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LECTURE– Introduction to FCH applications and hydrogen safety

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Introduction

Fuel cell and hydrogen (FCH) applications both in transport and energy sectors arrive to the market today, and it is quite likely that First Responders would deal with possible accidents/incidents in the near future. The development of FCH technologies requires a better, in-depth understanding by First Responders of the hazards, risks, processes and safety features associated with FCH systems and infrastructure. Hydrogen production by electrolysis and natural gas reforming; decentralised hydrogen production applications; gaseous and liquefied hydrogen storage; hydrogen transportation and materials handling applications; FC vehicles (e.g. cars, buses, forklifts); hydrogen refuelling stations; FC stationary applications; hydrogen-based energy storage systems remain largely unknown to First Responders. In addition to this, there is a lack of standardized procedures for intervention in the event of accidents or incidents on the above mentioned systems and infrastructures.

The purpose of this lecture is to introduce First Responders to a number of FCH applications, to familiarise them with the specific risks, and to outline the main approaches of hydrogen safety engineering. First Responders should realise that hydrogen is not more or less dangerous than any other common fuel. Hydrogen is different and the knowledge of its specific properties will facilitate in making appropriate decisions at the scene of an accident. First Responders should be professionally educated to deal with hydrogen systems at pressures up to 100 MPa and temperatures down to -253 ^{o}C (liquefied hydrogen) both outdoors and indoors. The developed International Curriculum in Hydrogen Safety Training for First Responders (http://www.hyresponse.eu/curriculum.php) was the first step in the establishment of the European Hydrogen Safety Training Platform for First Responders. The trainees are encouraged to use this document to assist them in their independent studies and to seek sources for further information.

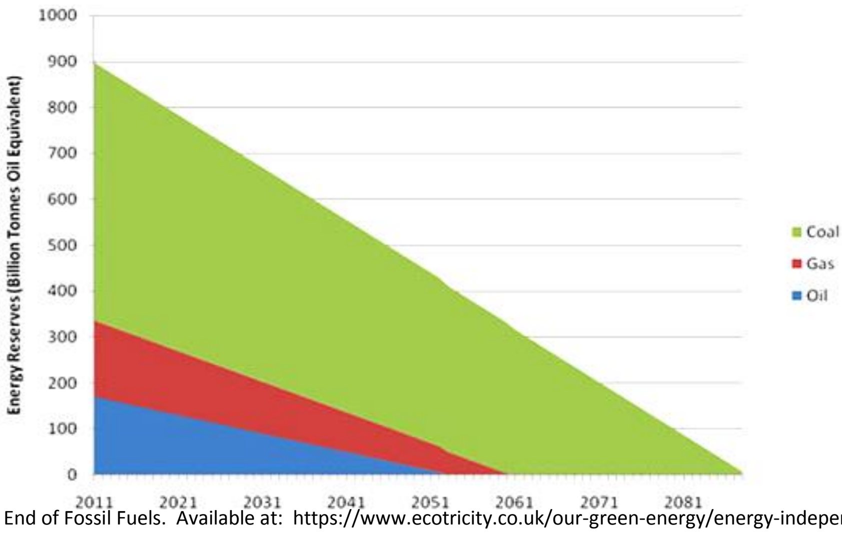
Objectives of the lecture

By the end of this lecture a First Responder/a trainee will be able to:

- Appreciate a novelty and a wealth of FCH technologies in modern society;
- Understand a role of hydrogen as a new energy carrier;
- Name the main routes of hydrogen production, transportation, delivery and use;
- Recognise the difficulties of the public perception towards hydrogen and fuel cell technologies;
- Define the main stream industrial hydrogen production methods. Although this lecture is not designed to provide learners with an in-depth knowledge of all production methods it gives a descriptive outline of a reformer, PEM and alkaline electrolysers with an emphasis placed on safety features and concepts;
- Describe the working principle of a fuel cell (FC) and a fuel cell stack;
- Explain the operational principles and safety aspects of a range of FCH applications including FC vehicles, refuelling stations, stationary hydrogen storage, materials handling and hydrogen distribution applications, back-up power generation and FC systems for combined production of heat and power;
- Give examples of incidents or accident that might occur on FCH applications;
- Give insight into the hydrogen safety engineering framework.

Why hydrogen is important?

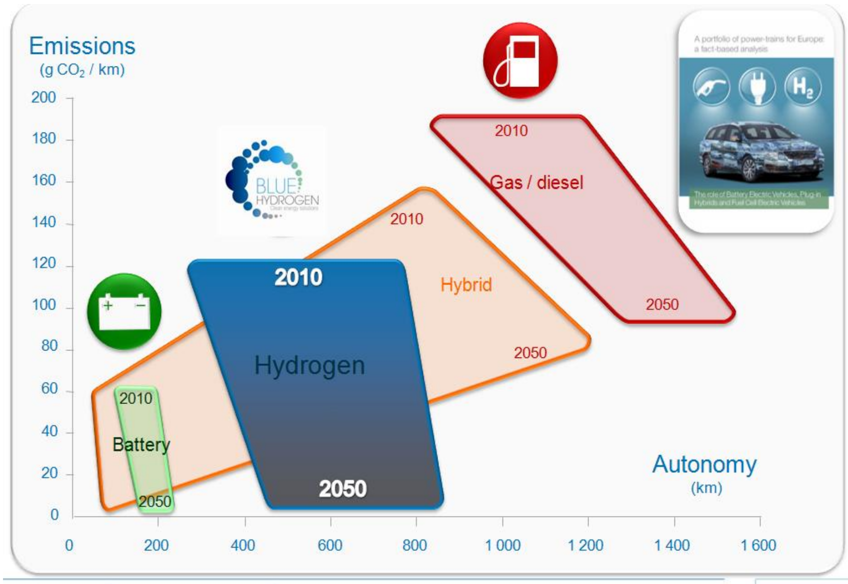
The scarcity of fossil fuel reserves (Figure 1), geopolitical fears associated with fossil fuel depletion, and issues of environmental pollution and climate change as well as the need to ensure independence of energy supply make the low-carbon economy with an essential hydrogen vector inevitable in the coming decades [1].



Source: Ecotricity. The End of Fossil Fuels. Available at: https://www.ecotricity.co.uk/our-green-energy/energy-independence/the-end-of-fossil-fuels

Figure 1. Prediction of the energy reserves for the coming years.

The role of renewable energy sources is expected to increase in the next decades. Hydrogen as an alternative to hydrocarbon-based conventional fuels currently enters the market. Zero emission road transport with medium to large size vehicles is a viable solution to negative environmental impact (Figure 2). Today first prototypes of FC buses and cars are already on the roads and hydrogen refuelling stations are operating in different countries around the world. Similar to electricity hydrogen is an energy carrier. Unlike the electricity hydrogen can be stored over long periods of times in extremely large quantities.



Source: AirLiquide, 2015

Figure 2. The emissions associated with transport powered with different energy sources.

The expected growth of hydrogen economy has raised many questions with regards to safety of hydrogen production, transportation, storage and end-use. Hydrogen safety engineering is defined as an application of scientific and engineering principles aimed to protect life, property and environment from adverse effects of incidents/accidents involving hydrogen. The use of hydrogen as an energy carrier presents several unusual hazards. The following sections will illustrate what we already know about hydrogen and what is the public perception of emerging FCH applications.

Hydrogen usage in industry

Hydrogen has been used in industry and stored safely as a compressed or liquefied gas for more than 100 years. Hydrogen is widely used for a range of applications including: crude oil refining; as a coolant in large turbine electrical generators; as a propellant in rocket propulsion and missiles applications; during production of ammonia for fertilizers; in metallurgy for extracting pure metals from their ores; in semiconductor, glass, pharmaceutical, petro-chemical, chemical and food industries; etc. The statistics on incidents related to hydrogen indicates that currently incidents occurring in laboratories are the most frequent (about 32 %) [2]. The low accident rate can be explained by the strict safety measures already in place for the production and end-use of hydrogen. However this trend might change in the coming years due to the expansion of FCH applications into public domain and more frequent use of FCH technologies by private individuals without a special safety training. The incident reporting also shows that from the total number of incidents recorded so far only a small proportion results in a loss of human life (4.6 %) [3]. Although hydrogen safety issues have been efficiently controlled in the industry until today, additional safety approaches especially with regards to emergency response procedures, will be required both in the transport sector and in residential fuel markets mainly due to high pressures utilised for storing hydrogen.

Hydrogen is not more or less dangerous than other flammable fuels including petrol and natural gas. In fact, some of its properties such as buoyancy provide safety benefits compared to other fuels. However, all flammable fuels must be handled responsibly. Like gasoline and natural gas, hydrogen is flammable and can behave dangerously under specific conditions. Hydrogen can be handled safely if simple guidelines are adhered to and the user has a good level of knowledge of its unique behaviour. Understanding of hydrogen specific properties and knowledge of FCH applications leads to safe implementation of hydrogen as a fuel. There is a need to establish a new safety culture in our society, to develop innovative safety strategies and breakthrough engineering solutions. It is expected that the level of safety at the consumer interface with hydrogen must be similar or higher than that present with the fossil fuel usage. Thus, safety parameters of hydrogen and fuel cell products will directly define their competitiveness on the market [1].

What we already know about hydrogen

As a unique gas hydrogen was discovered by Henry Cavendish in 1766. Seven years later it was given the name "water forming" by Antoine Lavoisier, who proved that water was composed of hydrogen and oxygen. The word "hydrogen" originates from the Greek words *hydōr* (water) and *gignomai* (forming). However, it has to be mentioned that hydrogen was observed and collected in 1671 by Robert Boyle, who dissolved iron in diluted hydrochloric acid, i.e. long before it was recognized as a unique gas by Henry Cavendish.

Hydrogen (symbol H) is a first element in the periodic table. Its atomic number is 1, and its atomic mass is 1.008 g/mol. The hydrogen atom is formed by a nucleus with one unit of positive charge (a

proton) and one electron. The electron has a negative charge and is usually described as occupying a "probability cloud" which surrounds the nucleus like a fuzzy, spherical shell. The charges of the proton and electron of each hydrogen atom cancel each other out, so that individual hydrogen atom is electrically neutral. The mass of a hydrogen atom is concentrated in its nucleus. Indeed, the proton is more than 1800 times heavier than the electron. The radius of the electron's orbit, which defines the size of the atom, is approximately 100,000 times as large as the radius of the nucleus. The size of hydrogen atom in its ground state is 10^{-10} m (1 angstrom) [1]. A neutron can be present in the nucleus of hydrogen isotopes: deuterium and tritium. The neutron has almost the same mass as proton and does not carry a charge.

Hydrogen is the lightest element in the periodic table and in the universe. Hydrogen is the most abundant element in the universe and constitutes 75 % of its elemental mass. Hydrogen is the third, after oxygen and silicon, most abundant element of Earth. It is found, in a free state, in trace quantities in the atmosphere. Hydrogen can be found only in compounds such as water, hydrides, hydrocarbons and many other organic substances; it does not exist in a pure form and therefore should be produced from its compounds.

Hydrogen forms diatomic molecules with chemical formula H_2. At normal conditions it is colourless, odourless, tasteless, and nontoxic gas and hence cannot be detected by human senses. It is the lightest of all gases (e.g. it is about 14 times lighter than air) that is why it was used to lift air balloons and airships. Hydrogen rises and disperses rapidly at a speed of around 20 m/s [4]. Low weight and small size of hydrogen molecules contribute to high diffusivity of gaseous hydrogen and propensity to leak through fittings, flanges, threads, etc. Hydrogen reacts easily with many substances. It is a flammable gas and should be stored away from any sources of heat, open flames and sparks. The main physical-chemical properties of hydrogen give rise to a variety of specific risks which will be discussed later in the Lecture on 'Hydrogen properties relevant to safety'.

Public perception towards hydrogen

In the minds of people, hydrogen is often synonymous with a danger especially since the Hindenburg disaster on 6 May 1937. On that day, the Zeppelin inflated with 200,000 m^3 of gaseous hydrogen ignited and burnt completely in less than a minute resulting in the death of 35 out of the 97 passengers, who in panic jumped out of the airship. Public perception of hydrogen technologies is still affected by this catastrophe and often referred to as the "Hindenburg syndrome". The catastrophe is often associated with hydrogen as a reason, even though the dominating hypothesis explains an ignition by an electric spark due to the electrical potential difference between the zeppelin mooring lines and the ground during "docking", which inflamed the dirigible canopy made of extremely combustible material. This was followed by a diffusive combustion of hydrogen in air without generation of a significant blast wave able to injure people [1]. Figure 3 shows a photo of the Hindenburg dirigible in a fire and demonstrates that there was no "explosion" [5].

Contrary to popular misunderstanding hydrogen helped to save 62 lives in the Hindenburg disaster. The NASA research has demonstrated that the disaster would have been essentially unchanged even if the airship was lifted by non-combustible helium, and that probably nobody aboard was killed by a hydrogen fire [6]. The 35% of those who died were killed by jumping out, or by the burning diesel oil, canopy, and debris (the fabric skin was coated with iron oxide and aluminium-impregnated cellulose acetate butyrate which nowadays serves as a solid propellant component of a rocket booster). The

other 65% survived, riding the flaming dirigible to the earth as the clear hydrogen flames swirled harmlessly above them [1].

Source: Environmental graffiti alpha, 2010

Figure 3. The Hindenburg dirigible fire [5].

Hydrogen safety studies were initiated a few decades ago as a result of accidents in the process industries, and were supported by safety research for nuclear power plants and aerospace sector. For example, a study of the Three Mile Island nuclear plant (USA) accident in 1979 demonstrated that almost homogeneous 8% by volume of hydrogen in air mixture deflagrated [7]. Fortunately, the deflagration pressure increases only to about 190 kPa that was considerably below the strength of the large concrete containment building. Recent disasters involving hydrogen such as the Challenger Space Shuttle explosion (1986) and the Fukushima nuclear tragedy (2011), demonstrated that our knowledge and engineering skills to deal safely with hydrogen even within these industries require more investment, from both intellectual and financial perspective [1].

FCH applications and technologies

At normal temperatures hydrogen is not a very reactive compound unless it has been activated somehow, e.g. by an appropriate catalyst. Hydrogen reaction with oxygen at ambient temperature is extraordinarily slow. However, if the reaction is accelerated by a catalyst or a spark, it proceeds with a high rate and an 'explosive' violence (Equation 1). This exothermic reaction between hydrogen and oxygen is capable to generate a significant amount of energy:

$$2H_{2\,(g)} + O_{2\,(g)} = 2H_2O_{(g)} + \text{Energy} \qquad (1)$$

Hence, hydrogen is considered to be a new energy carrier, which does not have a negative environmental impact as only water (i.e. steam) is produced during this reaction. The FCH systems and infrastructure are growing and expanding nowadays. Fuel Cell Today [8] mentions three broad fuel cell application categories:

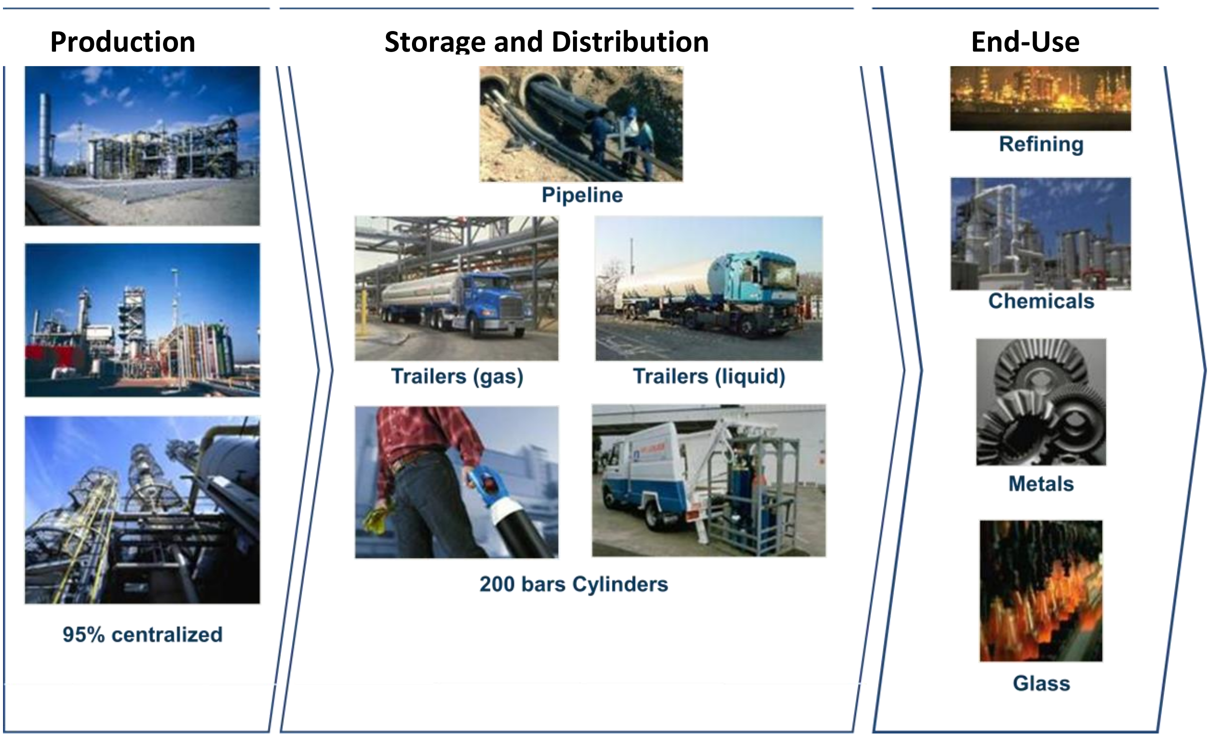
- Portable fuel cells which encompass those designed to be moved, including auxiliary power units (APU);
- Stationary power fuel cells are units designed to provide power to a fixed location;
- Transport fuel cells provide either primary propulsion or range-extending capability for vehicles. Also an infrastructure related to the production, storage and distribution of hydrogen for fuel cells should be considered (Figure 4). The summary of FC applications and technologies is given in Table 1.

Table 1. FC applications and technologies*

Application Type	Portable	Stationary	Transport
Definition	Units that are built into, or charge up, products that are designed to be moved, including auxiliary power units (APU)	Units that provide electricity (and sometimes heat) but are not designed to be moved	Units that provide propulsive power or range extension to a vehicle
Typical power range	5 W to 20 kW	0.5 kW to 400 kW	1 kW to 100 kW
Typical technology	PEMFC DMFC	MCFC PAFC PEMFC SOFC	PEMFC DMFC
Examples	- Non-motive APU (campervans, boats, lighting) - Military applications (portable soldier-borne power, skid-mounted generators) - Portable products (torches, battery chargers), small personal electronics (mp3 players, cameras)	- Large stationary combined heat and power (CHP) - Small stationary micro-CHP - Uninterruptible power supplies (UPS)	- Materials handling vehicles - Fuel cell electric vehicles (FCEV) - Trucks and buses

Source: The Fuel Cell Industry Today Review, 2012 [8].

* PEMFC – proton exchange membrane fuel cells; DMFC – direct methanol fuel cells; MCFC – molten carbonate fuel cells; PAFC – phosphoric acid fuel cells ; SOFC – solid oxide fuel cells.



Source: AirLiquide, 2015

Figure 4. An example of hydrogen and fuel cell infrastructure.

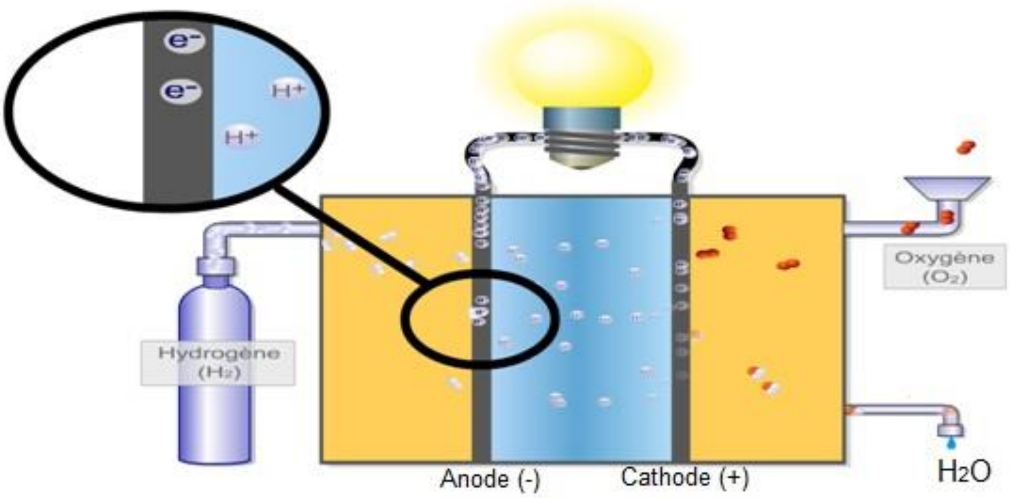
What is a Fuel Cell?

A fuel cell (FC) is an electrochemical generator, i.e. electricity is produced by the conversion of chemical energy. In the case of a hydrogen-fed FC oxygen and hydrogen are combined to produce electricity, heat and water. FC generates electricity but does not store it. FC includes two electrodes, positive (cathode) and negative (anode), immersed in an electrolyte solution, which provides a transfer of the ions in both directions, while a corresponding flow of electrons in an external circuit provides electricity [9]. An electrolyte is a substance that conducts charged ions from one electrode to another [10], and an electrode is a conductor, through which electrons enter or leave an electrolyte. A single FC is usually made of an electrolyte and two catalyst-coated electrodes: a porous anode and cathode. Normally several fuel cells are grouped together to form a fuel cell stack.

Although there are different types of fuel cells the working principle is similar. Hydrogen is fed to the anode where a catalyst separates hydrogen's negatively charged electrons from positively charged ions (protons) as shown on Figure 5. At the cathode, oxygen combines with electrons and, in some cases, with species such as protons or water, resulting in water or hydroxide ions, respectively. The oxygen is usually obtained from the ambient air around the FC. In some cases where hydrogen is produced by electrolysis, the pure oxygen co-produced in electrolysis may be used in the FC. The half-reactions occurring on both electrodes are shown in equations (2) and (3).

$$\text{At the anode: } H_2 \rightarrow 2H^+ + 2\,e^-, \quad (2)$$

$$\text{At the cathode: } \tfrac{1}{2}\,O_2 + 2H^+ + 2e^- \rightarrow H_2O. \quad (3)$$



Source: Areva, 2015.

Figure 5. The operating principle of a FC [11].

Hydrogen production

Hydrogen molecules H_2 cannot be found in their pure form in nature. Thus, hydrogen must be produced from the compounds, in which it contained, for example from water, methane, methanol, ammonia, ethanol, biomass, etc. Hydrogen production can be divided into two categories: large-scale centralised production and decentralised production of a small or medium scale. The centralised production refers to established, large scale chemical plants, mass producing hydrogen, which is then transported to customers. In this case, hydrogen is transported, sometimes over long distances, either via pipelines, by road or by ship. Examples include large steam reformers owned by

the major gas companies such as Linde, Air Products, AirLiquide and others. There are several established technologies currently available on the market for the industrial production of hydrogen. There are two commercial routes for the hydrogen production: electrolysis of water (dated back to late 1920) and reforming technologies (introduced in 1960).

Water electrolysis

Water electrolysis is a process, in which water is split into hydrogen and oxygen using electrical energy as shown in the equation (4):

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2. \tag{4}$$

This process occurs in an electrolyser that converts electrical energy into chemical energy and can be seen as a device opposite to a FC. The electricity can originate from different sources and depending on that the electrolysis can either be with or without carbon dioxide CO_2 emissions. If the electricity is produced from renewable sources (wind, hydroelectric, solar or tidal energy) no CO_2 will be emitted, if it is produced from fossil fuels then CO_2 is emitted (though distantly) as a result of hydrogen production. Produced gaseous hydrogen is very pure and can be utilized either immediately or stored for a later use. The electrolysers' capacities range from less than 500 m^3/h to more than 20,000 m^3/h.

The electrolyser contains two electrodes (positive and negative), water and an electrolyte, i.e. a substance containing free ions that make this substance an electrical conductor. The decomposition of water takes place when the electric current passes between two electrodes within the electrolytic cell. Hydrogen is produced at the negative electrode (cathode) and oxygen is formed at positive electrode (anode).

PEM electrolysers

When the electrolysis takes place in two rooms/chambers, which are separated by a Proton Exchange Membrane (PEM) we will be dealing with PEM electrolysers. By application of a direct current (DC) water dissociates into hydrogen (H_2) at the negative electrode and oxygen (O_2) at the positive electrode (Figure 6). The electrodes and the membrane usually form a Membrane Electrode Assembly (MEA) and a stacking similar to a FC stack. The gases are collected in the recovery containers. PEM electrolysers operate at low temperatures and PEM serves as the electrolyte.
As it shown in Figure 7 the PEM electrolyser consists of the following elements:

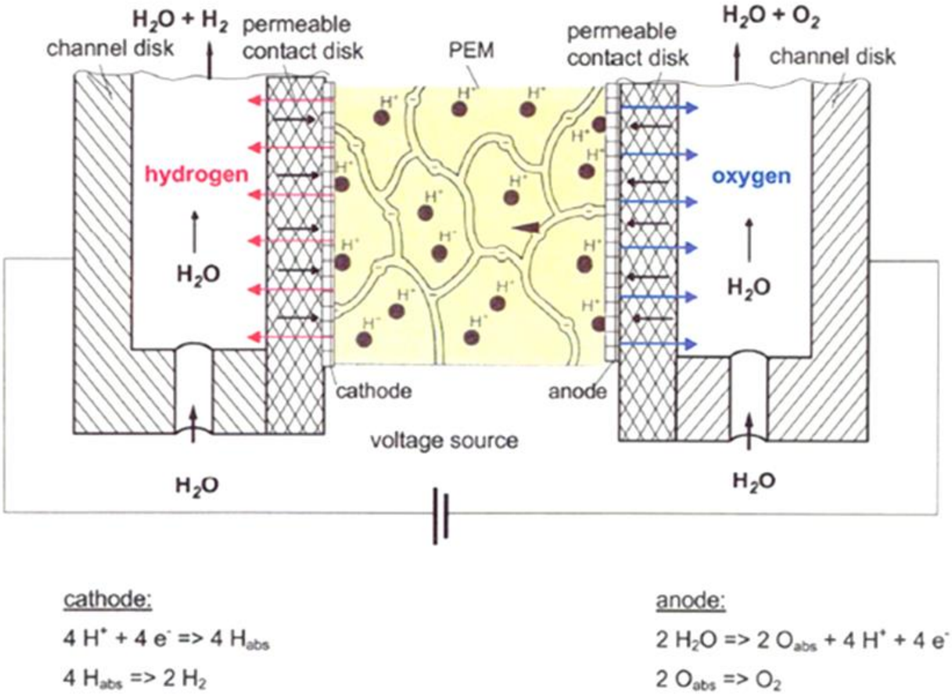
- a process cabinet containing all the process components such as valves, piping, gases and water, stack, pressurized vessels, pumps, etc.
- an electrical cabinet containing all electrical components (i.e. instrumentation and control, cabling, power conditioning).
- a cooling system for electrolysis process heat dissipation.
- a weather proof enclosure.

The unwanted events that might happen are associated with the formation of an ATEX[1] (i.e. H_2-O_2 explosive mixtures) either in the process compartment or in the separator (i.e. a device to separate gaseous H_2 and O_2 from water traces) usually installed downflow from a FC stack. To avoid the accumulation of hydrogen in the process compartment, the following measures should be taken:

- control pressure and pressure difference between hydrogen and oxygen lines;

[1] ATEX stands for **AT**mosphères **EX**plosibles

- control hydrogen concentration in the container (< 0.4 vol. % H_2);
- limit as much as possible the quantity of hydrogen in the gas layer of the separator to avoid the formation of a flammable hydrogen-air mixture in the container in case of a catastrophic leak [11].



Source: Areva, 2015.

Figure 6. A working principle of PEM electrolyser.

The formation of a hydrogen-oxygen ATEX in the separator may be caused by a malfunctioning of the water transfer line or by a membrane perforation. The following safety measures are considered to avoid ATEX event in the separator:

- impose a minimum water level in the gas separator above 55% of its height;
- control the water level in the H_2 and O_2 gas separators;
- control the pressure and pressure difference in-between the H_2 and O_2 lines;
- control hydrogen concentration at the exit of the oxygen gas separator.

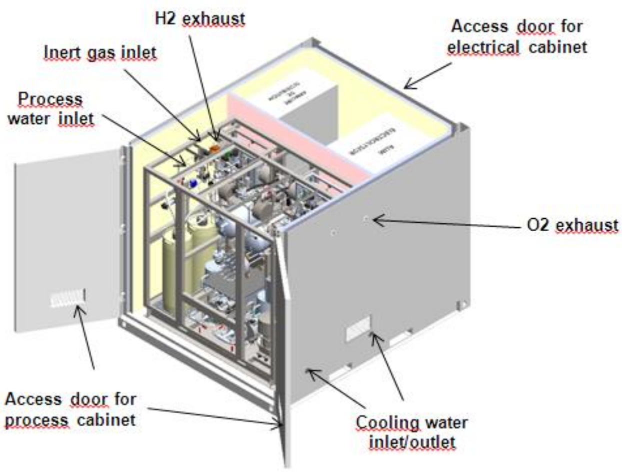


Figure 7. The scheme of a PEM electrolyser [11].

In the case of the activation of safety devices the electrolyser will shut-off, which involves not only closing of the isolation electro-valves connected to the storage tanks but also the depressurization of the system through the normally opened electro-valves.

Alkaline electrolysers

Alkaline electrolysis is a matured technology for hydrogen production and also the most employed in industry. Alkaline electrolysis uses the same principle as the PEM electrolysis that is the conversion of electrical energy into chemical energy.

Alkaline electrolyser has two electrodes immersed in a liquid alkaline electrolyte, potassium hydroxide or KOH aqueous solution at a level of 25% at 80°C up to 40% at 160°C. The use of KOH is preferable over the use of caustic soda NaOH due to its higher ionic conductivity, its lower chloride impurity contents and its lower saturated steam pressure. The electrodes are separated by a diaphragm as demonstrated on Figure 8. This diaphragm has two functions: first to keep the product gases (namely hydrogen and oxygen) separate and secondly to be permeable to the hydroxide ions (OH-) and water molecules. The diaphragm allows ions to pass but not hydrogen. Generally alkaline electrolyser is made of a number of electrolytic cells consisting of a membrane with electrodes sandwiched between bipolar flow plates as illustrated in Figure 9.

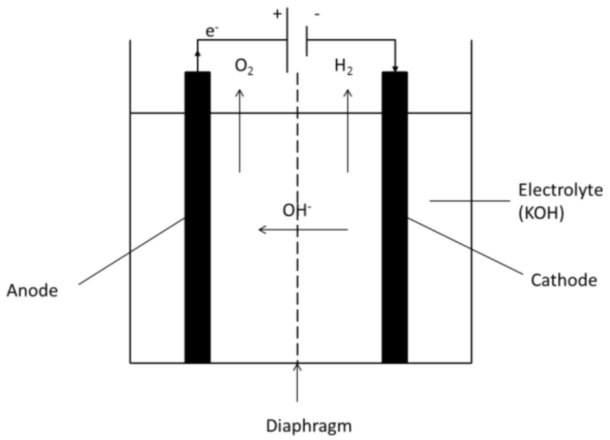


Figure 8. A scheme of an alkaline electrolyser [11].

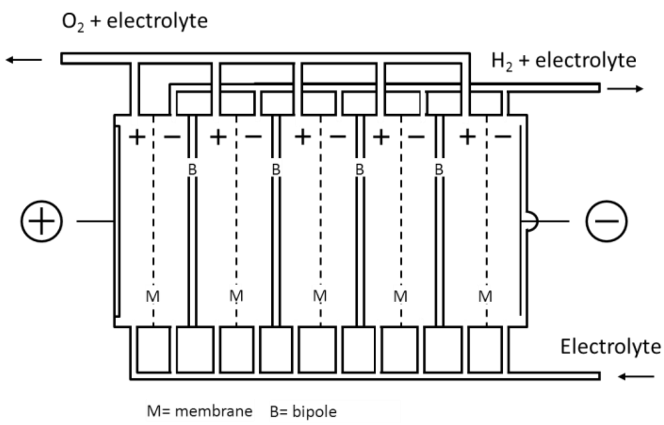


Figure 9. A scheme of electrolysis stack [11].

The reactions occuring on both electrodes are shown below:

At the anode: $2\,OH^- \rightarrow \frac{1}{2}\,O_2 + H_2O + 2\,e^-$ (5)

At the cathode: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$ (6)

Total reaction: $H_2O \rightarrow H_2 + \frac{1}{2}\,O_2$ (7)

A typical alkaline electrolyser is composed of:

- A power supply and a system of control and instrumentation;
- An electrolysis system containing a unit for water purification, a unit for hydrogen purification, a gas dryer, and a separator.
- A compressor.

The figures 10 and 11 show the examples of industrial alkaline electrolysers.

Figure 10. Alkaline electrolyser, IHT type S-556, 760 m^3/h and 30 bars [11].

Figure 11. Outdoor and indoor HySTAT from Hydrogenics electrolysers, 10-60m^3/h [11].

Similar to PEM electrolyser the main risk of alkaline electrolysis system comes from the formation of a hydrogen-oxygen mixture, which may lead to an internal explosion within the electrolyser. Several sensors are implemented in order to detect an electrolyser malfunction:

- measurement of hydrogen concentration in the oxygen line;
- measurement of voltage and current;

- measurement of the temperature at the entry and at the outflow of electrolysis cells;
- measurement of the ionic concentration of the electrolyte.

Another type of risk is associated with an exposure to a corrosive solution in the event of an electrolyte leak. The specification sheet of potassium hydroxide recommends the use of a leak tank in order to avoid the contact of KOH with the surroundings [11].

Reforming technologies

Currently the most common way of hydrogen production is by steam reforming of natural gas. The reaction of natural gas (methane CH_4) reforming is given in equation 8:

$$\underset{\text{natural gas}}{CH_4} + \underset{\text{steam}}{2H_2O} \rightarrow \underbrace{CO_2 + 4H_2}_{\text{syn-gas}} \quad (8)$$

This is an endothermic process (i.e. requires high temperatures) of methane and steam conversion into hydrogen and carbon dioxide CO_2. This is usually a two-step process with the typical by-products of reforming being carbon monoxide CO and carbon dioxide CO_2. A reformer can be operated on 24/7 basis at a constant load. The capacity of reformers ranges from 100 to more than 100,000 m^3/h. The efficiency of the reformer rarely exceeds 80%, the disadvantage of this method is that the produced hydrogen is not pure (it is contaminated with CO/CO_2) and it is at atmospheric pressure. To improve the sustainability of the reforming process CO_2 capture and sequestration are required. An example of steam reforming installation is shown on Figure 12.

Figure 12. AirLiquide steam reformer [11].

The steam reforming is a well-established industrial process and will not be treated in more detail in this lecture. For further technical details please refer to the papers on safety in the reforming industries provided in the International Curriculum on Hydrogen Safety Training for First Responders. As noted above the process occurs at high temperature and pressure, thus hydrogen safety issues addressed in the coming lectures on leaks, fires, detection, mitigation etc. are of course also relevant to steam reforming.

Other technologies for hydrogen production

An overview of hydrogen production non-main stream methods is given in this lecture. First responders should be aware of a variety of hydrogen production methods as FCH market is expanding rapidly. For further information on alternative hydrogen production technologies please

use the references from the International Curriculum on Hydrogen Safety Training for First Responders.

Hydrogen can be produced

- from water by:
  - Nuclear methods (radiolysis or thermolysis);
  - Photo-electrolysis (photovoltaic systems coupled with electrolysers);
  - Thermo-chemical cycle;
  - Ferro-silicon method (water, sodium hydroxide and ferrosilicon);
  - Photo-biological water splitting (two steps: photosynthesis and H production catalysed by hydrogenases);
  - Photo-chemical water splitting;
  - Biological routes (fermentation, enzymatic, microbiological and bio-catalytic)
- from fossil fuels by:
  - Partial oxidation of oil;
  - Coal gasification;
  - Plasma reforming (light hydrocarbons heated by plasma to 1600^{o}C and produce hydrogen and carbon, no CO_2 emissions);
  - Dry reforming (natural gas reformed in the stream CO_2)
- from complex metal hydrides:

- $NaBH_4 + 4H_2O \rightarrow NaOH + HBO_3 + 5H_2$ (36 wt. %) (9)

Sodium borohydride

- $LiBH_4 + 4H_2O \rightarrow LiOH + HBO_3 + 5H_2$ (46 wt. %) (10)

Lithium borohydride

These complex metal hydrides are currently under intensive research with the view to develop new materials suitable for solid storage of hydrogen.

Traditionally hydrogen is produced using reforming technologies, which are not “green” due to the fact that carbon dioxide is produced. Although hydrogen produced from natural gas is certainly a viable short-term option, it is not viewed as a long-term solution. It is envisaged that “greener” production routes such as electrolysis and nuclear will play an increasingly important role. Renewable resources for producing hydrogen include biomass, methanol, ethanol and land-fill gas, wind farms, tidal energy, hydroelectric energy, solar and gravitational energy. As renewable energy begins to play more significant role in meeting modern society energy demands the issues of grid balancing and energy storage are the subject of much investigation and this is where hydrogen as a new energy carrier comes in. A number of projects exist whereby wind or solar power is coupled to hydrogen production and storage, e.g. the Pure project (Scotland) and MYRTE platform (Corsica, France), which will be discusses later in this lecture.

Overview of hydrogen storage options

This section provides an overview of hydrogen storage options. Hydrogen leaks, fires and explosions as well as the interaction of hydrogen with materials used for storage are extremely relevant and will be considered in subsequent lectures. Hydrogen storage is an enabling technology across a range of FCH applications from on-board storage in FC vehicles to stationary FC applications. There is no universal storage solution that can be installed on all the systems. Hydrogen storage solution must be selected to suit the specific application. For example, size and weight are limiting factors for

passenger vehicles whereas weight can be a desirable attribute for forklifts. The storage solutions are one of the key challenges for the hydrogen economy and these technologies are a subject of considerable interest both for scientific and industrial communities.

The storage of the large quantities of hydrogen for long periods of time is a key step in the build-up of FCH infrastructure, which will regulate the hydrogen consumption and production and will ensure continuity in its supply to customers. Various underground hydrogen storage schemes are investigated. One option includes storage of gaseous hydrogen in geological formations such as depleted gas fields, aquifers, or salt caverns. Another option is the underground storage in tanks buried underground, and hydrogen is stored either as compressed gas or in a liquid form. Geologic storage is usually located close to a hydrogen production site, whilst the buried tanks are closer to the point of use, for example to refuelling stations.

Numerous hydrogen storage technologies are available and could be categorised into the following groups:

- Compressed gaseous storage
- Liquefied storage
- Solid storage

The most common way to store hydrogen as a compressed gas or as a cryogenic liquid is in metal or composite cylinders or tanks (Figure 13). Cryo-compressed technology, when gaseous hydrogen under high pressure cooled to low temperatures, is another useful alternative. The cylinders can have different sizes, capacities (from 20 to 300 L) and pressures (20-70 MPa) and for some applications can be connected into a bundle or gathered onto a basket for transportation.

a b c

Figure 13. On-board storage of hydrogen (a), a cylinder bundle (b) and a basket of cylinders for transportation (c).

Hydrogen gas can be compressed to 20-100 MPa. The primary issues with storing hydrogen as a compressed gas is the amount of energy needed for the compression process, the inherent safety issues with storing hydrogen at such high pressures and the additional costs and weight of cylinders designed to store hydrogen at high pressures. Issues such as permeation and embrittlement are proportional to gas pressure therefore at higher pressures these may be a greater issue. In Europe, most of transportable cylinders have only a valve as a safety feature. In USA transportable cylinders are equipped with pressure relief devices. This prescription is very controversial because they often become the sources of leaks. The storage of compressed gaseous hydrogen is usually integrated for stationary hydrogen storage systems and for on-board storage of hydrogen in FC vehicles [11].

Cryogenic hydrogen is formed when it is cooled to a temperatures below its boiling point 20K (-253 ^oC) is the second major category of hydrogen storage. In this form hydrogen can either be stored for some time or transported. This storage option is also very costly due to considerable energy required for liquefaction. The cost and weight of suitable materials to store and maintain the hydrogen at low temperatures must also be considered.

Hydrogen can also be stored either within the structure or on the surface of certain solid materials. This storage option does require neither high pressures nor low temperatures as in previous two methods; this offers advantages regarding the safety of the materials. There are three main mechanisms for storing hydrogen in materials: absorption, adsorption (Figure 14a), and chemical reactions (Figure 14, b-d). The examples of materials and compounds suitable for solid hydrogen storage are shown below on Figure 14.

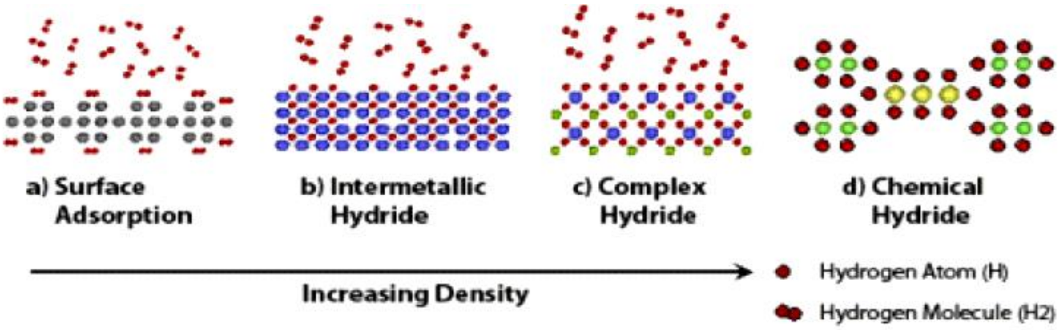


Figure 14. Materials used as solid storage of hydrogen [12].

All these three options have their own advantages and disadvantages, safety issues are also different and will be considered in detail in the Lecture 'Safety of hydrogen storage'.

Hydrogen storage systems can be used for different purposes: as containers for its transportation; as on-site (under- or above the ground) stationary storage systems, or as on-board storage tanks in FC vehicles.

Hydrogen transportation/distribution

As you have learnt hydrogen was used in industry for many decades. After hydrogen is produced at a centralized production site it is usually transported to the end-users or to the relevant FC applications. Hydrogen can be transported either as a compressed gas or as a cryogenic liquid. Thus there are a number of routes for its bulk transportation: by roads in trucks/trailers and containers or via pipes.

Trucks

Gaseous trucks

Truck fleets are currently used by industrial gas companies to transport seamless steel vessels of compressed gaseous hydrogen (CGH_2) for the distances of 200-300 km from a centralized production site. Single cylinder bottles, multi-cylinder bundles or long cylindrical tubes are installed on trailers (Figure 15). Storage pressure ranges from 200 to 300 bar and a trailer can carry from 2,000 to 6,200 Nm^3 of CGH_2 for trucks, subject to weight limitation of 40 tons. The amount of hydrogen transported this way is relatively low (from 180 to 540 kg depending on the number of tubes or bundles), which represents approximately 1-2 % of the total mass of the truck. Current trailers utilize Type I storage cylinders (i.e. all-metal). To increase their performance, bundles of light-weight composite hoop

wrapped cylinders or tubes (Type II) can be used. This mode of delivery is relatively easy but it has to be adapted to hydrogen quantities and distances to be cost competitive. The main restrictions in compressed gas truck delivery are capital costs, operation and maintenance including drivers' labour and fuel costs.

(a)

(b)

Source: AirLiquide, 2014.

Figure 15. Two types of CGH_2 trailers operated by AirLiquide in Europe: (a) tube trailer carrying 2,000 to 3,000 Nm^3 of hydrogen and (b) composite cylinder trailers carrying 6,200 Nm^3 of hydrogen.

The transportation by gaseous truck (tube trailer, cylinders) is one of the most mature modes selected for transportation on short distances and for small amounts of hydrogen. The major limitations are the low weight storage capacity for customers with high consumptions (requiring frequent delivery) and the low pressure of hydrogen delivered, which requires additional compression, for example at a refuelling station. Thus, alternative technologies with higher pressure, higher hydrogen-carrying capacity and lower-cost systems are investigated as described hereafter.

Lincoln Composites develops composite tubes of higher capacities. The material of a tank is a plastic liner fully wrapped with epoxy impregnated carbon fibre for gaseous hydrogen tube trailer delivery. For example, the TITAN™ tank (1.08 meters in diameter, 11.5 meters in length, 8,400 litres in water volume, and 2,087 kg in weight) operates at pressure of 250 bar. It can deliver 2-3 times more hydrogen compared to the amount of hydrogen stored/transported in steel tanks of similar masses. Figure 16 shows the storage unit holding four composite tanks capable of storing 600 kg hydrogen at 250 bar. The tanks suitable for higher pressures are currently under development.

Source: Lincoln Composites, 2014.

Figure 16. A trailer carrying four composite tanks developed by Lincoln Composites.

Hybrid technologies are explored at the Lawrence Livermore National Laboratory (LLNL) such as cryo-compression combining pressure and low temperature to increase the amount of hydrogen

that can be stored per unit volume and avoid the energy penalties associated with hydrogen liquefaction. Compressed hydrogen gas at cryogenic temperatures is much denser than in regular compressed tanks at ambient temperatures. These new vessels would have the potential to store hydrogen at temperatures as low as 80 K under pressures of 200-400 bar. This approach requires development of insulated pressure composite tanks. Alternatively one could consider using cold hydrogen gas tanks that would require less cooling. There may be some optimum combination of pressure and temperature over the range of 80-200 K. Recently, LLNL has identified inexpensive glass fibre materials for cold hydrogen gas storage (~ 150 K and up to 500 bar), expecting 50% trailer cost reduction.

The main safety devices used in gaseous trucks are manual safety valves. During transportation all hydrogen storage vessels are isolated by a valve. In service, there are different safety devices and procedures:

- The semi-trailer changeover procedure takes place as follows:
  - The driver parks the semi-trailer in the location provided,
  - The driver puts chocks in position and deploys the leg stand,
  - The driver unhitches the tractor unit,
  - The driver connects the hose from the full semi-trailer, tests the seal on the draw-off hose and disconnects the empty semi-trailer,
  - The driver hitches the empty semi-trailer to the tractor unit and departs.
- A manual leak tightness test when connecting to a semi-trailer. This is done in the following stages. The operator connects the semi-trailer hose to the installation's connection post. The hose is pressurised. The operator checks for a leak tightness using detection soap and stabilisation of the pressure measured locally using a pressure gauge.

Cryogenic liquid trucks

Hydrogen can also be transported by roads in a liquid form (cooled below 20 K or -253 °C) to distribute larger quantities (hundreds of m^3/h). In terms of weight capacity, super-insulated liquid hydrogen (LH_2) trucks can transport up to 10 times more hydrogen than the tube trailers used for conveying CGH_2. LH_2 trucks operating at atmospheric pressures have volumetric capacities of about 50,000 – 60,000 litres and can transport up to 4,000 kg (Figure 17). It is a preferred distribution mode for medium/large amounts of hydrogen on long distances, which explains the LH_2 business has been developed most extensively in North America (the hydrogen liquefaction capacity in North America is about ten times larger than in Europe). The liquid hydrogen transported in the truck is then vaporized to a high-pressure product for use at a customer site.

Source: AirLiquide Image Bank, 2015

Figure 17. A road tanker operated by Air Liquide for conveying LH_2 to the end-user.

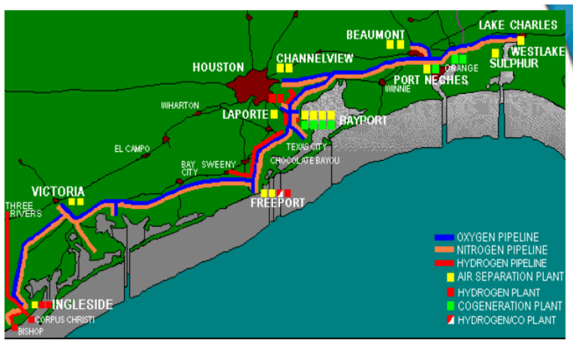
The main issue for this transportation route is a capital-intensive liquefaction process. The liquefaction process is costly as well. The energy input for liquefaction accounts for about 35% of the lower heating value of hydrogen (compared to 10% required for gas compression). Electricity costs account for 50-80% of the liquefaction costs. Distance is the main deciding factor between transportation of LH_2 and gaseous hydrogen CGH_2. The number of LH_2 trucks will depend on the hydrogen demand and the localization of the liquefaction point. However, the liquid truck capacity being much higher than that of a compressed gas truck, this mode of delivery is less dependent upon the transport distance. The truck capital cost and operating cost (fuel, labour) are much smaller. As a consequence, liquid trucking is more economical than gaseous trucking for long distances (from approximately 400 km to thousands of kilometres) and medium amounts of hydrogen.

However, one has to consider the availability of LH_2. Currently the industrial hydrogen market is served by four liquefiers in Europe and ten in North America. Larger markets would justify the construction of new liquefaction plants. Significant cost reductions due to scaling effects of liquefaction equipment are possible. However, this mode of delivery relies on the price of electricity and on the decision to install new liquefaction units. Better technologies could offer opportunities to reduce capital cost, to improve energy efficiency of liquefaction process and to reduce the amount of hydrogen lost due to boil-off during storage and transportation (the evaporation rate which depends on the size, shape, insulation of the container and time of storage, is typically of the order of 0.2 %/day for a 100 m^3 container). A number of studies are underway to improve liquefaction technologies and to propose novel approaches (for example, improvement of ortho-para conversion, development of magnetic refrigeration, etc.).

Pipes

A number of commercial hydrogen pipelines are used today to distribute large quantities (tens of thousands of m^3/h) of gaseous hydrogen to the industrial market. Their lengths range from less than one kilometre to several hundreds. The major actors are the industrial gas companies, namely Air Liquide, Air Products, Linde and Praxair. In response to an increased demand for hydrogen by mostly refineries, existing networks are expanding and new portions are built. For example, in March 2009 Air Products have announced 60 km extension to the U.S. Gulf Coast hydrogen pipeline network in Louisiana. The hydrogen network is estimated at around 1,600 km in Europe and 1,100 km in North America. Most of the pipelines are located where large quantities of hydrogen are consumed in refining and chemical sectors. These include systems in the North of Europe, (covering The Netherlands, Northern France and Belgium), Germany (Ruhr and Leipzig areas), UK (Teesside) and in North America (Gulf of Mexico, Texas-Louisiana, California, Alberta). Smaller systems also exist in South Africa, Brazil, Thailand, Korea, Singapore and Indonesia. Overall, the lengths of these pipelines are small compared to the worldwide natural gas transport pipeline system, which exceed 2,000,000 km.

Figure 18 displays parts of the worldwide hydrogen pipeline network. For example, the 240 km long pipeline in the Ruhr area of Germany (Figure 18 a) acquired by Air Liquide in 1998 has been in operation since 1938. Within the “Zero Region” European project for hydrogen energy applications Linde has installed a 900 bar hydrogen pipeline (1” in diameter) over a distance of 1.7 km in the Frankfurt-Hoechst industrial park to supply fuel cell passenger vehicles.



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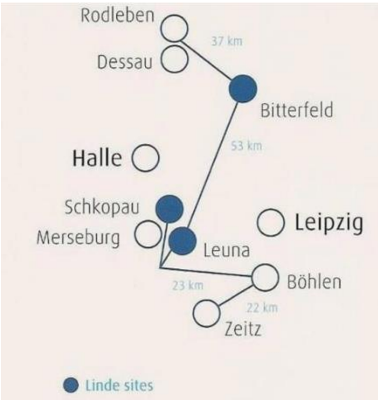

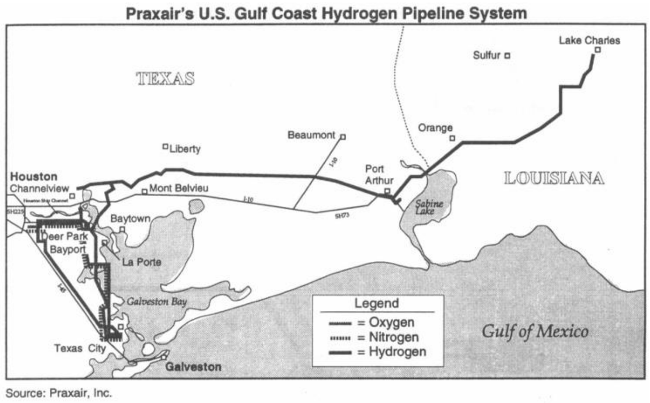

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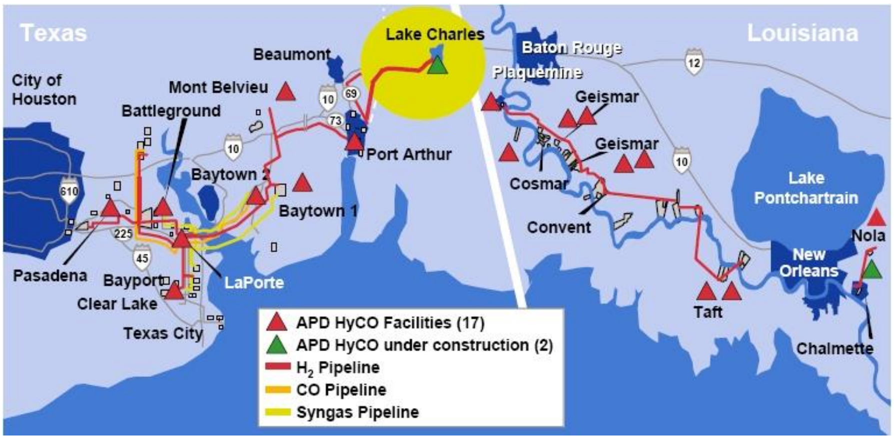


e

Figure 18. Main hydrogen pipelines in the world: (a) Air Liquide hydrogen pipelines in Benelux, France and Germany (Ruhr area); (b) Air Liquide hydrogen pipelines in the Gulf Coast (USA); (c) Linde hydrogen pipelines in Germany; (d) Praxair hydrogen pipelines in the Gulf coast (USA); (e) Air Product hydrogen pipelines in the Gulf Coast (USA).

The pipelines require an appropriate design, installation and maintenance procedures. The operating pressure of hydrogen pipelines is generally lower than 100 bar (most commonly between 40 and 70 bar) and the diameter of the pipelines (D) usually ranges from 10 to 300 mm. Current pipelines are made of steels. A technical concern is hydrogen embrittlement of metallic pipelines and welds, characterized by a loss of ductility and rupture when subjected to stress. The steels used for hydrogen pipelines are low-carbon, low-alloy and low strength steels to reduce the risk of embrittlement (e.g. API X42 steel with carbon content C < 0.2 wt. %, manganese content Mn < 1.3 wt. %). These steels combine economical affordability with an adequate range of physical properties such as strength, toughness, ductility and weldability. For safety reasons, most pipelines are buried and steels are protected with coatings or with a cathode protection to prevent corrosion.

Pipeline construction involves extensive welding for joining, with a minimum of inspections before operation for safety considerations. The exploitation of a pipeline network also requires compressor stations as hydrogen is generally available at low pressure. Hydrogen compressors feeding the pipeline system are usually found at locations where hydrogen is produced. The compressors are expensive and require high maintenance so they are not installed if another alternative is possible. For instance, when hydrogen is produced using natural gas (steam methane reforming), the natural gas feedstock can be compressed and the production plant operated at a higher pressure. Friction losses in pipelines with hydrogen are much lower than for those in natural gas as the viscosity of hydrogen is lower (the energy loss during transportation of hydrogen is about 4% of the energy content).

A hydrogen pipeline carries about 30% less energy compared to natural gas pipeline due to the lower volumetric density of hydrogen. The distribution of larger energy quantities in hydrogen pipelines requires a flow pressure increase (> 100 bar). This increase in pressure may have implications for the material which could be used in the pipeline construction. Furthermore, the operating conditions of a hydrogen pipeline for energy applications would be different from an industrial pipeline which today operates at nearly constant pressures, without significant pressure cycles. Hydrogen energy pipelines would have to bear variations of pressure. This may be a concern due to the susceptibility of steels to hydrogen embrittlement which affects their mechanical properties and decreases their resistance to fatigue crack. Hydrogen embrittlement phenomena will be discussed in the lecture ‘Safety of hydrogen storage’. There is a renewed interest in the research for the development of new pipelines’ materials compatible with hydrogen and their suitability to operate at higher pressure, and to reduce capital costs. New steels are explored to develop a better understanding of hydrogen embrittlement and to identify steel compositions and processes suitable for construction of a new pipeline infrastructure or potential use of the existing steel pipeline infrastructure.

Current research also concentrates on the alternative to metallic pipelines to achieve cost and performance targets for hydrogen transmission and distribution. Polymeric and fibre-reinforced polymeric pipelines, which present the advantages of being lighter, easier to handle, join and weld, non-sensitive to corrosion, non-sensitive to hydrogen embrittlement compared to steels are investigated. Polymeric pipes currently used in the natural gas distribution network are made of polyethylene and have a pressure rating limited to 10 bar. Polymers such as polyamide present more interest as the permeability of hydrogen is significantly reduced and its thermo-mechanical properties allow pipes to sustain a 20 bar operating pressure and 80°C operating temperature.

Therefore, plastic pipes can be a viable alternative to steel thanks to savings in installation and maintenance costs. However, the costs of these new polymeric materials can be very high. Pipes made of composite FRP materials are composed of a thermoplastic liner (mainly polyethylene) wrapped with high strength fibres (typically aramid fibres) coated with a thermoplastic layer. This last layer protects from environmental attacks and helps to retain the wrapping responsible for the mechanical properties. Compared to simple plastic pipes, wrapping with aramid fibres allows getting pressure up to 100 bar. These reinforced plastic pipes are already used for natural gas or crude oil distribution in the middle-East and their development for hydrogen delivery is currently part of the US DOE Hydrogen program (Figure 19). FRP pipes could be cost-effective substitutes of metallic pipes when long lengths (200 to 300 meters) are installed. However, the manufacturing process cannot produce plastic pipes with diameters as high as steel pipes (100 and 150 mm). Further developments are still needed to evaluate the feasibility of large-scale manufacturing operations, assess joining technology, and develop codes and standards for hydrogen-service FRP pipelines.

Figure 19. Composite FRP pipelines.

FC vehicles

FCH technologies for road and specialty vehicles are of a high importance today. Some car manufacturers, such as Toyota already launched sales of FCH vehicles in the regions where refuelling infrastructure is already in place. The examples of road vehicles include: passenger cars, buses, scooters, light trucks, etc. They use hydrogen as a fuel and have no engines as the FC and electric motor used instead. The availability of infrastructure is a key step towards commercial success of these products. These vehicles in appearance are similar to conventional vehicles. As opposed to conventional vehicles they emit no pollutants and are very quiet while in operation. Another important application is speciality vehicles. The speciality vehicles are designed for specific purposes and usually operate in fleets. FC forklifts is a good example of the specialty vehicles. This type of vehicles requires a power from 1.5 to 10 kW. At the moment many private companies are investing in a FC forklift fleet and refuelling infrastructure as they benefit from their use almost immediately.

The key features of FC vehicles

FC cars have an electric drive train powered by a FC that generates electricity in electrochemical reaction using hydrogen. Whilst there are a wide variety of prototype FC cars the following key features (Figure 20) are common for the most of them [13]:

- Hydrogen fuelling system;
- Hydrogen storage system;
- Hydrogen fuel delivery system;
- FC system;

- Electric propulsion and power management system.

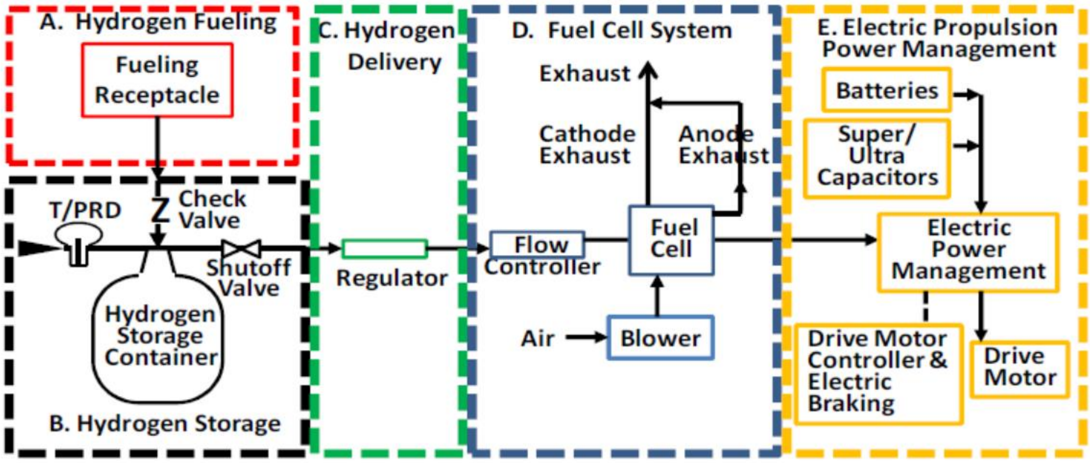


Figure 20. The key systems of an FC car [13].

During refuelling, hydrogen is supplied to the car through the fuelling receptacle (A) and flows to the hydrogen storage system (B). The hydrogen supplied and stored within the hydrogen storage system, usually in a compressed gaseous form. When a FC car starts, hydrogen gas is released from the storage system. Pressure regulators and other equipment within the hydrogen delivery system (C) reduce the pressure to the appropriate level for operation of the FC. The hydrogen is electro-chemically combined with oxygen in the FC system (D) to produce high-voltage electric power. That electric power is supplied to the electric propulsion power management system (E) where it is used to power electric drive motors or charge batteries and ultra-capacitors.

FC cars

Figure 21 illustrates a typical layout of key components of a typical FC car [13]. The fuelling receptacle is positioned on the rear quarter panel of the car as in other common vehicles. As with gasoline containers, hydrogen storage containers are usually mounted transversely in the rear of the car, but could also be mounted differently, such as lengthwise in the middle tunnel of the car. Fuel cells and ancillaries are usually located under the passenger compartment along with the power management, drive motor controller, and drive motors. Given the size and weight of traction batteries and ultra-capacitors, these components are usually located in the car to retain the desired weight balance for proper handling of the car.

Hydrogen fuelling system

Hydrogen may be supplied to the car at a refuelling station. At present, hydrogen is most commonly dispensed to cars as a compressed gas pressurised up to 125% of the nominal working pressure (NWP) of the car to compensate for transient heating from adiabatic compression during fuelling.

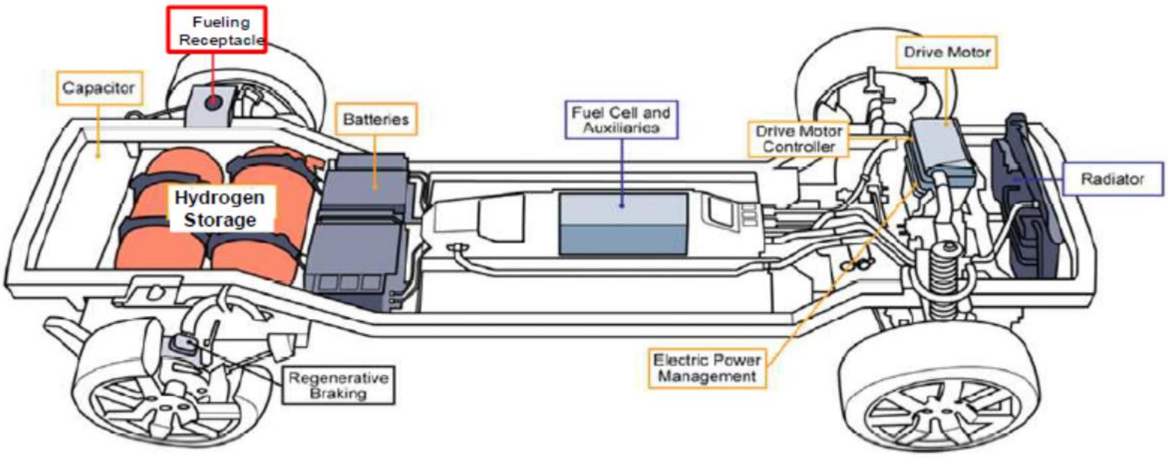
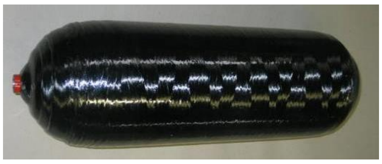


Figure 21. An example of a FC car [13].

Hydrogen storage system

The key functions of the hydrogen storage system are to receive hydrogen during refuelling, to contain it until needed, and then to release hydrogen to the FC system for use in powering the car. At present, the most common method of storing and delivering hydrogen fuel on-board is in compressed gas (CGH_2) form. The lightweight compressed gas cylinders at 700 bar are developed to increase storage capacity. They consist of a metallic (Type III) or polymeric (Type IV) liner placed in a fibre reinforced composite structure (Figure 22). The work is on-going to reduce the costs of these cylinders. More information related to on-board hydrogen storage systems will be available in the following lectures.



(a)

(b)

Figure 22. 700 bar cylinder prototypes developed and tested within the STORHY European project: (a) Type III technology, (b) Type IV technology.

Hydrogen fuel delivery system

The hydrogen fuel delivery system transfers hydrogen from the storage system to the propulsion system at the adequate pressure and temperature for the FC to operate. This is achieved *via* a series of flow control valves, pressure regulators, filters, fuel lines (pipes), and heat exchangers. Most of the fuel lines are silver in colour, but sometimes they could be red. If the tank is shut down due to an incident only a small amount of hydrogen will be in these lines. However, first responders should not cut the fuel lines during extrication procedures.

Fuel Cell (FC) system

The FC system generates electricity needed to operate the drive motors and to charge vehicle batteries and/or capacitors. There are several kinds of FCs but PEM fuel cells are the common type used in automotive applications due to their lower temperature of operation, which allows shorter

start up times. The PEM fuel cells electrochemically combine hydrogen and oxygen to generate electrical power. Fuel cells are capable of continuous electrical generation when supplied with hydrogen and oxygen, simultaneously generating electricity and water without producing carbon dioxide (CO_2) or other harmful emissions typical for petrol/diesel-fuelled internal combustion engines. In general, fuel cell stacks in a light duty passenger vehicle generate voltage of around 400 V DC. A converter also connects the fuel cell with the high voltage battery. The operating temperature of the FC is much lower than for internal combustion engine as it is more efficient.

Electric propulsion and power management system

The electric power generated by the FC system (FC stack) is used to drive electric motors that propel the vehicle as well as to power an air pump motor and an air conditioning motor. As shown in Figure 21, many passenger FC cars are front wheel drive with the electric drive motor and drive-train located in the "engine compartment" mounted transversely over the front axle; however, other configurations and rear-wheel drive are also viable options. Larger sport utility vehicle-type FC cars may be all-wheel drive with electric motors on the front and rear axles or with compact motors at each wheel. The high-voltage battery pack is usually placed in a metal case and firmly mounted into the frame. Different FC vehicles use different kinds of batteries such as nickel metal hydride or lithium ion. Other high-voltage components may include a FC contactor, a battery voltage control unit, a DC-DC converter, a power drive unit and an electric heater. Electricity from the FC stack and the high-voltage battery is delivered to the motors through a number of cables, which are typically located inside or behind enclosed high-voltage components and underneath the vehicle. They can be easily identified through the distinctive orange protective covers.

Safety features and concepts

The FC cars are fuelled through a special fuelling nozzle on the fuel dispenser at a refuelling station that connects with the fuelling receptacle on the car to provide a "closed system" transfer of hydrogen to the car. The fuelling receptacle on the FC car contains a check valve or other device that prevents leakage of hydrogen out of the car when the fuelling nozzle is disconnected.

The components of a typical compressed hydrogen storage system are shown in Figure 23. The system includes the container and all other components that form the "primary pressure boundary" that prevents hydrogen from escaping the system. There are three safety devices as parts of the compressed hydrogen storage system:

- A check valve;
- A shut-off valve;
- A thermally-activated pressure relief device (TPRD).

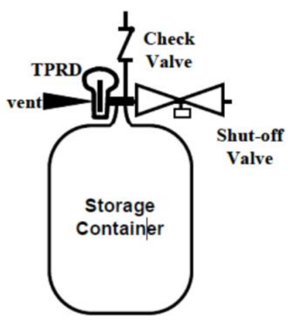


Figure 23. A typical compressed hydrogen storage system [13].

During refuelling, hydrogen enters the storage system through a check valve. The check valve prevents back-flow of hydrogen into the fuelling lines. An automated hydrogen shut-off valve prevents the out-flow of stored hydrogen when the car is not operating or when a fault is detected that requires isolation of the hydrogen storage system.

In the event of a fire, thermally activated pressure relief devices (TPRDs) provide a controlled release of the gas from the compressed hydrogen storage containers before the high temperatures in the fire weaken the walls of the containers and cause their hazardous rupture. TPRDs are designed to vent the entire contents of the container rapidly. They do not reseal or allow re-pressurization of the container. Storage containers and TPRDs that have been subjected to a fire are expected to be removed from service and destroyed. The hydrogen is usually (but not always) vented outside the FC vehicle through a vent line. The exact location of these vent lines depends on a vehicle manufacturer and its model, but it will be usually at the back of the vehicle, near the hydrogen tank [13].

The fuel delivery system shall reduce the pressure from levels in the hydrogen storage system to values required by the fuel cell system. In the case of a 70 MPa NWP compressed hydrogen storage system, for example, the pressure may have to be reduced from as high as 87.5 MPa to less than 1 MPa at the inlet of the fuel cell system. This may require multiple stages of pressure regulation to achieve accurate and stable control and over-pressure protection of down-stream equipment in the event of a pressure regulator failure. Overpressure protection of the fuel delivery system may be accomplished by venting excess hydrogen gas through pressure relief valves or by isolating the hydrogen gas supply (by closing the shut-off valve in the hydrogen storage system) when a down-stream overpressure condition is detected [13].

A number of hydrogen sensors are located in FC vehicles. When a potentially hazardous hydrogen leak is detected the system controller will automatically stop the flow of hydrogen from the tank. There are several areas where sensors can be found: on the instrumentation panel; beside hydrogen storage tanks; near an exhaust pipe; underneath the bonnet; above the headliner in the passenger compartment, etc. When the propulsion system is "ON," these sensors continuously monitor hydrogen concentration in these areas. For example, according to the US First Responders SOP, when hydrogen is detected at a "Warning Level" (that is, above 12% of the LFL), the driver will be alerted by the "H_2" icon located in the instrument panel cluster, and the Driver's Information Centre (DIC) will show a "H_2 Detected" message. If hydrogen is detected at an "Alarm Level" (above 50% of LFL), the "H_2" icon will blink, an audible beep will sound, and a "H_2 Detected – Evacuate Vehicle" message will appear on the DIC [14].

FC buses

FC buses use the same technology as in FC cars. Hydrogen is stored in tanks usually located on the bus roof. The total capacity is in the 40 kilogram range. The fuel cell stack is located in the rear engine compartment. The bus fuel cell stack is bigger than that for FC car and generates higher voltage, of around 600 V. The main advantages of FC buses compared to the conventional ones are reduced pollution; lower concentration of greenhouse gases; increased energy efficiency and a quieter operation.

There is a range of European projects associated with a hydrogen-based transport. For example, Clean Energy Partnership (CEP) [15] is the project that aims to test and to demonstrate the use of

FCH technologies in transport applications. CEP, established in 2002, is an international cooperation of 18 partners including leading car manufacturers such as BMW Group, Honda, Daimler, Ford, Hyundai, GM/Opel, Toyota and Volkswagen. In 2011 CEP moved to its third phase 'Market preparation'. Another project is HyFleet: Cute (http://www.global-hydrogen-bus-platform.com/Home), which seeks to develop and operate the world's largest fleet of FC buses. There are between 40 and 45 FC and Internal Combustion Engine (ICE) hydrogen-driven buses in operation around the world, most of which are in regular public service [16]. These buses have been successful in providing valuable data to developers and operators as they are used under harsh conditions, through uninterrupted operation and extreme climatic conditions. Another important aspect of this project has been to familiarize the public with this new technology and to thereby gain public acceptance of its introduction [16]. London now has a fleet of 8 FC buses running on route RV1 between Covent Garden and Tower Gateway (Figure 24).

Figure 24. Wright Pulsar 2 hydrogen-powered bus on route RV1 in London.

"FC-buses have evolved substantially in the last decades. A number of different design configurations have been used, including hydrogen in ICE, and various fuel cell technologies. In addition, companies have used direct drive systems and hybrid drive systems, where an energy storage device (battery or ultra-capacitor) is included within the drivetrain to reduce peak loads and allow regenerative braking" [17]. A brief comparison between the main hydrogen bus technologies is presented in the review curried out within NextHyLights project [17].

Figure 25 shows a layout of SunLine's "All American" FC bus [18]. In this example hydrogen is stored as a compressed gas (CGH2). Adams [19] carried out a research looking into the optimum on-board storage pressure that would be required for buses equipped with CGH2 tanks. It was concluded that a standardised on-board storage pressure restricting device is required in order to ensure that a vehicle is not refilled to a pressure greater than the storage pressure to which it was designed. This standardisation would also be necessary to reduce unnecessary system development costs for vehicles and the associated refuelling infrastructure as well as reducing the risk of damaging refuelling interfaces due to incompatibility. The compression energy within the gas in a container increases for a given mass of hydrogen with increasing storage pressure; therefore sudden expansion of the gas due to the container rupturing could have severe consequences that would increase with higher pressures. Therefore when considering storage systems for buses, where volume is not as critical a constraint as in cars, optimum pressures for non-articulated single deck city buses were found to be between 20 and 35 MPa [19].

Safety devices used in FC buses are similar to those used in FC cars. Pressure relief device (PRD) is a non-reclosing thermally activated device that is designed to protect a pressurised hydrogen tank from a catastrophic failure should an emergency situation such as a fire occur. It is used to ensure that the thermal impact caused by flames does not increase the pressure in the storage vessel beyond its structural capacity. It should be noted however that fires that cause a PRD to open may not result in the hydrogen immediate ignition upon release. The hydrogen tanks are equipped with thermally activated pressure relief device (TPRDs) and the stainless steel fuel and vent lines. There is an Emergency Shut-down Device (ESD) button located at the driver's panel, and one on the fuel cell itself in the engine compartment.

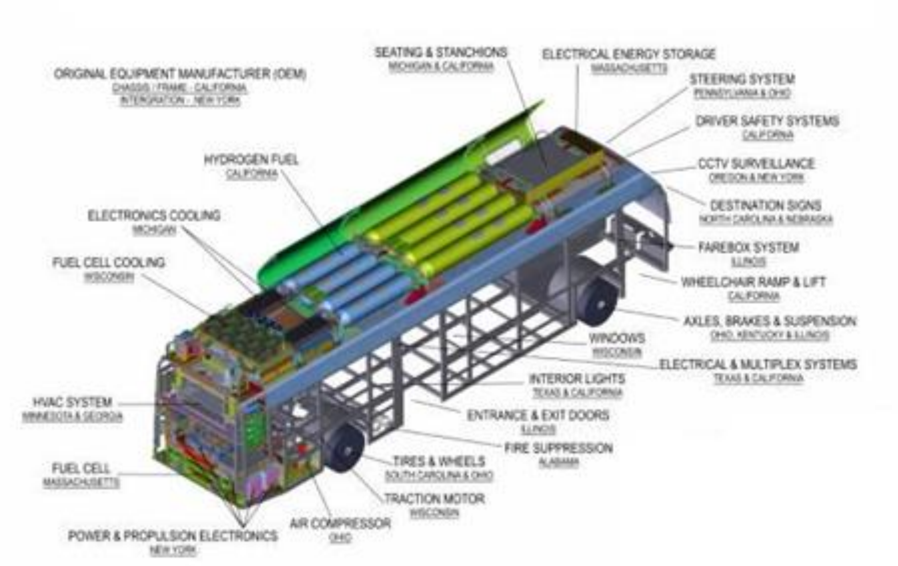


Figure 25. A layout of the main components of a FC bus [18].

First responders have to learn how to deal with FC vehicles in case of the traffic accidents. The main hazards are associated with a high voltage (up to 600 V) and with high gas pressures (up to 70 MPa). For different types of road vehicles regulation EC79/2009 in conjunction with EC406/2010 requires labelling of FC vehicles: for light duty vehicles the label has to be visibly placed near the fuelling receptacle (another label should be inside the engine compartment). The Rescue Data Sheets should be available for all FC vehicles and should be found on-board the vehicle. Fire brigades usually have access to this information via communication links. The vehicle identification parameters should also contain all high voltage and high pressure characteristics informing first responders well in advance. Similar to conventionally fuelled vehicles, the following components may pose hazards to first responders in case of a road accident: bumpers; shock absorbers; tires; hood and trunk struts; airbags; seat belt pre-tensioners; air-conditioning system; batteries. Please note that disconnecting a low-voltage cable will isolate and shut-off all vehicle systems (e.g. the hydrogen storage, high-voltage and low-voltage systems) in a FC vehicle.

FC forklifts

Many companies with large warehouses or distribution centres currently deploy FC forklift trucks to move goods, which operate on 24/7 basis [11]. FC forklift trucks are hybrid vehicle that couple a fuel

cell, usually from 1.5 to 10 kW, with a battery. Hydrogen cylinders are stored outside the facility/warehouse. Hydrogen is either delivered to the site by an industrial gas supplier or produced on site using natural gas reforming or water electrolysis methods. A refuelling of a FC forklift with hydrogen mostly occurs indoors (but outdoor dispensers are also possible) and only takes a few minutes. Compared to battery powered specialty vehicles FC forklifts have longer life-span; have more power for a longer period of time and can be refuelled in less than 3 minutes. Another plus point of FC forklifts are lower operating costs and increased productivity due to a lower number trips to a battery charging station. Since there is no need for battery chargers, storage, or battery swap areas more warehouse space is available for other uses. Main industrial suppliers sell warehouse hydrogen refuelling stations for FC forklifts.

An example of a FC forklift and the fuel cell unit are depicted in Figure 26.

A FC forklift

FC fuel cell of a forklift

Figure 26. A FC forklift truck and its FC unit [11].

The main components of a FC unit are demonstrated on Figure 27. They include:

- fuel cell (called PAC);
- fuel cell auxiliaries;
- hydrogen storage vessel, the volume of which varies between 20 and 70 L in water and fitted with a regulator system;
- lithium ion battery, which passed the tests required by the United Nations (UNO) specified in the United Nations Manual of Tests and Criteria, Section 38.3;
- water collection tank.

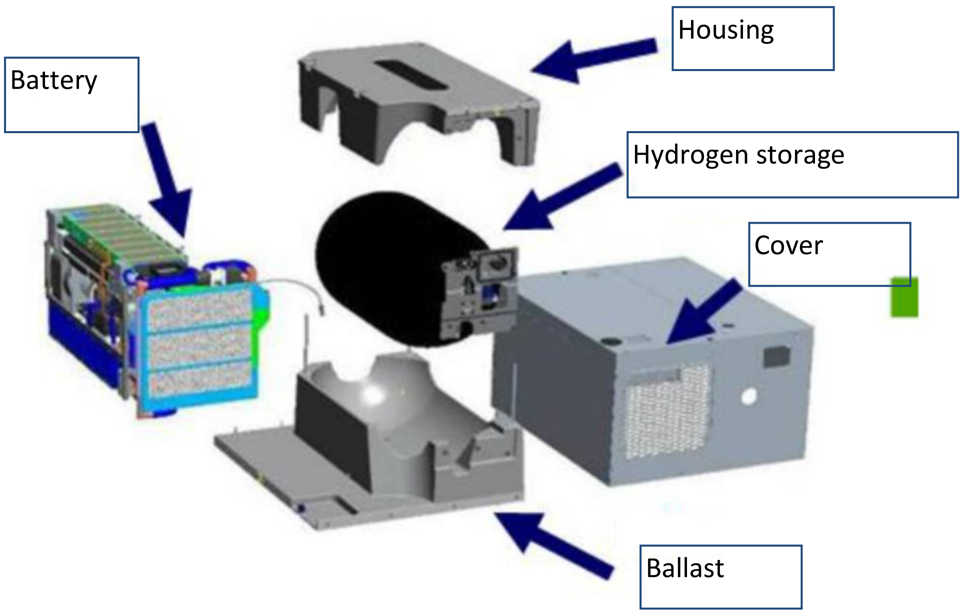


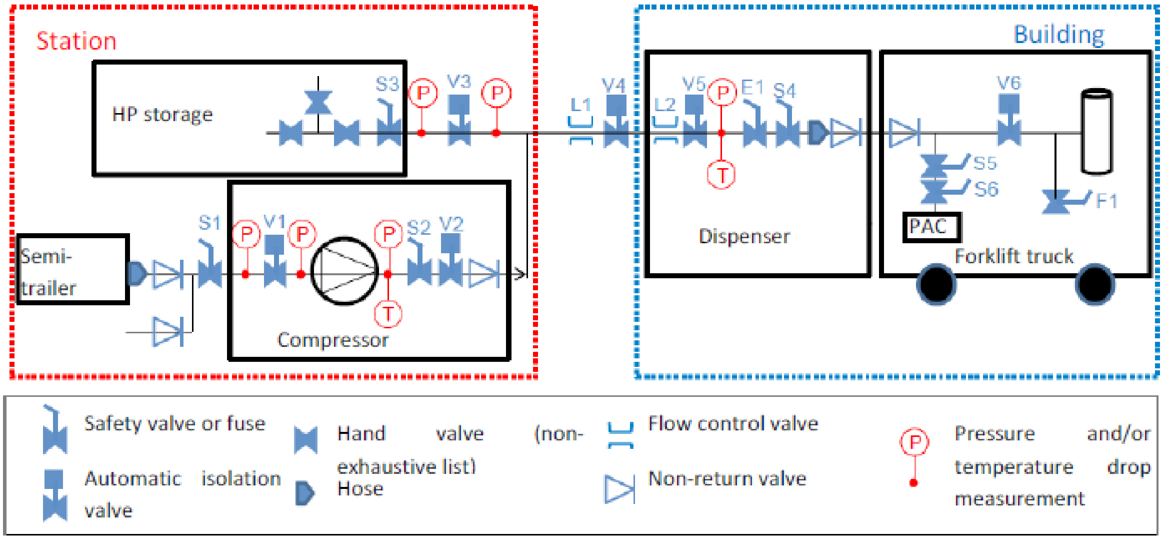
Figure 27. Forklift fuel cell unit components.

From a safety point of view, the hydrogen storage is protected with a TPRD (triggered by a thermal fuse) situated between the forklift's isolation valve and the cylinder. The fuse opens at 109°C and allows the rapid release of pressurised hydrogen. There is also a non-return valve on the filling port to prevent gas in the storage from escaping. Also all the components of the FC are built into a cast iron casing, which is in turn, is protected by a cover. There are two advantages to this cast iron casing: it provides protection against external mechanical damage and allows the flow of hydrogen to be vented out in the event of an external thermal attack.

Hydrogen refuelling stations

Refuelling of a FC vehicle is not much different from a conventional vehicle refuelling process. In most demonstration programmes FC vehicles are refuelled by trained/authorised personnel. There more than 200 hydrogen refuelling stations around the globe tested in the last ten years. Hydrogen either delivered to the station or produced on-site. A map of hydrogen refuelling stations is available at: http://www.netinform.net/h2/H2Stations/Default.aspx. Similar to compressed natural gas CNG refuelling systems hydrogen vehicle refuelling is a closed-loop system, thus preventing any leaks. The dispensing nozzle must be "locked on" to a receptacle before any hydrogen can starts flowing. Hydrogen dispensers are equipped with safety devices including breakaway hoses, leak detection sensor and grounding platforms. These measures enhance safety in the case of human error such as trying to drive away while the dispenser is still connected to the vehicle. Indeed, the passenger vehicles do not allow an operator to drive away with the nozzle attached/fuel door open. This is not the case with FC forklift trucks.

The main function of the installation is to fill the tanks of FC vehicles with gaseous hydrogen. A block diagram of the fork-lift truck refuelling installation is shown in **Error! Reference source not found.**. The gaseous hydrogen contained initially in a semi-trailer at a pressure of 200 bar, and then is compressed in the high-pressure (HP) storage. During refuelling process the tank is filled by a balancing of the pressure. The pressure in HP storage is between 450 bar for forklifts and buses and 1000 bar for cars. The pressure in the on-board storage tanks is between 350 bar for forklift trucks and buses and 700 bar for a car. To fill a car as fast as possible hydrogen is cooled during filling by cryogenic liquid nitrogen or in a cold unit.



Source: Air Liquide, 2015.

Figure 28. A block diagram of a hydrogen refuelling station [11].

The semi-trailer, the compressor and the HP storage are located outside in an area called the outdoor area (Figure). The dispenser can be located in the dedicated building and/or in a warehouse and/or outside depending on the applications. The volumes of these areas could vary from hundreds to 10,000 cubic metres. A connecting pipe runs between the filling area and the dispenser.

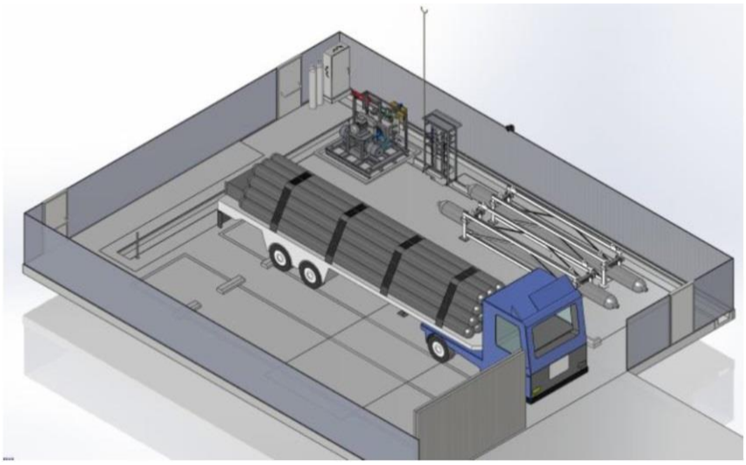


Figure 29. A typical layout of the outdoor area.

The compressor system is installed on a concrete slab and is placed in a shed or a container. It consists of a diaphragm or a hydraulic compressor for the hydrogen, a compressor cooling system and miscellaneous equipment (valves, pressure relief devices, etc.). The HP storage (sometimes called the buffer) provides a buffer capacity and meets the Pressurised Equipment Directive (DESP). Its total volume ranges between 1,000 and 3,000 L. It may consist of several storage units, volumes of which vary between 50 and 1,500 L. The storage is protected by a relief valve (S3 on Figure 28). The discharge from this relief valve is evacuated through the same vent stack as that used for the compressor system [11].

The pipework connects the HP storage to the dispenser. Depending on the station site the pipework total length can vary between ten to several hundred metres. An outdoor pipes routing is preferable in order to avoid the risk of a leak indoors. Those parts of pipelines that cross any access roads are contained in a channel or supported on a gantry or buried with exposed parts physically protected. Pipework enters the building at the last possible moment for connection to the dispenser. The materials used for the pipes should be compatible and suitable for the use with hydrogen (for example, stainless steel). The pipe diameter is usually less than 1" depending on the length of the pipework.

The dispenser may be installed in one of three different places: in a storage cell, in a dedicated room/building or outside. The dispenser consists of the following:

- a mast equipped with a hose (fitted with an anti-tear-out system and connected to a filling gun) and a cabinet containing the pipework connection and the system of valves;
- a station-vehicle communication system and a vehicle earth cable (when needed);
- a pipe for draining water from the water tank;
- a remote interface allowing the operator to remotely control the filling of the forklift (Figure 30).

Figure 30. The examples of the outdoor and indoor hydrogen dispensers [11].

In general, the following safety systems are in place [14]:

- Pressure relief systems:
  - Burst disks
  - Pressure relief valves/devices (PRV/PRD)
  - Safety vents
- Fire and leak detection systems:
  - Telemetric monitoring
  - Hydrogen gas detectors
  - UV/IR cameras
  - Fuelling line leak check on nozzle connect
- Design elements:
  - Engineering safety margins and analysis
  - Hydrogen compatible materials
  - Siting to satisfy established regulations
  - Cross-hatched areas for user attention

- Other systems:
    - Emergency stops
    - Dispenser hose break-away devices
    - Impact sensors at the dispenser
    - Controlled access
    - Excess flow control (fuelling)
    - Pre-coolers

The outdoor area is easily identified, marked out, physically protected and has controlled access. It complies with "industrial" hydrogen installation rules. The access to the outdoor area is restricted to the authorised personnel only [11].

The hydrogen compressor is equipped with two automatic isolation valves at the intake and exit (V1 and V2), a safety relief valve (S2) and a non-return valve (**Error! Reference source not found.**). Discharges from the relief valves are directed through a vent stack, which is sized according to the maximum permitted flow rate, the noise on exiting the vent, the heat flow caused by the hydrogen flame and expected overpressures in the event of the discharged hydrogen cloud igniting. Also, the compression system includes a retention tank sized according to the quantity of oil used. The connecting pipework includes an automatic isolation valve (V3 in **Error! Reference source not found.**), normally closed and located in the outdoor area [11].

The measures contributing to the dispenser safety are as follows:

- The dispenser is located away from roadways. If it is needed protective barriers are put in place around it to prevent any collision with a vehicle approaching to be filled or with another one manoeuvring in the area. The dispenser is placed on a raised platform.
- Combustible substances are stored at least 4 m away from the dispenser. Markings on the floor make the perimeter clearly visible.
- The vehicles' speed is limited. An area is marked on the floor to indicate the position of the vehicle during filling.
- When the operator handles the hose it is no longer under pressure.
- The filling control interface is 2 m away from the hydrogen mast (ATEX zoning).
- A break-away system is fitted to the hose. If the hose is torn out, the device quickly closes two valves to isolate the leak on the station side and the truck side. It is therefore a weak point in the line.
- The dispenser is fitted with: a regulator/a flow limiter (L2), a closed isolation valve (V5), a safety reducing valve (S4) and an open vent valve (E1) as shown on Figure 28. During normal operation of the station the flow restrictor L2 is used to regulate the downstream flow rate in a way that a rise in pressure in the vehicle's storage is limited. In the event of an accidental rupture occurring downstream of this item it is expected that it will limit the rate of leakage. Discharges from S4 and E1 are collected in a second vent stack which is sized according to the maximum permitted flow rate, the noise on exiting the vent, the heat flow caused by the hydrogen flame and expected overpressures in the event of the released hydrogen cloud igniting. It is situated on the building.
- If the dispenser is located in the building, a flame detector (UV/IR sensor appropriate to the radiation characteristics of a hydrogen flame) could be positioned above the dispenser.

- Hydrogen detector is installed in the dispenser at the top of the mast. If during the filling hydrogen concentration greater than 25% of the LFL or if the flame is detected all isolation valves (V3, V4 and V5) will be closed and vent valve (E1) will open (**Error! Reference source not found.**).
- If the dispenser is located in the building hydrogen detector is installed in the upper part of the building (ambient detection). In actual fact the low volume inside the building may not allow sufficient dilution of the hydrogen discharge to prevent it from forming an explosive atmosphere. An air extractor is also installed as required by standard M58-003.
- Many stations are also telemetrically monitored by the supplier such that they will know if an equipment problem arises, in addition to notifying any onsite personnel [11].

FC stationary applications

Combined Heat and Power (CHP) systems

In the traditional CHP plants electricity and heat are produced by combustion of natural gas in the internal combustion engine or turbine. CHP systems based on FCs generated electricity, heat water in the electrochemical reaction described earlier. Two FC technologies are considered: Solid Oxide Fuel Cell (SOFC) and PEM FC. Natural gas is converted to produce hydrogen and a mixture of hydrogen, carbon dioxide and carbon monoxide (called syn-gas) with impurities is fed directly to the FC to generate energy. In PEM FC systems, which use lower temperatures, the syn-gas needs further purification to remove carbon monoxide and sulphur-containing compounds. MicroCHP installations have been introduced in Europe within the Callux project (http://enefield.eu/).

Back-up power generation

A back-up system connected to a data-centre

The main objective of this type of technology is to provide instantaneous power in case of a blackout. The power capacity of this installation is between 16 and 80 kW with up to nine hydrogen cylinders. The main advantages of this application are:

- High reliability and fast start-up
- Scalable autonomy, only depending on gas storage volume
- Low maintenance
- Clean and silent operation [11].

Potential users of this type of application include: telecom, datacentres, hospitals, military, industries, luxury hotels, etc. An example of the system is depicted in Figure 31 showing a FC back-up power unit used in IP Energy project (Aix-en-Provence, France). 30 kW backup power system installed in 2008 is first containerized solution. Internal gas storage allowed a 4-hour operating capacity.

Figure 31. A FC back-up power coupled with IP Energy data centre.

The safety features and concepts for the system are as follows:

- The FC system has two separated vent lines, one for oxygen and one for hydrogen, that discharge the gas on the roof of the container at a hazard distance to avoid mixing of oxygen and hydrogen during discharge. After a discharge, a residual amount of hydrogen subsists within the system.
- The process compartment is equipped with two hydrogen sensors that can trigger an emergency stop if the hydrogen concentration in the containers is above 0.4 vol. %. If an abnormal hydrogen concentration is detected a safety stop is triggered and the following actions will take place:

  - Stop all system processes
  - Activate the mechanical ventilations
  - Insulate the gas storages by closing the solenoid valves.
- Detection of hydrogen is monitored continually even when the system is in a standby mode. In the event of loss of detection the system triggers a safety stop.
- The containers are equipped with fire detectors. In case of their activation the following actions should be undertaken:
  - Stop all system processes
  - Insulate the gas storages by closing the solenoid valves
  - Cut off ventilations
- The hazardous explosive atmospheres resulting from potential hydrogen leaks or releases shall be prevented in the FC enclosure. Passive prevention measures include but not limited to: a use of joints that are permanently secured and constructed in a way that they limit the maximum release rate to a predictable value; and natural ventilation. Active prevention methods include but are not limited to: active ventilation; a flammable gas detection system; other means of leak detection (e.g. through pressure measurements relative to control settings).
- Inside the container, where hydrogen may leak or diffuse into, is not classified since safety barriers ensure no dangerous hydrogen ATEX at the leaking point or by accumulation. Nonetheless, all equipment installed just below the container ceiling and capable to ignite flammable hydrogen-air mixtures is certified for ATEX zone 2. In particular, it concerns the hydrogen and fire sensors and the ventilation system. Besides the electrical compartment is systematically separated from the process compartment.
- Oxygen is not flammable in air but it supports combustion process. An oxygen leak can be an origin of a fire. The fire risk is increased when the atmosphere is enriched with oxygen. Any contacts must be avoided between oxygen and the organic matters due to the fire risk.
- General measures of risk prevention are taken with the design and in the exploitation of this system:
  - Correct choice of materials (i.e. degreased stainless), use of protected pipes and without abrupt elbows, tight connections, etc.
  - Limitation of the oxygen flows according to the pressure
  - Protection of the oxygen lines by filters in order to trap dust that is likely to ignite
  - Natural and forced ventilation in the process compartment
  - Lengths reduction of the pipes under high pressure, sufficient hazard of the pipes from the electric components
  - Re-grouping of the units containing oxygen in a delimited zone (compartment)
- Adherence to the procedures of control and maintenance (periodic tests) of the facility [11].

Decentralised hydrogen production

The decentralised (or distributed) hydrogen production refers to the systems over a range of scales, from an island community to a home electrolyser for a personal use. A move towards distributed production can result in energy independence for the end use; however it also means there is a need for a new “safety culture” as the public will have a greater responsibility. Some examples of home systems have been presented by Honda and ITM:

- Honda home energy station: http://automobiles.honda.com/fcx-clarity/home-energy-station.aspx
- ITM home system: http://www.itm-power.com/page/17/Hydrogen+Home.html

Hydrogen-based energy storage systems

As an example of hydrogen-based energy storage system we will consider the Greenenergy Box. The Greenenergy Box^{TM} is a containerized hydrogen chain comprising of an electrolyser, a fuel cell, a water and heat management system, and electrical converter systems coupled with hydrogen and oxygen storages. The Greenenergy Box^{TM} is an integrated modular system that can offer a power from 50 to 500 kW with a storage capacity from 0.2 to 2 MW. Its principle is indicated in Figure 32. Several systems can be coupled to increase the power and the energy capacity providing the function of a back-up system for few hours at high power [11].

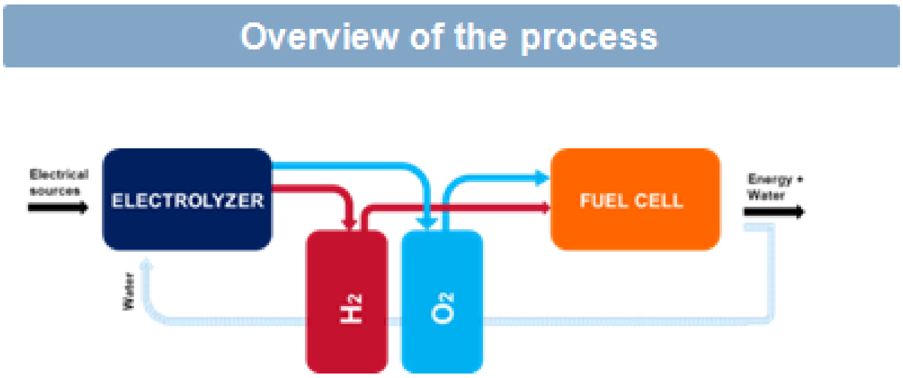


Figure 32. An overview of Greenenergy Box process.

The photovoltaic panels provide electricity to the electrical network and its surplus is used by the electrolyser to generate gaseous hydrogen and oxygen. Once produced gaseous hydrogen and oxygen are stored in separated tanks installed aside of the Greenenergy Box^{TM}. Owing to the FC system stored hydrogen and oxygen can be used to produce electricity to ensure partial energetic autonomy of the buildings as well as the backup system in case of power cuts. The Greenenergy Box^{TM} manages itself the electricity received by the photovoltaic panels to electrolyze water or to provide electricity to the network. Furthermore heat, which is also produced by the system during both electrolysis and fuel cell processes, is also managed and valorised for the adjacent buildings.

The water-proof and wind-resistant Greenenergy Box^{TM} has three different compartments: an electrical compartment, a fuel cell compartment and an electrolyser compartment as shown in Figure 33.

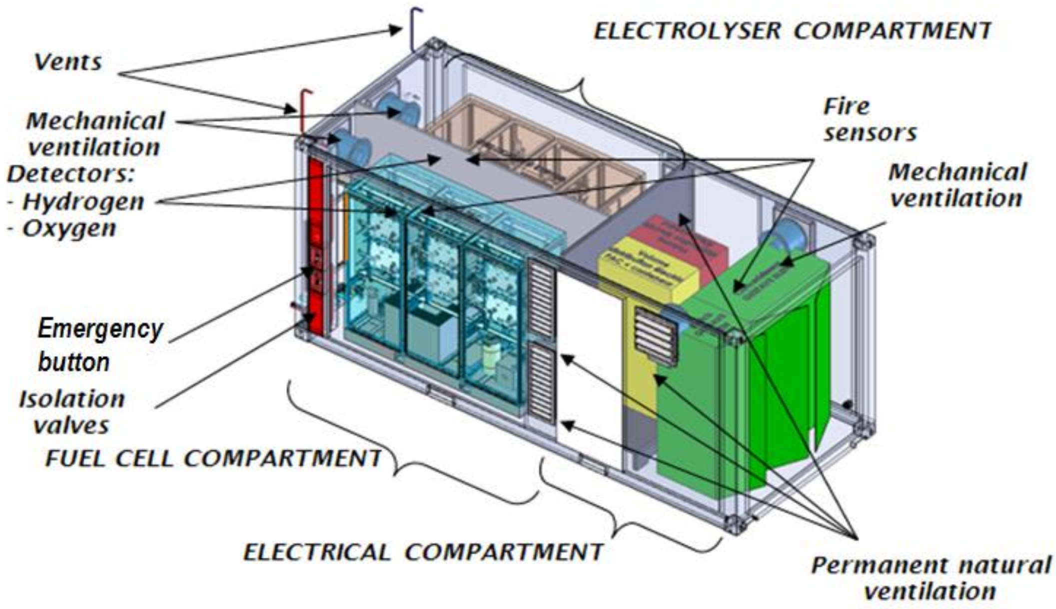


Figure 33. A schematic of the Greenenergy Box™ [11].

The Greenenergy Box™ is CE certified by following the Low Voltage Directive LVD 73/23/EEC, the Electromagnetic Compatibility Directive EMC 89/336/EEC, Machinery Directive MD 98/37/EC, Pressure Equipment Directive PED 97/23/EC.

The risk assessment for this system is carried out in three steps. First, a document called "Basic safety considerations" describing the main safety requirements, which should followed for the architecture and conception stages of the hydrogen chain, is prepared. Once the architecture of the system is sufficiently detailed, a HAZOP (HAZard and OPerability Study) review of each subsystem is performed to define the potential causes of each process deviations, associated potential consequences and assess the existing barriers. As third stage, a fault tree analysis completes the HAZOP review to highlight the conception failure, inappropriate system configuration and external sources of danger. All the safety study is collected in a document entitled "Synthesis of the safety studies of the Greenenergy Box™ [11]. The overall safety strategy of the hydrogen chain is detailed below in six different parts.

1. Leak suppression and control

- Equipment and piping materials are chosen to be compatible for hydrogen and oxygen use. In particular, hydrogen material embrittlement and oxygen corrosion are selected from the IGC15/06, ISO/TR 15916 and ISO 11114-4. Steel cylinders are commonly used to store pressurized hydrogen and oxygen. The maximum carbon equivalent for hydrogen is 0.43 as described in the IGC 121/04, § 3.
- Welded connections are preferred and are used in a practical way to minimize potential leak sources. The number of joints and fitted connections is minimized.
- Both electrolyser and fuel cell compartments of the Greenenergy Box™ are equipped with two hydrogen sensors and an oxygen sensor. A safety shut-off valve triggers at 10% of the hydrogen LFL (0.4 vol. % H_2 in air) and an emergency shut-off occurs at 25% of the LFL (1 vol. % H_2 in air). Oxygen detection triggers whenever the oxygen concentration reaches more than 23 vol. % in air.

- Furthermore, hydrogen and oxygen leaks are also detected by difference of pressure during standby phases. If a tank or a portion of pipe loses pressure during a standby stage, it potentially means that there is leak. If there is a minor loss of pressure during the standby stage, an alarm triggers and if the pressure loss is too significant the system will not be able to restart.
- Before commissioning, hydraulic and leak tests are performed as required by the Pressure Equipment Directive.
- Regular inspections and preventive maintenance program are organized to ensure the maximum safety level. In particular, leak tests on pressure regulators, valves, pipes, joints and connections etc. are realized regularly. Regular visual inspections are organized to check the level of corrosion. Information regarding inspection and maintenance frequency is in the Appendices F of the IGC 121/04 and IGC 13/02.

2. Prevention of formation of flammable or over-oxygenated atmospheres
   - Three compartments of the Greenenergy Box™ are naturally ventilated thanks to lateral vents located on both sides of the container (Figure 33).
   - The fuel cell and electrolyser compartments are both equipped with ATEX type ventilation that triggers for hydrogen and oxygen concentration above respectively 0.4 vol. % hydrogen or 23 vol. % oxygen in air. The maximum flow rates are set for thermal dissipation i.e. 2,500 m^3/h for the FC compartment and 2,700 m^3/h for the electrolyser compartment.
   - Modelling of an accidental hydrogen leak of 750 L/min flow rate using the LES (Large Eddy Simulation) approach developed at the University of Ulster highlights that it takes about 10 s for a hydrogen sensor to detect a hydrogen concentration greater than 0.4 vol. % in the naturally ventilated electrolyser compartment. Considering the conservative hypothesis of 30 s for a response time of the hydrogen sensor, it can be observed that after 40 s of continuous constant release the hydrogen-air concentration formed below the ceiling is still below the LFL of hydrogen in air i.e. less than 4 vol. % by air. From this moment, the hydrogen sensor sends a signal to the control command that triggers the air intake fan to its maximal speed. It can be observed that the hydrogen air cloud is entirely diluted in less than 2 s.
3. Suppression/Reducing ignition sources
   - The inside of the Greenenergy Box™ where hydrogen may leak or diffuse into is not classified since safety barriers ensure no dangerous hydrogen ATEX at the leaking point or by accumulation. Nonetheless all equipment installed just below the container ceiling and capable to ignite a flammable hydrogen-air mixture is certified for ATEX zone 2. In particular, it concerns the fire detectors, hydrogen and oxygen sensors and the ventilation system.
   - The Greenenergy Box™ and reservoirs are earthed and bonded to give protection against the hazards of stray electrical currents and static electricity.
4. Protection against overpressures
   - Each reservoir and piping lines from the Greenenergy Box™ to the storage tanks are equipped with a pressure relief valve (PRV). The tare pressure of the pressure relief valve is set so that the PRV actuates when the pressure within the reservoir reaches 1.15 of the maximal operating pressure.

- The storage tank vents are mounted vertically at a minimum high of 3 m. They are equipped with a 'hat', for which the weight is calibrated to lift under pressure in order to avoid the introduction of water within the vent.
- The Greenenergy Box^{TM} is equipped with two distinct hydrogen and oxygen vents located at a minimum height of 1 m above the roof of the container and well separated to avoid oxygen-enriched hydrogen-air mixture. Each distinct venting line is common to the electrolyser and the FC and allows the depressurization of the system in less than 2 minutes in case of emergency shut-down.

5. Emergency and safety shut-down
   - The control command that is used for piloting automatically the system is also used to trigger the safety functions. About 70 safety functions are recorded into the control command to detect any process deviation or gaseous leak or fire within the system. Depending on the amplitude of the deviation compared to the safety threshold of the parameter, an emergency or and safety shut-down is triggered and is followed by power shut-down, system depressurization, inerting and ventilation activation (except for fires).
   - The main safety functions i.e. hydrogen, oxygen and fire detections, emergency shut-down button and watchdog of the control command are realized by logic cable and respect a SIL (Safety Integrity Level) 1 [11].

Hydrogen storage coupled with renewable energy sources

MYRTE platform

MYRTE (i.e. Mission hYdrogen – Renewable for the inTegration on the Electrical grid) is a project, which concerns among other tasks on the supply of the grid connected by a photovoltaic plant and on hydrogen hybrid system acting as energy storage. The project is coordinated by the University of Corsica at the site of Vignola (Ajaccio, Corsica, France) with the support of the Corsican Regional Authority, the French Government and the European Union (European regional development fund ERDF). The platform is illustrated in Figure 34. The hydrogen platform has to fulfil two main objectives:

- daily peak load saving of the electrical demand of the Corsican electrical grid by using a photovoltaic (PV)/Fuel Cell (FC)/Electrolyser (EL) renewable energy system;
- use of hydrogen for the PV production smoothing to prevent the strong energy variations to the load.

The overall functioning principle of the MYRTE platform is similar to the one deployed in the Greenenergy Box. The photovoltaic panels provide electricity and its surplus is used by the electrolyser to produce hydrogen and oxygen. Then gaseous hydrogen and oxygen are stored in individual reservoirs. The FC combines hydrogen and oxygen, producing electricity to electrical grid network. Furthermore the heat produced by the system during both electrolysis and hydrolysis processes is also managed and valorised [11].

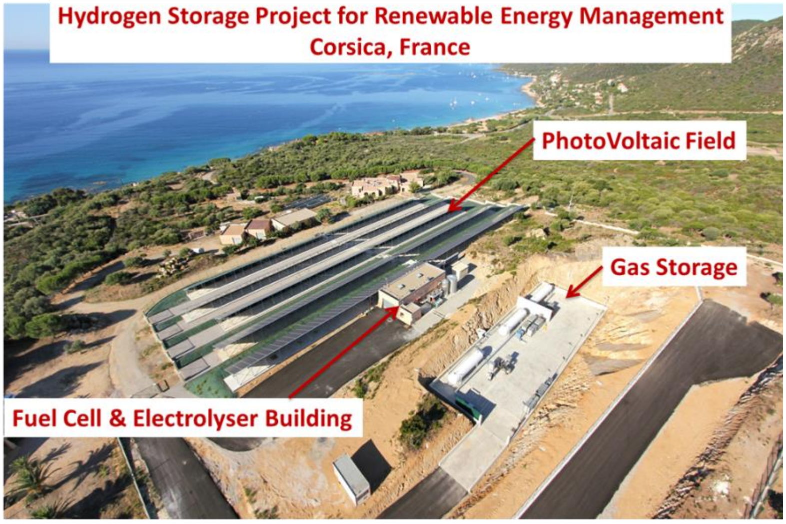


Figure 34. An overall view of the MYRTE platform.

The platform consists of several sub-systems:

- A photovoltaic farm, which provides electrical energy to the electrical network as well as to the electrolyser;
- A hydrogen building that includes:
  - an electrolyser that generates gaseous hydrogen and oxygen using the electricity surplus;
  - a FC that provides electricity using the gas stored in the reservoirs to deliver electricity to the network;
  - The electric management sub-system that ensures the conditioning of the electrical energy to provide the electrical network
  - The control command room to pilot the whole system;
- Hydrogen and oxygen storages in the storage zone;
- Heating managing system that ensures the storage and the management of the heat produced by the system.

The potential hazardous zones and illustration of safety measures are shown in Figures 35-38.

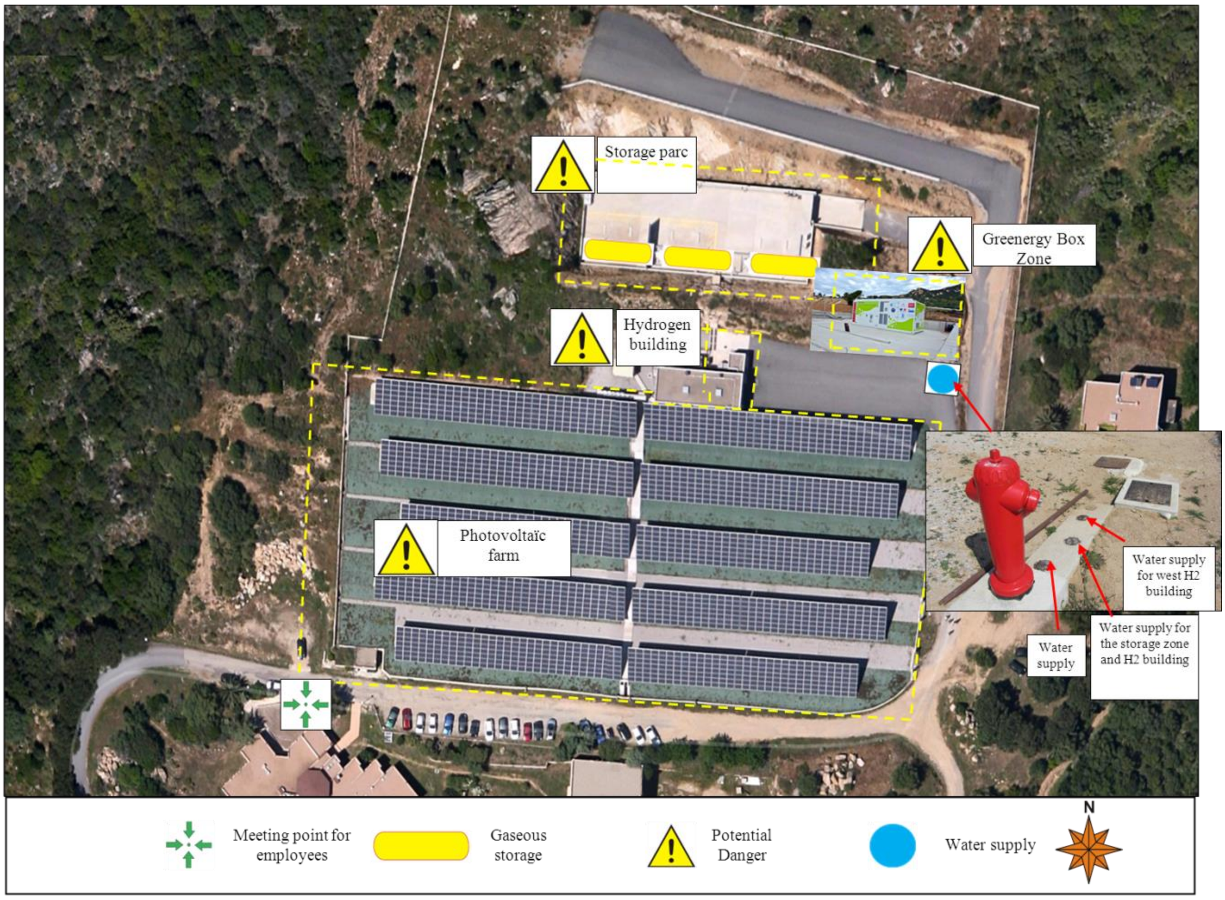


Figure 35. An overview of hazardous zones within MYRTE platform.

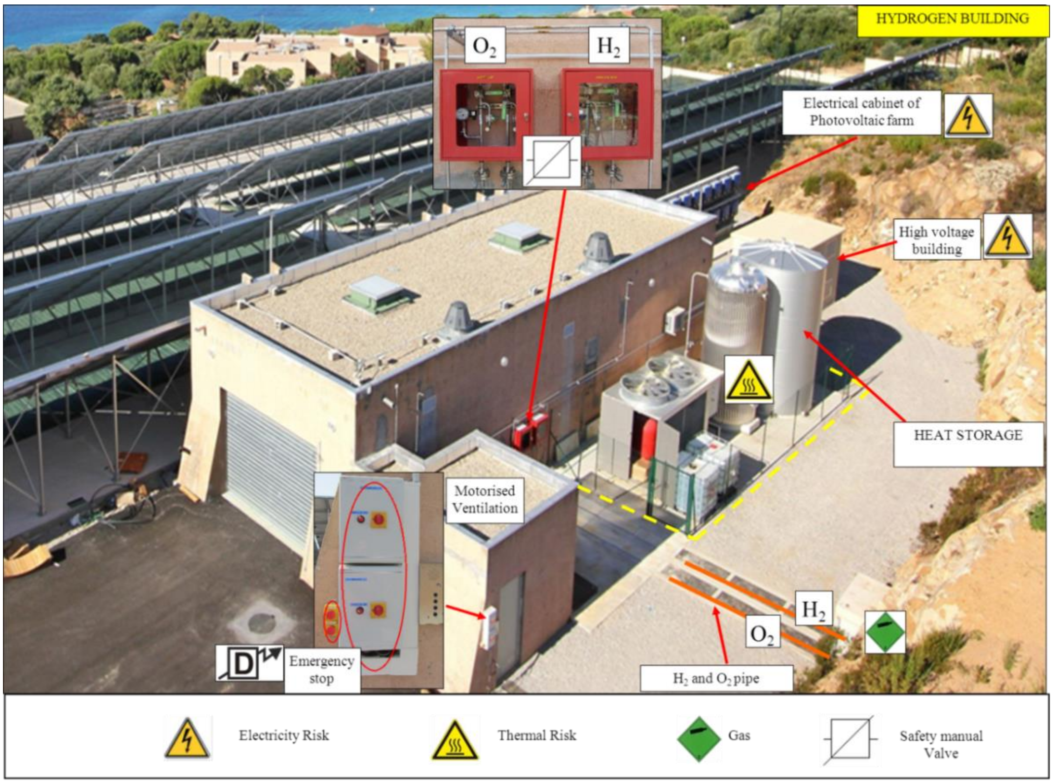


Figure 36. Safety measures in place for the hydrogen building.

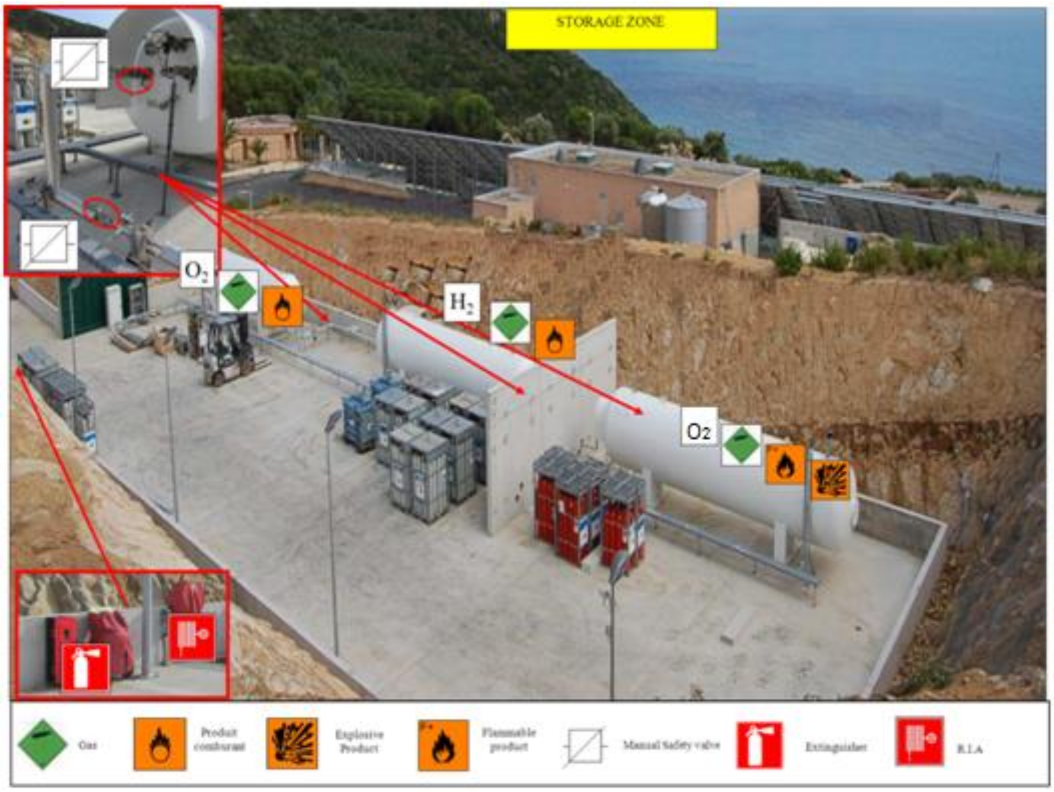


Figure 37. Safety measures in place for the storage zone.

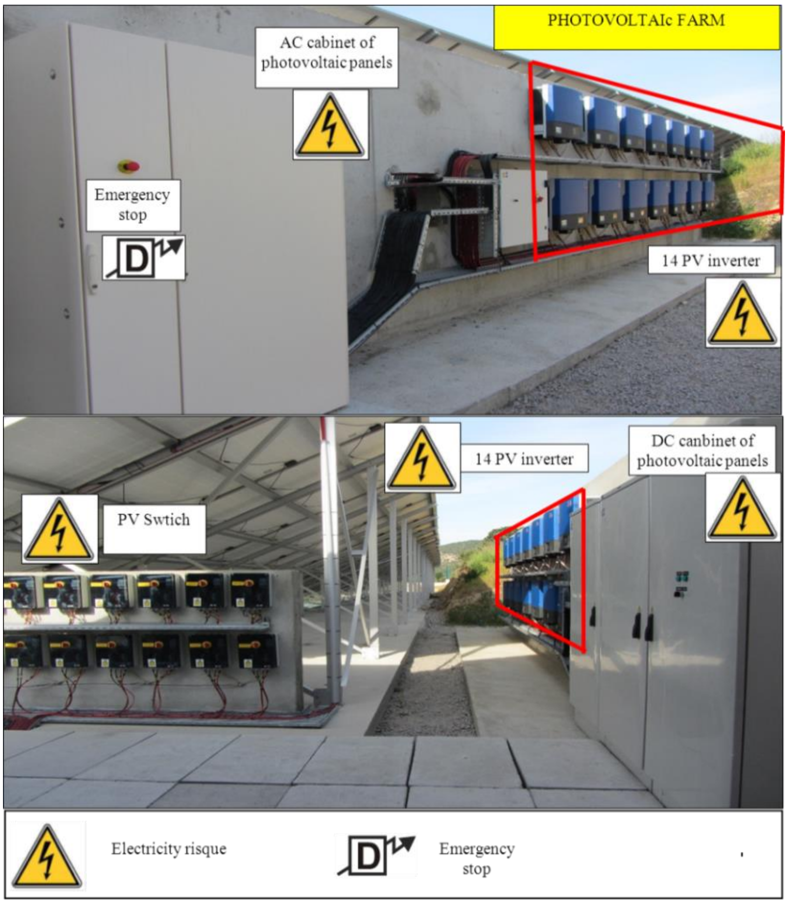


Figure 38. Safety measures in place for the photovoltaic farm.

Incidents and accidents on FCH systems and infrastructure

An incident is an event that has the capacity to lead to loss of or a disruption to operations, services, or functions – which, if not managed, can escalate into an emergency, crisis, or disaster [20], and an accident is an unforeseen and unplanned event or circumstance causing loss or injury. Reporting incidents/accidents, which occurred on the FCH systems or infrastructures, as well as a complex evaluation of their principal causes and the lessons learnt from them, are extremely valuable exercise for both private and public sectors. Information on accidents or incidents related to FCH technologies can be found in the following well-known databases:

- Hydrogen lessons learned from incidents to and near-misses: http://h2tools.org/lessons/
- Hydrogen Incidents and Accidents Database HIAD database:
https://odin.jrc.ec.europa.eu/engineering-databases.jsp
- Bureau d'Analyse des Risques et Pollutions Industries (BARPI) http://www.aria.developpement-durable.gouv.fr/about-us/barpi-contact/?lang=en

All the databases should be regularly updated.

For example, H2Incidents database (recently renamed to Hydrogen Tools. Lessons Learned) has been created by the Pacific Northwest National Laboratory with funding from the U.S. Department of Energy (https://h2tools.org/lessons). In this database, incidents and near-misses are reported without including the names of the companies and other details in a way that confidentiality encourages reporting the events. The incidents are classified according to settings, equipment, damage and injuries, probable causes and contributing factors [2].

Rigas and Amyotte [2] defined the following major causes of incidents/accidents:

- Mechanical material or equipment failure
- Corrosion attack
- Over-pressurisation
- Hydrogen embrittlement at low temperatures
- Boiling Liquid Expanding Vapour Explosion (BLEVE)
- Storage tank rupture due to impact of shock waves or missiles from adjacent explosions
- Human error

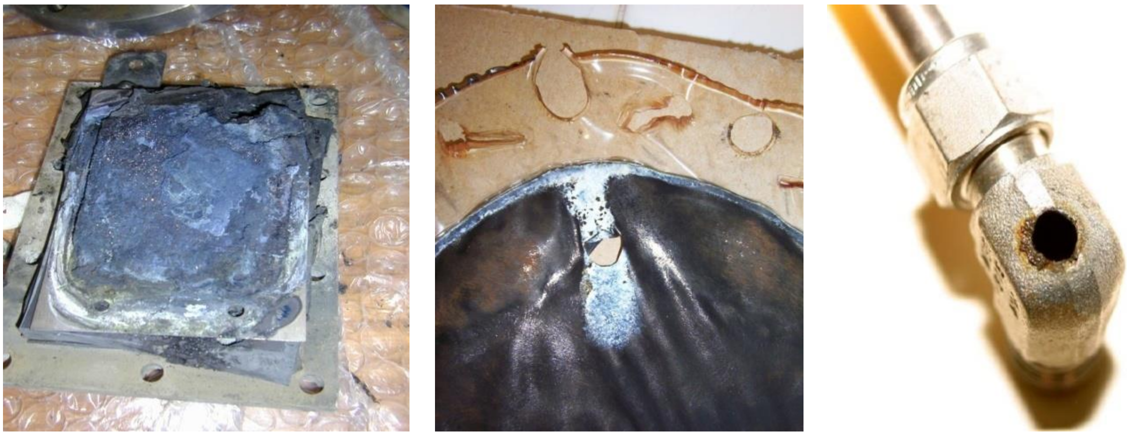
In this first lecture we will only discuss a few examples of incidents/accidents related to FCH technologies. However the following lectures will include a number of relevant examples to each FCH system studied.

Accidents occurred during hydrogen production

An explosion of an electrolyser at the operational pressure of 40 MPa happened on the 7th of December 2005, at a demonstration hydrogen stand at the Kyushu University (Japan) [1]. Possibly, following a membrane leak, an internal hydrogen-oxygen jet fire resulted in a metal (titanium) fire and explosion or rupture of the electrolyser shell. The internal fluid and combustion products were released into surrounding including parking area outside the laboratory building. The windscreens of several vehicles were damaged due to the exposure to hydrogen fluoride which formed during the decomposition of a membrane polymer material [1].

A French-Russian study [21] reported the analysis of the failure mechanisms of PEM water electrolytic cells, which can ultimately lead to a destruction of the electrolyser. A two-step process involving initially the local perforation of the solid polymer electrolyte followed by a catalytic

recombination of hydrogen and oxygen stored in the electrolysis compartments has been evidenced. The photographs of a stainless steel fitting and a nut perforated by a hydrogen-oxygen flame formed inside the PEM stack are presented on Figure 39.



Source: Millet et al, 2011 [21]

Figure 39. Damaged parts of high pressure PEM electrolyser.

An incident at a refuelling station

Hydrogen gas release occurred at **Emeryvile fuelling station**. A PRD had failed, 300 kg of hydrogen released and subsequently ignited. The gas ignited at the exit of the vent pipe and burned for 2.5 hours until technicians were permitted by the local fire department to enter the station and stop the flow of gas. During this incident the fire department evacuated nearby businesses and schools, closed adjacent streets.

The identified root causes of this event are:

- the use of incompatible materials in the manufacturing of the PRD,
- improper assembly resulting in over-torquing of the inner assembly,
- over-hardening of the inner assembly materials by the valve manufacturer.

These problems could have been avoided by adequate quality assurance/quality control procedures during the design and safety reviews.

Hydrogen safety engineering

Hydrogen safety engineering (HSE) is defined as an application of scientific and engineering principles to the protection of life, property and environment from adverse effects of incidents/accidents involving hydrogen [22]. Despite the progress in hydrogen safety science and engineering during the last decade, especially through the HySafe partnership [23], an overarching performance-based methodology to carry out HSE is still formally absent.

HSE comprises a design framework and technical sub-systems. A design framework for HSE, developed at the University of Ulster, is similar to British standard BS7974 for application of fire safety engineering to the design of buildings [24] and is expanded to reflect specific hydrogen safety related phenomena, including but not limited to high pressure under-expanded leaks and dispersion, spontaneous ignition of sudden hydrogen releases to air, high momentum jet fires, deflagrations and detonations, mitigation techniques, e.g. venting of deflagration and natural/forced ventilation, etc. The HSE process includes three main steps as indicated in Figure 40.

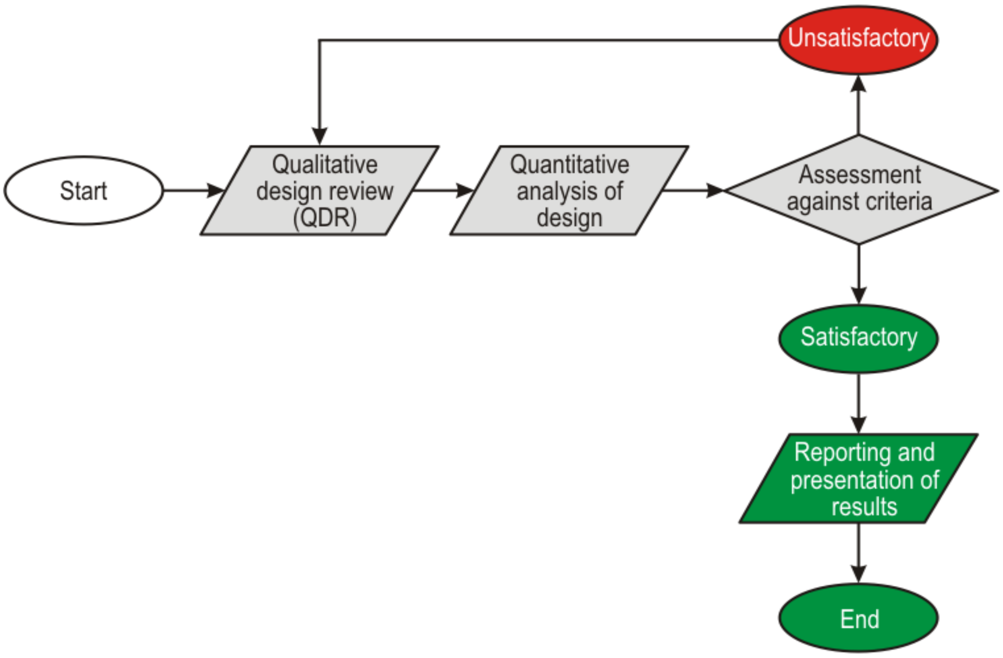


Figure 40. Steps of hydrogen safety engineering process [1].

At first, a qualitative design review (QDR) is undertaken by a team that can include owner, hydrogen safety engineer, architect, representative of authorities having jurisdiction, e.g. emergency services, and other stakeholders. The team defines accident scenarios, suggests trial safety designs, and formulates acceptance criteria. Secondly, a quantitative safety analysis of selected scenarios and trial designs is carried out by qualified hydrogen safety engineer(s) using the state-of-the-art knowledge in hydrogen safety science and engineering and validated models and tools. Thirdly, the performance of a hydrogen and/or fuel cell system under the trial safety designs is assessed against predefined acceptance criteria.

The QDR is a qualitative process based on the team's experience and knowledge. It allows its members to establish a range of safety strategies. Ideally, QDR has to be carried out early in the design process and in a systematic way, so that any substantial findings and relevant items can be incorporated into the design of HFC application or infrastructure before the working drawings are developed. In practice however, the QDR process is likely to involve some iterations as the design process moves from a broad concept to greater detail.

Safety objectives should be defined during the QDR. They should be appropriate to the particular aspects of the system design, as HSE may be used either to develop a complete hydrogen safety strategy or to consider only one aspect of the design. *The main hydrogen safety objectives* are safety of life, loss control and environmental protection. The QDR team should establish one or more *trial safety designs* taking into consideration *selected accident scenario(s)*. The different designs could satisfy the same safety objectives and should be compared with each other in terms of cost-effectiveness and practicability. At first glance, it is essential that trial designs should limit hazards by implementing prevention measures and ensuring the reduction of severity and frequency of consequences. Although HSE provides a degree of freedom, it is mandatory to fully respect relevant regulations when defining trial designs.

The QDR team has to establish the *acceptance criteria* against which the performance of a design can be judged. Three main methods can be used: *deterministic, comparative, and probabilistic*. The

QDR team can, depending on trial designs, define acceptance criteria following all three methods. The QDR team should provide a set of qualitative outputs to be used in the quantitative analysis: results of the architectural review; hydrogen safety objectives; significant hazards and associated phenomena; specifications of the scenarios for analysis; one or more trial designs; acceptance criteria and suggested methods of analysis. Following QDR the team should decide which trial design(s) is likely to be optimum. The team should then decide whether quantitative analysis is necessary to demonstrate that the design meets the hydrogen safety objective(s).

Following the QDR a *quantitative analysis* may be carried out using Technical Sub-Systems (TSS) where various aspects of the analysis can be quantified by a deterministic study or a probabilistic study. The quantification process is preceded by the QDR procedure for two main reasons: to ensure that the problem is fully understood and that the analysis addresses the relevant aspects of the hydrogen safety system; and to simplify the problem and minimise the calculation effort required. In addition, the QDR team should identify appropriate methods of analysis among: simple engineering calculations; CFD simulations; simple probabilistic study; full probabilistic study, etc. A deterministic study using comparative criteria will generally require fewer data and resources than a probabilistic approach and is likely to be the simplest method of achieving an acceptable design. A full probabilistic study is only likely to be justified when a substantially new approach to hydrogen system design or hydrogen safety practice is being adopted. The analysis may be a combination of some deterministic and some probabilistic elements.

Following the quantitative analysis, the results should be compared with the *acceptance criteria* identified during the QDR exercise. Three basic types of approach can be considered to access the performance of safety system against criteria:

- Deterministic approach shows that on the basis of the initial assumptions a defined set of conditions will not occur;
- Comparative approach shows that the design provides a level of safety equivalent to that in similar systems and/or conforms to prescriptive codes (as an alternative to performance-based HSE);
- Probabilistic approach shows that the risk of a given event occurring is acceptably low, e.g. equal or below the established risk for similar existing systems.

If none of the trial designs developed by the QDR team satisfies the specified acceptance criteria, QDR and quantification process should be repeated until a hydrogen safety strategy satisfies acceptance criteria and other design requirements. Several options can be considered when re-conducting QDR following recommendations [24]: development of additional trial designs; adoption of more discriminating design approach, e.g. using deterministic techniques instead of a comparative study; re-evaluation of design objectives, e.g. if the cost of hydrogen safety measures for property loss prevention outweighs the potential benefits. When a satisfactory solution has been identified, the resulting HSE strategy should be fully documented.

Depending on particularities and scope of the HSE study, the reporting of the results and findings could contain the following information similar to requirements [24]:

- Objectives of the study;
- Full description of the HFC system/infrastructure;
- Results of the QDR;

- Quantitative analysis (assumptions; engineering judgments; calculation procedures; validation of methodologies; sensitivity analysis);
- Assessment of analysis results against criteria;
- Conclusions (hydrogen safety strategy; management requirements; any limitations on use);
- References (e.g. drawings, design documentation, technical literature, etc.).

To simplify the evaluation of a HSE design, the quantification process is broken down into several technical sub-systems (TSSs). The following requirements should be accounted for development of individual TSS:

- TSS should together, as reasonably as possible, cover all possible aspects of hydrogen safety engineering;
- TSS should be balanced between their uniqueness or capacity to be used individually, and their complementarities and synergies with other TSSs;
- TSS should be a selection of the state-of-the-art in the particular field of hydrogen safety, validated engineering tools, including empirical and semi-empirical correlations and contemporary tools such as CFD models and codes;
- TSS should be flexible to allow update of existing or use of new appropriate and validated methods, reflecting recent progress in hydrogen safety science and engineering.

The following TSSs are currently suggested and under development for [22]:

- TSS1: Initiation of release and dispersion;
- TSS2: Ignitions;
- TSS3: Deflagrations and detonations;
- TSS4: Fires;
- TSS5: Impact on people, structures, and environment;
- TSS6: Mitigation techniques;
- TSS7: Emergency services intervention.

Hydrogen safety engineering is a key to the success of the hydrogen economy. It is the powerful tool for provision of hydrogen safety by qualified specialists in the growing market of HFC systems and infrastructure. Last not least the HSE can secure high level of competitiveness for hydrogen and fuel cell products.

Summary

Hydrogen has been extensively used in industry for quite a long period of time as a compressed gas or in a liquefied form. Hydrogen is not more or less dangerous than other common fuels, but it is different, with its own specific properties and associated risks. A growing use of FCH applications requires a deep understating of processes, hazards and risks, safety features and concepts as well as professionally trained personnel to deal with possible incidents or accidents in a safe manner. This all requires a significant change in a safety culture, especially for first responders, who will be the first ones to deal with emergency situations that might involve pressurised or liquefied hydrogen, both indoors and outdoors, in urban residential areas, on the roads, in the countryside and in many other different settings.

An overview of FCH systems and infrastructure has been given in this lecture. Potential hazards, risks, safety measures and concepts associated with both stationary and transport FCH applications were considered. An overview of the main hydrogen uses, main production methods, storage options, and distribution modes was also given. In addition, the main principles of hydrogen safety engineering were discussed.

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