BACHELOR THESIS

IMPLEMENTATION OF A FUEL CELL SYSTEM ON BOARD OF A SMALL FERRY

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1.SUMMARY

This thesis is focused on a preliminary study of the viability of using fuel cells in small ferries for its propulsion. In order to reduce emissions, make necessary to study new naval propulsion systems in solidarity with the environment. Fuel cell system manages to reduce pollutant gas emissions and as a secondary effect reduce noises. Therefore, it could be a reasonable alternative to a conventional engine.

This thesis begins in chapter 2 by an introduction about the necessity of replace the conventional engine power with a new green alternative. Furthermore, it is mentioned the difficulties of installation a fuel cell system due to the lack of regulatory framework and facilities to provide the hydrogen. In chapter 3 it is explained the main thermodynamic characteristics of hydrogen. These properties are useful for understanding why it is so difficult to store discrete amounts of energy in small spaces and the challenges ahead with this fuel. Then, chapter 4 is focused on the main technologies investigated of storage hydrogen, analysing which of them is the best option for this particular case and the companies worldwide that provide them. Chapter 5 describes the operation of fuel cells and the classification according to the type of electrolyte used. Finally, a table has been created as a summary of the characteristics of each one. To conclude this part of the thesis, chapter 6 explains the state of the art of the use of fuel cells and batteries in the naval field.

The last part of this thesis is a preliminary study of the feasibility of implement a hybrid system made up of fuel cells and batteries in a passenger ferry in Venice. This issue is discussed in chapter 7.

2.INTRODUCTION

Fossil fuels are the main resource in order to produce energy and in transport sector. However, they are limited, and it used causes greenhouse gases, acid precipitation, acceleration of climate change, atmospheric pollution… Despite of the fact society is concern about taking care of the environment, they have a high dependency from fossil fuels.

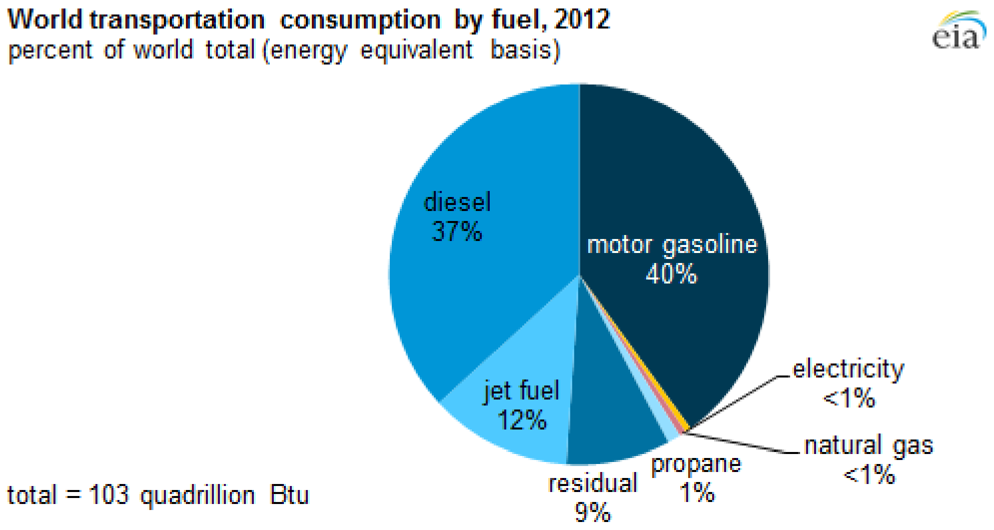


Figure 1: World transportation consumption by fuel, 2012. [1]

The graphic above illustrates that global transport fuel consumption is dominated mainly by diesel and gasoline engines. Together, they represent 77%. Almost all fuels used for transport are derived from fossil fuels.

For this reason, researchers are investing in other alternatives. Using hydrogen as a substitutive of fossil fuels is one of them. Apart from reducing emission of greenhouse gases, hydrogen is an unlimited and secure resource. It is the 1st element most abundant on Earth. Although hydrogen as an element is found in very small amounts, it is found combined in all components of living matter, as well as in hydrocarbons and organic matter. And of course, it is found in the most abundant compound on Earth, water (H_2O).

Shipping industry is one of the most urged to addressing changes in order to comply with upcoming pollutant emissions regulations. Thus, the new International Convention for the Prevention of Pollution from Ships (MARPOL) and Sulphur Emissions Control Areas (SECA) regulations limit the sulphur content in fuel oil, so ships need to use fuel oil which is inherently low enough in sulphur, [49]. Therefore, the use of fuel cells in ships is a promising alternative due to its greater efficiency, flexibility, reduce emissions and less noise. However, the current main challenges for application of fuel cell installations are the high cost of the equipment, the lack of experience on their long-term performance in a marine environment and the mastering of safety issues.

Although safety issues have been addressed for terrestrial applications, civilian applications at sea are still limited to a few pilot projects. As a matter of fact, the key hurdle for the wider application of fuel cells in ships is the lack of a comprehensive regulatory framework covering the technology. The lack of regulatory framework limits the possibilities of building and testing prototype applications, which in turn are essential for qualifying and improving the performance of the systems and for gaining a better insight in the safety issues, which is necessary for establishing rules. "Classified Ships" are ships that have been designed and built under certain rules and have the survey of a Naval Register (Lloyd, RINA, ABS, DNV…). For the time begin, these classification societies have not established any rule about hydrogen propulsion yet.

In addition, in Italy there is a locally rule, DPR 435 (1991), about the safety of navigation and human life at sea. Article nº 81 explains that liquid fuel for internal combustion engine propulsion and auxiliary equipment must have a flash point of not less than 60°C.

Furthermore, currently there is no hydrogen infrastructure comparable to diesel or gasoline yet. Due to the increasing use of hydrogen in fuel cell passenger cars, the expansion of the infrastructure will continue and be pushed ahead with the development of the market. The refuelling of ships with liquid hydrogen could be analogous to the current bunkering of inland waterway vessels with LNG, which are characterized by bunkering directly from truck to ship at an appropriate berth. Even though, these infrastructures remain complicated and difficult to manage. Especially, the problem is increasing in cities like Venice where bunkering is so close to citizens´ homes and it can cause safety problems. As it is shown in Figure 2, the boat is moored closely to homes, approximately 33 metres. It is also important to understand that Venice has a great architectural, artistic and historical value, thus any change in the city's architecture like building new hydrogen supplies systems can have a social impact too.

Figure 2: Distance from pier to citizens´ homes

3.HYDROGEN

3.1. Introduction to Hydrogen Technology

Hydrogen is the simplest and most abundant element in the universe. It consists of an electron and a proton. It is also the lightest element due to its lack of neutrons. Because of this, hydrogen is not found in its pure state on our planet, but in various compounds such as water and in the majority organic compounds. It is therefore expensive to obtain compared to fossil fuels. It is necessary to develop systems capable of producing it efficiently.

Hydrogen is not considered a primary energy source, but rather a means of transporting energy, which is why it is known as an **energy vector**. It is transformed into electrical and thermal energy in a clean and efficient way, by means of an electrochemical process called "fuel cell".

To produce pure hydrogen, it is necessary to extract it from compounds which are made up of it. A common process is the **electrolysis of water** to obtain hydrogen and oxygen. It is an endothermic reaction which needs a contribution of energy either through renewable energies or from fossil fuels.

As mentioned above, fossil fuels are "hydrogen carriers", it would suffice to make them react with water using a catalyst to facilitate the reaction. This process is called **reforming**.

Biomass is another source of hydrogen. Biomass is matter that comes from living beings in which hydrogenated compounds abound. When biomass is treated, a **synthesis gas** is obtained consisting of hydrogen and carbon dioxide.

3.2. Thermodynamics Properties

For analysing correctly, the mechanism of a fuel cell and the store of hydrogen, it is essential to know some thermodynamics properties about hydrogen.

Under Standard Conditions according to NIST (National Institute of Standards and Technology), temperature 20°C and atmospheric pressure, hydrogen is in a gaseous state. At atmospheric pressure is required to get -252,87°C in order to obtain hydrogen in a liquid state.

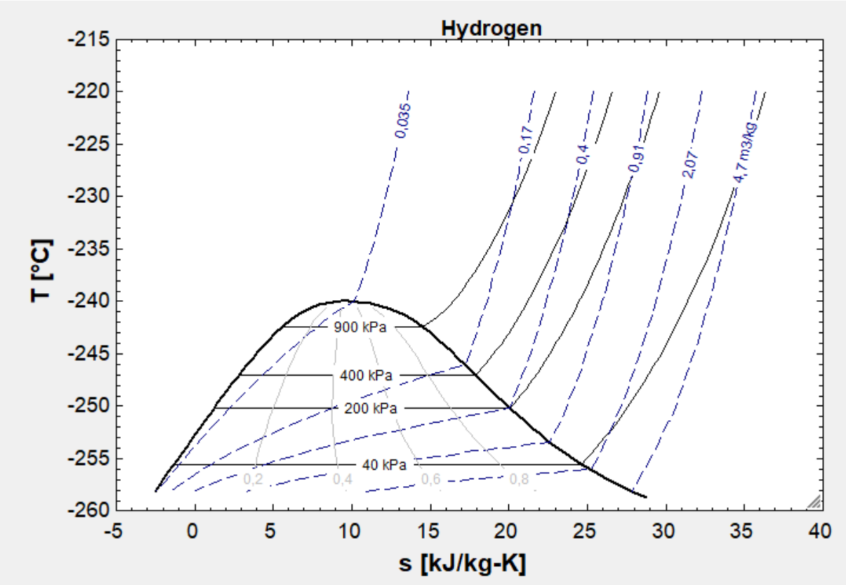


Figure 3: Hydrogen Temperature-Entropy diagram [2]

The critical point in the diagram T (°C) – s (KJ/KgK) is 12,96 bar and -240 °C.

About **density**, hydrogen is the lightest element. Under Standard Conditions, its density is 0,0838 kg/m^3. However, liquid hydrogen has a higher volume density; 70,8 kg/m^3. In order to qualify the difference:

$$\frac{70{,}8\ \mathrm{kg}/m^3}{0{,}0838\ \mathrm{kg}/m^3} = 844{,}87$$

The density of liquid hydrogen is 845 higher than in gas state. The issue is that to obtain liquid hydrogen must get the cryogenic temperature of -253 °C and keep it. A lot of energy is required. It is explained with more details in chapters below.

Just to avoid liquefaction, it is possible to compress hydrogen at environmental temperature. As it is illustrated in Figure 4, hydrogen behaves as an ideal gas in low pressure environments, but in higher pressures not:

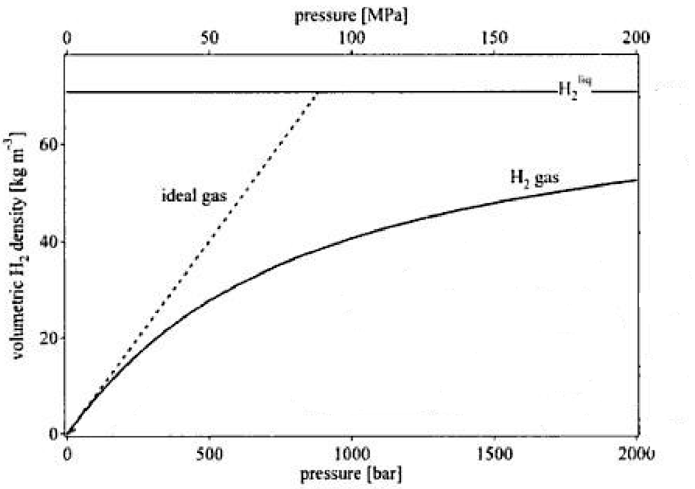


Figure 4: Hydrogen Pressure-Volumetric H_2 density Diagram [3]

At high pressures hydrogen in gas state does not behave as an ideal gas.

In terms of **calorific values**, in other words, the amount of energy produced by the complete combustion of a material or fuel could be measured in energy per unity of mass (specific energy; MJ/Kg) or per unity of volume (density energy; MJ/m^3).

SPECIFIC ENERGY:

This parameter is important to study to know the energy that hydrogen can provide per unit of mass. Above all, comparing this parameter with that others conventional fuels makes it possible to evaluate hydrogen as a possible fuel. Hydrogen has a specific energy of LHV 120 MJ/Kg. It is the highest specific energy in comparison with conventional fuels.

DENSITY ENERGY:

However, when the energy density of hydrogen is studied, it is observed that it is considerably lower than other fuels. This means that, for the same volume, conventional fuels provide more energy than hydrogen. And this difference is very noticeable.

$$Density\ Energy\left(\frac{MJ}{m^3}\right) = LHV\left(\frac{MJ}{Kg}\right) * \rho_{H_{2(GAS)}}\left(\frac{Kg}{m^3}\right) = 120 * 0{,}084 = 10{,}08\frac{MJ}{m^3}$$

It is possible to increase this density energy increasing its density. Then, if the gas is compressed or in a liquid state, higher energy densities are achieved. The table below illustrates a comparison at different pressures:

STATE	PRESSURE (bar)	Density (Kg/m^3)	LHV (MJ/Kg)	Energy Density (MJ/m^3)
Gas	1	0,084	120	10,08
Gas	250	17,86	120	2143,2
Gas	500	31,22	120	3746,4
Gas	700	39,69	120	4762,8
Liquid	1	70,80	120	8496

Table 1: Calculation of the energy density of gaseous hydrogen at different pressures and in liquid state

3.3. Comparison other fuel properties

By focusing on the energy associated with a fuel, the properties of hydrogen are compared with different conventional fuels that are currently used to study the viability of using hydrogen in the future.

Focus on LHV shown in Table 2, hydrogen almost triples the amount of energy provided per unit of weight than other fuels. Therefore, hydrogen could storage more energy quantity than the rest of fuels at equal of mass.

The next table resumes energetic properties of hydrogen and the most common fuels used:

FUEL	VOLUMETRIC DENSITY (Kg/m^3)	LHV (MJ/KG)	ENERGY DENSITY (MJ/m^3)
Diesel	832	43,1	35860
Gasoline	708	43,448	30761
Propane	493	46,296	22824
Liquid Hydrogen	70,80	120	8496
Compressed Hydrogen (700 bar)	39,69	120	4762,8

Table 2: Volumetric density, LHV and energy density of hydrogen and common fuels

Despite of compressing or liquified hydrogen, the energy density of the rest of fuels are higher than hydrogen. It means that, to storage the same quantity of energy, it must be required bigger tanks.

In general, fuel cells have an energy efficiency between 40-60% and can reach up to 85%-90% in cogeneration, if the residual heat is captured again for use. In contrast, conventional engines do not exceed 50%. For this reason, fuel cells required less storage energy than conventional engines and volume problem it is compensated.

3.4. Current Situation and Perspectives of Hydrogen

Following is a list of positive and negative effects about hydrogen propulsion in order to understand the current situation and its perspectives for the future.

On one hand, positive effects are:

- **Low or even zero emissions:** During the normal operation of the ship, this propulsion system does not carry any emissions that damage the environment. It is therefore the cleanest possible, totally non-polluting fuel. However, throughout its whole Life Cycle Assessment (LCA) some pollutant gases are involved. Currently, the most commonly method used for obtaining hydrogen is a process called reforming with natural gas which involve greenhouse gas emissions.
- **Low noise:** As a secondary effect, noise and vibration are minimized.
- **Carbon free fuel:** When hydrogen is burnt it gives off water instead of carbon dioxide.
- All the rules for emissions are changing and the last stage is 2021, so in a medium future hydrogen could be one of the possible solutions after the changes of statutory rules, and after the edition of Naval register rules for hydrogen propulsion**.**
- **Simple and compact system**

On the other hand, there are still problems to be solved:

- Locally rules, like DPR 435 previously mentioned, does not permit use hydrogen or other liquid fuels with a flash point lower than 60°C. In addition, there are no rules of Classification Ships of any Naval Register of IACS (International Association of Classification Societies).
- **Safety Issues:** Hydrogen is the element with the highest thermal conductivity, the lowest molecular weight, the lowest density and viscosity of the periodic table. These qualities make hydrogen diffuse very quickly (2,8 times faster than methane and 3,3 times faster than air). Any leak of hydrogen will rapidly dissipate upwards. In open or well-ventilated areas, the probability of creating a detonating atmosphere is low. On the other hand, in closed rooms and in presence of electrical devices, the risk of explosion increases. Especially if the ignition source is close to the leakage zone.
  Like gasoline and natural gas, hydrogen is flammable and can pose a danger under specific conditions. Hydrogen can be handled safely when simple guidelines are observed, and the user understands its behaviour.

Property	Hydrogen	Methane (NG)
Flammability in air	4 to 75%	5 to 15%
Burning velocity	3 m/s	0,45 m/s
Minimum Ignition Energy	0,019 mJ	0,1 mJ

Table 3: Comparison types of fuel cells

  As it is shown in the previous table, hydrogen has a low ignition energy. This means that, it needs ten times less energy to ignite than gasoline or natural gas and at low concentrations (<10%) this energy is equal or higher than gasoline or natural gas. In addition, its high flammability range makes a significant risk that a confined hydrogen/air mixture will detonate.
  Hydrogen is an odourless, colourless and tasteless gas so it is not detectable by humans. For this, it is necessary to install on board sensors to detect leaks.
  Related to the issue of storage, the most common method is the use of pressurized tanks. The higher the pressure, the greater the amount of hydrogen stored. However, it increases the risk of tank rupture by releasing tremendous energy. This can be avoided by choosing a suitable location and materials for the tank.
  Fortunately, several classification societies have produced guidelines for ensuring safety issues in fuel cells application. From a safety point of view, similar with gas piston engines, fuel cells also represent a potential for gas leakage and formation of explosive atmospheres. The main philosophy of the rules is that there is no way to decrease the safety level when gas is used, compared to conventional machinery.
- **Fuel costs production, transport and distribution:** A fundamental obstacle is the lack of an economical hydrogen production, transport and storage infrastructure as it is mentioned in the introduction. Each hydrogen production method has an associated carbon footprint. For the use of hydrogen to be competitive, it is necessary to improve its production methods: reduce costs and reduce the associated emissions of greenhouse gases. In order to achieve this, the current sources of hydrogen production must be replaced by others of totally renewable origin.

Its transport and distribution are also a difficulty. Currently, most hydrogen is produced in-situ or near the point of consumption, usually in large industrial plants; and distribution is by pipeline or land transport (in pressurized or liquefied tanks). However, the consolidation of hydrogen as a fuel at a global level would require a much broader transport and distribution network.

Pipeline distribution of hydrogen is not technologically very complex. The problem is that building a general network of pipelines is too high an initial outlay. One option is to take advantage of the natural gas distribution infrastructure by injecting hydrogen into pipelines and separating it from natural gas at the point of destination, but this can carry many problems at least.

Focus on the case of study, bunkering procedure in a heritage city like Venice becomes a more acute issue, also the port bunkering procedures don't allow, according to now, fuels like LNG or Hydrogen. The procedure of bunkering is quite complicated, and it mean also supervision of many institutions.

4.HYDROGEN STORAGE TECHNOLOGIES

4.1. Types of Storage

In order to boost hydrogen energy generation, hydrogen storage must be improved. There are different types of storage depending on their use. The main forms of storage are compressed hydrogen, liquid state or in the form of hydrocarbons.

In the storage of hydrogen under pressure it manages to introduce large quantities of hydrogen, but this entails the use of high-cost materials that can withstand high pressures. However, liquid storage requires very low temperatures and cooling is a major energy expense.

A developing technology is the use of metal hydrides. If heat is applied to the metal hydride, hydrogen is released. This technology is stable and safe, but the process is slow and sometimes expensive to extract hydrogen.

Linked to this problem, researches have been studying many ways of storage to solve it. In the next figure it is shown how storage hydrogen works.

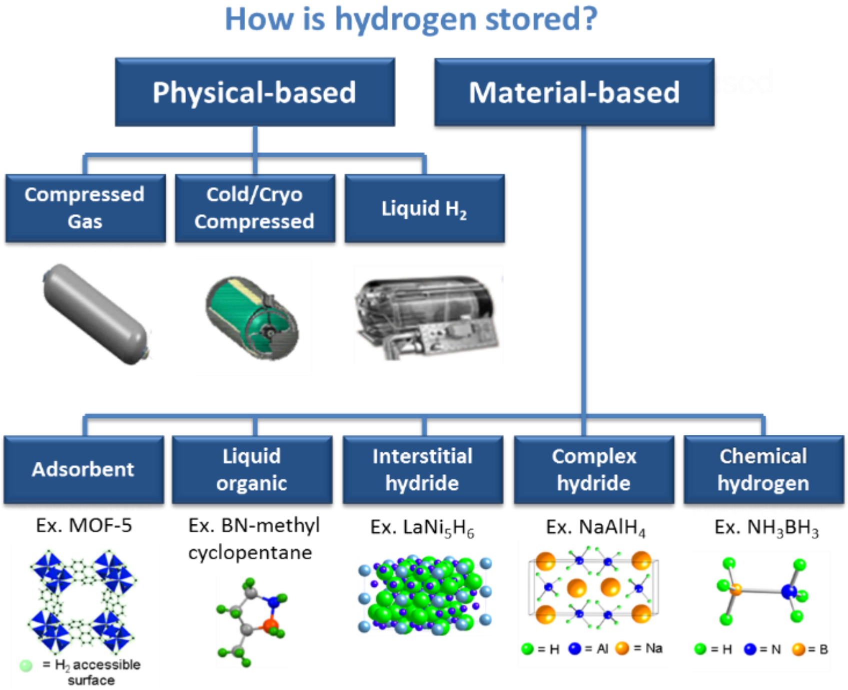


Figure 5: Main hydrogen storage technologies [9]

As it is mentioned previously, despite of the fact that hydrogen has a high specific energy (MJ/kg), its volumetric density (MJ/m^3) is too low. This means that in equal volume with other fuels, hydrogen has little energy; in equal weight, a very high energy. Therefore, for the application of hydrogen in transport, it is necessary to store as much hydrogen as possible in the smallest possible volume and with the least possible weight.

As the previous figure shows, hydrogen stored is divided in two main groups: Physical-Based and solid or Material Based. Physical-Based methods are the most mature and known because they are like other gases storage methods. However, Material-Based is also been investigate in order to solve the problem. Physical methods store hydrogen molecules in their free form, without being joined or absorbed by other materials. Therefore, we play fundamentally with pressure and temperature, with them we try to maximize the volumetric and gravimetric capacity of hydrogen stored above all for applications in the transport sector.

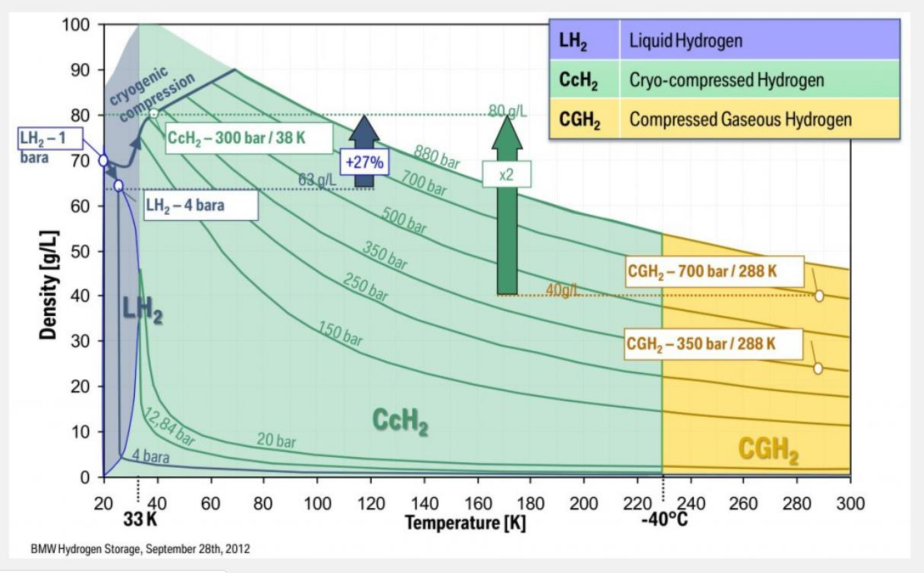


Figure 6: Hydrogen Density versus Pressure and Temperature [10]

Figure 6 shows the regions corresponding to the three forms of physical storage of hydrogen: compressed, cryo-compressed and liquid, as well as the variation in density for different pressures and temperatures. It is clearly seen how liquid hydrogen and cryo-compressed have a much higher density than compressed hydrogen. Despite the great advantages of liquid and cryo-compressed storage, they are currently in an experimental phase solving certain problems. The most commonly used method for storing hydrogen today is compressed hydrogen.

Each hydrogen storage technology is described in detail in the following sections.

4.1.1. Gas Compressed

Nowadays, the easiest and economical method is storage hydrogen as a gas compressed. Hydrogen density increases by compressing then, more kilograms of hydrogen can be stored which occupies the same volume as uncompressed. But at high pressures, hydrogen does not behave as an ideal gas.
The gas temperature´s increases by compressing. Therefore, during the filling of the tank it is necessary to control the temperature inside and more difficulties appear.

TYPES OF TANKS:

There are four types of tanks according to the pressure they can afford; [52]:

- **TYPE I:** Traditional bottles. Metal tanks. Approximate maximum pressure they can afford is aluminium 175 bars and steel 200 bars. Elevate weight.
- **TYPE II:** Cylinder metal tanks with filament windings like glass fibre or carbon fibre around. Maximum pressure they can afford is 250 bars for aluminium/glass and 300 bar for steel/carbon. They are lighter than the previous type. However, they are only used in stationary activities.
- **TYPE III:** These cylinders are made up of a thin metallic layer called liner, cover of compounds materials. The liner prevents hydrogen leaks. This type of tank support

higher pressures than previous. Maximum pressure 700 bars. So, weight and volume are lower.

- **TYPE IV:** They are like type III, but the liner is a polymer. They work with the same pressure and they have a lower weight. This polymer liner is not good as the previous one, but it achieves a lower weight tank.

Energy consumption in this method is linked to the necessity of compress hydrogen until the pressure required. Energy is needed to compress gases and the compression work depends on the thermodynamically compression process, as well as on the nature of the gas. This is presented by the comparison of hydrogen with helium and methane:

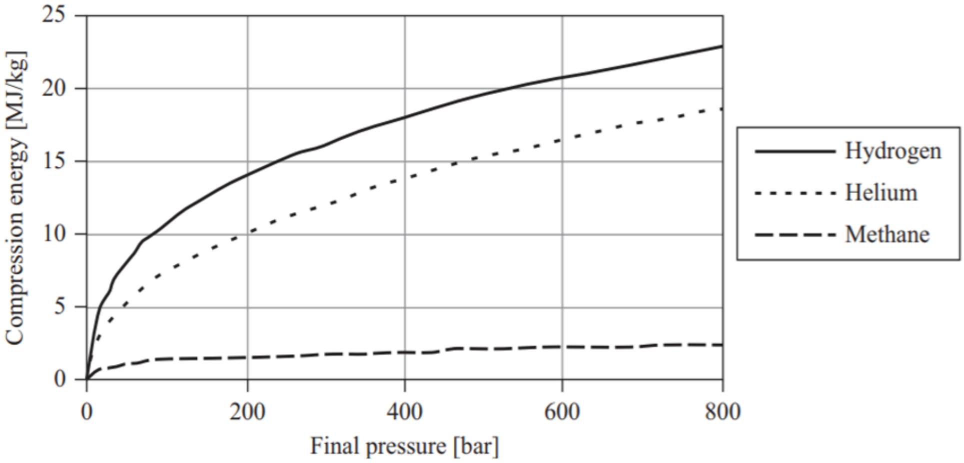


Figure 7: Adiabatic compression work as a function of the pressure of certain gases including hydrogen [11]

Energy required for compression: Two levels of compression (350, 700 bar) are considered in this study. We start with hydrogen at 300K and 20 bars. In the table below, it is collecting the theorical energy required in isothermal compression:

COMPRESSION ISOTHERMALLY	THEORICAL ENERGY (kWh/kg H_2)
20-----350	1,05
20-----700	1,36

Table 4: Theorical energy required for compression [12]

The lower heating value (LHV) of hydrogen is 33,3 kWh/kg H_2. This means that 3,15% of the LHV of hydrogen is required to compress hydrogen from 20 bars and 300K to 350 bars and 300K. And the 4% of the LHV of hydrogen is required to compress hydrogen from 20 bars and 300K to 700 bars and 300K.

Cooling previously H_2 can help in order to reduce the energy for compression. Due to compression heating, overpressures are required to achieve a complete fill. A 350 bar system can require an overpressure as high as 440 bar and the maximum vessel temperature must be limited to 85°C and a 700 bar fast fill systems can require an overpressure as high as 880 bars with pre-cooling as low as -40°C. Compressing hydrogen (isothermally) from 20 bar to 350 bar requires just 1,05 kWh/kg H_2, with an additional 0.10 kWh/kg H_2 to reach a pressure of 440 bars. Only 1.35 kWh/kg H_2 is required for compression to 700 bars, with an additional 0.12 kWh/kg H2 to reach 880 bars. All these data are taken from [12]

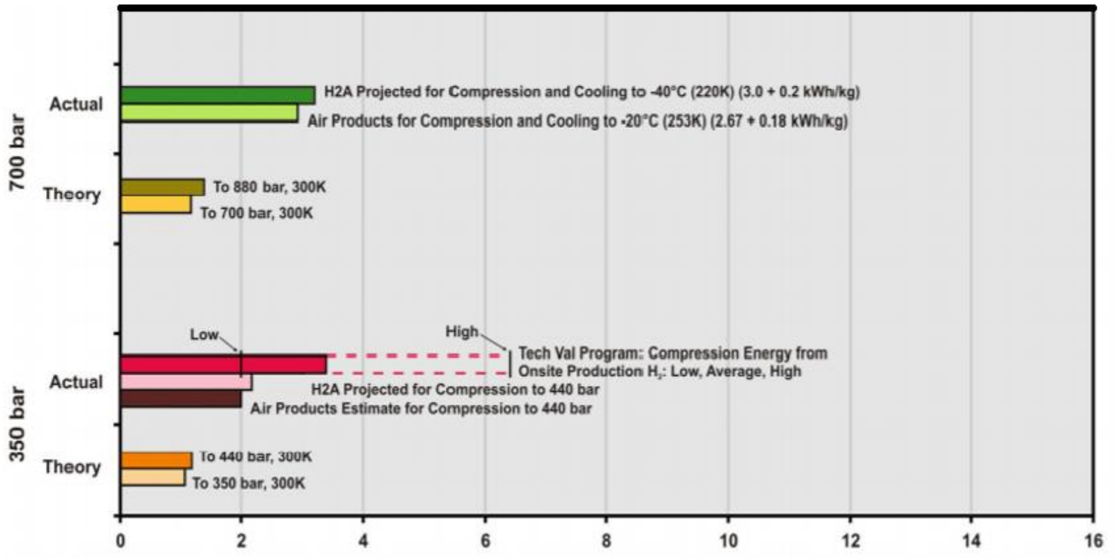


Figure 8: Energy consumed (KWh/KgH_2) for compress hydrogen from 20 bar, 300 K [12]

Figure 8 shows the energy consumed for compression at 350 bar and 700 bar. At each pressure level, a distinction is made between the theoretical energy consumed and the actual energy consumed. The actual energy consumed has been obtained from experimental case studies. It is observed that there is always a higher consumption of energy than in the theoretically calculated compression process because it is not an ideal process, there are imperfections such as the efficiency´s compressor, leaks, heating...

4.1.2. Liquid Hydrogen

A viable option is the storage of hydrogen as a liquid. Liquid hydrogen has a density of 70,8 Kg/m^3, 845 times more than in a gaseous state at atmospheric pressure. Therefore, the main advantage of this type of storage is that the tanks required are smaller than in the gaseous state for the same quantity, thanks to the increase of its density. LH2 storage does not require high pressures. With LH2 stored on the vessel, it can in principle be fuelled directly from a LH2 tanker brought to the waterfront by the gas supplier. In principle, this would not require a "hydrogen station," providing more flexibility for refuelling. LH2 tank technology scales well. Building much larger LH2 tanks does not introduce new problems and can readily be accomplished. The main problem is liquefaction.

Energy required for liquified: The minimum theoretical energy to liquefy hydrogen from ambient (300 K; 1,01 bar) conditions is 3,3 kWh/kg LH2. Actual liquefaction energy requirements are substantially higher, typically 10-13 kWh/kg LH2, depending on the size of the liquefaction operation. Liquefaction with today's processes requires 30 - 40% of LHV. Beginning with 20 bar H2 gas, liquefaction adds a theoretical minimum work of only 2,3 kWh/kg LH2; [12].

Hydrogen liquefaction involves multiple process steps and some degree of complexity in addition to compression. This leads to significantly higher energy requirements and a broader range of actual energy requirements which vary with liquefaction plant scale. Energy requirement of 10 kWh/kg LH2 for a conventional LH2 plant.

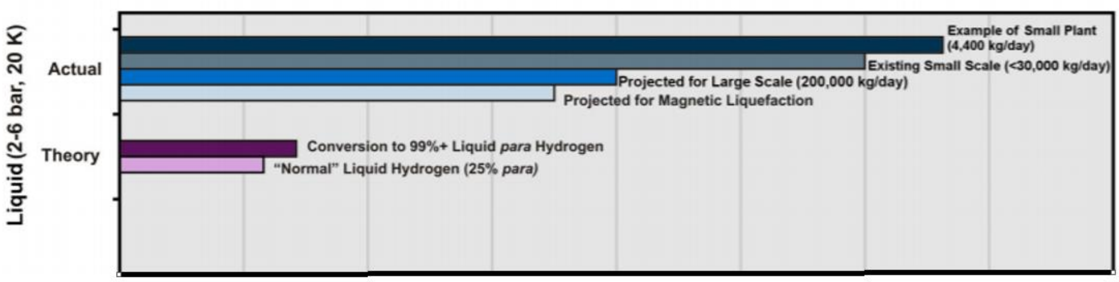


Figure 9: Energy consumed (KWh/KgH_2) for liquified hydrogen from 20 bar, 300 K [12]

4.2. Commercial Compressed Hydrogen Storage Tanks

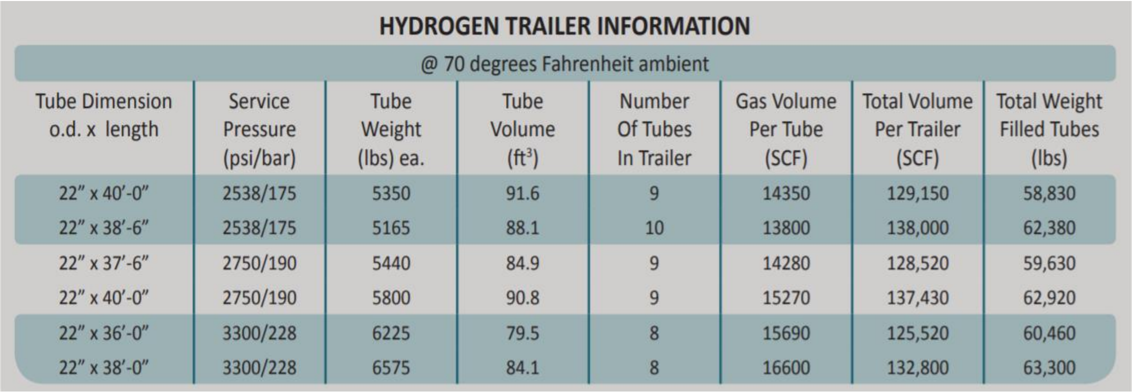
In this section, the main companies that commercialize compressed hydrogen tanks have been defined:

- **NPROXX:** This company is a global leader in designing, developing and manufacturing Type 4 pressure vessels for the storage of hydrogen under high pressure. In one hand, this company has created solutions for the storage in large volumes of hydrogen for stationary activities such as: Hydrogen Storage for Filling Stations, Hydrogen Infrastructure… NPROXX is in advanced stages of developing a new hydrogen storage system that can store more than 1,000kg of H_2 at a nominal working pressure of 500 bar. In the other hand, NPROXX is working to develop and produce high pressure hydrogen storage solutions for use in transport applications, such as: hydrogen powered buses, hydrogen powered heavy vehicles, hydrogen powered cars and vans, hydrogen powered rail vehicles and shipping and maritime hydrogen applications. [37]
- **HYON:** Deliver integrated systems including renewable hydrogen production, storage, distribution, dispensing, and electricity generation via fuel cells. Hyon is equally owned by Nel ASA, Hexagon Composites ASA and PowerCell Sweden AB, and utilises each partner's respective world leading technologies and competencies to manage and develop projects for effectively integrated and optimal zero-emission power solutions for the customers. [38]
- **H2 GO POWER:** H2GO Power is an award-winning spin-out company from the University of Cambridge developing safe and low-cost hydrogen production and storage technologies. Their mission is to bring affordable reliable energy to millions across the globe in a green way for large social and environmental impact. [39]
- **CALVERA:** It is a company founded in 1954 and based in Spain with an international presence for the distribution of cylinders for the transport of gas under pressure of different types. Its activity is divided into three divisions that form the group: Calvera Industrial Gases, Calvera Gas Technology (CNG-BIOGAS) and CalveraHydrogen. [36]
- **CP INDUSTRIES INC:** It is a company from Pennsylvania, with great experience in the field of large type 1 seamless steel cylinders for the transport of hydrogen under pressure. The company offers a wide range of possibilities to customize the cylinders listed in the price list according to your needs. [13]
- **SIAD:** is one of the most important chemical groups in Italy and supplies a full range of industrial, specialty, food and medical gases, in addition to operating in the following sectors connected with the world of gases: engineering, healthcare, LPG and Natural gas. Hydrogen supply options and services available to SIAD customers include, [40]:

  - Transport in cylinders, cylinder packs or cylinder trucks
  - Design and installation of gas distribution systems
  - Supply of equipment for the correct use of the gas
  - Assistance and technical consultancy for the transport, distribution and application of the gas.
- **FABER INDUSTRIES:** It is founded in 1972 with headquarters in Udine (Italy), can boast a great deal of experience in the production of steel and composite cylinders (Type 1, 2, 3 and 4) for the storage of high pressure gas with a capacity between 1 and 700 liters. Its products guarantee high quality standards and comply with various specifications established by international bodies, local authorities or at the request of its customers. [54]

CP INDUSTRIES (TUBE TRAILER):

CP Industries' tube trailers are a cost effective, reliable solution for transporting hydrogen. A tube trailer is a trailer made up of small tubes which contain the gas hydrogen compressed inside. There are many types of it depending on its length and pressure. Here is a table of the hydrogen trailers provided:



HYDROGEN TRAILER INFORMATION

@ 70 degrees Fahrenheit ambient

Tube Dimension o.d. x length	Service Pressure (psi/bar)	Tube Weight (lbs) ea.	Tube Volume (ft³)	Number Of Tubes In Trailer	Gas Volume Per Tube (SCF)	Total Volume Per Trailer (SCF)	Total Weight Filled Tubes (lbs)
22" x 40'-0"	2538/175	5350	91.6	9	14350	129,150	58,830
22" x 38'-6"	2538/175	5165	88.1	10	13800	138,000	62,380
22" x 37'-6"	2750/190	5440	84.9	9	14280	128,520	59,630
22" x 40'-0"	2750/190	5800	90.8	9	15270	137,430	62,920
22" x 36'-0"	3300/228	6225	79.5	8	15690	125,520	60,460
22" x 38'-0"	3300/228	6575	84.1	8	16600	132,800	63,300

Figure 10: Main features of some cylinders proposed by the company CPI [13]

Next, it is studied how the distribution of the tubes could be with the example of storing 200 kg of hydrogen. For this, the following conversion factors are used:

$$1\ ft^3 = 0{,}0283168\ m^3$$

$$1\ lbs = 0{,}45359237\ kg$$

$$1\ SCF = 0{,}002623\ kg\ H_2$$

For this case, it is used one distribution of each pressure shown, changing the number of tubes per trailer:

Tube Dimension o.d x length	Pressure (bar)	H_2 Storage (kg)	H_2 Storage (SCF)	Tot.Volume Gas/Trailer (SCF)	Tube Weight (kg)	Tube Volume (m^3)	Number tubes in trailer	Total Volume (m^3)
22´´x 40´-0´´	175	200	76249	14350	2426,72	2,5938	6	23,3442
22´´ x 37´-6´´	190	200	76249	14280	2467,54	2,4041	6	21,6369

22´´ x 36´ - 0´´	228	200	76249	15690	2823,61	2,2512	5	18

Table 5: Results of the storage of 200 kg of hydrogen with cylinders from the CPI company [13]

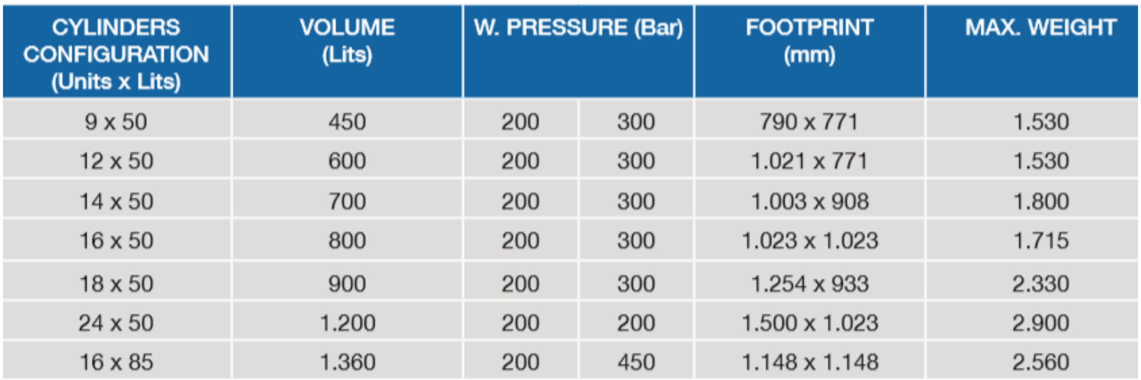
Any of these configurations can be used to store the same amount of hydrogen. It is observed that as the pressure increases, the weight of the tubes increases too because they contain more kilograms of hydrogen inside, however the volume is smaller.

CALVERA:

This company develops different ways of storing compressed hydrogen. They fall into three main categories; [36]:

- **Bundles of cylinders for high pressure gas transportation:** This storage technique consists of bottles of small capacity but forming a package of many these bottles. Figure 11 and Figure 12 represent a bundle with all cylinders interconnected making one lonely tank and all the configurations available:

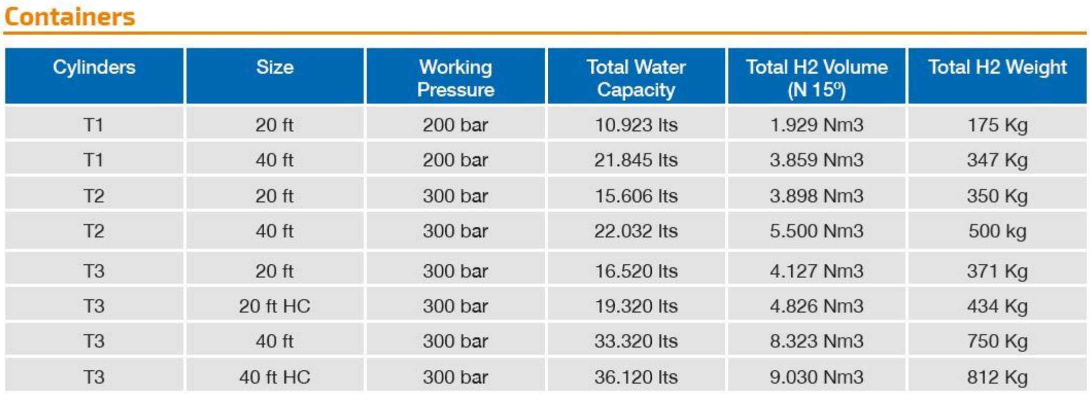
Figure 11: Bundle of cylinders from Calvera



CYLINDERS CONFIGURATION (Units x Lits)	VOLUME (Lits)	W. PRESSURE (Bar)		FOOTPRINT (mm)	MAX. WEIGHT
9 x 50	450	200	300	790 x 771	1.530
12 x 50	600	200	300	1.021 x 771	1.530
14 x 50	700	200	300	1.003 x 908	1.800
16 x 50	800	200	300	1.023 x 1.023	1.715
18 x 50	900	200	300	1.254 x 933	2.330
24 x 50	1.200	200	200	1.500 x 1.023	2.900
16 x 85	1.360	200	450	1.148 x 1.148	2.560

Figure 12: Main features of the cylinder packs (200 bar for hydrogen) proposed by the company Calvera

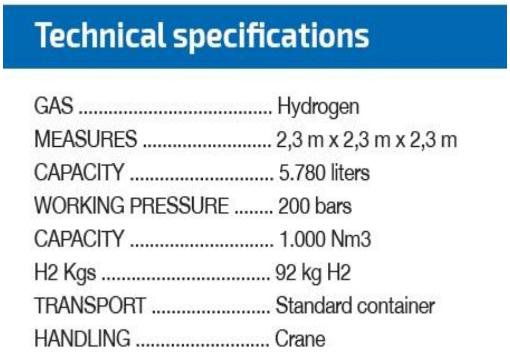
- **Multiple Element Gas Container (MEGC):** They have a disposition like the tube trailer, they are formed by bottles of small dimensions (volume<150 L).



Containers

Cylinders	Size	Working Pressure	Total Water Capacity	Total H2 Volume (N 15º)	Total H2 Weight
T1	20 ft	200 bar	10.923 lts	1.929 Nm3	175 Kg
T1	40 ft	200 bar	21.845 lts	3.859 Nm3	347 Kg
T2	20 ft	300 bar	15.606 lts	3.898 Nm3	350 Kg
T2	40 ft	300 bar	22.032 lts	5.500 Nm3	500 kg
T3	20 ft	300 bar	16.520 lts	4.127 Nm3	371 Kg
T3	20 ft HC	300 bar	19.320 lts	4.826 Nm3	434 Kg
T3	40 ft	300 bar	33.320 lts	8.323 Nm3	750 Kg
T3	40 ft HC	300 bar	36.120 lts	9.030 Nm3	812 Kg

Figure 13: Main features of the containers proposed by the company Calvera



Technical specifications

GAS	Hydrogen
MEASURES	2,3 m x 2,3 m x 2,3 m
CAPACITY	5.780 liters
WORKING PRESSURE	200 bars
CAPACITY	1.000 Nm3
H2 Kgs	92 kg H2
TRANSPORT	Standard container
HANDLING	Crane

Figure 14: Main features of a fixed bottles pack (200 bar for hydrogen) proposed by the company Calvera

5.FUEL CELLS

5.1. Definition and operation of a fuel cell

A fuel cell is an electrochemical battery capable of converting the chemical energy of a fuel into electrical energy, without any thermodynamic process. The electrolysis of a water molecule requires a supply of energy. By contrast, a fuel cell puts hydrogen and oxygen back together in a way that the energy released is in the form of electricity.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + \Delta H \quad where\ \Delta H = -285\frac{kJ}{mol}$$

A fuel cell is made up of three different parts: cathode, anode and electrolyte.

- **Anode**: In this electrode, the fuel enters, in this case, the hydrogen. It dissociates, releasing electrons that will pass through the cell to generate electricity and the ions formed will pass through the electrolyte to the cathode.

$$H_2 \rightarrow 2H^+ + 2e^-$$

- **Cathode**: In this electrode, air is injected. Oxygen from air reacts with the hydrogen ions giving rise to water.

$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O$$

- **Electrolyte**: It is the layer that divides the anode from the cathode and prevents electrons from passing through it. It could be solid or liquid.

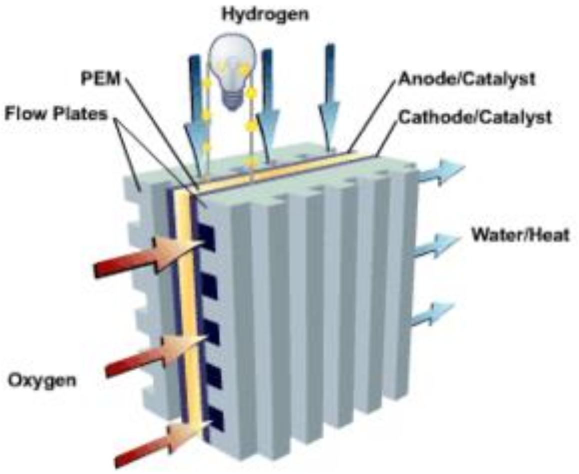


Figure 15: Proton Exchange Membrane Fuel Cell [4]

To facilitate the reaction, a catalyst is used on both electrodes. The most commonly used element is platinum. However, new lines of research are being opened to improve efficiency and reduce cost.

5.2. Voltage Losses

The Gibbs free energy (ΔG) is the maximum electrical energy that a fuel cell can achieve of the reaction above:

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

The theoretical potential of fuel cell, E, is then:

$$E = -\frac{\Delta G}{nF}$$

Where n is the number of electrons involved in the reaction and F is the Faraday's constant. So, the theoretical hydrogen/oxygen fuel cell potential can also be calculated:

$$E = -\frac{\Delta G}{nF} = \frac{237{,}340}{2 * 96{,}485}\frac{J * mol^{-1}}{As * mol^{-1}} = 1{,}23\ V$$

If all the Gibbs free energy can be converted into electrical energy, the maximum possible (theoretical) efficiency of a fuel cell is a ratio between the Gibbs free energy and hydrogen higher heating value ($HHV_{H_2} = 286\frac{KJ}{mol}$):

$$\eta = \frac{\Delta G}{\Delta H} * 100 = \frac{237{,}34}{286} * 100 = 83\%$$

Actual cell potentials are always smaller than the theoretical ones due to irreversible losses. In the figure below shows a typical resulting polarization curve from a fuel cell considering the four main losses: activation, fuel crossover and internal current, ohmic and mass transport-concentration losses.

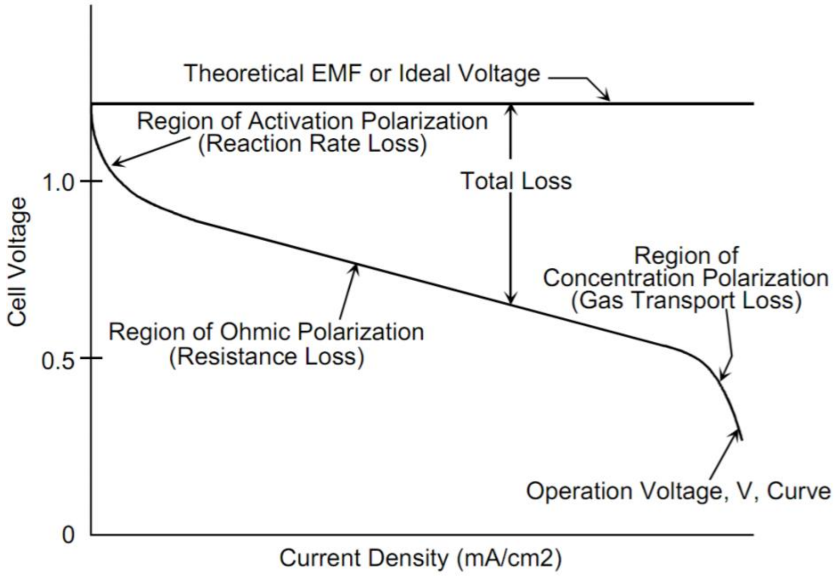


Figure 16: Cell Voltage vs Current Density [25]

- **Activation losses**: This type of voltage loss occurs because energy is needed to activate the reaction, at both the anode and the cathode, and thus chemical energy that could have been transformed to electrical energy is wasted. A slower reaction requires more energy to be started and therefore lead to a more substantial energy loss than a reaction with a higher reaction rate. In PEM fuel cells, activation voltage losses occur mainly at the cathode. These losses can also be lowered by raising the temperature, increasing the roughness (which increases the active surface area), increasing reactant concentration or increasing the pressure. For low- and medium-temperature fuel cells, activation losses are the most important cause of voltage drop. Therefore, it is of the utmost importance to look for better catalyst materials so that the current density is increased and with that the overall performance of the fuel cell.

- **Fuel crossover and internal current** When fuel passes through the electrolyte without reacting at the anode but instead reacts with oxygen at the cathode, it generates two electrons that does not run through the circuit and cannot be utilised in the electrical engine. This issue is called fuel crossover. If hydrogen is split-up at the anode but the two electrons instead go through the electrolyte to the cathode without passing the circuit, what is called an internal current occurs. In both scenarios, two electrons are considered lost. The resulting loss in voltage from these two reasons is dependent on how many moles of reactant gas that is used per second, the more gas usage the higher is the loss in current considered to be.
- **Ohmic losses Voltage:** losses due to electrical resistance in the electrolyte and the bipolar plates are called ohmic losses. The bipolar plates are used to connect multiple cells in series. A few things can be done to reduce the ohmic losses, including to use electrodes with the highest possible conductivity, optimisation of the bipolar plates and to make the electrolyte thinner. However, one cannot make the electrolyte too thin, because it needs to be thick enough to prevent shorting between anode and cathode as well as being a robust structure for electrodes to be built upon.
- **Mass transport and concentration losses:** The partial pressure of reactants is a crucial part to the cell voltage because the higher the reactants partial pressures are the higher voltage becomes. When current is extracted from the fuel cell the partial pressure of both hydrogen and oxygen decreases. The hydrogen partial pressure decreases at the electrode due to a flow back into the supply tubes, so when the rate of supply of hydrogen to the electrodes is not as fast as the consumption of hydrogen the pressure will drop and with that the voltage. At the cathodic side, if the oxygen is fed with air the consumption of oxygen at the electrode requires a good circulation of the air in order to replenish oxygen and keep the oxygen partial pressure at the electrode stable. By designing the flow and circulation of hydrogen and air in the optimal way, the loss of voltage due to mass transport and concentration losses can be minimized.

5.3. Classification

Fuel cells can be classified attended work temperatures, but the most common classification is in order to the type of the inner screen (electrolyte) that defines its applications:

- AFC (Alkaline Fuel Cell)
- PAFC (Phosphoric Acid Fuel Cell)
- SOFC (Solid Oxide Fuel Cell)
- MCFC (Molten Carbonate Fuel Cell)
- DMFC (Direct Methanol Fuel Cell)
- PEMFC (Proton Exchange Membrane Fuel Cell)

5.3.1. AFC (Alkaline Fuel Cell)

The electrodes consist of an organic layer, a hydrophobic layer that prevents the electrolyte from escaping and a conductive metal mesh. The chemical reaction speed is high, and there are several components that can serve as catalysts, without the need for precious materials that make the price more expensive. The electrolyte generally used in this type of fuel cell is an aqueous mixture of potassium hydroxide (KOH) or sodium hydroxide (NaOH), in concentrations of 30-35% by weight. They are low temperature (60-100ºC) cells. The disadvantage is that the oxygen and hydrogen introduced must be pure because the electrolyte reacts with the CO_2 by blocking it. Therefore, air cannot be used to introduce oxygen.

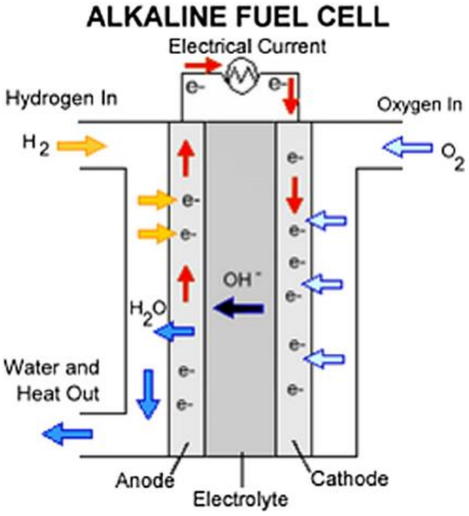


Figure 17: Schematic representation of an alkaline fuel cell (AFC) [5]

5.3.2. PAFC (Phosphoric Acid Fuel Cell)

They use phosphoric acid (H_3PO_4) as an electrolyte. The acids have the advantage that they do not react with CO_2 and therefore the use of pure oxygen and hydrogen is not necessary. In addition, overall yields of up to 85% are achieved.

As a disadvantage, phosphoric acid has a melting point of 42,35 ºC, so at ambient temperature it is normally in a solid state in which it is a very bad ionic conductor. On the other hand, in gas phase conductivity improves, with an optimum temperature between 150 and 200 ºC. Therefore, in order to start operating, a preheating system is necessary which causes the state of the phosphoric acid to change and the temperature to increase. This process will cause the start to be slow.

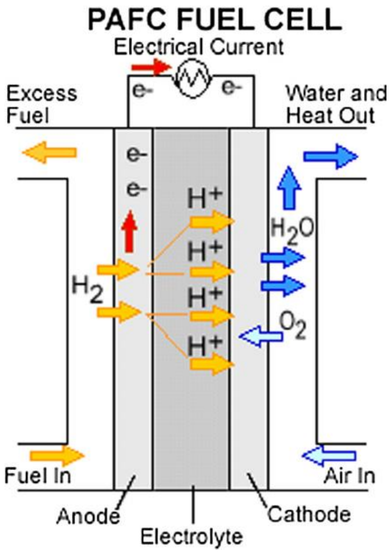


Figure 18: Schematic representation of Phosphoric Acid Fuel Cell (PAFC) [6]

5.3.3. SOFC (Solid Oxide Fuel Cell)

They use solid oxides as electrolyte, that is, impermeable ceramics capable of conducting charge carrying oxygen ions through a crystalline network at high temperature, 800 - 1000 ºC. The electrolyte is a solid and this provides advantages such as stability, safety and reduction of losses due to infiltrations. However, working at high temperature increases the rate of degradation of the materials.

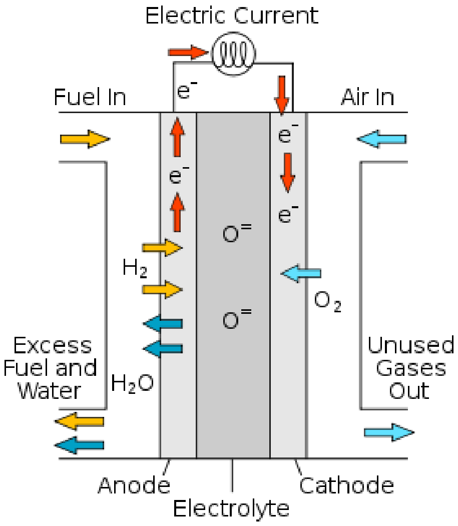


Figure 19: Schematic representation of Solid Oxide Fuel Cell (SOFC) [7]

5.3.4. MCFC (Molten Carbonate Fuel Cell)

It's a molten electrolyte, a mixture of alkaline metal carbonates. It is transported by carbonate ions (CO_3^{2-}) that are consumed at the anode and regenerate at the cathode. The temperature flows in 600 – 650 ºC. It takes this temperature for the electrolyte to be able to conduct. Therefore, its start is very slow, several hours. In this way, platinum is not needed as a catalyst and this reduces the economic costs.

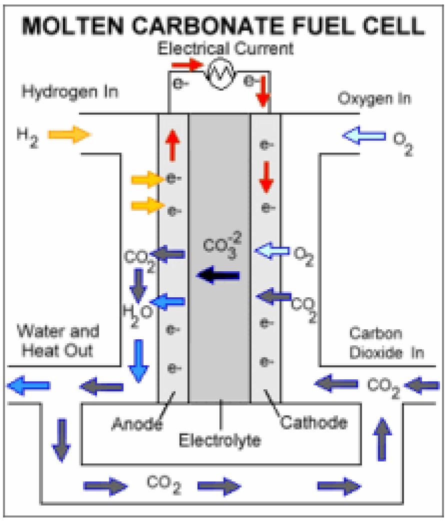


Figure 20: Schematic representation of Molten Carbonate Fuel Cell (MCFC) [8]

5.3.5. DMFC (Direct Methanol Fuel Cell)

The fuel used in this type of cells is not hydrogen, but liquid methanol. The maximum working temperature is 150ºC. Its main use is in the automotive field.

The main advantage is its reduced start-up time and its adaptability to any power. However, it has several disadvantages. One of them is the slow oxidation reaction of the methanol that takes place at the anode. Another disadvantage is due to a fuel crossing as the membrane absorbs methanol and mixes with the water reducing the voltage.

5.3.6. PEMFC (Proton Exchange Membrane Fuel Cell)

In this type of fuel cells, the electrolyte is a polymeric membrane attached to functional groups. It is capable of transporting H^+ ions and the anions are immobilized in the polymer structure. The reactions that occur in the electrodes are:

$$Anode: H_2 \rightarrow 2H^+ + 2e^-$$

$$Cathode: \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

$$Overall\ reaction: H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

The PEMFC produces warm water and electricity using hydrogen and oxygen.

The operating temperature ranges from 60 - 100ºC, temperatures above 100°C are not feasible as the membrane needs to stay humid. There must be enough water content in the polymer electrolyte. The proton conductivity is directly proportional to the water content. However, there must not be so much water to the extent that the electrodes which are bonded to the electrolyte, flood, blocking the pores in the electrodes or the gas diffusion layer. A balance is therefore needed for the water content. The water production from fuel cell and the water drag are both directly proportional to the current. The back diffusion of water from cathode to anode depends on the thickness of the electrolyte membrane and the relative humidity of each side. They are capable to achieve the operative temperature quickly. Also, a low temperature allows for flexible operation and less stringent material requirements that makes it a suitable fuel cell for transportation.

Traditional PEM fuel cells use a solid proton conducting polymer membrane called Nafion, a polyfluorinated sulfonic acid (PFSA) material, which facilitates proton transfer between the anode and cathode. Porous carbon electrodes containing a platinum catalyst act as the metal electrode assemblies (MEAs).

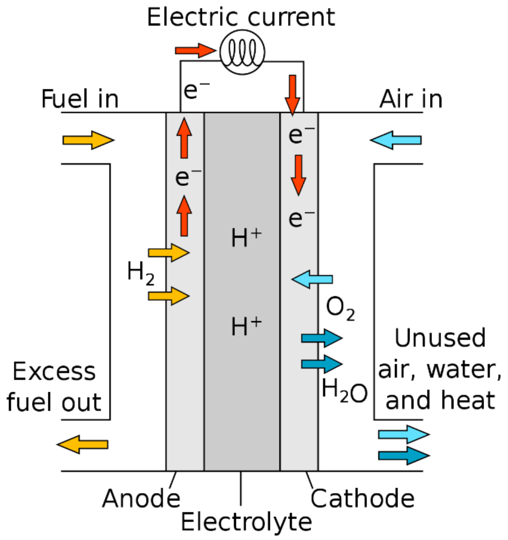


Figure 21: Schematic representation of Proton Exchange Membrane Fuel Cell (PEMFC) [14]

PEMFC is very sensitive to impurities, especially CO, even at very low concentrations. On the other hand, PEMFC has a high tolerance to CO2, so it is possible to use air as an oxygen supply.

The efficiency of this type of fuel cell is relatively lower than the rest, 50-60%, but it's still a high score compared to conventional motors. PEMFCs also have the highest energy density of all current fuel cells.

Its most common use is in the automotive industry due to its simplicity and compactness. The main producer of PEMFC in the world is the Canadian company Ballard Power Systems.

5.4. Comparison of technical characteristic of fuel cell technologies

Fuel Cell Type	Electrolyte	Operating Temperature (°C)	System Output (KW)	Efficiency (%)	Application
AFC	aqueous mixture of KOH or NaOH	60-100	10-100	60	Military, space, backup power
PAFC	H_3PO_4	150-200	50–1000	>40	Distributed generation
SOFC	Solid Oxides	800 - 1000	1-2000	60	Auxiliary power, electric utility, distributed generation
MCFC	Molten lithium, sodium, and/or	600 – 650	1-1000	50	Electric utility, large distributed generation

	potassium carbonates				
DMFC	Liquid methanol	150	0.001–100	40	Transportation, replace batteries in mobiles; computers and other portable devices
PEMFC	Perfluorosulfonic acid	60 - 100	1-250	50-60	Transportation

Table 6: Comparison types of fuel cells [26]

6.STATE OF THE ART OF FUEL CELL AND BATTERY APPLICATION IN SHIPPING

6.1. Conventional Engine in shipping

The most common marine propulsion systems are diesel and only a small part use other systems, based mainly on gas turbines, steam or alternative steam engines.

However, diesel engines have several disadvantages:

- Manufacturing cost;
- Maintenance Complexity;
- Efficiency;
- Noise;
- High emission of pollutants into the atmosphere;

Carbon dioxide (CO2), nitrogen oxides (NOx), sulphur dioxide (SO2), carbon monoxide (CO), hydrocarbons, and primary and secondary particulates are noted as the most important ships emission pollutants due to their role as e.g. greenhouse gas, their contribution to acid rain, and/or their impact on human health.

It is therefore necessary to act on the maritime and port fronts. The International Maritime Organization (IMO) aims to reduce global maritime emissions by 50% by 2050 through the creation of low emission zones. [41]

More specifically, in the Mediterranean area, which is the objective of the study in this project, it has been decided to launch a joint initiative to obtain the declaration of an ECT. It is the combination of SECA and NECA (sulphur and nitrogen oxide emission control area) for the entire Mediterranean Sea.

The application of an ECT in the Mediterranean Sea could reduce SO2 and NOx emissions from international shipping by 80% and 20%, respectively, compared to current legislation. Reducing air pollution concentrations will save 16,000 premature deaths and up to 25 billion euros in health costs. [42]

Another issue to solve in conventional engines is the noise they make. This issue directly affects the studied ferry (RO-RO San Nicolò) because Venice is a city where there is an abundance of ships transporting passengers and cars from one island to another and has an immediate effect on the population.

6.2. New Marine Propulsion System: Fuel Cells

In order to solve the main problems previously mentioned about using traditional engines on board, now it is studied the possibility of implement fuel cells as an alternative.

Fuel cells technology, which is already applied in many land-based systems, is one of many green technologies that have started to be introduced on board vessels. One of the advantages of fuel cells over other technologies is environmental effect of it. The fuel cells have minimum impact of the environment; the only 'exhaust' is water and heat. Other advantages of fuel cells are minimized noise, vibration and less maintenance are required.

The study is based on a comparison between diesel engines and fuel cell systems. Therefore, the feasibility of this new option can be quantified.

6.2.1. Comparing technologies: Fuel Cells and Conventional Engines

In conventional engines, there is always some heat wasted, an efficiency of 100% can never be reached because they are subjected to the Carnot limit. Fuel cells are not subjected to this limit, so high efficiency is possible to reach but they have irreversible losses as already discussed. Next figure shows the efficiency of a fuel cell and a heat engine as function of the operating temperature. From 100°C to 750°C fuel cell efficiency limit is greater than heat engines. As the operating temperature increases above 750°C, the heat engines will have a Carnot limit higher than that of fuel cell efficiency limit.

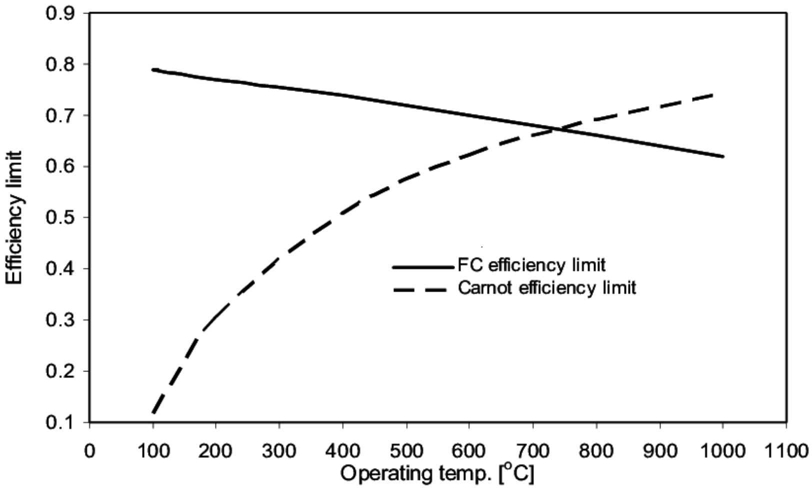


Figure 22: FC limit vs Carnot limit [27]

In heat engines, fuel and oxygen react to generate heat, then heat energy it is converted to mechanical energy and finally into electrical energy. On the contrary, fuel cells convert chemical energy directly into electrical energy. This means that, this direct conversion has a profound impact on the maximum theoretical efficiency of electrochemical devices. With simple thought, there is heat given off to the environment which is considered as a waste product. Thus, the waste heat given off as inefficiency in the fuel cells is less than the combustion engine.

In the figure below it is shown different configurations and their efficiency.

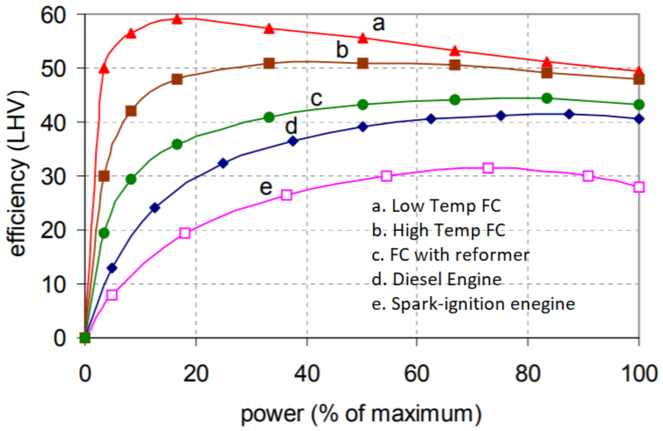


Figure 23: Efficiency vs Power from different configurations [53]

Fuel cells are efficient in part load application. So, they could maintain efficiency through a range of loads. On the contrary, conventional systems are less efficient at partial load.

6.2.2. Fuel Cells Technical Consideration

All systems on-board must be designed and installed in such a way to ensure that general safety is not prejudiced in any way. Therefore, fuel cells systems should meet the specific requirements including such criteria as operational conditions on-board, e.g., temperature, humidity, salinity, system concepts, redundancies, operating methods and noise.

6.2.2.1. Ship integration issues

For it to be possible to integrate fuel cells on board the ship, they must be able to withstand certain conditions to which they may be subjected such as:

- Machine room temperature range from 0 to 55 degrees Celsius;
- Relative humidity up to 96%;
- Adjusting and Pitching…

Considering the functional and operational characteristics of each vessel, the type of fuel cell that best suits the needs and maximizes efficiency is chosen. For example, a cruise ships the most important parameters are comfort, reducing vibrations and noise.

Fuel cells are used as power generation propulsion systems or as Auxiliary Power Units (APUs).

Existing demonstration projects also show the use of various types of fuel cells on board different types of ships with different power ranges.

PEM fuel cells are the most popular type. They were selected because of their high-power density, simplicity of the system and state of the art. MCFCs have been demonstrated for high power units (from 300 kW). The technology is not considered viable for small-scale applications. The efficiency of MCFCs is also superior to that of PEMFCs and does not need noble metals as catalysts.

In addition, the working temperatures of the MCFC are optimal for reforming inside the ship in the case of light hydrocarbons or CH_4, thus taking advantage of the amount of heat released by the stacked cells themselves.

6.2.2.2. Power density

One deficiency of fuel cells is that they are volumetrically inefficient, especially those that use hydrogen as fuel due to its low energy density (MJ/m^3). As it is explained in section 3.2., hydrogen has the lowest energy density comparing with conventional fuels. In addition, methane seems to be the highest power density; nevertheless, other issues such as fuel cells reformers should carefully be considered.

On the other hand, hydrogen has the highest gravimetric energy density (MJ/kg). This means, for the same amount of energy, less kilograms of hydrogen are required in comparison with other fuels.

6.2.2.3. Response to abrupt change or accident

there is still little information available regarding fuel cells response to abrupt changes, such as temperature change due to sudden or large load change during ship manning. There is also not enough literature to show fuel cells resistance to flood, fire and collision or other accident scenarios.

Ballard PEMFCs have been tested in different environments in order to verify the capacity of support critical conditions.

A shock and vibration test of 500W PEM fuel stack was done by Rajalakshmi in order to screen and ascertain the reliability of the stack, mechanical integrity and to assess the mounting requirements. The result showed that the mechanical integrity of the stack is good. The physiochemical properties like electrochemical performance of the stack are in good agreement before and after the vibration and shock test revealing that the individual components of all the 30 cells are intact after the test. Although there was a minor compression force release at the bolts, it is suggested that they can be prevented by damping the vibrations to protection equipment like padding or spring suspension. [29]

6.2.2.4. Maturity of technology

With several demonstration projects all over the world, it seems that fuel cells diffusion on board ships is still in a model stage, which is still in the bottom of the Scurve type in innovation adoption. It is obvious that the fuel cells system on board is still considered an immature technology. And to compete with the existing well understood, proven and reliable technology, with well-established infrastructure and well define economy is not an easy thing.

Small scale existing prototypes will require extrapolation for large commercial ships, with the assumption that fuel cells will behave rationally. Furthermore, performance characteristics traditionally based on historical data, especially those for availability, reliability and maintainability (ARM) with derivation of Mean time to overhaul (MTTO), Mean time between overhaul (MTBO) and Mean Time Between Failure (MTBF) are highly desirable. If supporting evidence is not available, the assessment may be viewed with suspicion; [29]

6.3. LTPEM and HTPEM fuel cell for marine use

The most used and developed type of fuel cells so far is the PEMFC. For this reason, the feasibility of the application of this type of fuel cell in ships will be further explored in this section. Also, the HTPEMs are studied as fuel cells that improve the defects of the PEMs, but that still need to be studied in greater detail.

The PEM fuel cell is a mature technology that has been successfully used in marine and other high energy applications. The technology is available for several applications.

The main advantages of using PEM fuel cell on board are:

- Low working temperatures prevent many corrosion problems and therefore it is not necessary to use materials of such high quality.
- Simplicity and compact construction make them ideal for transport application.
- If it is used pure hydrogen in energy conversion with a PEM fuel cell, would essentially produces water and low-quality heat as the only emissions with zero-emissions.
- Its relative maturity leads to a relatively low cost.
- PEM fuel cells have a large density current. Its range is about 0,1-0,15 $\frac{A}{cm^2}$.
- Tremendous flexibility in power supply.
- Due to low operating temperature, PEM fuel cell has a fast start-up.
- Deliver high power density and offer lighter weight and smaller volume than other fuel cell systems because they have been specifically developed for lower-scale mobility power applications.
- PEM fuel cells are also insensitive to the rocking motions, vibrations, and shocks that can be found on-board maritime vessels.

On the contrary, PEMFCs present some disadvantages:

- The operation requires pure hydrogen because PEMFC is very sensitive to impurities, especially CO and sulphur, even at very low concentrations. CO concentration must be less than 20 ppm.
- If other fuel sources than hydrogen is to be used it needs to be converted to hydrogen prior to injection to the PEMFC. So, fuel reforming must be external.
- Its efficiency is moderate, around 50-60%.
- Due to low temperatures, heat recovery is considered not to be feasible.
- A complex water management system.
- Moderate lifetime.
- A catalyst such as Platinum is needed to accelerate the reaction. This leads to an increase the cost of the fuel cell and it can be poisoned by carbon monoxide (CO) and sulphur (S).

An alternative to solve PEMFCs´ problems are HTPEMs (High Temperature PEMs). The HTPEMFC is a technology that is less mature than conventional low temperature PEM, addressing however some of the problems with the low temperature of the PEM. Operates at 150-180 ºC by using a mineral acid electrolyte instead of water. This gives more CO tolerance, allowing the use of reformed liquid fuels (methanol, ethanol, natural gas...) instead of pure hydrogen. As a result of not needing the humidifiers, air compressor and oversized radiator as in the LTPEM systems, the HTPEM system architecture seems very simple.

	LTPEM	*HTPEM*
CO tolerance	20 pp	30 ppm
Sulphur tolerance	1 ppm	20 ppm

Table 7: CO and S tolerance in LTPEM and HTPEM Fuel Cells [15]

In addition, it is possible to harness the excess heat from the fuel cell in a heat recovery system. The efficiency of HTPEM is like PEM, but the overall efficiency is higher thanks to heat recovery and due to less parasitic losses.

The HTPEMs are arranged in independent modules normally of 5-15 kW, with small reforming units incorporated. The modules are easily assembled into large power sets, which can reach up to 1MW.

The higher operating temperature allows eliminating the need for a clean-up reactor after the reformer. Owing to the tolerance for fuel impurities, simpler, lighter and cheaper reformers can be used to produce hydrogen from a broad range of fuels such as LNG, methanol, ethanol or even oil-based fuels. The operational temperature of up to 200˚C is assumed moderate enough so that tolerance for cycling is not significantly weakened.

As to what fuel cell technology have the best prospects, the question is best answered by considering the application. Smaller and medium applications may favour low and medium temperature technology, such as Proton Exchange Membrane (PEM) and High Temperature PEM. Larger application which can more easily accommodate waste heat solutions, such as industrial and large maritime, are better for the high temperature solutions such as Molten Carbonate or Solid Oxide fuel cells.

6.3.1. Comparison PEMFC and HTPEMFC

The following table illustrates the main parameters of the most promising fuel cell technologies for marine use. The parameters are:

- Cost
- Power (KW)
- Lifetime
- Tolerance for cycling
- Flexibility towards type of fuel cell
- Technological maturity
- Physical size
- Sensitivity for fuel impurities
- Emissions
- Safety aspects
- Efficiency

These above criteria were chosen because they are vital for evaluating if a fuel cell technology is suitable for marine use soon, and for comparing different technology.

	LTPEM	**HTPEM**

Cost	Low	Moderate
Power	Up to 120 KW	Up to 30 KW
Lifetime	Moderate	Unknown
Tolerance for cycling	Good	Good
Fuel	Hydrogen	LNG, Methanol, Diesel, Hydrogen
Maturity	High, extensive experience from several applications including ships	Low, experience some applications including ships
Size	Small	Small
Sensitivity to fuel impurities	Medium	Low
Emissions	No	CO_2 and low levels of NO_x if carbon fuel is used
Safety Aspects	Hydrogen	High temperature (up to 200°C). Hydrogen and CO in reforming unit
Efficiency	50-60%	50-60%

Table 8: Comparison LTPEM vs HTPEM [16]

6.4. Hybrid Fuel Cell/Battery System

The power system of a pure fuel cell has disadvantages like a large power configuration, slow dynamic response and wide range of output voltage variation. In order to overcome these shortcomings, a fuel cell hybrid system is proposed. Hybrid fuel cell propulsion system, which combines a fuel cell and an energy storage system, have been used successfully in different applications which contributes to higher efficiency and reduced CO_2 emissions. This system combines the high energy density of fuel cells and the high-power density of storage. Since fuel cells have a time-delayed response due to their slow dynamics, energy storage devices are usually combined with fuel cells to meet the dynamic and rapid changes in power requirement. For transport applications, batteries, super-capacitors, hydrogen and flywheels are being considered.

Batteries and electrochemical capacitors are higher dynamically than fuel cells as shown in figure 23. Comparing batteries to electrochemical capacitors, batteries have slower response times and charging rates, lower power density and slower discharge cycles. However, batteries have more energy density and higher power range which is important in transportation applications that is why batteries are the main energy storage device for fuel cell applications.

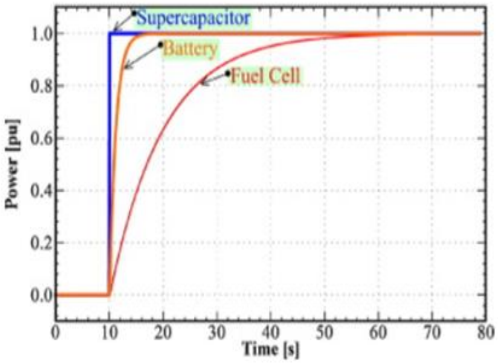


Figure 24: Dynamic classification of fuel cells, batteries and capacitors [18]

The feasibility of using batteries in hybrid applications and the reduction of emissions will depend on the cycle efficiency of the batteries. There are different types of batteries but because of weight and space limitation of naval applications, higher energy density and lighter types must be identified. Table 9 shows a comparison between different battery types:

TYPE	SPECIFIC ENERGY (Wh/Kg)	ENERGY DENSITY (Wh/L)	DURABILITY (years)	COST ($/KWh)
LEAD-ACID	40	65	5-15	300
NIKEL-CADMIUM	60	105	5-20	1150
LITHIUM ION	160	400	5-20	1550
SODIUM-SULPHUR	195	195	15	400
ZINC-BROMINE	73	45	5-20	575

Table 9: Comparison of certain types of batteries [17]

6.4.1. Configurations

Different connection modes of the fuel cell and auxiliary power battery systems are:

- **Simple topology of a hybrid power system**: The fuel cell and the battery systems are directly connected to the load, and the bus voltage will be determined by the battery terminal voltage. In this topology, the voltage level of the fuel cell and the battery is determined by the rated voltage of the load. Only when the voltage level of the DC bus is matched with the load will the system obtain the best energy and economic efficiency. In addition, the output voltage of the fuel cell changes with the output current, which is like the current source, with soft output characteristics and slow dynamic response. In most cases, the output voltage of a fuel cell is lower than the required voltage of the DC bus when the load changes, which makes the energy management of the hybrid power system very difficult and, hence, reduces the efficiency and reliability of the system.

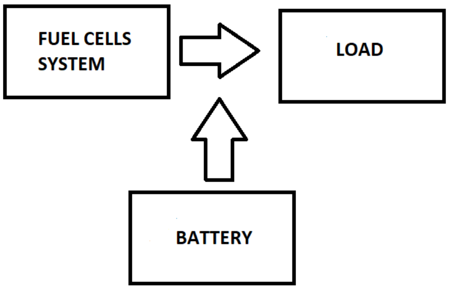


Figure 25: Simple topology without DC/DC converter

- **Battery directly connected to the low voltage bus:** accumulator is connected directly to the low voltage bus, in parallel with the fuel cells: the battery functions as an energy buffer covering peak demand without being able to control the charge and discharge cycles, recharging when the voltage at its extremes is higher than that corresponding to its state of charge, in addition, the necessary correspondence of production and storage voltage levels leads to less system flexibility and difficulty in the choice of components, which can lead to an increase in the complexity of the system. With this configuration, the DC-DC converter is unique and processes all the power required by the user;

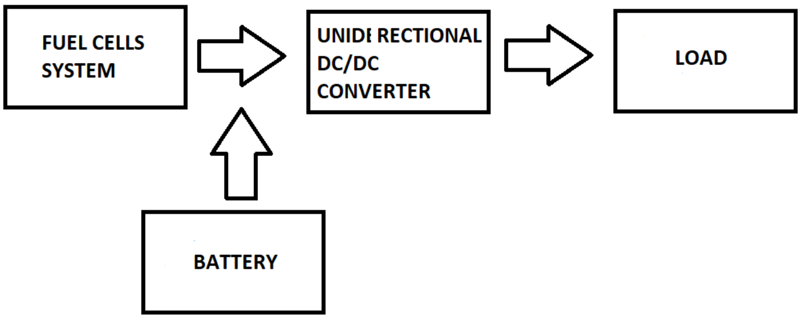


Figure 26: Battery directly connected to the low voltage bus

- **Battery and fuel cell system are connected to two different converters:** the output power of each converter can be controlled and the charging and discharging cycles of the accumulator can be totally managed so as to ensure the correct functioning of the accumulation system; for this configuration it is much easier and more flexible to choose the components and it offers better performance in terms of battery management and coverage of load peaks provided, however, that two DC/DC converters are installed.

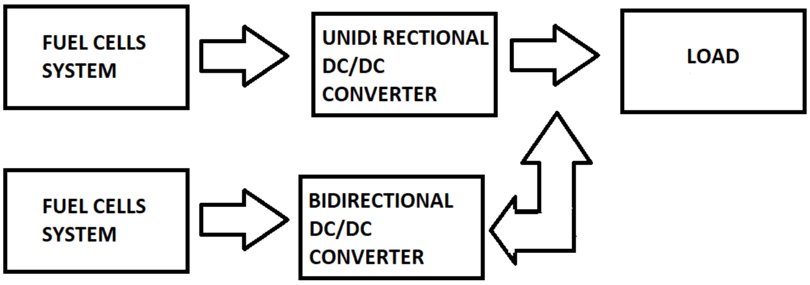


Figure 27: Battery directly connected to the high voltage bus

6.5. Application PEM Fuel Cells in land transport

The vehicles provide the main stimulus for the development of fuel cells, due to the large number of them and being also one of the main contributors to pollution.

Many automobile companies are immersed in automotive fuel cell development programs, including Mazda, Toyota, Nissan, Hyndai...

In following sections, it is described the "Toyota Mirai," a car that is already running based on fuel cells around the world.

6.5.1. Toyota Mirai

An electric vehicle in which electricity is obtained from a hydrogen fuel cell. It is currently commercialized in Japan, the United States and in some European countries such as Denmark, the United Kingdom, Belgium or Germany. The commercialization of the Toyota Mirai in Italy is still not possible since by law the gas stored on board a vehicle cannot exceed the pressure of 350 bar, while the Toyota stores it at 700 bar. Although currently this law has been corrected allowing therefore the sale of this vehicle soon.

The car body has four doors and the passenger compartment has four seats. The exterior dimensions are 4,89 metres long, 1,82 m wide and 1,54 m high. The mass of the Mirai is 1850 kilograms (including the driver and the fluids necessary for the operation of the vehicle). The propulsion system moves the Mirai from 0 to 100 km/h in 9,6 seconds and allows it to reach a top speed of 178 km/h [43]. The Mirai's propulsion system is basically composed of the following elements: an electric motor, a fuel cell, two hydrogen tanks and a battery.

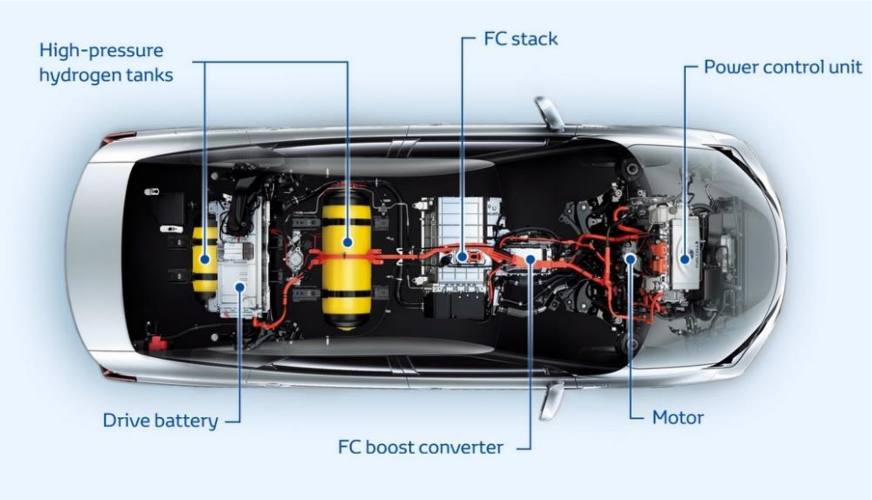


Figure 28: Toyota Mirai Components [33]

6.5.1.1. Electric Motor

The electric motor is positioned in front of the front axle and gives a maximum power of 154 hp. The electricity that feeds it comes mainly from the hydrogen fuel cell, which is located under the front seats. It is a permanent magnet synchronous motor that can produce 154 hp maximum power and 335 Nm maximum torque. It operates at a rated voltage of 650 volts and has its own cooling system, differentiated from that used for the fuel cell. The electric motor is located below the control unit and just in front of the front axle. [43]

6.5.1.2. Fuel Cell

The fuel cell is the main source of power for the electric motor.

The hydrogen cell is a device that makes hydrogen react with oxygen and as a result generates water and electricity. It is made up of 370 cells connected in series (so if one cell fails, the battery stops working). Each cell consists of two porous electrodes (anode and cathode, through which hydrogen and oxygen respectively enter) separated by a polymeric membrane electrolyte that only allows protons to pass through and with a platinum-cobalt alloy catalyst that covers one side of each electrode. Each cell is separated from the consecutive cell by a separator plate and a current collector. The separator plate is metal (contains titanium) and provides battery rigidity and thermal insulation.

The cathode has a special design, such as overlapping flakes, instead of straight and parallel channels as usual. Toyota gives it the name of 3D fine-mesh. It has two advantages over conventional design: first, a better diffusion of oxygen to the catalyst and, second, a better evacuation of water produced during the reaction.

Each cell is 1,34 millimeters thick and can produce a theoretical voltage of 1,23 volts. Since they are all connected in series, the theoretical battery voltage is 455,1 volts (1.23 volts/cell x 370 cells). As the efficiency is not higher than 75%, the actual voltage is lower. [43]

The fuel cell is located below the row of front seats, weighs 56 kilograms and occupies a volume of 37 liters. These values do not take into account the mass and volume of the auxiliary elements (such as the hydrogen recirculation pump), nor the transformer that is coupled to the output of the cell to raise the voltage to 650 volts (the latter has a volume of 13 liters). The fuel cell can produce a maximum power of 154 hp (114 kW). It therefore has an energy density of 3,1 kW/l or 2,0 kW/kg. [43]

The solid electrolyte is permeable to positive H+ ions (protons). The electrolyte must be replaced every 60000 km and in order for it to perform its function correctly, it needs to have a certain level of humidity. This is usually achieved by a specific circuit with a humidifier. Toyota has dispensed with it because they use the water generated in the hydrogen's reaction with oxygen as the water source to regulate the humidity.

Toyota has tested the fuel cell at very low temperatures to make sure that the water produced in the reaction does not freeze or cause problems as a result. One of these was held in Yelowknife, Canada, and consisted of leaving a Mirai parked for 17 hours at temperatures between 20 and 30 degrees below zero. Thirty-five seconds after starting the vehicle, the fuel cell gave 60% of its performance when the accelerator was fully depressed. At seventy seconds, the performance of the battery reached 100%.

To prevent the water generated by the battery from freezing when the vehicle is parked, the circuit must be purged at the push of a button. All the accumulated water is then expelled through a nozzle at the rear of the car's underbody. The Mirai produces an average of 7 litres of water per 100 kilometres.

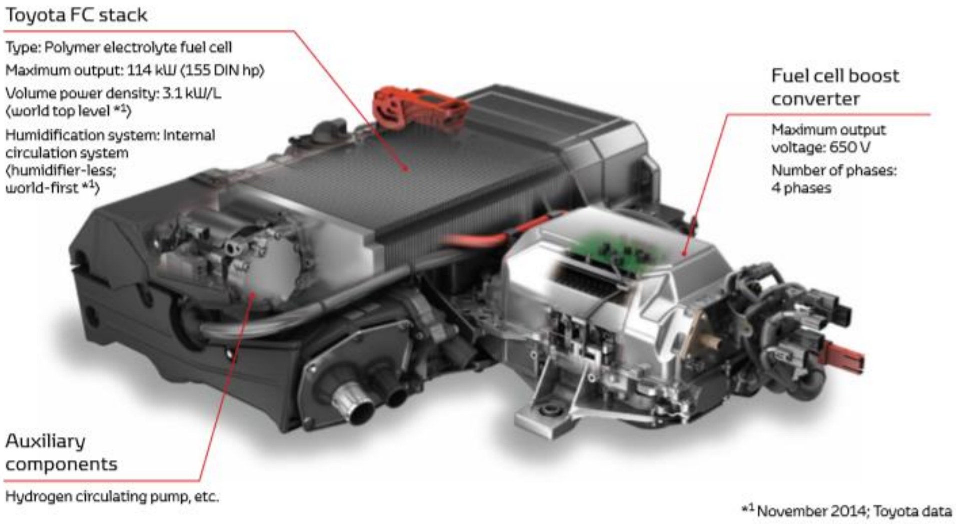


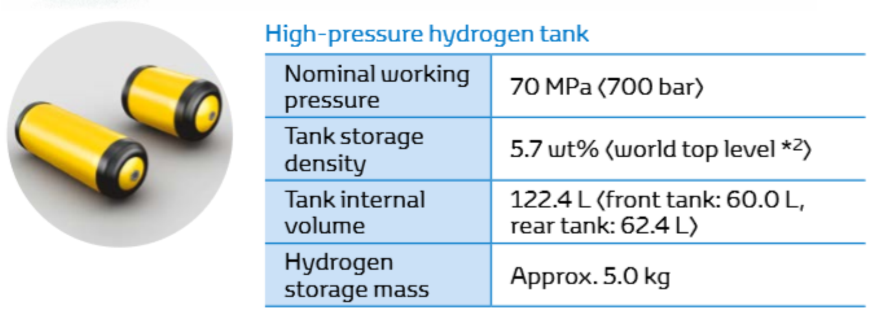
Figure 29: Fuel Cell stack assembly Toyota Mirai [33]

6.5.1.3. Hydrogen Storage

Oxygen is obtained from air and hydrogen is stored in two tanks, one under the rear seats and the other behind them. One of them has a capacity of 60 liters and another of 62,4 liters, in total there are 122,4 liters in which approximately 5,0 kilograms of hydrogen can be stored at 700 bar pressure. With higher pressure more hydrogen can be introduced into the tanks, however, the extra energy cost and material reinforcements required are not compensated for by the increased storage, [43]. On the other hand, 700 bar is the filling pressure that has been agreed as standard in Europe, the United States and Japan. The tanks are manufactured by Toyota and use three layers of material. The inner face is made of a plastic polymer with very low hydrogen permeability. The intermediate layer is made of carbon fibre reinforced plastic and is the one that gives the rigidity to the tank to withstand the pressure. The outer layer is made of fiberglass reinforced plastic.

In order to fill the tanks, it is necessary to use a jet that can supply hydrogen at 700 bar (this pressure is a standard used in Europe, the United States and Japan). It takes between 3 and 5 minutes to fill the hydrogen tanks.

The pressure and temperature of the hydrogen inside the tanks are controlled by sensors, whose information is transmitted via infrared to the hydrogen pump nozzle to determine how much fuel needs to be supplied.



High-pressure hydrogen tank

Nominal working pressure	70 MPa (700 bar)
Tank storage density	5.7 wt% (world top level *2)
Tank internal volume	122.4 L (front tank: 60.0 L, rear tank: 62.4 L)
Hydrogen storage mass	Approx. 5.0 kg

Figure 30: High-pressure Hydrogen Tanks Toyota Mirai [33]

6.5.1.4. Battery

The battery is NiMH (nickel metal hydride) type and has a capacity of 1,6 kWh. It has two functions: the first is to store the electricity generated in the deceleration phases and by the battery; the second is to feed the electric motor to move the Mirai (either alone or adding its force to that of the battery). By itself it gives an autonomy of about two kilometres.

The battery is placed above the second hydrogen tank, i.e. between the backrests of the rear seats and the luggage compartment. It is made of nickel and metal hydride, consists of 34 cells connected in series, has a capacity of 1,6 kWh and generates a voltage of 244 volts, [43].

Its function is to move the car during the first metres, support the fuel cell during the acceleration phases that require it and store the energy produced during the deceleration phases, as well as that produced by the fuel cell.

6.5.1.5. Consumption calculation

According to the NEDC homologation cycle, the Mirai consumes an average of 0,76 kilograms of hydrogen per 100 km and has a range of 550 km, [43].

An electronic control unit manages the energy flows between the battery, the battery and the electric motor and determines how much power is required from the battery and the battery according to the driver's demand for acceleration. For example, under strong acceleration demand, the fuel cell and battery together provide power to the electric motor.

During the deceleration phases, a part of the car's kinetic energy is transformed into electrical energy, which is directed to the battery for recharging. During these phases, as well as in others where the power demand is low, the fuel cell also helps to recharge the battery.

In the case of the fuel consumption (g/s) of the Toyota Mirai fuel cell as it is not provided by the supplier, then it has been calculated in the following estimated way:

Bottle 1 has a volume of 62,4 litres and the other bottle 60 litres. In total there are 122,4 litres in which approximately 5 kg of hydrogen is stored. Therefore, the density of hydrogen under these conditions can be calculated as:

$$\rho_{H_2} = \frac{5\,kg}{122{,}4 * 10^{-3}\,m^3} = 41\frac{Kg}{m^3}$$

The fuel cell data sheet indicates that the capacity storage density of both bottles is 5.7% by weight. Therefore:

$$Bottle\ 1 \begin{cases} m_{H_2} = 62{,}4 * 10^{-3} * 41\dfrac{Kg}{m^3} = 2{,}55\,Kg \\ m_{H_2+bottle} = 2{,}55\,Kg + 100 * \dfrac{2{,}55}{5{,}7}Kg = 47{,}27\,Kg \end{cases}$$

$$Bottle\ 2 \begin{cases} m_{H_2} = 60 * 10^{-3} * 41\dfrac{Kg}{m^3} = 2{,}45\,Kg \\ m_{H_2+bottle} = 2{,}45\,Kg + 100 * \dfrac{2{,}45}{5{,}7}Kg = 45{,}45\,Kg \end{cases}$$

The autonomy in time can be calculated from the relationship between the autonomy in distance and the average speed. An average speed of 100 km/h is assumed:

$$\text{Autonomy (h)} = \frac{\text{Autonomy (km)}}{\text{Velocity}\left(\frac{\text{km}}{\text{h}}\right)} = \frac{550}{100} = 5{,}5\,h$$

$$Fuel\ Consumption = \frac{m_{H_2}}{Autonomy(h)} = \frac{2{,}55 + 2{,}45}{5{,}5} = 0{,}91\,\frac{kg}{h} = 0{,}25\,\frac{g}{s}$$

If a 20% error is made in the calculations, the hydrogen consumption is finally 0,3 g/s.

6.6. Application PEM Fuel Cells in Ferries

PEM Fuel Cells offer a zero emission and low noise polluting alternative especially for short distance connections.

This section it is focus on the study of two passenger ships: Alsterwasser and SF-BREEZE.

6.6.1. “Alsterwasser”, Hamburg

In August 2008, “Alsterwasser” was the first inland passenger ship in the world to set off under fuel cell propulsion, and with hydrogen as its source of energy. This is made possible by integrating a hybrid fuel cell and battery-based propulsion system, instead of using a diesel electric system.

This project was launched in November 2006 and ended in April 2010. It is leaded by the company ATG in Hamburg. The hybrid electro-fuel cell system has been developed by Proton Motor and responsible for the development and operation of the hydrogen fuelling station is the Linde Group.

The ZemShip project consists of designing, building and test an emission-free passenger boat called “Alsterwasser”. Alsterwasser was built to sail on regular trips around Alster lake at the heart of the city. The main aim is to test practical emission-free ship operation and to promote the use of this technology for maritime applications, [44].

From November 2006 to December 2008 took placed planning phase for FCS Alsterwasser and fuelling station. After that, began construction phase ship and hydrogen fuelling station including the integration of fuel-cell system. In August 2008, the prototype ship FCS Alsterwasser was delivered and started its regular service. Collection and evaluation of operation data and the hydrogen fuelling station began. In 2010, the battery system and parts of the vessel were damaged by a fire onboard. All damages were repaired and in 2013 Alsterwasser returned to regular operation but in 2014 was a decommissioning of the refuelling station. [45]

Figure 31: Alsterwasser Ship [20]

- **The vessel:**

SPECIFICATIONS OF THE SHIP	
Length	25,56 m
Width	5,20 m
Passenger capacity	100
Displacement of water	72000 kg
Maximum speed	15 km/h

Table 10: Features Alsterwasser Ship [44]

- **Engine and propulsion system:** Alsterwasser integrate a hybrid system: fuel cell and battery-based propulsion.

  The fuel cell system is made up of two identical PEM fuel cells, which operate in a separated way, one of each with a peak output of 48 kW. They are of the ‘PM A Basic 50 maritime’ construction series by Proton Motor. Not only are they particularly powerful, they are also extremely robust. The fuel cell stacks are installed optimally together, with all the important peripheral systems such as cooling, and air supply incorporated in a single compact assembly. This means that, the system is suitable for various applications and can be used on ships of different sizes and powers. The electro-chemical fuel cell process is entirely pollutant-free.

Figure 32: PM Basic A 50 maritime PEMFC from Proton Motors [21]

The other element that completes the hybrid propulsion system is the pack of seven batteries with a total capacity of 560 V and 360 Ah delivered by Proton Motor. The battery pack integrated in the system buffer temporarily the energy delivered by the fuel cell to supply the electric motor on demand. Due to the convenient fact that the system can run in partial-load or load-change mode, its effectiveness under normal operation is twice that of diesel propulsion. Demand-controlled energy management by battery is intended to guarantee operation at peak user hours. On the other, it lightens the load on the fuel cells while docking and casting-off procedures and so prolongs their life cycle substantially. Apart from having an intelligent energy management, the FCS Alsterwasser also has a low-energy water management system. It saves time, energy and work by moistening the external fuel cell membrane and re-filling de-ionised water.

SPECIFICATION FUELL CELLS AND BATTERIES	
Type of fuel cell	Proton Motor PM 600 Proton-Exchange-Membrane (PEM)
Type of fuel cell system	Proton Motor “PM Basic A 50 maritime”
Fuel cell peak power	48 x 2 KW
PEMFC voltage	140-260 V
PEMFC current	280-520 A
Max. System Efficiency	> 50 %
Total weight of fuel cell system	1000 kg
Size of single fuel cell system	2200 x 1100 x 900 mm
Buffer Battery	Lead-gel Battery 560 V (7 x 80 V), 360 Ah
Type of electric motor	AC motor, (100 kW)

Table 11: Specifications about fuel cells and batteries installed onboard [46]

- **Hydrogen Storage:** The Alsterwasser can store up to 50 kg of compressed hydrogen distributed in 12 tanks at a pressure of 350 bar. This quantity is enough to provide a continuous autonomy power of approximately three days of operation.
  The Linde Group is the company in charge of the design and assembly of the hydrogen refuelling station. It has designed a totally innovative and pioneering solution in the sector. It is a service station that uses a unique process based on **ionic compression**, without the need of mechanical pistons.

The ship filling process has several phases. First, a tank truck transports the liquid hydrogen to the refuelling station. Once there, it is stored in cryotanks at -253ºC. When the vessel is being refuelled, the liquid hydrogen evaporates and is compressed to an initial pressure of 25 bar. The pressure of 290 bar is then reached using ionic compression. And finally, it is compressed to 350 bar. [46]

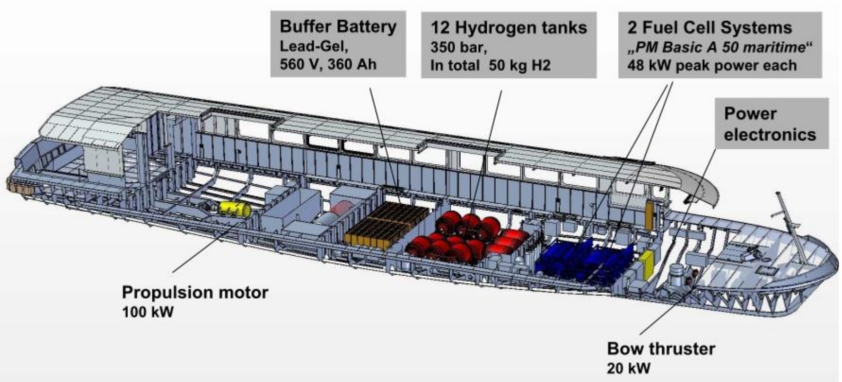


Figure 33: The FCS "Alsterwasser" [22]

IONIC COMPRESSOR IC90, LINDE GROUP:

It is made up of five-stage compression that allows continuous and fast high-performance fuelling at lower operating costs. Efficiency is also a big plus with energy savings of around 30% compared to traditional compressors.

Ionic compression has several advantages over the conventional method:

- It is a highly efficient process providing the required quantity.
- Ordinary compressors use mechanically driven pistons in reciprocating motion to compress the gas in cylinders before being discharged. The pistons cannot be lubricated by oil, since the oil would evaporate and impurify the hydrogen; hence they need to run dry, which is a big challenge to materials and mechanics. One difference of Linde's ionic compressor lies in the fact that the pistons are lubricated by an ionic liquid which moves up and down in a similar fashion. The main advantage of the liquid, however, is that it allows nearly 100% of the compression space to be used. The specially designed ionic liquids are nearly incompressible and because they do not have a vapour pressure, they do not evaporate or mix with the hydrogen. What is even more, they cool the hydrogen during the compression and make sure there is no dead volume at the end of the cylinder, which increases the energetic efficiency of the compressor.
- In addition, it is a fast compression. It only takes 12 minutes to fill up to 50 kg of compressed hydrogen.

It is a high-performance solution that has an approved design and is easy to operate. It allows for quick, safe, highly efficient and economical fuelling of hydrogen vehicles at 35 or 70MPa. The basic principle is the replacement of the conventional metal piston with a specially designed, nearly incompressible **ionic liquid**. The gas is compressed in the cylinder by the up-and-down motion of the liquid column, like the reciprocating motion of an ordinary piston. The ionic compression technology has been approved and is already in operation at several hydrogen fuelling stations around the world. The setup consists of either a cryogenic liquid or compressed gaseous hydrogen tank, or an on-site production unit for hydrogen supply. The compression station is built into a transportable steel container. The electrical system and the compressor/storage compartments are separated by a gas-tight wall. All controls and electrical power switch gear are in electronics compartments. A pressure discharge vent is in the roof of the gas compartment. In order to use stored pressure and compressor capacity in the most cost-efficient manner, the station has a three-bank cascade system. It consists of three pressure storage banks (buffer sections), in which the hydrogen for the fuelling is stored. Subsequently, the fuelling can be carried out through Linde's external 35/70-MPa hydrogen dispenser. The initial vehicle pressure is determined by a test pulse. Based on this test measurement and taking the ambient and hydrogen temperature into account, the final vehicle target pressure is calculated. The fuelling process starts with the equalisation of the low-pressure bank, followed by the equalisation of the medium pressure and the high-pressure bank. The selection of the bank system is based on the pressure ramp. The quantity of hydrogen dispensed is recorded using a mass flow meter with support for standard trading systems, [30].

Figure 34: Ionic compressor IC90 [30]

6.6.2. "SF-BREEZE", San Francisco

SF-BREEZE (San Francisco Bay Renewable Energy Electric vessel with Zero Emissions) is a collaboration project between Sandia National Laboratories, The red and White Fleet, the American Bureau of Shipping, the U.S. Coast Guard and naval architect Elliott Bay Design Group.

The project started in 2015 and is a feasibility study to examine the technical, regulatory and economic aspects of building and operating a high-speed hydrogen fuel cell passenger ferry and hydrogen refuelling station in San Francisco. The project aims to design, build and operate a 150 passengers high-speed hydrogen fuel cell passenger ferry using a PEM fuel cells and liquid hydrogen as fuel. Two branches of the project were formed: one task focused on technical and regulatory feasibility of the high-speed ferry and the other on the feasibility of the required of a refuelling infrastructure. In January 2018 another report was done in order to optimize the fuel cell ferry design, [48].

- **Technical specifications:** SF-BREEZE is designed to carry passengers from Vallejo to San Francisco. This route is shown in Figure 35: **Route SF-BREEZE [31]**.

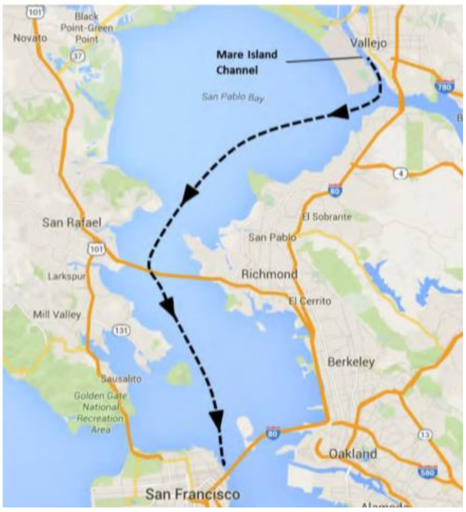


Figure 35: Route SF-BREEZE [31]

The maximum speed achieved is 35 knots. The route takes around one hour and 44,45 km of distance.

- **Fuel Cell selection:** In this section the different propulsion possibilities for the ship "SF-BREEZE" are studied. It focuses especially on PEM-type fuel cells from the world's largest suppliers: Ballard Power System, Hydrogenics and Proton Motors.

Ballard Power Systems: This company is a developer and manufacturer of Proton Exchange Membrane (PEM) fuel cell products for markets such as heavy-duty, portable power, material handling as well as technology solutions including engineering services. Ballard has designed and shipped over 250 MW of fuel cell products to date. Ballard was founded in 1979 to conduct research and development on high-energy lithium batteries. In 1983, In the course of investigating environmentally clean energy systems with commercial potential, Ballard began working on the development of PEM fuel cells. The company manufactures fuel cells for different transport sectors such as buses, trains, ships, etc.

In the marine field:

- Ballard provides modular power solutions from 100kW to multi-MW power systems for marine applications.
- Marine environment compliant with hydrogen safe stack compartment.
- Integrated power management systems and controls.
- Scalable and flexible integration of the one-deck-high system into the ship architecture and grid.

FCveloCity is a PEM fuel cell developed specially for mobility applications. It is available in various configurations between 30 KW and 200 KW. In the table below is summarize the main models:

PRODUCT SERIES	FCveloCity MD	FCveloCity HD	FCveloCity XD

Net Power Level	30 KW	60 KW, 85 KW, 100 KW	200 KW
Application	Small transit buses, battery hybrid range extenders	Full size hybrid electric buses	Light rail and marine applications

Table 12: Products from Ballard Power System company [23]

Specially, FCveloCity 90 KW HD is described in the following table:

Net Power	90 KW
Operating Voltage Range	280 - 420 V
Rated Net Current	288 A
Dimensions	1130 x 869 x 506 mm
Weight	256 kg

Table 13: FCveloCity 90 KW HD characteristics from Ballard Power System company [23]

Hydrogenics, Inc: It is the worldwide leader in designing, manufacturing, building and installing industrial and commercial Hydrogen generation, Hydrogen fuel cells and MW-scale energy storage solutions. They offer:

- PEM and alkaline Hydrogen generators for Industrial processes and Fueling stations.
- Hydrogen fuel cells for electric vehicles, such as urban transit buses, commercial fleets, utility vehicles and electric lift trucks.
- Fuel cell installations for freestanding electrical power plants, critical power and UPS systems (uninterruptible power supply).
- “Power-to-Gas” the world’s most innovative way to store and transport energy.

Hydrogenics manufactures a “building block” 33 kW PEM fuel cell, the model HyPM HD30. The table below shows the main specifications of the fuel cell:

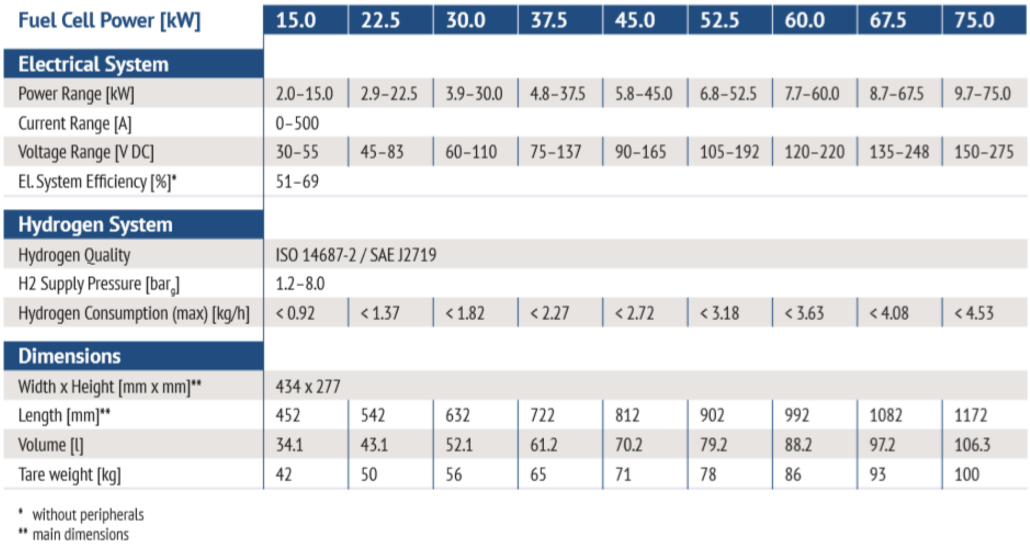
Net Power	33 KW
Operating Voltage Range	60-120 V
Rated Current	0-500 A
Dimensions	719 x 406 x 261 mm
Weight	72 kg

Table 14: HyPM- HD30 characteristics from Hydrogenics [19]

Proton Motors: It was founded in 1980, Germay. Began with “Missing Link Development” of hydrogen fuel cell technology for a fully electric vehicle platform. Nowadays, Proton Motor address stationary, mobile and maritime applications with integrated energy supply concepts. Applications for buses, commercial vehicles, ships and stationary power generation.

Proton Motors have designed two PEM fuel cells prototypes: PM 200 AND PM 400 which are ideal for multiple energy applications.

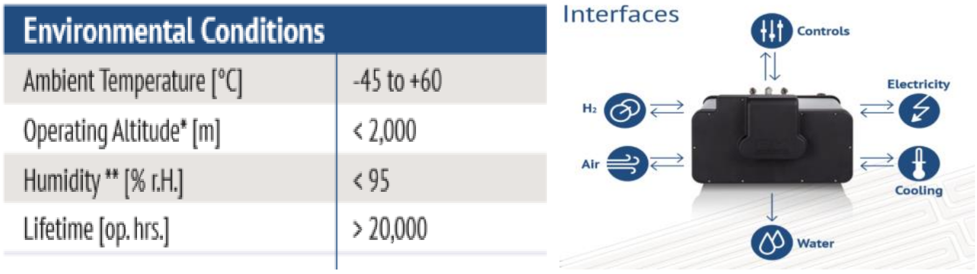
The following images illustrate the PEM 400 DataSheet:



Fuel Cell Power [kW]	15.0	22.5	30.0	37.5	45.0	52.5	60.0	67.5	75.0
Electrical System									
Power Range [kW]	2.0–15.0	2.9–22.5	3.9–30.0	4.8–37.5	5.8–45.0	6.8–52.5	7.7–60.0	8.7–67.5	9.7–75.0
Current Range [A]	0–500								
Voltage Range [V DC]	30–55	45–83	60–110	75–137	90–165	105–192	120–220	135–248	150–275
El. System Efficiency [%]*	51–69								
Hydrogen System									
Hydrogen Quality	ISO 14687-2 / SAE J2719								
H2 Supply Pressure [bar_g]	1.2–8.0								
Hydrogen Consumption (max) [kg/h]	< 0.92	< 1.37	< 1.82	< 2.27	< 2.72	< 3.18	< 3.63	< 4.08	< 4.53
Dimensions									
Width x Height [mm x mm]**	434 x 277								
Length [mm]**	452	542	632	722	812	902	992	1082	1172
Volume [l]	34.1	43.1	52.1	61.2	70.2	79.2	88.2	97.2	106.3
Tare weight [kg]	42	50	56	65	71	78	86	93	100

* without peripherals
** main dimensions

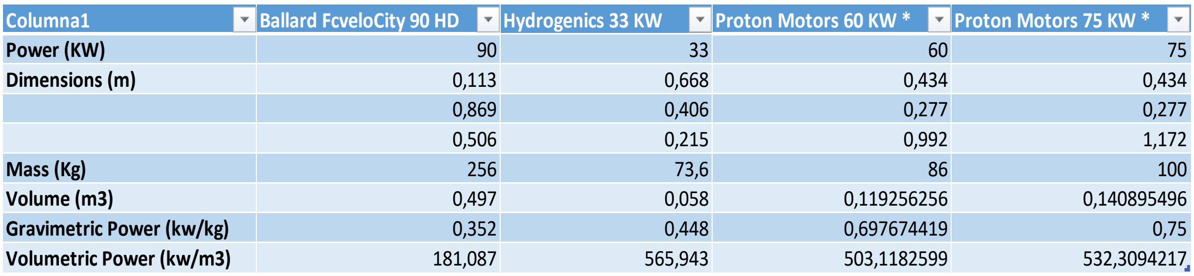
Figure 36: DataSheet PEM 400 from Proton Motors Company [21]



Environmental Conditions	
Ambient Temperature [°C]	-45 to +60
Operating Altitude* [m]	< 2,000
Humidity ** [% r.H.]	< 95
Lifetime [op. hrs.]	> 20,000

Figure 37: DataSheet PEM 400 from Proton Motors Company [21]

Next table lists the gravimetric and volumetric power specification for the fuel cell systems examined. The last two columns with (*) of the table have been calculated with Excel. In this case, the Proton Motors units provide the highest gravimetric power density. However, the Hydrogenics unit provides the highest volumetric power density.



Columna1	Ballard FcveloCity 90 HD	Hydrogenics 33 KW	Proton Motors 60 KW *	Proton Motors 75 KW *
Power (KW)	90	33	60	75
Dimensions (m)	0,113	0,668	0,434	0,434
	0,869	0,406	0,277	0,277
	0,506	0,215	0,992	1,172
Mass (Kg)	256	73,6	86	100
Volume (m3)	0,497	0,058	0,119256256	0,140895496
Gravimetric Power (kw/kg)	0,352	0,448	0,697674419	0,75
Volumetric Power (kw/m3)	181,087	565,943	503,1182599	532,3094217

Table 15: Comparison gravimetric and volumetric power from different companies [31]

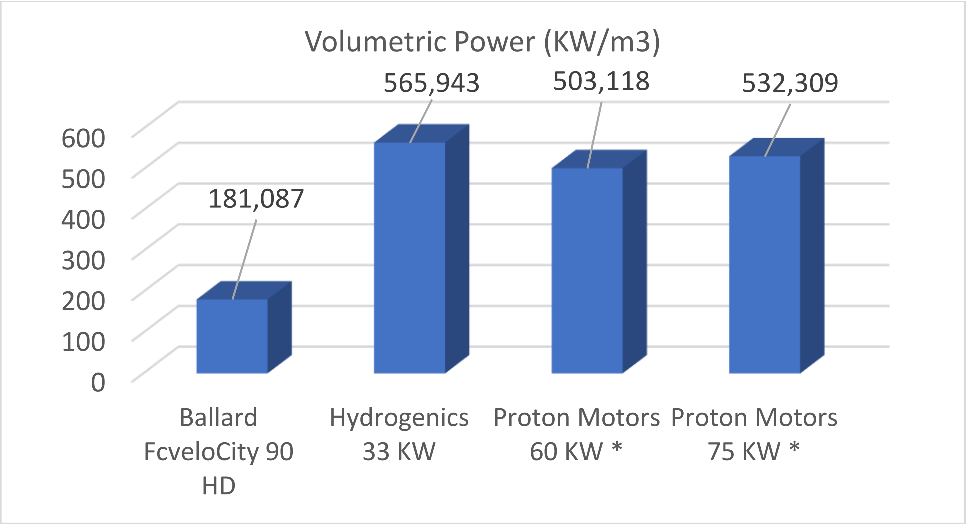


Figure 38: Volumetric Power (kw/m^3) of fuel cells from different companies [31]

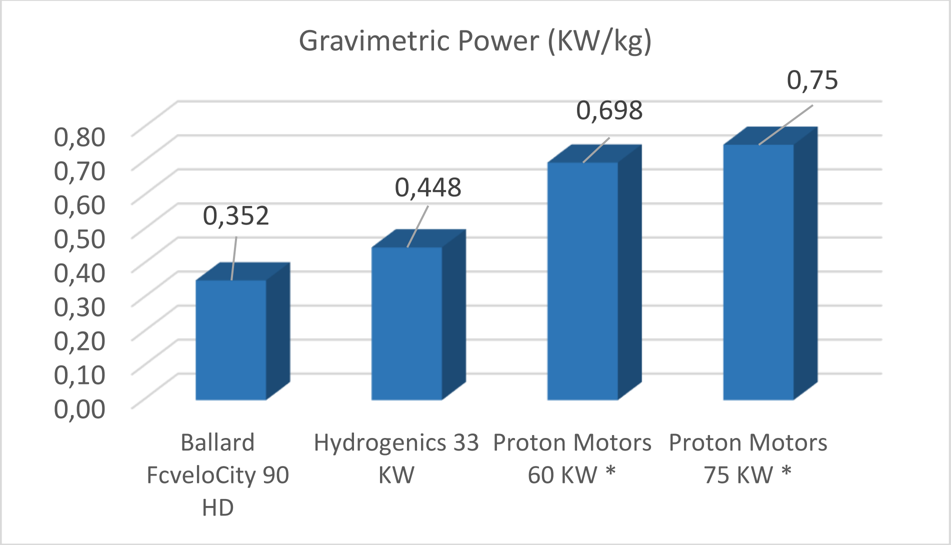


Figure 39: Gravimetric Power (kw/kg) of fuel cells from different companies [31]

In conclusion, the best suitable fuel cell for SF-BREEZE is Hydrogenics 33 KW due to its higher volumetric power density. Although it has not the highest gravimetric power density, the difference is minimal.

7.Analysis of the application of a fuel cell system on board of a Venice ferry

In following sections, the project focuses on the study of a specific ship. It is a ferry RO-RO that transports passengers and vehicles through the Venice area. The aim is to study the preliminary technical feasibility study of replacing the principal conventional engines and auxiliary’s engine currently used, by a hybrid system consisting on PEM fuel cells and a Battery

Energy Storage that work together. In this way, the power is satisfied without harming the environment and with a satisfactory efficiency. The model and calculations were performed using Matlab and Microsoft Office Excel software.

This ferry studied is called San Nicolò and belongs to the company ACTV. ACTV is a public transport company founded in Venice in 1881. Currently, it provides naval service in Venice, urban bus service in Mestre, Lido and Chioggia and extra-urban bus service in 45 communities in the provinces of Venice, Padua, Treviso and Rovigo. The ACTV Naval Fleet consists of 151 mobile units. In detail, the type of fleet includes steamboats, motorboats, single agent motorboats, powerboats and seven ferry ships for the transport of vehicles. All mobile vessels are registered by RINA (Registro Navale Italiano), which certifies their structural efficiency, safety and quality of maintenance operations, [50].

7.1. San Nicolò - Passanger/RO-RO Cargo Ship

The San Nicolò maritime ship was built in 1998 and is currently sailing under the Italian flag. Its function, as a RO-RO ship, is to transport passengers and cars from the port of Lido (San Nicolò) to the Tronchetto Ferry Terminal and vice versa. It belongs to line 17 of the company ACTV. The ferry is in service 24 hours a day, 7 days a week. The journey takes 35 minutes to cover 8 km.

Figure 40: San Nicolò Ferry [24]

The following table shows the main features of the ferry and route specifications:

NAME:	San Nicolò	**FUEL:**	Diesel
LENGTH:	57,85 m	**ENEGINE POWER:**	2 x 637 kW (tot. 1274 kW)
MAXIMUM WIDTH:	13,12 m	**PROPELLERS:**	2 fixed pitch
MAXIMUM SPEED:	8 kn	**AUX. POWER**	2 x 200
AVERAGE SPEED:	6 kn	**TRAVEL DISTANCE:**	8000 m
GROSS TONNAGE:	630 t	**TRAVEL DURATION:**	35 min
DEADWEIGHT:	500 t		

Table 16: Main features of San Nicolò and route specifications [24]

The route is defined in the following image:

Figure 41: San Nicolò´s route

7.2. Analysis Power/Speed Curve

A graphic has been made using Excel programme. It represents the engine´s power as a function of speed. The plotted curve is approximately a third-degree polynomial curve [47], whose equation is given in the graphic. The curve has been calculated from the data provided by the company ACTV summarized in Table 17**Table 17: Power (kW) and fuel consumption (kg/h) provided by ACTV**. These power data refer to the final power, i.e. it is the final power after discounting all system losses (electrical efficiency, mechanics, friction losses, etc...). Therefore, in the Matlab simulation higher power values will be used.

	POWER (kW)	CONSUMPTION (Kg/h)
VELOCITY = 6 kn	132 x 2	27,5 x 2
VELOCITY = 8 kn	192 x 2	39,9 x2

Table 17: Power (kW) and fuel consumption (kg/h) provided by ACTV

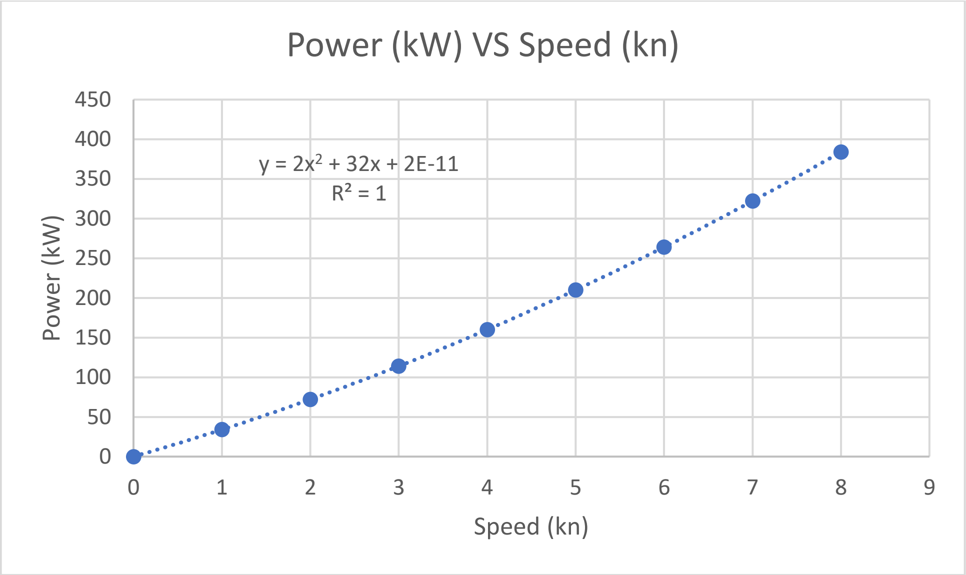


Figure 42: Power (kW) vs Speed (kn)

7.3. Energy Model

The energy variability in a system relative to time is defined by the following equation:

$$\frac{dE}{dt} = P_{IN} - P_{OUT}$$

Where:

P_{IN} : This is the power supplied by electricity generation systems, such as in this case the fuel cell.

P_{OUT} : It is the power consumed by propulsion and auxiliary engines.

If the equation is integrated by taking a particular time range, Δt, now the equation is:

$$E_{t_i+\Delta t} - E_{t_i} = \left(P_{IN} - \sum P_{OUT}\right)_{t_i} \cdot \Delta t$$

This formula has been implemented in Matlab fixed a certain period of time, of the order of seconds until completing the 24 hours of the day.

Before starting the simulation in Matlab, a preliminary estimation has been done in order to know about the amount of hydrogen that the new system may use. For this purpose, the company ACTV has kindly provided us with the diesel consumption of the main and auxiliary engines of the last three months. From this information, it is obtained that the average consumption of diesel is 78 kg/h. Assuming an efficiency of the main and auxiliary engines of 30% and a fuel cell which has an efficiency of 47%, the hydrogen consumption is approximately 430 kg.

For the design of the model power consumption of the ferry throughout the day has been based on the schedules provided by the company ACTV of line 17 a weekday. In addition, a certain number of hypotheses have been assumed:

- The study day is a usual working day from midweek.
- San Nicolò does twenty-four trips during the day. Each one takes 35 minutes, of which the first 8 minutes are at full power (8 kn), when the ferry is sailing between the two islands of Giudecca and Venice, slow down to 6 kn and it takes 20 minutes. The last 7 minutes, the ferry sails again at full power. In order to simplify, it has been estimated that the first 15 minutes are at full power (velocity 8 kn), and the remaining 20 minutes the ferry runs at approximately 0,69 of full power (velocity 6 kn).
- A ferry like this, which operates for short distances, is mainly composed of the propulsive power required only during navigation and a minority share always present due to auxiliary services.
- The power of the auxiliaries has been fixed at 150 kW in operation 24 h, even if the ferry is moored. Except during the night, the consumption is totally null.
- The mechanical propulsive power used during navigation varies between 452 and 362 kW during the day, to take into account the lower traffic intensity during the afternoon and night.
- An overall efficiency of the system of 85% has been hypothesised.
- A load curve has been estimated that peaks in the central hours of the morning and decreases throughout the afternoon until night. Its values range from 0,8 to 1.
- In this preliminary analysis the weight and volume for the power electronic has not been considered.

7.4. Results

The first figure resulting from the simulation is the load profile of the propulsion engine from the above assumptions. Figure 43 shows the pattern of demand on each journey with its maximum power requirement.

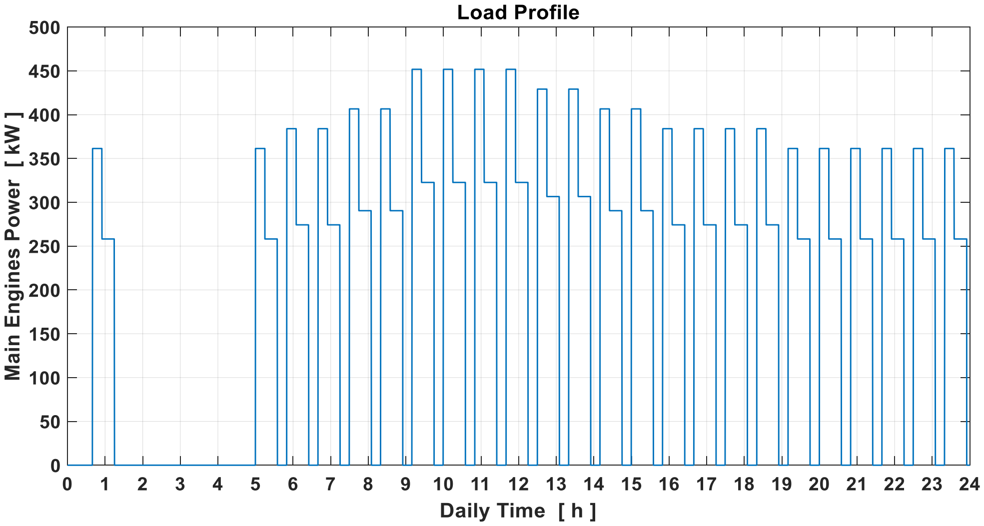


Figure 43: Load Profile Main Engine

By ordering the data in the graph in Figure 43, we obtain the graph in Figure 44 which shows the cumulative load profile. It is observed that during 10 hours per day the ship is moored, therefore the engines that consume are only the auxiliary ones. The power average is around:

$$\frac{Total\ Energy\ (kWh)}{Total\ Hours\ (h)} = \frac{7673{,}9}{24} \approx 320\ kW$$

Finally, the graphic illustrates the total power required at the end of the day, 600 kW.

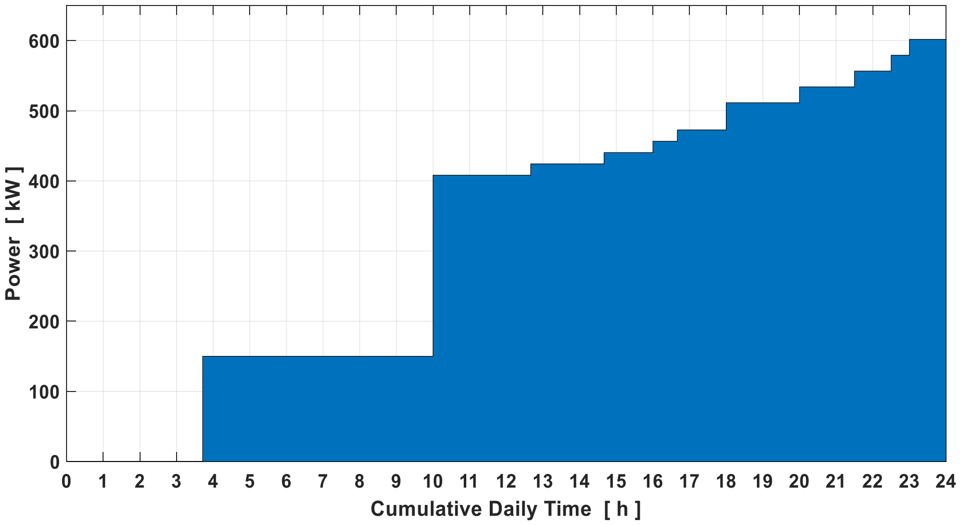


Figure 44: Cumulative Power during a day

Having studied the energetic model of the ferry, it is concluded that the most adequate fuel cell is the "HyPM 180 kW" of Hydrogenics commercial home. In order to satisfy the demand, it is necessary to install two fuel cells identical to this model. This fuel cell is decided to work providing 160 kW, and it is assumed to have an efficiency of 49%.

Implementing and simulating the model in Matlab gives a hydrogen consumption equal to 470 kg. The fuel cells system injects a 24-hour continuous power of 320 kW.

Figure 45: HyPM-HD 180 Kw Fuel Cell [32]

Table below shows the operation conditions from one “HyPM HD-180 kW” Fuel Cell:

TECHNILCAL DATA	HD-180
Power	160 kW
Efficiency	49 %

Operating Voltage	460 V
Oxidant	Ambient Air
Dimensions	955 x 1525 x 690 mm (excluding air delivery and water pump)
Mass	654 Kg (including air delivery and water pump)

Table 18: Operation conditions HyPM-HD 180 kW [51]

The following figure shows the operating point of a fuel cell:

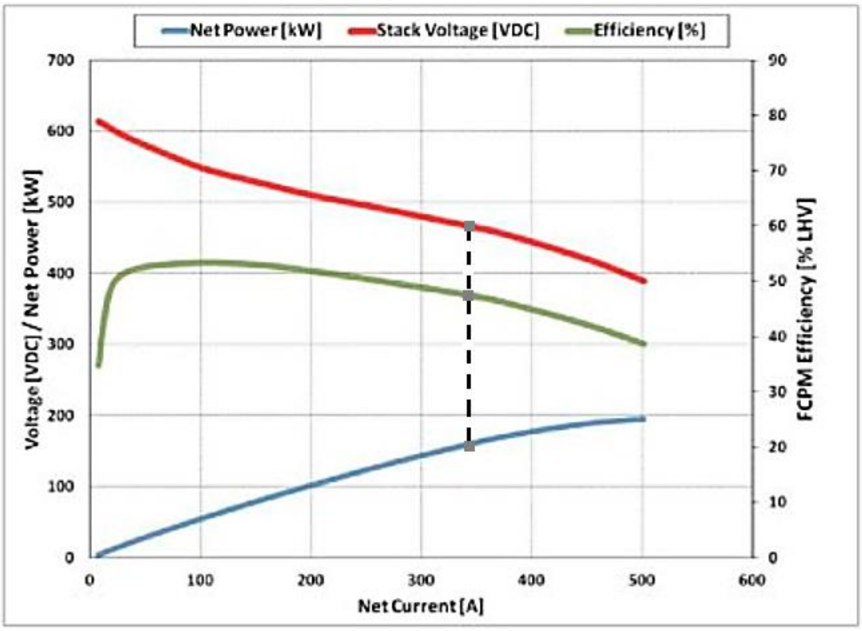


Figure 46: Selected operating point [51]

Nevertheless, this system of fuel cells is not enough to satisfy the power requested by itself, but instead it requires a set of batteries which complement it.

The selected battery pack belongs to PBES. By simulating it indicates that the total energy that the batteries must supply to satisfy the demand is 1548,3 kWh. Therefore, among the different models offered by PBES the most suitable is "Eneergy 88". It has the following characteristics:

ENERGY 88	
Type	Lithium Industrial Battery
Dimensions	896 x 2550 x 632 mm
Weight	950 kg
Energy	88 kWh
Capacity	100 Ah
Nominal Voltage	880 VDC
Max Discharge Current	200 A
Max Charge Current	100 A
Internal Resistance	28 mΩ
Integrated Racking System	Included

Table 19: Energy 88 specifications from PBES

As the energy to be supplied is 1028 kWh, 18 identical units of Energy 88 are needed:

$$\frac{1548{,}3\ kWh}{88\ kWh} \approx 18\ units$$

Table 20 illustrated the total volume and weight from fuel cells and batteries system:

	VOLUME AND WEIGHT CALCULATION	
	Volume (m^3)	**Weight (Kg)**
Fuel Cells	2,01	1308
Batteries	23,10	15200
Total	25,11	16508

Table 20: Total Volume and Weight from FCs and Batteries

Fuel cells´ volume have been calculated without including the air delivery and water pump.

The following figure represents the instantaneous battery power during the day:

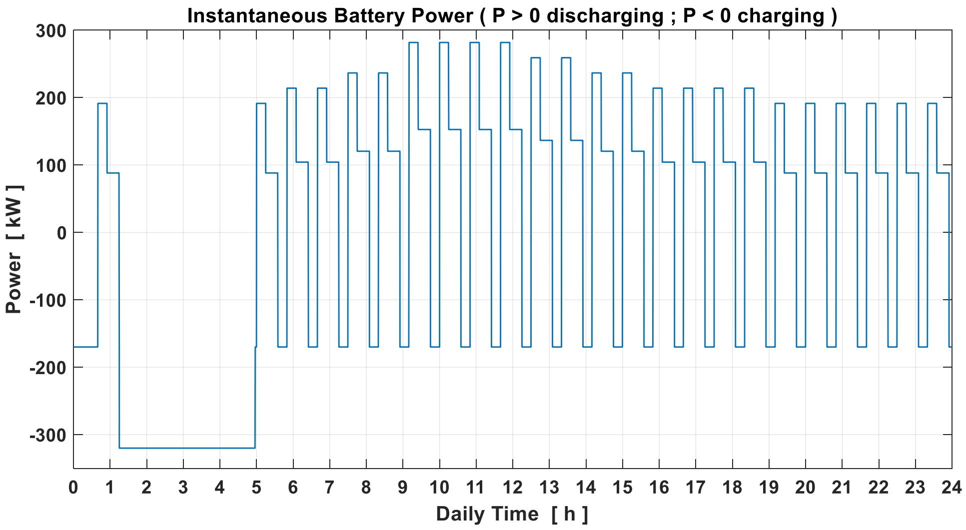


Figure 47: Instantaneous Battery Power

Maximum power charge and maximum power discharge are 320 kW and 282 kW, respectively.

So, the total power, including propulsion and auxiliaries, is illustrated in the figure below:

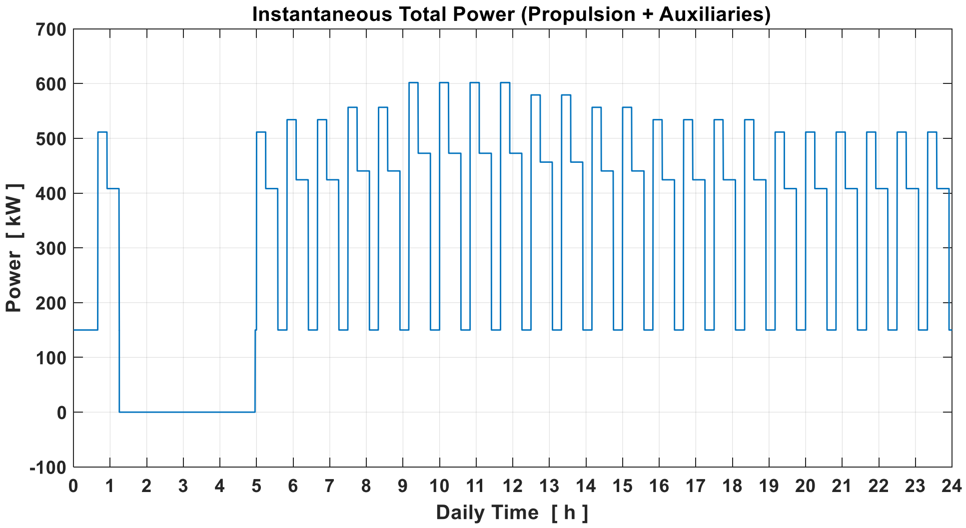


Figure 48: Instantaneous Total Power (Propulsion and Auxiliaries)

Regarding the state of charge of the battery pack, Figure 49 shows that the battery is initially at 20% of its total capacity. However, it manages to complete its charge (SOC 100%) during the hours when the ferry is moored. From 05:00 h, the ferry starts its day and therefore the batteries are discharged until they reach the same state of charge as initially (20%) completing the day.

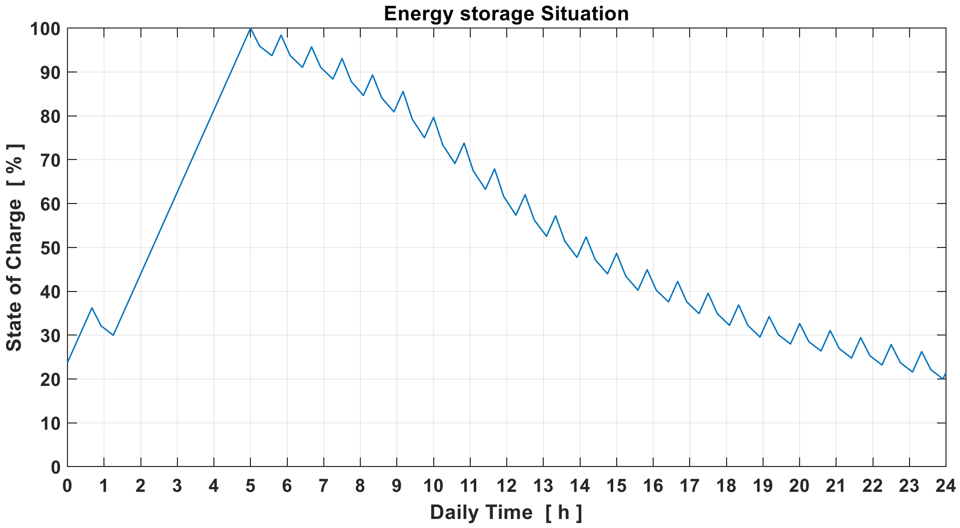


Figure 49: State of Storage (SOC)

7.5. Hydrogen Storage

This part of the project aims to find a compact system to store the amount of hydrogen demanded by the fuel cells installed in the ship for one day. In this case, 470 kg of hydrogen are needed. To this purpose, a search has been carried out on the different models for storing compressed hydrogen from several commercial companies.

Finally, it has been chosen the compression of hydrogen into steel cylinders of Type III at 300 bar inside a standard container of 40 ft size from the Italian company Faber Industries. The storage system selected has the following technical characteristics:

FABER 190 L TYPE 3 CARBON FIBER	
Hydrogen Stored	470 kg
Working Pressure	300 bar
Single Unit Volume	190 L
Single Unit Net Weight	57 kg
Ext. Diameter	440 mm
Height	1400 mm
Number of Units	121
Container Size	40 ft
Container Empty Weight	3800 kg
Number of Containers	1
Total Container Volume	77 m^3
Total Weight	11136 kg

Table 21: Technical Specifications for the hydrogen storage

For the arrangement of this hydrogen reserve a trailer is needed in order to mount the cylinder pack which would be connected to the hydrogen system on board by a flexible hose and which would be parked on the pier during all day until the exhaustion of hydrogen, and then be replaced by a loaded cylinder pack during a stop, thus avoiding the loading of hydrogen from outside simplifying the procedure and increasing safety.

7.6. Electric System

The conventional propulsion system currently installed in the ship is illustrated in Figure 50.

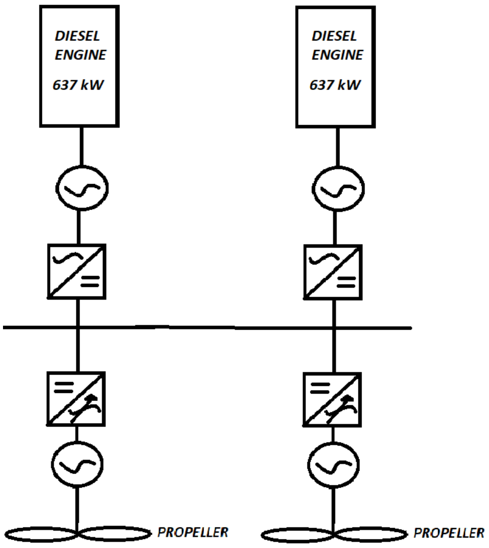


Figure 50: Electric Conventional System

Nevertheless, Figure 51 shows the hybrid system proposed. Fuel cells require a DC-DC unidirectional converter and the battery pack needs a bidirectional DC-DC converter in order to supply energy when it is not enough with fuel cells and storage energy from fuel cells when the energy production is higher than the energy required.

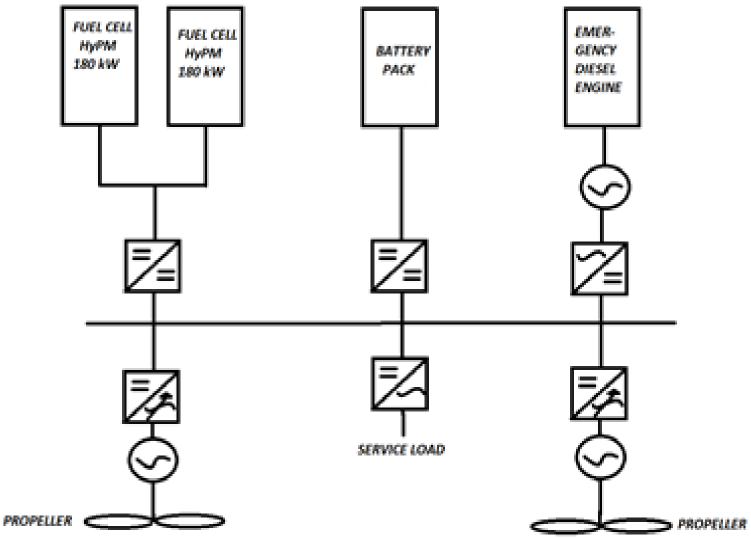


Figure 51: Fuel Cells and Battery System

8.CONCLUSIONS

The main purpose of this thesis has been to study the feasibility of using hydrogen fuel cells in the naval sector.

In the first part of the project, a balance has been made of the advantages and disadvantages involved in the use of hydrogen. Particularly, it has been studied the positive and negative impact that its use could have on a small ferry Venice. This analysis has shown that hydrogen could be in the future an alternative to conventional propulsion systems in solidarity with the environment. However, it still presents some problems that must be solved in order to make its use not dangerous, also regulated under certain institutions and not expensive to produce, store or transport.

As for the issue of ways of storage hydrogen, it emerges that the method with the greatest technological maturity and provides facilities to be used in naval applications is storage in pressurized bottles. Although storage at very high pressure (600-700 bar) offers a higher energy density, its complexity and safety issues make its application difficult. Therefore, the use of small bottles storing hydrogen at 200-300 bar is advisable.

Another conclusion obtained from the study of fuel cells is that the most developed and researched for marine use is the PEM type. Its fast start-up owing to its low working temperature, simplicity, flexibility and maturity gives advantages over the rest.

Finally, the very preliminary technical feasibility study for the application of a propulsion hybrid system consisting of Fuel Cells/Batteries with compressed hydrogen on a RO-RO ferry has demonstrated its viability. However, the absence of stipulated rules that allow the safe regulation of the use of hydrogen is the main obstacle to the implementation of the project. Nevertheless, the new rules for emission expected to be enforced in 2021 will mark a turning point for the implementation and modification of standards on this issue.

9.ACKNOWLEDGEMENTS

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11. List of figures

12. List of tables