow for faster charging and to reduce thermal inertia. The system does not contain any control systems, only sensors (level transmitters and pressure transmitters), actuators (two electrovalves controlling the input/output of each bank), and safety devices (two safety valves which release the hydrogen if the system reaches more than 45 bar).

Each bank consists of a series of tubular pressure vessels, which are in turn placed inside a larger vessel containing water, which is used to control the temperature of the hydrides.

Figure 15. The hydride bank being assembled. Clockwise: the modules stacked; the water vessel; and the soldering of the modules.

The dimensioning of the hydrides can be calculated using the nominal consumption of the fuel cell, around 15 l/min. If the fuel cell provides 1kw, and we need 24kWh, that means we need to provide 21600 normal liters of hydrogen or 964.25 mol. Assuming 1% of the weight of the hydrides is usable stored hydrogen[3], we need around 200kg of hydrides.

[3] Although the MH system can go up to around 1.5% hydrogen by weight, the lower range of that is unusable due to the fact that the hydrides are unable to provide enough pressure for the fuel cell.

As a comparison, the Tesla Powerwall provides 13.5 kWh in a 114 kg system, or around 118W per kg[25]. The metal hydrides provide 120W per kg, although the necessary accessory systems such as the electrolyser and fuel cell bring that down. However, since this density has been calculated using the performance of the fuel cell, it will increase together with the evolution of fuel cell technology.

2.5.3.1 Mechanical

Due to the nature of the system, the hydride banks are objects of considerable weight and size as they contain 200kg of hydrides inside and are rated pressure vessels. Furthermore, they will be filled with water on site.

They are set on a stand so they can be lifted with a pallet jack and moved around and simply rest on the floor.

2.5.3.2 Line management

The hydride banks have a single hydrogen connection which will flow towards the inside when charging and towards the outside when discharging. It is important to constantly monitor the pressure and to release it before the safety valves kick in.

The input and output of water is what controls the temperature of the hydrides, and consists of an open (e.g. non-pressurized) vessel which will spill over if overfilled. Therefore, care must also be taken to constantly monitor the level of water, which will reduce due to evaporation.

2.5.4 Fuel cell

The fuel cell for this project has particular requirements which make it difficult to find. In particular, the fuel cell needs to be water-cooled, a feature common in larger fuel cells, but not in ones of this size. For this reason, contacts have been established with multiple companies until a Swiss group was able to provide us with a reasonable offer.

This fuel cell has the following general specifications:

Main System Parameters:

- System based on [redacted] FC stack platform
- Output power: 1,5 [kW]
- Maximum current: 180 [A]
- System output voltage: 17 – 33 [V] (to be confirmed)
- Load modulation: 30 – 100 [%]
- Operation modes: Idle, Stand-by, RUN mode, Emergency

Anode (Hydrogen) Line:

- Swagelok standard fittings
- Hydrogen pressure required: 8-12 [bar g]
- Hydrogen quality: according to ISO 14687

As seen, the FC does not provide a constant voltage output. This is unfortunately a drawback that is inherent to the design of fuel cells. To solve this issue, a DC/DC converter will have to be included.

The hydrogen flow required and quality are perfectly in line with the hydride system.

Unfortunately, due to time constraints, there are no more details available on the structure or power connections of the fuel cell. For this reason, the model uses data available regarding comparable models to configure the parameters of the cell.

2.5.5 Hydrogen flow control system

The whole system is designed with a Piping and Instrumentation Diagram (P&ID) which defines every single one of its components. The complete diagram is available in the annex but some partial representations will be presented in this description for clarity.

2.5.5.1 Purge lines

The system has two separate purge or vent lines. As the electrolysis process produces oxygen which is not used in this system it needs to be vented. There is another line for purged hydrogem which comes from the electrolyser's purge port (it expels hydrogen at regular intervals to clean and dry itself) and from the purge ports of the other components. Pure oxygen and pure hydrogen cannot be combined in order to avoid an explosion, so two different lines are needed.

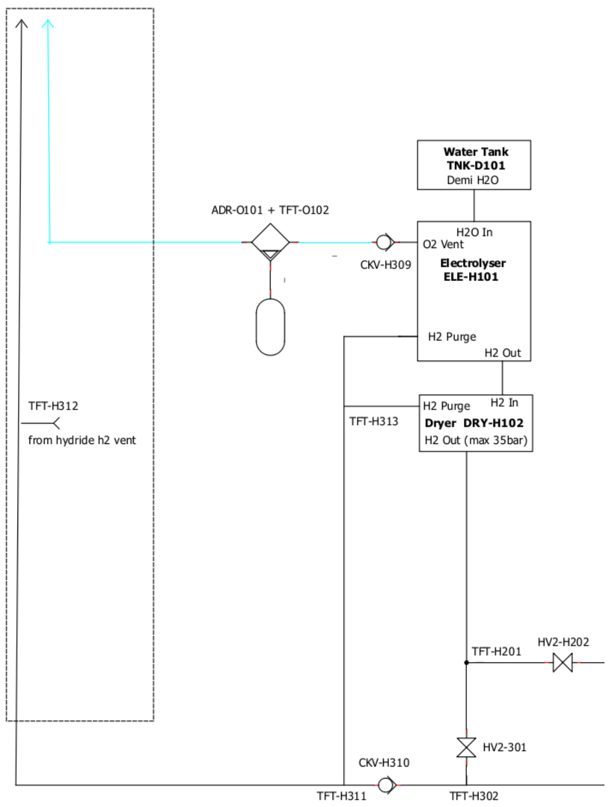


Figure 16. Purge lines schematic

2.5.5.2 *Central hydrogen interface*

The three main components (electrolyser, MH banks and FC) are interfaced with each other by the following system. The system contains manual valves to facilitate testing and maintenance, however the control of the flow is done using a single electrovalve. Since the hydrogen should only flow from the electrolyser to the hydride bank and not in reverse, a check valve (CKV-H204) is used to guarantee that direction.

When the electrolyser is being used or the system is in standby, SV2-H208 is closed, therefore closing the FC from the system. When it is being used, any residual pressure from the EL will flow into the FC side and then the check valve will prevent any pressure from being lost to the EL side.

A pressure sensor (PT-H401) is located to measure the pressure in case the ones located in the hydrides are not available.

Finally, in terms of safety, there is a purge valve (SV2-H303) which is used in case that the gas needs to be rapidly vented to the exterior to avoid overpressure situations, and a safety valve before the FC to protect the membrane against any accidental overpressure.

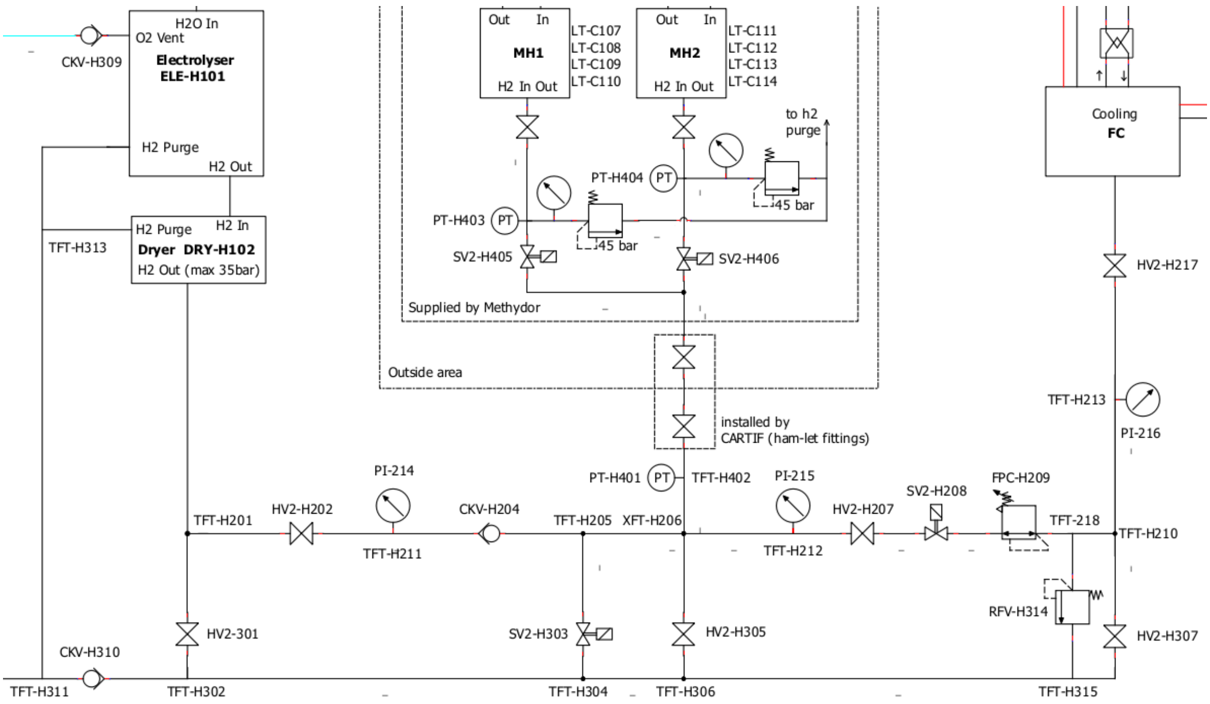


Figure 17. Central hydrogen interface schematic

2.5.6 Thermal control system

The thermal loop is one of the critical parts of this system. Since the fundamental objective is to make it as efficient as possible, the system needs to control the thermal flows precisely in order to keep as much energy inside the system as possible.

Figure 18 shows the schematic of that system. It consists of a central loop to which components can be connected and disconnected freely. This topology has been decided in order to allow for flexibility in terms of programming and testing instead of choosing a more static scheme.

All the objects are connected via 3 way diverting valves. If the valves are straight, the water bypasses the component, and if they are not they divert the flow towards the component.

The MH banks have check valves since the vessel they contain is open and cannot hold pressure. The rest do not as the backpressure keeps water from flowing in, but if it is determined that there is heat loss through those exits, check valves will also be added.

The radiator can be connected and disconnected to avoid heat loss.

There are temperature transmitters set at the entry and exit of the hydrides, inside the water tank, and between the water tank and the cooler for testing reasons.

Finally, a heat exchanger is connected to the FC to maintain its operating temperature while insulating its cooling circuit (it contains its own pump which it controls independently) from the rest of the loop.

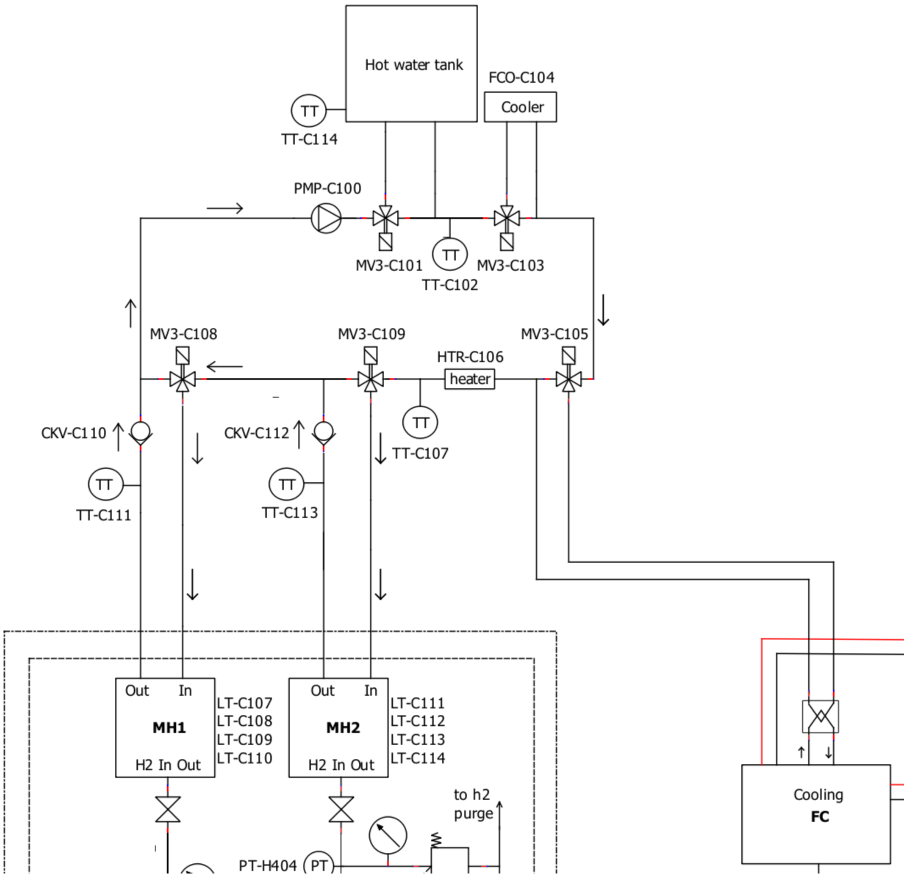
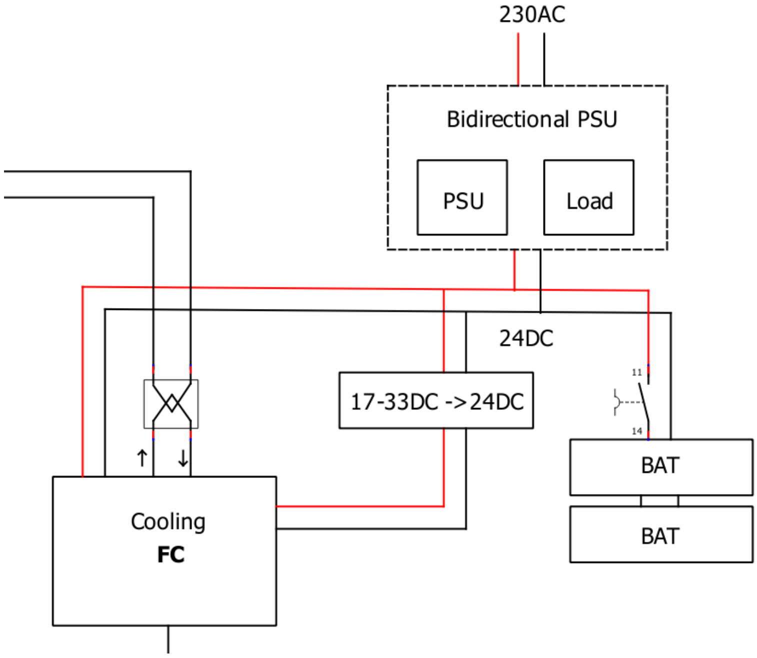


Figure 18. Thermal control system schematic

2.5.7 Electrical system

The design of the electrical system is poised to vary with the further definition of the fuel cell, however the client has explained that they will use a bidirectional power supply unit, which will act as a power supply or a load. In load mode, the DCDC will control the voltage of the system. The power supply will also be used to charge the batteries, acting as an energy buffer, while having the FC and DCDC disconnected, and in that scenario it will be the PSU that is managing the voltage of the circuit.



2.5.7.1 DC/DC converter

The converter chosen for this project is the BB MP device from BrightLoop. This converter has an input and output range of 10-56V, and it is capable of handling up to 240A, therefore making it perfectly in line for the output characteristics of the fuel cell.

Figure 19. The BB MP DC/DC converter from BrightLoop

2.5.7.2 Battery bank

The battery for the buffer will be a 24V 100Ah system from Victron Energy. This product has been chosen due to its advanced and easy to use Battery Management System which facilitates integration with our control system. These batteries also have very good safety mechanisms which are in line with our safety goals.

Figure 20. A 24V 100Ah battery from Victron Energy

2.5.8 Control network

The particular behaviour of the control system is described in Section 4. This section deals with the hardware configuration of the control network.

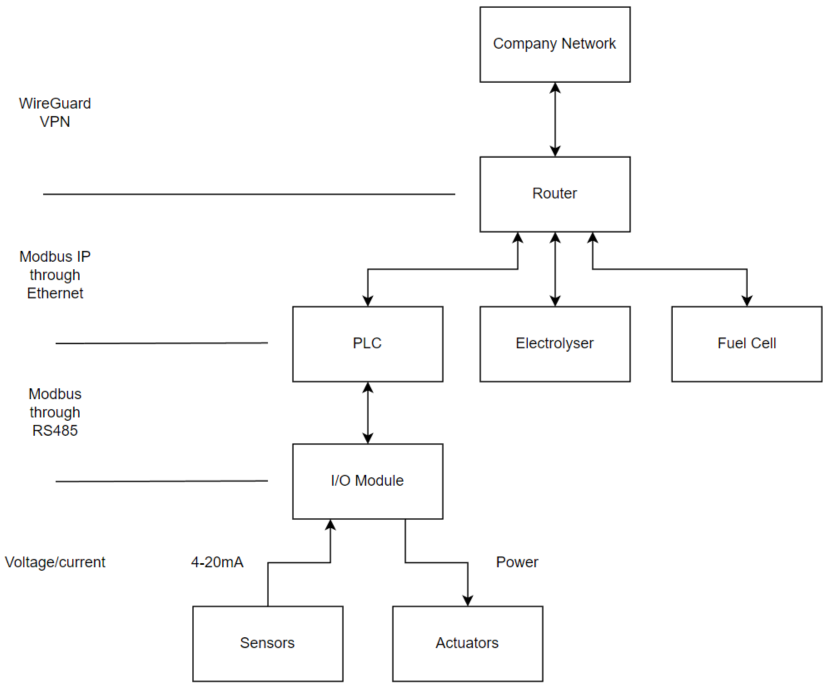


Figure 21. Control network schematic

The control network is set up in a stratified way that abstracts the signals further as the components rise in the hierarchy. Starting from the bottom, the passive components (sensors and actuators such as pressure transmitters or electrovalves) interface with an I/O module which digitalizes these readings and transmits them to the PLC, or uses relays to control the delivery of power to the actuators.

The module chosen for this project is the MIX38 by Isma Controlli, due to its great flexibility and number of inputs and outputs.

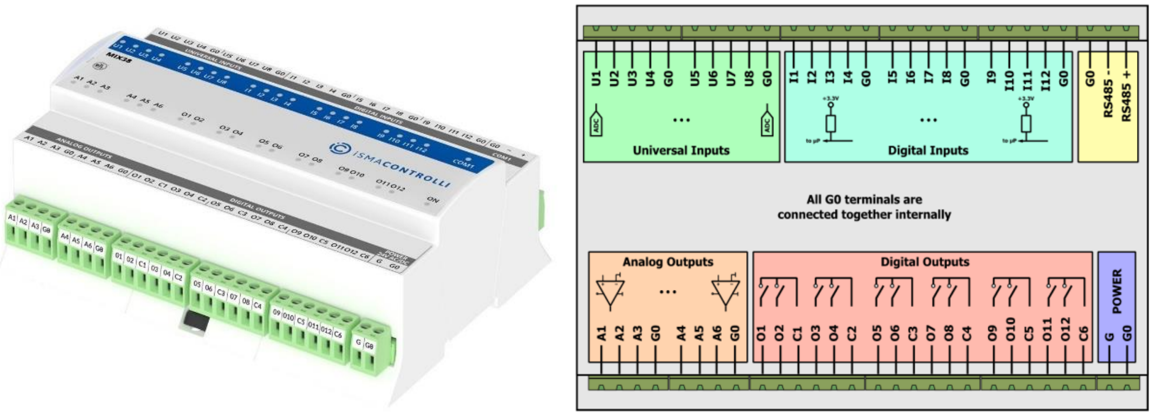


Figure 22. View and schematic of the Isma Controlli MIX38

In terms of the PLC, with flexibility in mind, the Revolution Pi Flat has been chosen. It is specifically designed for energy management systems in mind and due to its Linux architecture it is particularly flexible. It also contains an internal router, switch and WLAN, which will be useful to connect multiple IP based devices, and has good integration with CODESYS, since the manufacturer provides a specific programming library to program for its interfaces.

Figure 23. View of the RevPi PLC

2.5.9 General assembly

As the finished system will have to be shipped to another country, it is in our interest to make the whole system as transportable as possible. In the case where the system was being developed where it would be installed, ad-hoc solutions would be more adequate, but in this case the installation time needs to be limited as much as possible. For this reason, as much as possible of the system will be installed inside an industrial rack.

The one that has been chosen is 1700 mm high, 800 mm deep, and 600 mm wide. The extra width and depth give us the possibility to put the hydrogen and water lines inside, so that the system has simplified connections to the outside, approaching a “plug-and-play” installation as much as possible within the obvious limitations of a novel and experimental system.

Figure 24. The industrial rack that holds everything together

2.6 Acquisitions and supply chain issues

At the time of writing, all of the items necessary for the construction of the system have been purchased. Unfortunately, due to the current supply chain crisis that has been caused by a multitude of global political and economic events, some of the suppliers have been unable to fulfil their expected delivery dates, mainly due to themselves not being able to obtain the required components.

This has led to a delay of the project and therefore this document cannot provide the real results of the system as assembled, but will provide the results using an accurate model of the system which can interact with the real control network.

As an interesting datapoint, at this point this project has entailed the exchange of circa 900 email messages, with the client, suppliers, and colleagues.

3 System model

This system is complex, innovative, and safety critical. As such, the scenarios that it will face and its behaviour must be studied before its initial deployment. For this purpose, a full virtual model of the system will be developed that will attempt to simulate the physical side of the system, so that the virtual control side can interact with it as if it was there in real life.

3.1 Purpose

The purpose of this model is to provide a close to real life model and interface, so that the developers can create a control system and test it against the model to improve performance and prevent unforeseen scenarios.

As there are many unknowns, especially regarding heat exchange and performance of subsystems that might be variable, the system will aim to at least model faithfully the states of the system.

For example, if the charging process takes 1h or 1h20m is not relevant, as the control system will not “wait” but will be reactive to the sensor readings. What is important is that the states in which the system finds itself are coherent with real life.

The model will be developed using the NodeRED framework [26], which allows for a versatile mix of traditional and flow-based programming. It is based on a flow and message model, in which connected blocks send messages to one another via visible pathways. Each of these blocks can contain other blocks, therefore allowing for increasingly high-level design. This message flow can be paralleled to the real life behaviour of substances moving in pipes, allowing for a highly visual and comprehensible model design experience.

3.2 Scope

The model will fundamentally model the hydrogen flow and the thermal flow. As seen in Figure 25, the industrial control side, done in Codesys, will be the same in both the live system as in the modeled system, allowing the programming of the PLC as if it was interacting with the live systems.

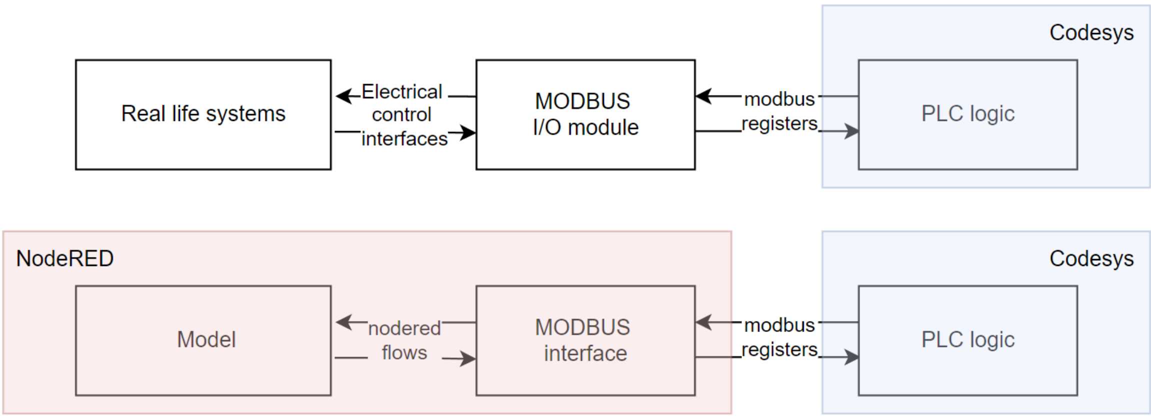


Figure 25. Environments of real and modeled system

The model will initially simulate the flow of water along the thermal loop. Each block will receive the water message and then modify its temperature according to its internal operation. The blocks which produce, store, and consume hydrogen will perform similar actions for this substance.

3.3 Model description

3.3.1 General overview

As previously described, the model consists of a series of objects which receive, modify and send a message containing an amount and quantity of water with its characteristics. This message runs through the system once per second.

For example, if the pump is running at 10 liters per second, the message specifies that it contains 10 liters of water which is at 25ºC. When that message arrives to the heater block, the heater script does the following:

calculates by how much it is able to heat that much water in one second at its current power;

changes the temperature of the water message to the calculated one;

and sends the message on to the next block.

By running the message through the whole system and then setting the initial temperature as the last one, one can continually simulate the behaviour of the system using its discrete elements.

The hydrogen flow system is rather simpler, since there is only one device that consumes hydrogen, one that creates it, and one that stores it, so the first two simply add and subtract hydrogen from the last.


```
05/10/2022, 17:08:03   node: debug 9
flow : msg.payload : Object
▾object
  loopId: 1
  temperature: 19.998587939391772
  flow: 10
  CP: 4186
  DT: 0.000007304297390189842
  connected: 0
  fan_effect: 1
  out_temp: 20
  timeFactor: 1
  soc: 1.2478141016696496
  pressgas: 19.998464427215588
  p_eq: 19.99846442721559
  n_diff: 3.8751407461314387e-7
  n_gas: 16.626755455466533
  n_mh: 371.3732445445386
  h_diff: -0.010741890148276347
  n_exchange: 0
  tactive: 1
  tmass: 19.998464927274988
  ismh: true
```


Figure 26. An example of a temperature message with debugging values

The basic structure of the model flows is the following:

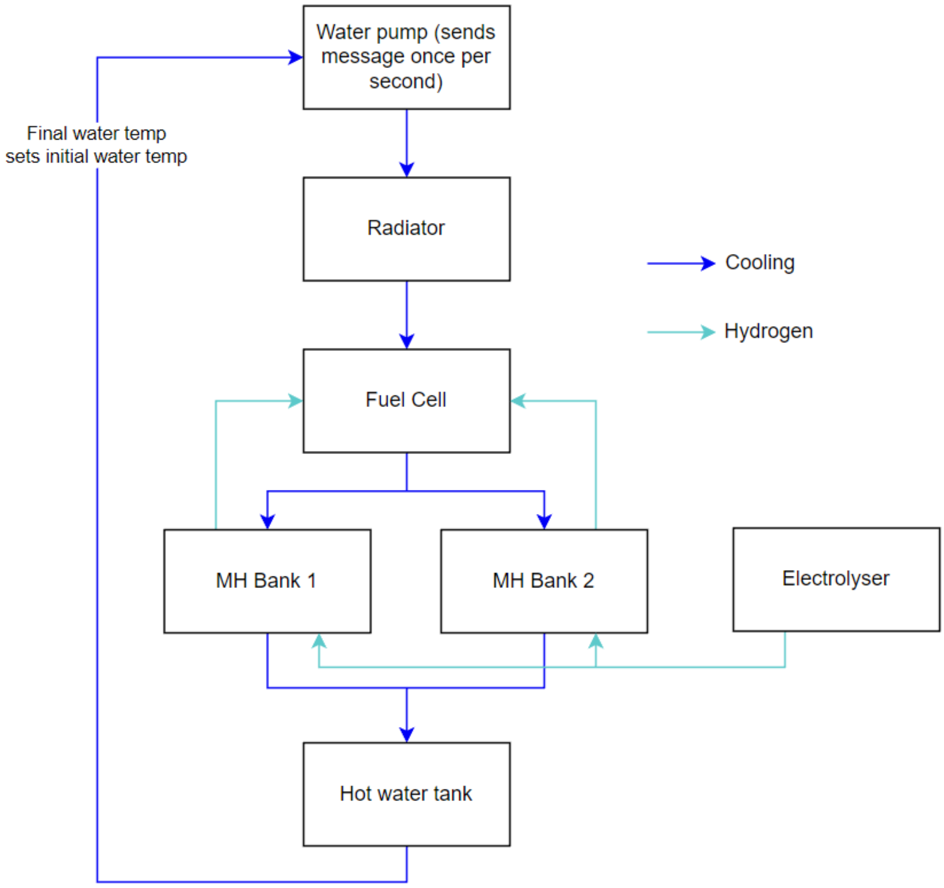


Figure 27. Model structure schematic

3.3.2 Water pump

The "water pump" is simply a Node-RED periodic trigger which sends a message every second containing the water flow rate (the amount it will have delivered that second) and the temperature of the last returning message.

3.3.3 Radiator

For clarity, in this and other devices the temperature difference to be applied to the water is calculated in several steps. Initially, the total thermal power exchange of the system (in this case, the heat dissipated into the environment) is calculated (3.1). It is positive if the device adds heat to the water and negative if it absorbs it. Using that value, the temperature difference to the water is calculated using the flow rate of water and its specific heat capacity (3.2)

$$\Delta H = (T_{ambient} - T_{waterIn}) * h_{exchange} * C_{fan} \tag{3.1}$$

Where:

ΔH = energy transfer

$T_{ambient}$ = temperature of the air around the radiator

$T_{waterIn}$ = temperature of the water as it enters the radiator

$h_{exchange}$ = heat transfer coefficient of the radiator

c_{fan} = multiplier to simulate the effect of the fan

$$\Delta T_{water} = \frac{\Delta H}{F_{water} * Cp_{water}} \tag{3.2}$$

Where:

ΔT_{water} = temperature difference to be applied to the exiting water

ΔH = previously calculated energy transfer

F_{water} = flow of water

Cp_{water} = specific heat capacity of water

3.3.4 Fuel cell

On a thermal level, we consider the fuel cell to act similarly as a heater. Although they have some response times, on a larger scale and especially in the thermal side this is considered trivial, especially since the worst possible case is that where it functions at 100% power.

Due to their design, fuel cells usually produce as much thermal energy as electrical energy [27]. Therefore, since our cell is 1kW, we will assume that it produces 1kW of thermal energy. The method to calculate the temperature change is therefore relatively trivial and the same as (3.2)

In terms of hydrogen consumption, our fuel cell consumes around 15 normal liters per minute, so when it is in operation, we will subtract 0.25 normal liters from the hydride storage system per second.

3.3.5 Heater

Similarly to the Fuel Cell’s thermal behaviour, the heater has a specific amount of wattage that it applies to the water, so we again use equation (3.2).

3.3.6 Metal Hydrides

The functioning of the metal hydride modules is the most complex of the model. In Figure 28, the main interactions of the system are demonstrated. To understand the operation of the hydrides, first we must analyze their internal composition. They are fundamentally pressure vessels which contain gaseous hydrogen and the metal hydride powder. The hydrides have an “objective” equilibrium pressure which is fundamentally defined by the temperature. This pressure is also defined by how much hydrogen they have already absorbed. As seen in Figure 29 this last relationship is not very influential during the middle stages of charging/discharging but does change the pressure substantially when the hydrides are close to being depleted or filled.

When the pressure is calculated, it is compared with the current pressure of the gas in the tank. If the equilibrium pressure of the hydrides is higher, they will release hydrogen, an endothermic process, which in turn will make them cool down and lower the equilibrium pressure, until a systemic equilibrium is reached.

In turn, if the pressure of the gas in the vessel is higher than the equilibrium pressure, the hydrides will absorb the gas, in this case an exothermic reaction; therefore they will heat up and raise their equilibrium pressure.

Therefore, if we maintain a higher gas pressure and control the temperature so that it doesn’t raise, the hydrides will be charged until they are filled, and if we lower the gas pressure and raise the temperature the hydrides will release hydrogen until they are depleted.

The unit used to quantify the exchanges of hydrogen between parts of the system is the mol.

Having understood this method of operation, we can start modeling more precisely the detailed interactions of this system, analysing the full calculation step by step.

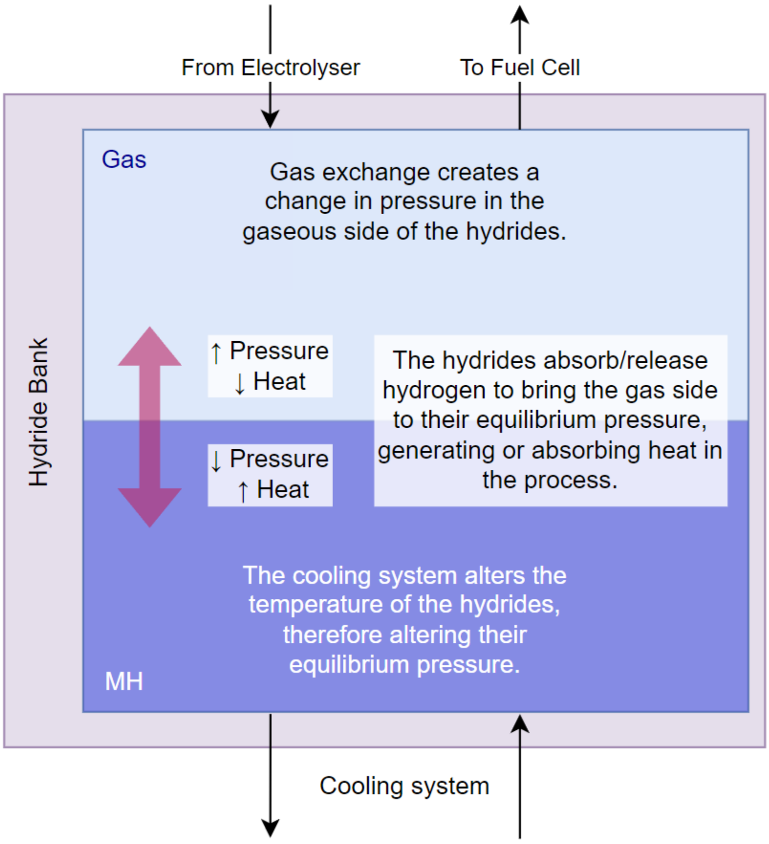


Figure 28. MH material and energy flows

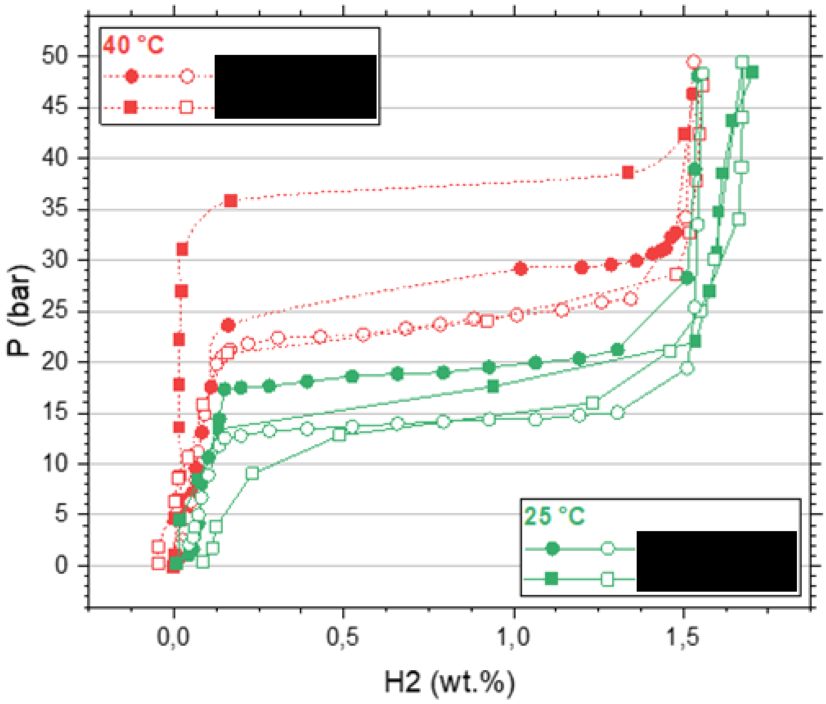


Figure 29. Internal test results. Composition of hydride material covered for IP protection

1. *MH side*

On the solid storage side, the equilibrium pressure is calculated according to the laboratory tests (Figure 29) performed and provided by Methydor, the manufacturer.

2. *Gas side*

The gas side pressure is initially calculated by calculating the net flow of hydrogen in moles from the exchange with the electrolyser or the fuel cell. Since we know the current amount of moles in the gas vessel we can know the current pressure thanks to the ideal gas equation (3.3).

$$PV = nRT \tag{3.3}$$

$$P_{final} = \frac{(n_{gas}+n_{exchange})RT}{V} \tag{3.4}$$

3. *Gas exchange*

At this point, we know the equilibrium pressure of the hydrides and the current pressure of the tank. The hydrides will exchange hydrogen gradually in order to minimize the difference between these values. The rate of exchange is not fully defined experimentally, since it depends on a multitude of factors, including vessel design and surface area of the hydrides, a value which varies with use. However, experiments show that in practical terms the exchange rate is not very significant since the equilibrium pressure and the gas pressure are highly coupled, due to the fact that gas pressure does not vary quickly enough in most systems to cause a significant difference.

$$\frac{PV}{RT} = n \tag{3.5}$$

$$\Delta n = \frac{P_{gas}V_{vessel}}{RT} - \frac{P_{eq}V_{vessel}}{RT} \tag{3.6}$$

$$\Delta n = \frac{(P_{gas}-P_{eq})V_{vessel}}{RT} \tag{3.7}$$

4. *Gas side update*

Since we now know the amount of gas that will be released by the hydrides, we can adjust the final pressure of the gas side using the same method as in step 2.

5. *Thermal exchange*

The final step is to calculate the amount of heat produced or absorbed by the exchange of gas of the hydrides. The experimental results calculated by Methydor Srl indicate the heat produced or absorbed by the hydrides in joules per mole of hydrogen exchanged. For this reason it is trivial, having defined the amount of hydrogen exchanged between the gas and hydride sides, to calcualate the heat produced or absorbed by the material.

For IP protection purposes, the exact amount of heat exchanged by the hydrides cannot be displayed here, but as an indication the heat absorbed during desorbtion of hydrogen is about 1.2x that of the heat produced during absorption.

The MH stack also loses heat to the environment at a specified rate.

3.3.7 Water tank

The water tank works similarly to the formula describing the radiator, but with the difference that the ambient temperature is the temperature of the tank water, and that the heat is not simply lost into the environment, but it is added to the tank water in the same way. In this way, the tank slowly heats up, reducing the difference between the tank water and the cooling water, ultimately equalizing and not exchanging any further heat.

3.4 Software stack

The Node-RED service runs in a physical server, which is accessible through a WireGuard VPN. This makes it possible to access the server from anywhere in the world. The Modbus connection with the PLC runs through the local network on-site. Finally, the data from the model is published every second to an InfluxDB database, which is visualized using Grafana. (Figure 30)

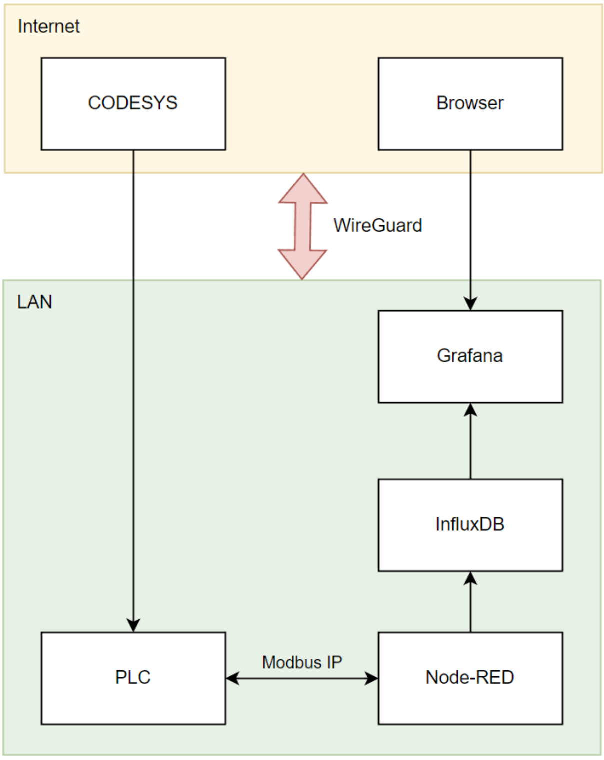


Figure 30. Structure of software stack

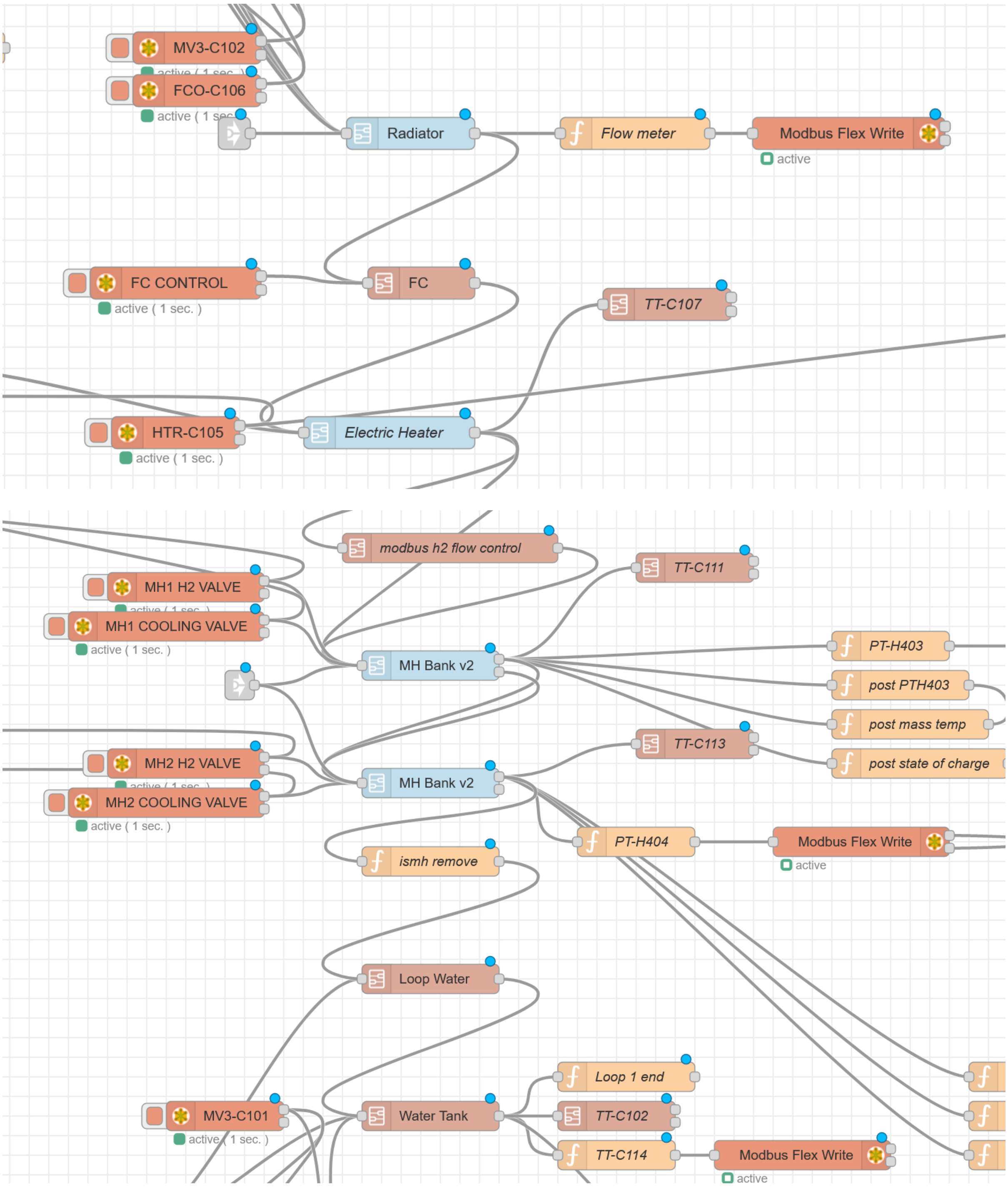


Figure 31. Screenshots of the model

4 Control system

4.1 Purpose

The aim of this part of the thesis is to design a control system that will abstract the internal functioning of the system in order to expose a simplified charge/discharge/standby interface. Therefore, every internal process of the system must run at a high level of automation and be able to respond to any scenario that the system can face without user interaction.

4.2 Scope

The scope of this control system is integral and involves the whole control stack, from the control of electrovalves and the reading of sensors to the user interfaces and data broadcast.

4.3 Description

As this is a commercial project that will be physically built, the control system needs to be built in a way that it can be used for the true control after testing. For this reason, the system has been developed directly on CODESYS, a PLC programming platform that allows for flexibility when interacting with devices and also provides an array of high-level functions and modules that facilitate the usage of certain algorithms.

This is beneficial for this particular project, since due to the supply crisis there hasn't been the chance to choose items according to their communication protocol and CODESYS allows the developer to interface with multiple protocols.

4.3.1 General overview

The control system is mostly programmed using graphical programming. This has its benefits and drawbacks, but it is useful for this purpose since it can keep complex logic relationships clear and understandable.

The system is organized in the following manner.

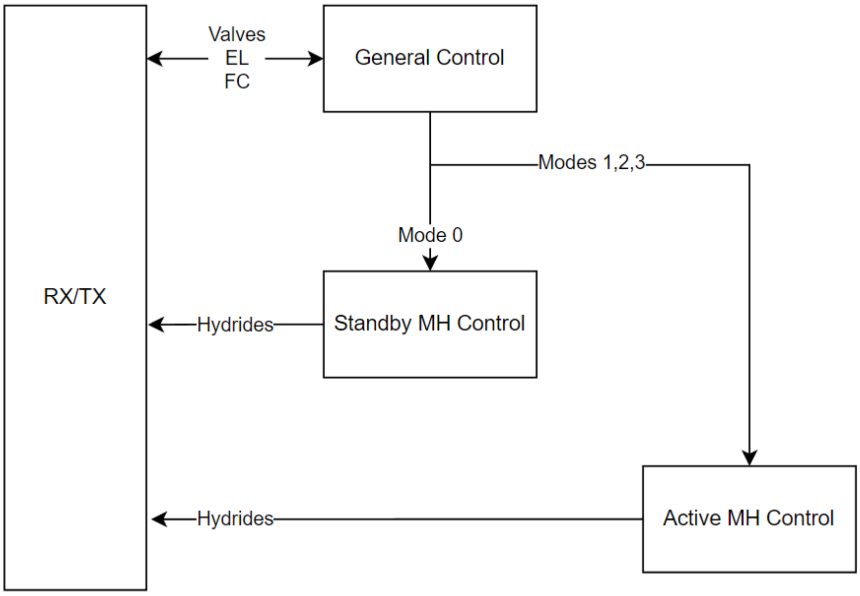


Figure 32. General overview of control system

As seen in the diagram, the control system has a "General Control" program. This runs every 200ms and is the parent entity to the rest of the control. It manages the valves and "talks" to the electrolyser and the fuel cell.

Note: The descriptions of the control flows are accompanied by simplified flowcharts in order to facilitate communication of the algorithms. Processes particular to the machine, such as the process for opening valves, calculating hystereses, and others are ommited for clarity.

4.3.2 General control

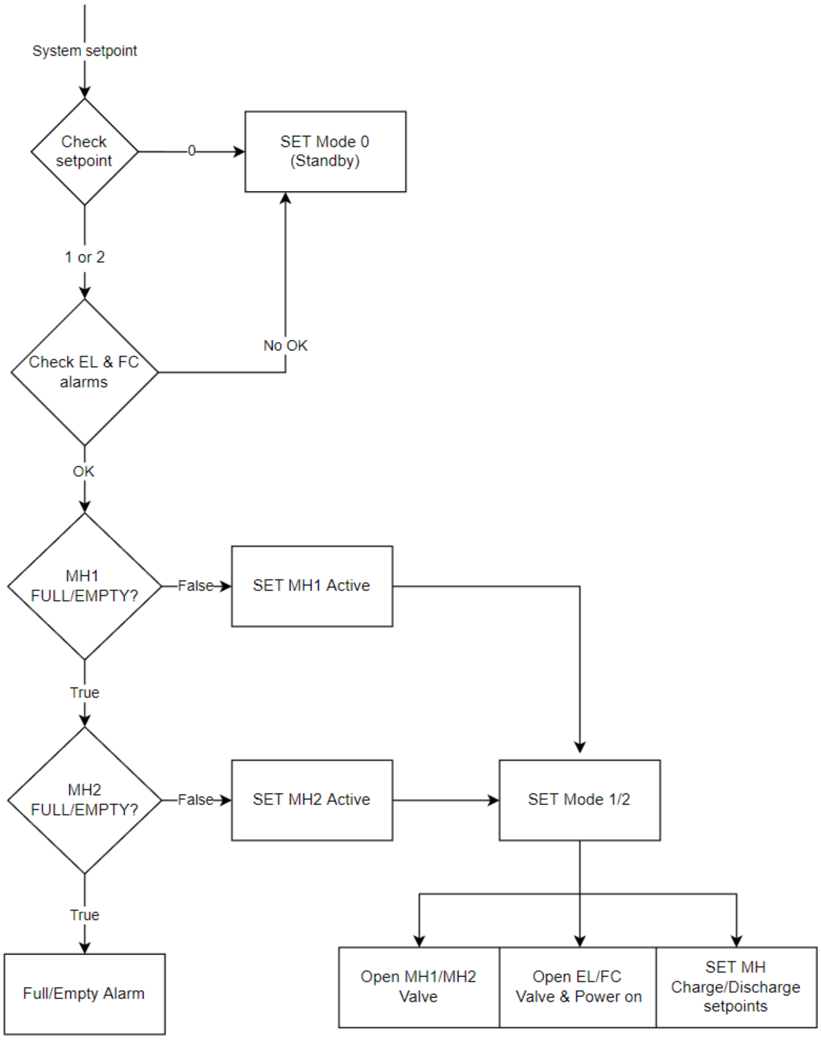


Figure 33. Description of General Control flow

The general control flow is in charge of receiving inputs from the controller. As requested by the client, the control is as high-level as possible to facilitate use and consists of three modes (and one "internal" mode):

0. Standby mode
1. Charging mode
2. Discharging mode
3. Purge mode

These will be described further in the next sections, but from the point of view of the general control, 0 is controlled by a specific program, called Standby Control, 1 and 2 are controlled by another program, called Active Control, and finally, if the pressure limits are exceeded, General Control takes back direct authority and controls the valves in order to ensure safe operation of the hydrides. When the purge is finished, the program goes back to its previous states.

As seen, the program initially checks if either the electrolyser (EL) or the fuel cell (FC) are showing any alarms. If that is the case, the system stays in standby mode unless manually overridden.

Next, the program checks the state of charge of the hydrides (MH). It does this by checking the pressure, so if it is above a certain point they are considered full and if they are under they are considered empty. Although the pressure varies according to temperature, therefore allowing for slightly higher quantities of stored hydrogen at higher temperatures, the graph (Figure 29) indicates that the pressure stays within a narrow range while charging and rapidly shoots up when fully charged. The limits are set at these higher levels so the pressure limits are coherent at any temperature.

Another method could be to use the experimental results in other to consult the state of charge according to the temperature and pressure values. This can be used for an indicative display of the state of charge and could allow for higher storage amounts, but due to the fact that the morphology and performance of the hydrides varies with use [28] the pressure method has been chosen since it is safer and more strict.

There a system state which is important to take into account. If the system is fully charged at a certain temperature, the valve is closed and then the temperature rises, the pressure inside the MH could rise and approach high pressure values. For this reason, the system ensures that when the system is charging it is done at the highest possible temperature, around 38ºC, so that when the charging process is finished the temperature will lower. If the temperature rises above that, a very unlikely possibility in our mediterranean climate, the change in pressure will not be very significant. If it were to raise further, for example during a fire, the purge flow will take care of controlling the pressure, and if that were to fail, there are mechanical pressure safety valves attached to each bank.

If the mode set is Charge and both hydrides are full, the system stays in Standby and throws an alarm. Similarly, if the mode is Discharge and both are empty, the system does not change mode. If one or the other are available, the system sets the adequate bank as active.

Since the program is run cyclically, these checks are performed continuously, and if MH1 becomes full or empty, it switches automatically to charging or discharging MH2.

General Control also takes care of the valves connecting each of the devices (only on the hydrogen side), controls their settings using their respective communication protocols and also sets the setpoints of the metal hydrides. Although the setpoints are “enforced” in each of the Standby or Active control programs, they are set here. The setpoints control the objective pressure of each hydride, depending on if they are active and if they are being charged or discharged.

For example, if MH1 is being charged, there will be no minimum pressure, as there is no requirement to provide pressure while charging. Similarly, as MH2 is in standby, it will not have a minimum pressure (however, they must always maintain the absolute, emergency limits set by the program).

If the system is in discharge mode, a minimum pressure for the active MH will be set, since the FC requires a certain pressure to function. The programs described in the following section, which are executed by General Control in a cyclical manner, take care of ensuring this.

To further understand the operation of the program, partial screenshots of the actual program are presented in Figure 34 and Figure 35.

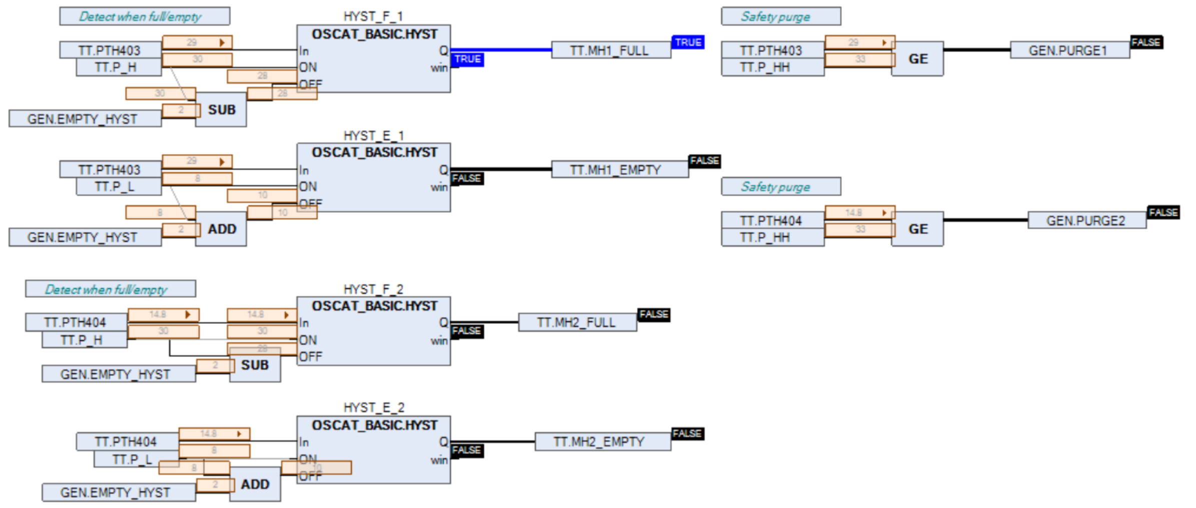


Figure 34. Setting of empty/full flags and purge control

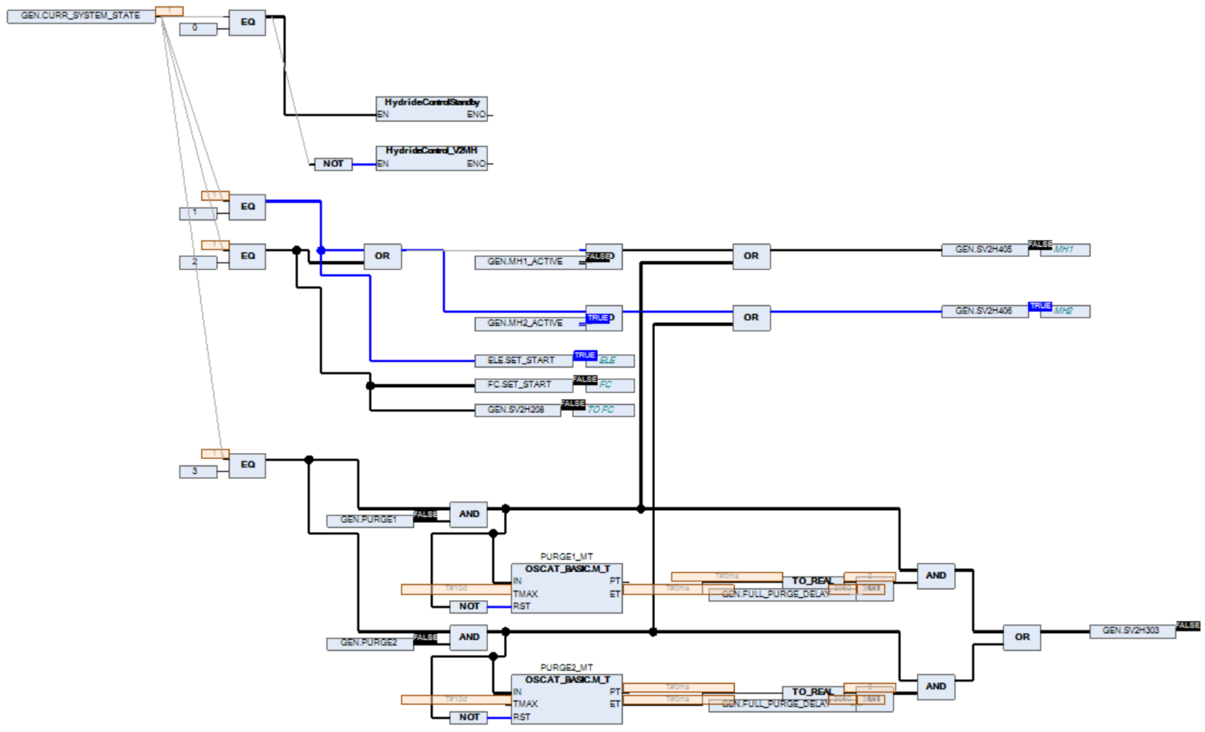


Figure 35. General control state management

In Figure 34 the process for detecting when the hydrides are full or empty or at overpressure is described. PTH403, MH1's pressure sensor, is under the limit of 30 bar, but since there is a hysteresis module, it will be considered full until it goes under 28 bar. This avoids situations such as pressures variating very close to 30 bar and turning on and off the "full" flag rapidly.

In Figure 35, after the checks have been completed and the state has been assigned, this part of the program takes care of operating the hydrogen valves. In the first row, if the mode is 0 (standby) the Standby program is run. If it is in any other state, the Active Control program is used.

Further down there is the management of each of the operational states. In the situation shown, the system is in Charging mode with MH2 as active, since MH1 is full. It closes MH1's valve, opens MH2's valve, turns on the electrolyser, and ensures the FC and the FC valve are off. Not shown in this screenshot are the controls that ensure the conditions necessary to turn on the EL or the FC. For example, the fuel cell cannot be started if a certain hydrogen pressure has not been reached or if the electric system is not ready. These will be developed when the particular requirements of the devices are known.

Finally, the purge system can be seen. If the purge is activated (as seen above) the valve settings for the MH are overridden, and the necessary valves are opened.

4.3.3 Standby MH control

This is the program which the system is in when it is not in active operation. Its purpose is to continuously monitor the hydrides, ensuring that they do not exceed or fall below certain absolute limits in terms of pressures and temperatures.

In this mode, the pump and all thermal management systems stays off most of the time except in the case that the limits are exceeded, and the valves that connect the MH to the inside system are open, in order to equalize residual temperature changes. When required, the program activates the fan or the heater in order to correct the temperatures or pressures and sends an alarm to the operators to make them aware of the situation.

All temperature controls in this system use hysteresis in order to avoid constant activations of systems. For example, if the temperature of the hydride reaches the maximum of 40ºC, for example, the radiator and the fan will be turned on until it goes down to 36ºC. These are not included in the flowcharts for clarity.

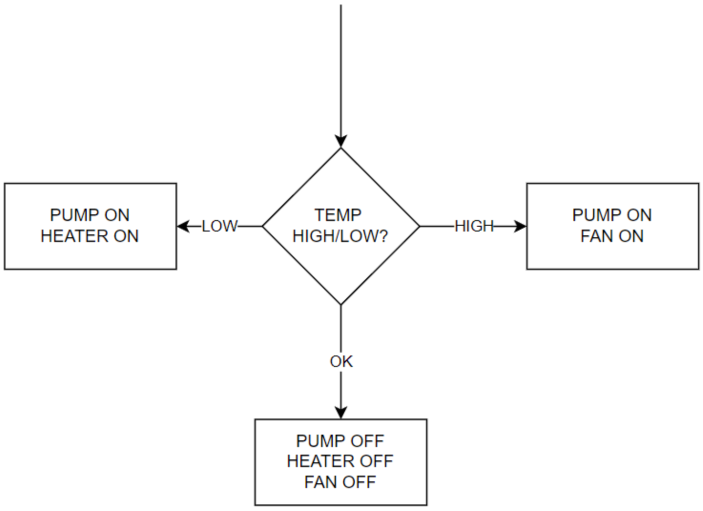


Figure 36. Standby MH Control flowchart

4.3.4 Active MH control

The Active Control program is the one in charge of controlling the hydrides during charge or discharge. This system is particularly complicated since it needs to monitor and act upon both pressure and temperature values. The following algorithms run in parallel:

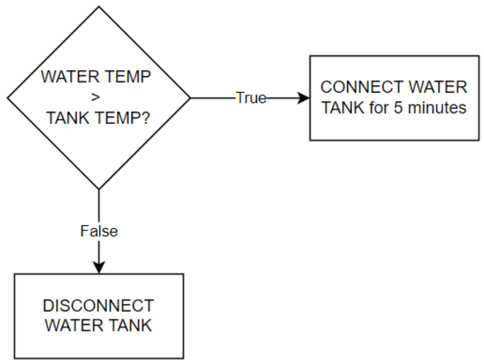


Figure 37. Water tank heat buffer control

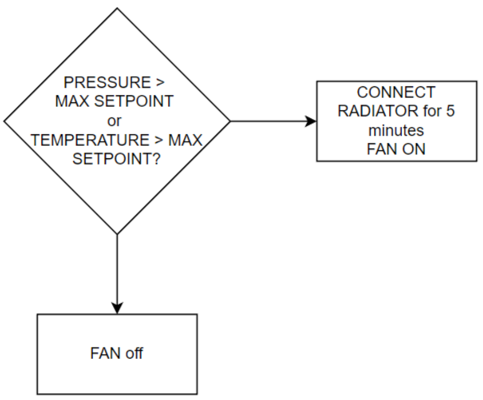


Figure 38. Overpressure overtempt control

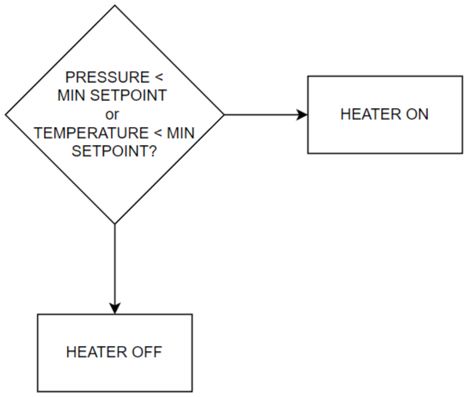


Figure 39. Underpressure undertemp control

The reason why the last two programs run in parallel is because due to the fact that there are two different, independent banks, different combinations might occur in different moments. In the program, these are prioritized and then the output is defined, using an interlock that keeps the program from heating and cooling at the same time.

As an example of this complicated behaviour, the process of changing from one hydride bank to the other can be observed. In this state timeline, we can see that when MH1 is full, the hydrogen valve turns to MH2, but the cooling valve remains on until MH1 returns to its equilibrium pressure. If MH1 were to go back to a high temperature or pressure, the system would deal with it while also controlling MH2. These situations are detailed in further depth in the Results section.

Figure 40. MH1 to MH2 transition (state timeline)

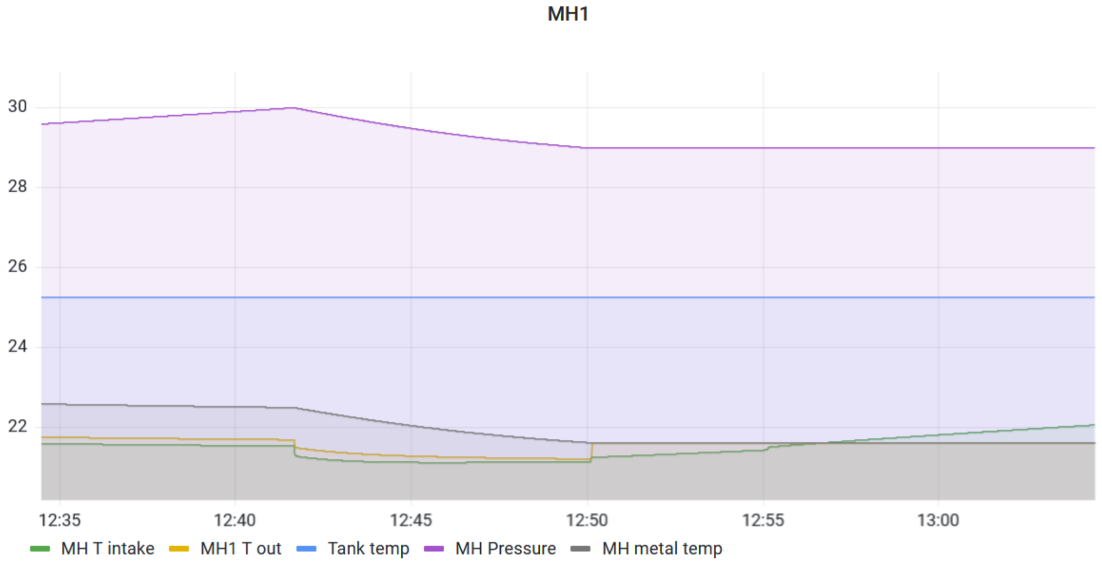


Figure 41. MH1 to MH2 transition (MH1 plot)

As with the other programs, the flowcharts are a simplification of what is otherwise a complicated ensemble of logic gates. For example, this is a part of the Active Control program:

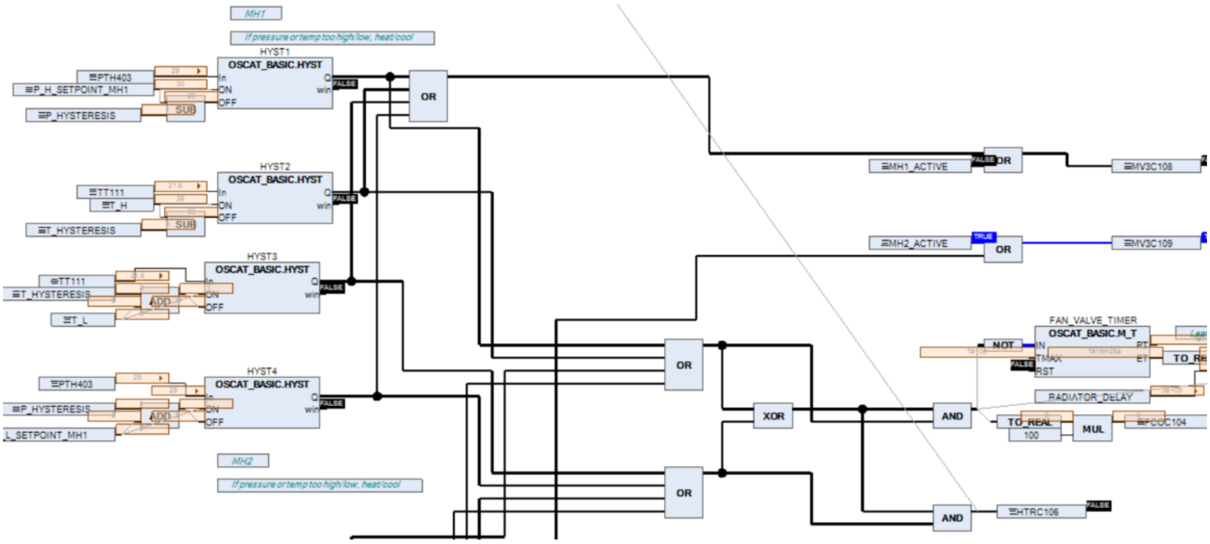


Figure 42. MH1 section of Active Control

Although it might seem convoluted, the system can be understood in the following manner. This screenshot shows only the MH1 side, although the MH2 is symmetrical. At the very left there are the hysteresis modules which activate when temperature is over or under a certain setpoint and hasn't receded back to the setpoint minus the hysteresis values.

When any of the hysteresis modules activate, indicating that MH1 needs thermal management, the first OR gate activates, connecting the appropriate water valve and thus connecting MH1 to the thermal management loop. As seen in the top right, when a bank is active the valve is always connected, but if it is not active it can still connect when needed.

The second and third OR, near the middle, accumulate the signals from MH1 and MH2 requiring heating and cooling, respectively. If the top OR is activated, cooling is started, if the bottom OR is activated, heating is started.

The XOR gate serves as an interlock. If there is a situation where cooling and heating are required, none are given; although this might seem counterintuitive, it will lead to the system going in either direction by itself, ultimately leading to a situation where it is exclusively too hot or too cold. In that case the system goes back to its normal operation and activates the required thermal management system.

4.3.5 Industrial communication

The PLC and the Node-RED model (and in the future, each of the components) communicate using an established Modbus IP interface. As seen in Figure 43, CODESYS has two channels configured, one for input and one for output, with different addresses each. The purpose of having two channels is that only one device should write on a particular address and the other should read, so that there are no conflicts.

Variable	Mapping	Channel	Address	Type	Current Value
		Channel 0	%IW89	ARRAY [0..9] OF WORD	Only subelements upd...
Application.RX.FLOW_RATE		Channel 0[0]	~~%IW89~~	WORD	1000
Application.RX.TT102		Channel 0[1]	~~%IW90~~	WORD	2494
		Channel 0[2]	%IW91	WORD	0
Application.RX.TT107		Channel 0[3]	~~%IW92~~	WORD	2494
Application.RX.TT113		Channel 0[4]	~~%IW93~~	WORD	2496
Application.RX.TT111		Channel 0[5]	~~%IW94~~	WORD	2163
Application.RX.TT114		Channel 0[6]	~~%IW95~~	WORD	2526
Application.RX.PTH401		Channel 0[7]	~~%IW96~~	WORD	0
Application.RX.PTH403		Channel 0[8]	~~%IW97~~	WORD	2899
Application.RX.PTH404		Channel 0[9]	~~%IW98~~	WORD	1633
		Channel 1	%QW3	ARRAY [0..13] OF WORD	Only subelements upd...
Application.TX.MV3C101		Channel 1[0]	~~%QW3~~	WORD	0
Application.TX.MV3C103		Channel 1[1]	~~%QW4~~	WORD	0
Application.TX.MV3C105		Channel 1[2]	~~%QW5~~	WORD	0
Application.TX.MV3C108		Channel 1[3]	~~%QW6~~	WORD	0
Application.TX.MV3C109		Channel 1[4]	~~%QW7~~	WORD	1
		Channel 1[5]	%QW8	WORD	0
		Channel 1[6]	%QW9	WORD	0
Application.TX.HTRC106		Channel 1[7]	~~%QW10~~	WORD	0
Application.TX.FCOC104		Channel 1[8]	~~%QW11~~	WORD	0
Application.TX.ELE_SIM		Channel 1[9]	~~%QW12~~	WORD	1
Application.TX.FC_SIM		Channel 1[10]	~~%QW13~~	WORD	0
Application.TX.SV2H303		Channel 1[11]	~~%QW14~~	WORD	0
Application.TX.SV2H405		Channel 1[12]	~~%QW15~~	WORD	0
Application.TX.SV2H406		Channel 1[13]	~~%QW16~~	WORD	1

Figure 43. CODESYS Modbus communication table

The temperatures and pressures are transmitted multiplied by 100 and then divided, as the WORD datatype does not allow decimals. The outputs are mostly binary, except the fan speed, which is 0-100.

5 Testing and results

To better understand the behaviour of the control system and the model, testing has been undertaken at significative states of the system.

5.1 MH1 to MH2 transition (charging)

This test shows the process by which charging is switched from MH1 to MH2 when the former is full.

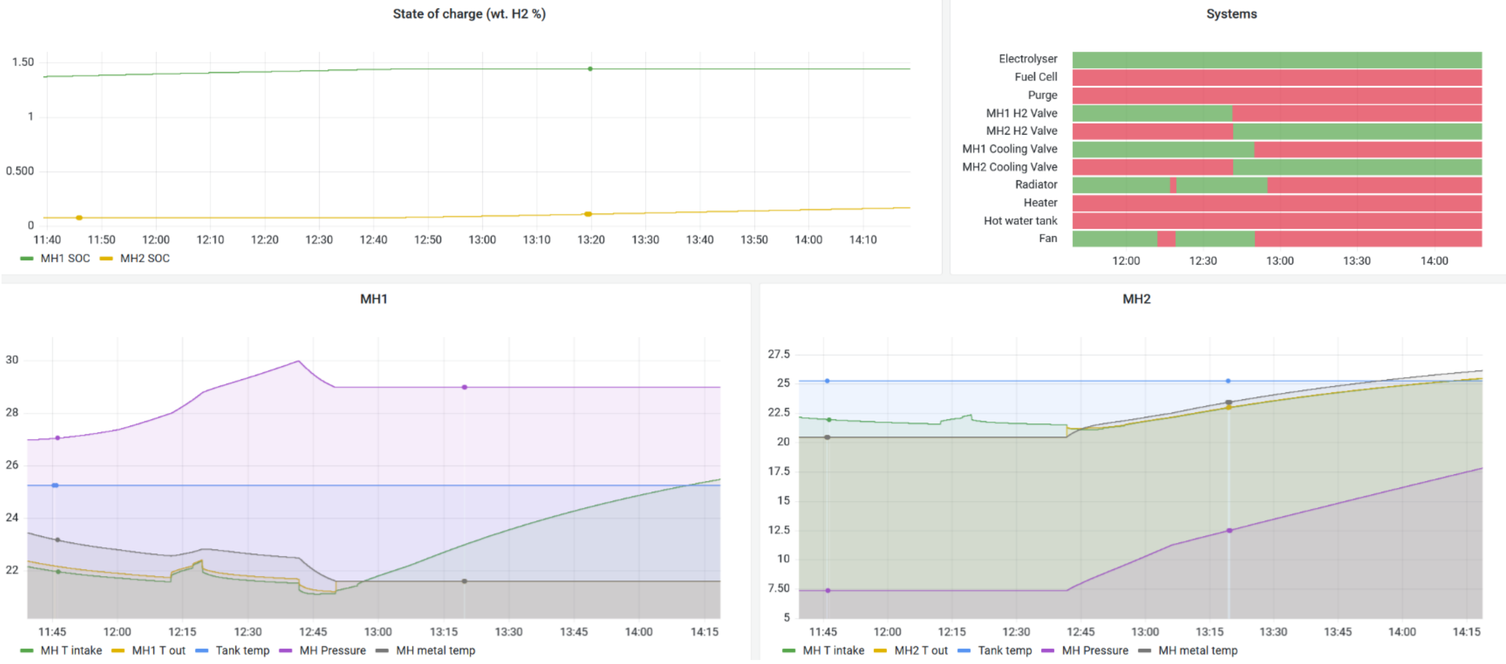


Figure 44. Full MH1 to MH2 transition while discharging

Note: the moment when the radiator and the fan stop around 12:20 is due to a brief reset of the system during the test and can be ignored.

This test is particularly useful since we can see what the system does when a bank becomes full, how it changes from one hydride bank to the other, and what it does when it starts charging an empty bank.

As the state of charge rises, so does the pressure, and due to the constant absorption of hydrogen the temperature also rises. When the pressure reaches its "charged" setpoint, the hydrogen valve of MH1 closes and that of MH2 opens, however the system still stays in control over the temperature of MH1 and keeps its thermal management connected until the remaining gas is absorbed and the temperature is brought to normal levels.

It can also be seen how at the maximum charging capacity of the hydrides, both the radiator and the fan must be on in order to contain the temperature rise as much as possible.

We can also see how MH2 starts to pressurize and heat up.

5.2 Controlling temperature with the hot water tank

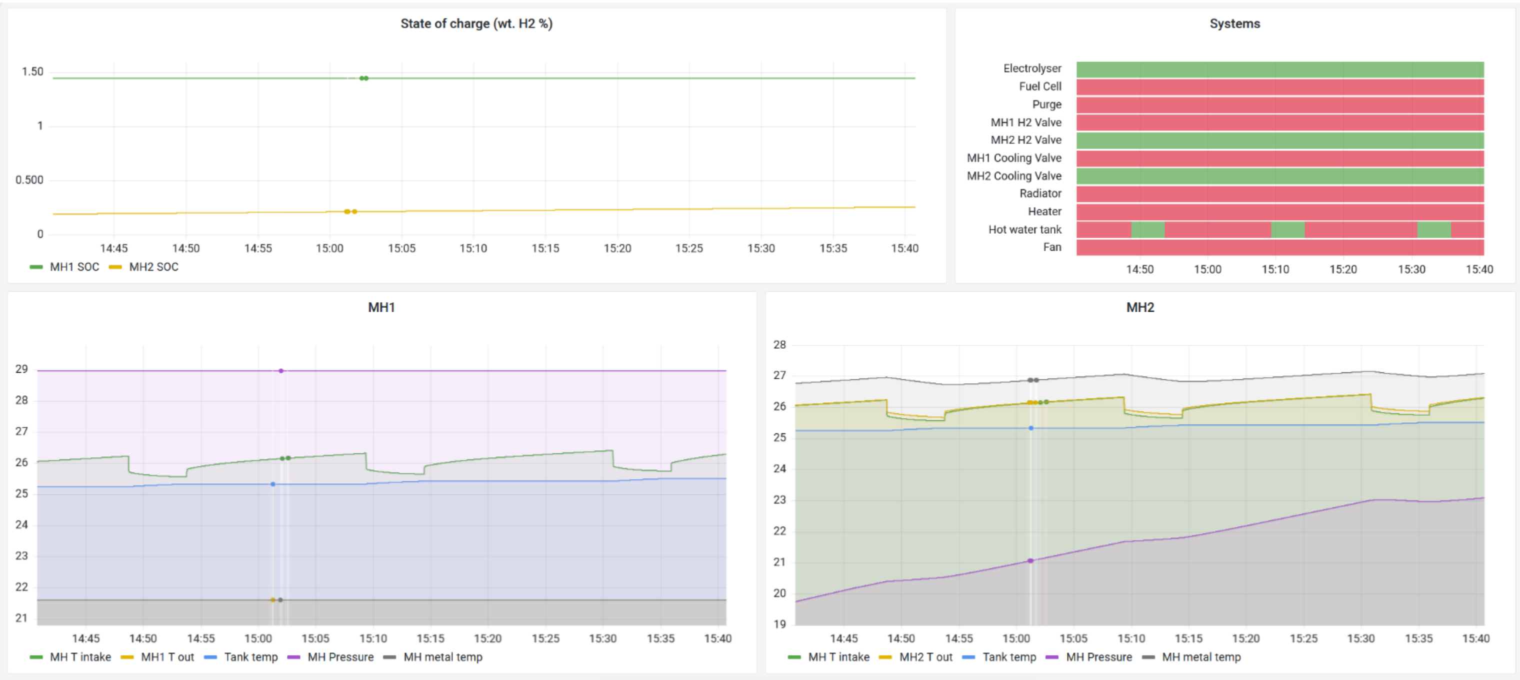


Figure 45. Charging and cooling with the hot water tank

In this case, we can see how the hot water tank is used to slow the rise in temperature of the system. As MH2 charges and rapidly pressurizes (as it does during the initial phase of charge) the hot water tank connects when the temperature of the cooling water is 1ºC over the temperature of the tank. It then stays connected for 5 minutes, and then disconnects until the difference is large enough again. The reason why the water tank is not always connected is that since the expected rise in temperature is so slow, there is no need to constantly have the increased load on the pump, and also that the decreased thermal mass of the system when the tank is disconnected allows for a quicker reaction time by the heater and the radiator. The cycles rather long so the effect on the lifetime of the valves is reduced, and the temperature difference can be further optimized in the real system to find an adequate balance.

5.3 MH1 to MH2 transition (discharging)

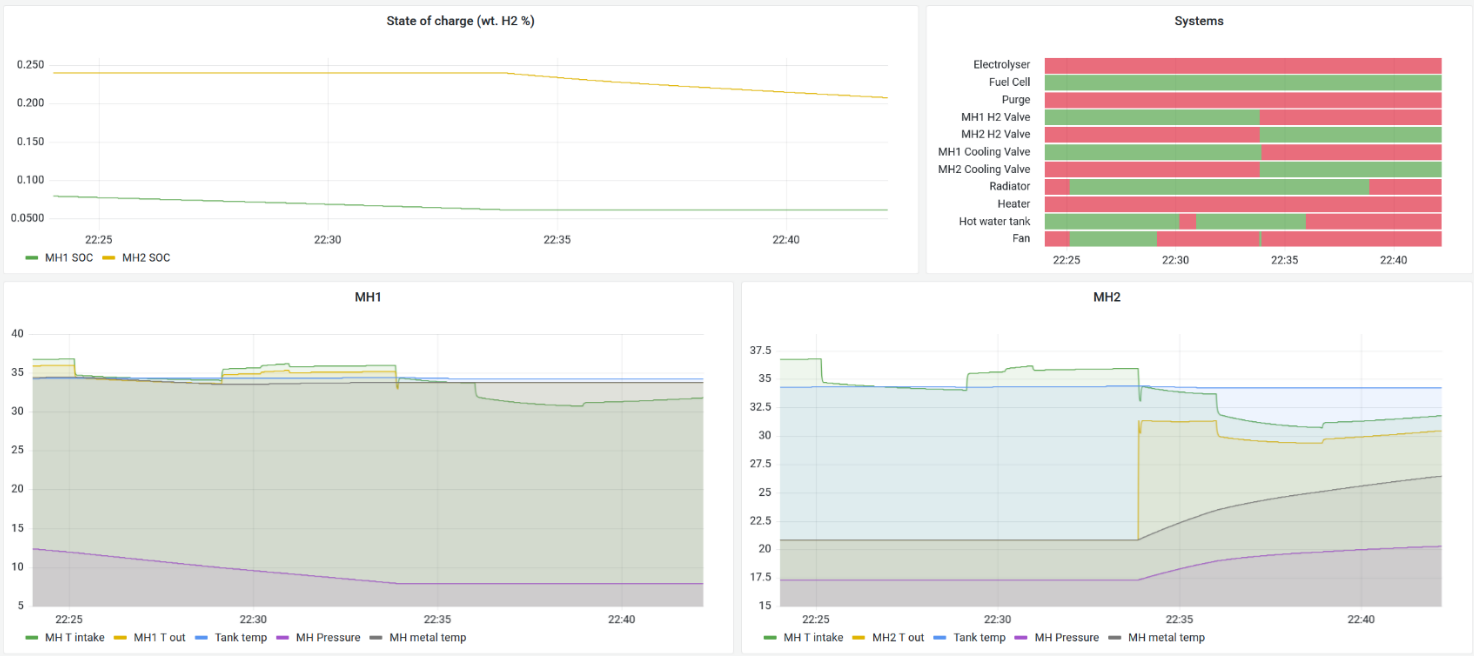


Figure 46. Full MH1 to MH2 transition while discharging

This scenario shows a similar transition timeframe but in the opposite way, that is when a hydride bank become empty and discharging switches to the other one. It can be seen that the temperature is brought to the maximum in order to use as much hydrogen as possible, to the point that the fan briefly engages as the temperature reaches its absolute maximum, which is prioritary. The pressure then decreases to under the minimum and the valves change in order to disconnect MH1 and connect MH2. There is a drop in the temperature of the water as MH2 heats up therefore bringing its pressure up. Temperature will remain uncontrolled until itself or the pressure reaches the setpoints.

5.4 End of production

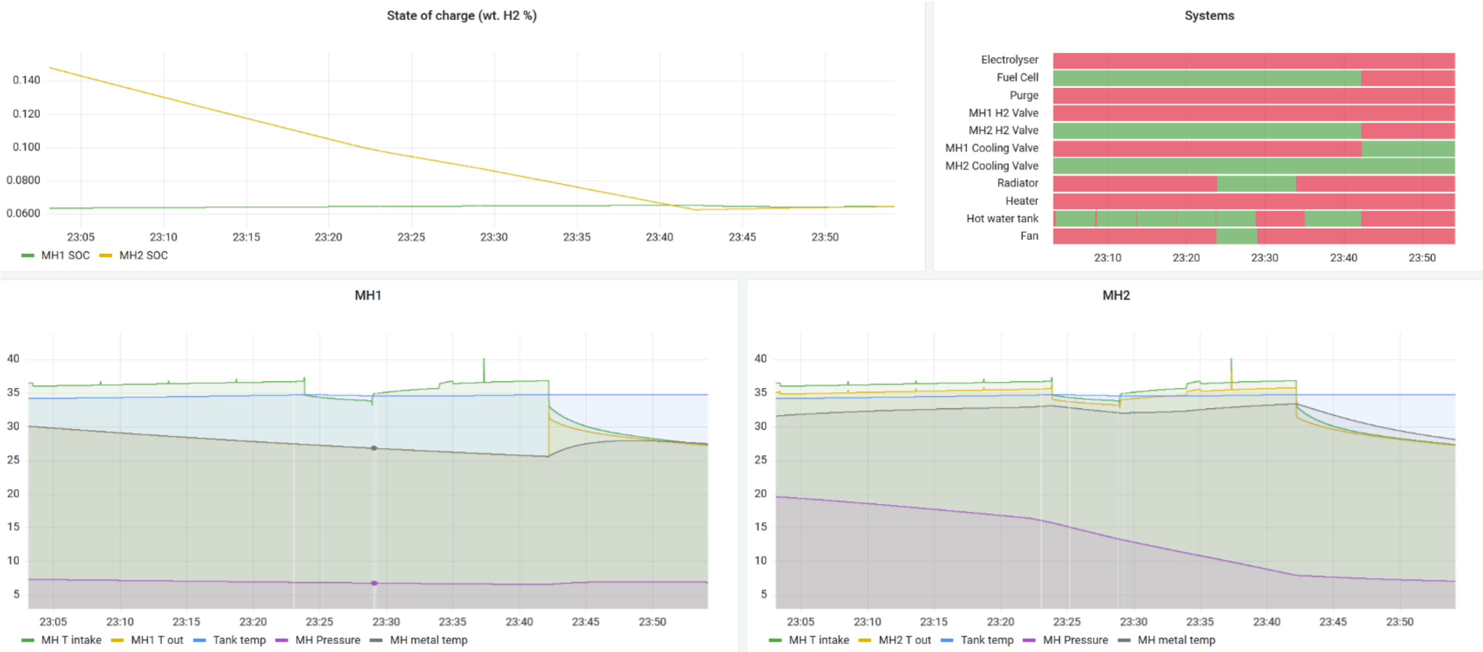


Figure 47. End of production

As seen in the SoC graph, this shows how the system responds when both hydride banks become empty. In this situation MH2 is becoming depleted and therefore the temperature is slowly rising in order to maintain the pressure above the minimum. At around 23:23 there is a drop in temperature since it reaches the absolute maximum temperature, which has priority, so the fan turns on until it is under its hysteresis. The temperature then goes back up until the pressure cannot be maintained under the minimum working pressure and the system then considers the MH depleted and turns to standby mode, maintaining the temperatures of both hydrides, which slowly equalize to the ambient temperature. The slight increase in temperature and pressure of MH1 is due to the valve being open during standby and both hydride banks equalizing.

5.5 Purge mode

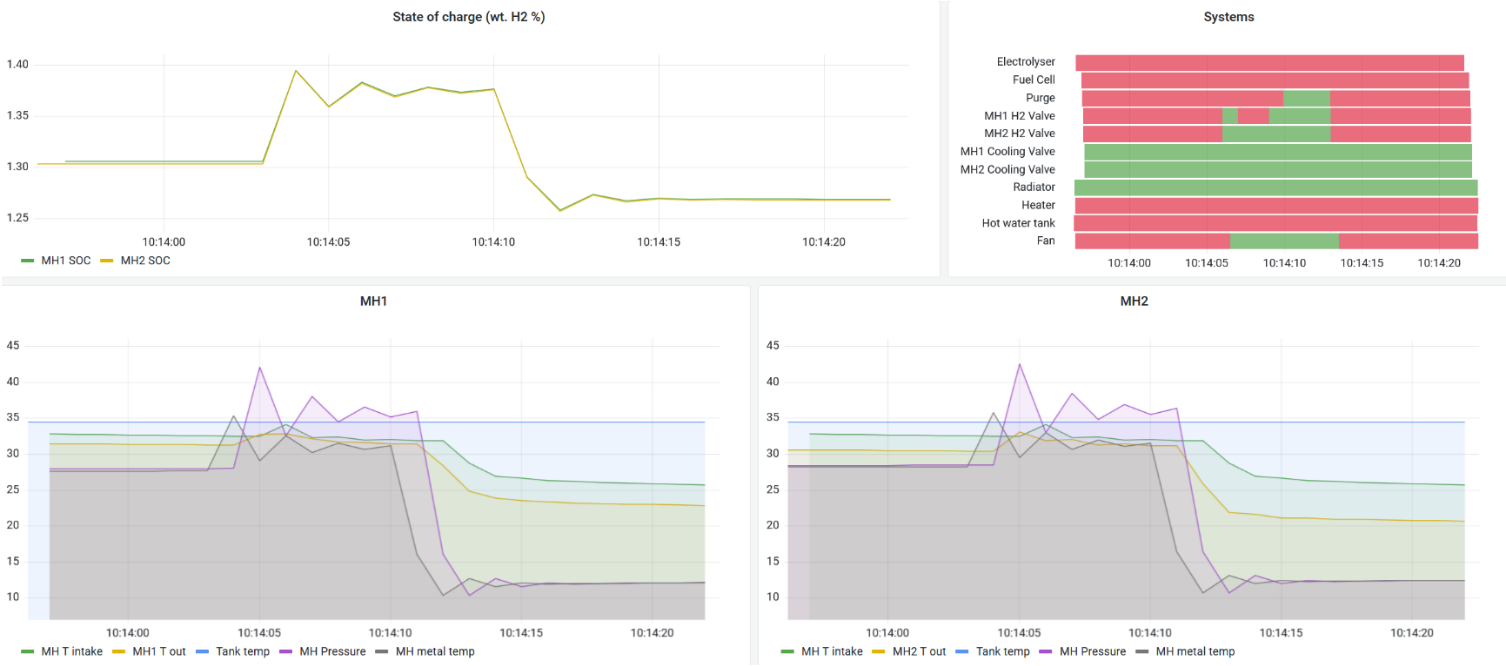


Figure 48. Purge mode

This graph shows the brief moment where the pressure is artificially set to a value above the maximum allowed pressure, therefore triggering the purge system. This is an unlikely scenario in real life, but it must be accounted in order to guarantee as many layers of safety as possible. In this case, shortly after 10:45:05, the pressure is raised and the purge system opens the valve that leads the MH to the hydrogen management interface. After 3 seconds, if that has not been sufficient to lower the pressure, the general purge valve is opened until the pressure has decreased to a sufficient level. Since the simulation runs every second, that is the maximum amount of precision that the control can respond to, so the pressure decreases significantly, but in real life the control is run every 200ms and can be lowered if deemed necessary and not computationally intensive. The hydrides respond by cooling themselves since they are releasing hydrogen to compensate for the sudden loss in pressure.

5.6 Uncontrolled rise in temperature of the hydrides

In this scenario simulating a situation akin to a fire, the temperature surrounding the hydrides has been set to 500ºC. In this situation, the system limits and the control, as long as they function, are able to contain the situation and discharge the hydrides using the purge mechanism. An interesting phenomenon happens, which is that due to the rapid release of hydrogen due to the heat and the large differential pressure due to purging, the hydrides absorb a lot of heat and therefore cool themselves, achieving a sort of system equilibrium that keeps the temperatures controlled. When the hydrides are depleted the temperature will rise uncontrollably (as can be seen in the graph, where the temperature decouples from the pressure), but, since the hydrides are empty, there will be no risk of a hydrogen explosion. The system completely empties itself in the span of 10-15 minutes. There is also the option of adding a system which empties the hydrides as fast as possible while limiting the minimum temperature in order to avoid freezing of the water.

6 Conclusions

The current state of development of this project, consisting of the full system design, including the control system, and the development of a model, has proved that it is feasible to construct a system that can create, store and consume hydrogen in order to store energy.

Although the model has many unknown variables that don't allow for exact predictions of efficiency, it has made possible the design and optimization of a control system that will be able to respond to dynamic situations when the full machine is assembled.

The next step in this project will be to assemble the prototype and test it under real conditions. This will allow for the refinement of the model and the control system, as well as the development of a business plan to commercialize the technology.

When the model is iterated and improved, it will be able to be modified to simulate the effectiveness and efficiency of real-world systems before they are fully designed, therefore assisting the dimensioning of the parts, and providing a technical and commercial advantage to its users.

This project has also contributed to the understanding of the current state of the hydrogen market, its strengths and shortcomings, and has made evident the difficulties posed to industry by the current global supply crisis.

Looking forward, this project has set a strong baseline for future developments in the field of low-power compact hydrogen storage systems. By further understanding and integrating different components and subsystems, improvements can be found in cost, efficiency, and environmental impact. Additionally, control structures have been developed which can be iterated on and improved with the help of real systems.

These developments will be accelerated by the ability to use a strong model in order to better aim the resources dedicated to this purpose. Using it, the user can identify the points where energy is not used adequately or lost and can optimize the behaviour of the components in order to maximize efficiency. Furthermore, by changing the settings of the components, different configurations of products can be tested to see how the energy balance evolves.

In conclusion, this project and thesis have succeeded in completing their objectives and set a strong foundation for future research and development in this field.

7 Tables

7.1 Figures

8 Bibliography

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