HyResponder

European Train the Trainer Programme for Responders

Lecture 3

Hydrogen storage

LEVEL I

Firefighter

The information contained in this lecture is targeted at the level of Firefighter and above.

This topic is also available at level I-III.

This lecture is part of a training material package with materials at levels I – IV : Firefighter, crew commander, incident commander and specialist officer. Please see the lecture introduction regarding competence and learning expectations

FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

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Acknowledgments

The project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (JU) under grant agreement No 875089. The JU receives support from the European Union's Horizon 2020 research and innovation programme and United Kingdom, France, Austria, Belgium, Spain, Germany, Italy, Czechia, Switzerland, Norway.

Summary

This lecture introduces different hydrogen storage options – compressed, liquefied and in solid materials, as well as hazards and safety issues associated with them. Specifically catastrophic rupture of the vessels is introduces along with online tools which may be used.

The HyResponse project is acknowledged as the materials presented here are based on the original HyResponse lectures.

Keywords

Hydrogen storage, compressed hydrogen, storage vessel, liquefied hydrogen, hydrogen storage materials, burst prevention, leak-no-burst

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1. Target audience

The information contained in this lecture is targeted at LEVEL 1: Firefighter. Lectures are also available at levels II, III and IV: crew commander, incident commander and specialist officer.

The role description, competence level and learning expectations assumed at crew commander level are described below.

1.1 Roll description: Firefighter

A firefighter is responsible and expected to be capable of carrying out operations safely in personnel protective equipment including breathing apparatus using equipment provided, like vehicles, ladders, hose, extinguishers, communication and rescue tools, under any climatic conditions in areas and to emergency situations which can be reasonably anticipated as requiring a response.

1.2 Competence level: Firefighter

Trained in the safe and correct use of PPE, BA and other equipment which it is expected they will operate first responders must be supported by appropriate knowledge and practice. Behaviours that will keep them and other colleagues safe should be described by Standard Operating Procedures (SOP). Practiced ability to dynamically assess risk to self and others safety is required.

1.3 Prior learning: Firefighter

EQF 2 Basic factual knowledge of a field of work or study. Basic cognitive and practical skills required to use relevant information in order to carry out tasks and to solve routine problems using simple rules and tools. Work or study under supervision with some autonomy.

2. Introduction and objectives

Hydrogen is typically stored and transported in two forms: as a compressed hydrogen gas or as a cryogenic liquid. The most common way to store hydrogen is in metal or composite cylinders/tanks of different sizes and capacities. Sometimes they can be connected into a bundle or gathered onto a basket for transportation. Due to a small size of its molecules, hydrogen is prone to leak easily through some materials, cracks, or poor joints of the storage tanks, as opposed to other common gases at equivalent pressures. Although hydrogen is generally non-corrosive and does not react with the materials used for storage containers, at certain temperature and pressure conditions it can diffuse into a metal lattice causing a phenomenon known as '*hydrogen embrittlement*.' In addition, in case of fires, the composite materials used for storage vessels may degrade and a loss of hydrogen containment may occur. In the worst-case scenario, this may lead to a catastrophic rupture of a hydrogen storage tank, generating a blast wave followed by a fireball and flying projectiles/missiles. For this reason, hydrogen storage equipment must be designed and maintained to high safety standards to ensure the integrity of the container.

The present lecture gives an overview of hydrogen storage options and also addresses the main safety and technical issues associated with them. It also covers the topics of hydrogen interaction with different types of materials and hydrogen permeation, which are extremely relevant to hydrogen storage technologies. It should be mentioned that the topic of hydrogen storage is vast; thus, this lecture is mainly focused on high-pressure, liquefied and solid hydrogen storage systems, with a close attention to high-pressure storage technology, as it is most common. The phenomena such as unignited releases, fires and explosions will be discussed in the subsequent lectures.

3. Hydrogen storage options

Hydrogen storage is an enabling technology across the entire range of Fuel Cell and Hydrogen (FCH) applications, from on-board vehicles to stationary and portable power generation [1]. There is no universal solution for hydrogen storage. Instead, the solution must be carefully selected to address specific system requirements. For example, the space and weight are critical factors for FC passenger vehicles, whereas weight can be a desirable attribute for FC forklifts or marine applications. For space applications NASA has been utilising liquid hydrogen for years [2].

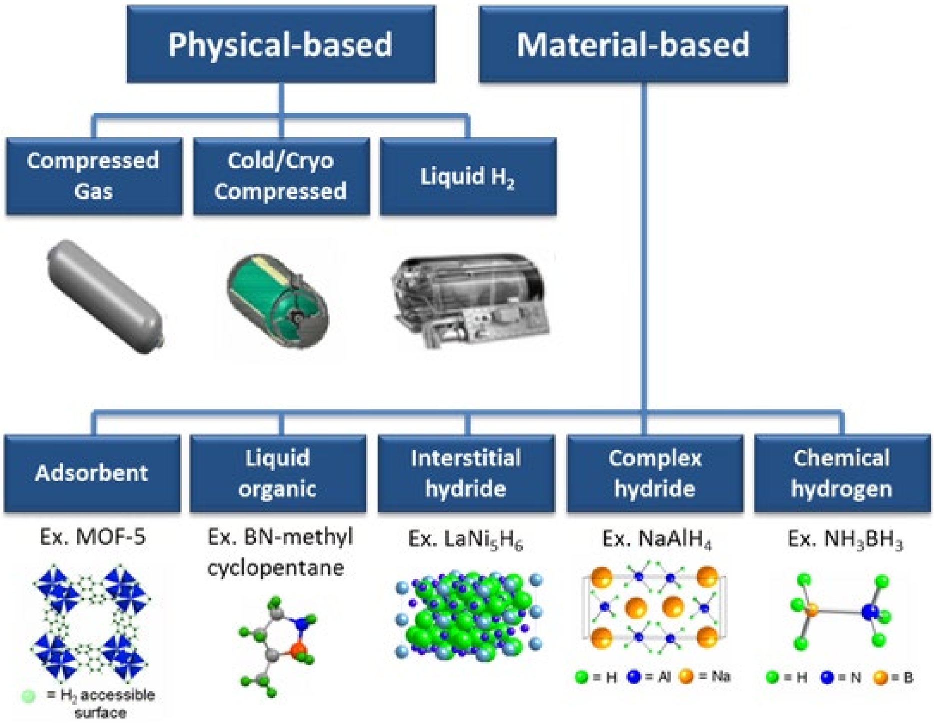
Hydrogen is the lightest gas with a low normal density of 0.09 g/L (at 288 K and 1 bar). As it follows from Table 1 it has very high energy content per mass of any fuel (about three times more than petrol). However, due to its low density, hydrogen has very low energy content per unit volume (about four times less than petrol). As a result, storing hydrogen, particularly within the size and weight constraints of a vehicle, represents a challenge [3]. The research is underway to develop safe, reliable, compact, light-weight, and cost-effective hydrogen storage technology.

Volumetric and *gravimetric capacities* (densities) are two terms often used when describing gas storage approaches. In the case of hydrogen, research activities are geared towards increasing both capacities, i.e. higher both volumetric and gravimetric [1]capacities are desirable. As it is shown in Table 1 there is more energy in 1 kg of hydrogen than in one 1 kg of petrol. However, it is also evident that the same mass of hydrogen occupies a larger volume. Hydrogen is not a liquid at ambient temperature and, therefore, to store the amounts sufficient for a certain driving range on a vehicle (above 500 km) it is necessary to either compress it to very high pressures (for example to 700 bar for automotive applications), or to cool it significantly to obtain a liquid form. These extremes of pressure and temperature present safety challenges for the materials used and in the event of a loss of containment.

[1] Gravimetric capacity determines the weight of a storage tank required to store a given amount of H_2

Table 1. Energy content by weight and by volume for hydrogen and other common fuels [4]

	Hydrogen	Natural gas	Petrol
Energy content per unit mass	**2.8 times** more than petrol	**~1.2 times** more than petrol	**43** MJ/kg
Energy content per unit volume	**4 times** less than petrol	**1.5 times** less than petrol	**120** MJ/Gallon

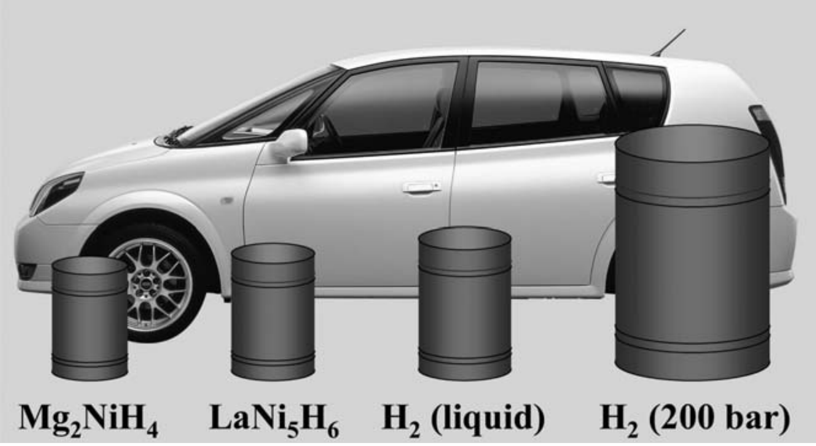


Source: US Department of Energy (DoE): http://energy.gov/eere/fuelcells/hydrogen-storage

Figure 1. An overview of hydrogen storage technologies

Hydrogen can be stored *physically* as a compressed gas (cGH_2) or as a cryogenic liquid (LH_2). The gaseous hydrogen storage systems typically require compressed gas vessels, i.e. tanks (to withstand up to 700 bar pressure). Storage of hydrogen as a liquid requires extremely low temperatures because its boiling point at 1 atm pressure is -253°C. The LH_2 storage is commonly used for bulk hydrogen storage and transportation (please refer to Lecture 'Introduction to FCH applications and hydrogen safety'). Hydrogen can also be stored in *materials*: on the surfaces of solids (by adsorption) or within solids (by absorption) [1]. An overview of hydrogen storage options is given in Figure 1.

Figure 2 from references [5, 6] illustrates the volumetric densities achieved or expected to be achieved for the various storage options in on-board vehicle applications. The US DOE has set targets in their research programme [7] for each of the parameters so that research can be discontinued if it appears that one of the targets cannot be reached.



Source: Risø Energy Report 3, 2004.

Figure 2. The volume occupied by 4 kg of hydrogen stored in different ways, relative to the size of a car.

4. Storage of gaseous hydrogen

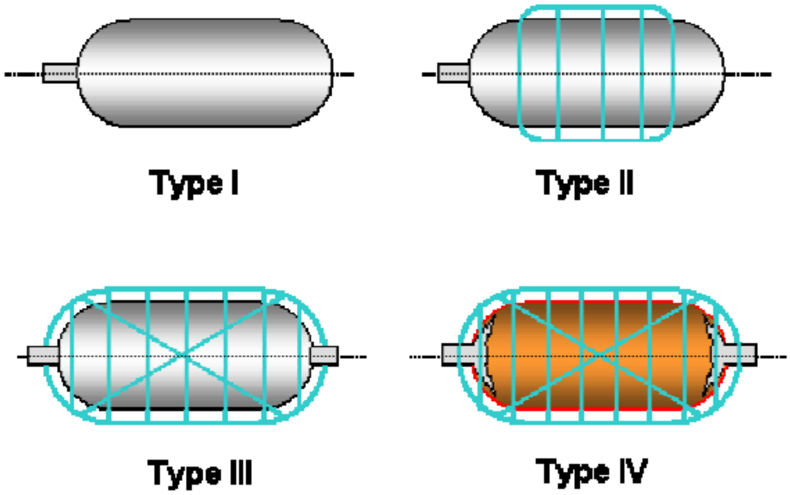
Currently, the most common way of storing hydrogen is as a compressed gas in metal and composite overwrapped cylinders at different pressures. As it was shown in previous lectures many FC applications use hydrogen at higher pressures.

4.1 Types of cGH_2 storage vessels

Due to a number of unique hydrogen properties (please see the Lecture 'Hydrogen properties relevant to safety') hydrogen should be compatible with the materials the walls of the storage tanks are made of. Four types of vessels have been developed and used for hydrogen transportation and storage:

- Type I: made of metal seamless metallic container
- Type II: seamless metallic container hoop-wrapped with fibre resin composite
- Type III: metallic liners fully wrapped with fibre resin composite
- Type IV: polymeric liner fully wrapped with fibre resin composite

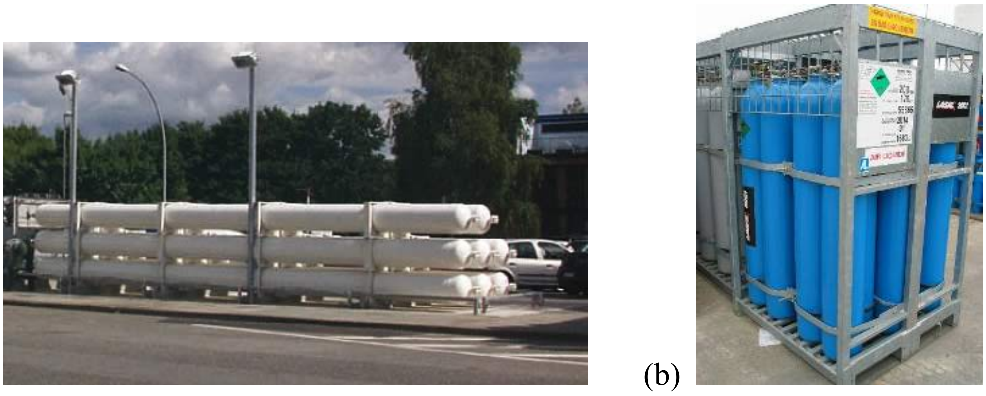
In 2014 the first prototype of type V tank was produced. It is an all-composite vessel without a liner [8]. The schematic representations of the vessel's types used for cGH_2 are shown in Figure 3.



Source: Barthelemy, 2009 [10].

Figure 3. Types of hydrogen tanks used for compressed gaseous hydrogen storage

The examples of storage vessels, which can be found at stationary applications include: a bundle or a basket of cylinders, fixed tube bundles or tube trailer used to deliver hydrogen to refuelling stations (Figure 4).

(a)  (b)

Source: AirLiquide Image Bank

Figure 4. The examples of hydrogen storage vessels common for stationary applications: (a) fixed bundle of cylinders, (b) a basket of cylinders.

4.2 On-board hydrogen storage

As mentioned earlier, the most suitable vessels to store hydrogen on-board of vehicles are Type III and Type IV. These technologies are also widely used for storage of other gases (e.g. natural gas or air), but the main difference is the need for much higher pressures in the on-board hydrogen storage: 35 to 70 MPa for hydrogen compared to 20 MPa for natural gas. Hydrogen storage systems installed on-board should perform the following functions:

- to receive hydrogen during (re-)fuelling;
- to contain hydrogen until needed;

- to release hydrogen to FC system to power the vehicle.

Today's light-duty passenger fuel cell vehicles (FCVs) typically store up to 6 kg of hydrogen on-board needed to provide a driving range in the region of 400-500 km [4]. Similar to CNG buses, the hydrogen fueled buses store hydrogen on the roof in several tanks. The fuel cell stack is usually located in the rear engine compartment of the bus. Up to 50 kg of hydrogen can be stored on-board of a FC bus.

4.3 Pressure Relief Devices

The main safety feature of the hydrogen storage systems (both for automotive and stationary applications) is *pressure relief devices (PRDs)*, with the definition given as follows: a PRD is a safety device that protects against a failure of a storage vessel by releasing some or the entire tank content in the event of high temperatures, high pressures or a combination of both [9]. In the event of a fire, *Thermally Activated Pressure Relief Device (TPRD)* provides a controlled release of the gaseous hydrogen GH_2 from a high pressure storage container before its walls are weakened by high temperatures, leading to a *catastrophic rupture*. TPRDs vent the entire contents of the container rapidly. They do not reseal or allow re-pressurization of the container for hydrogen systems.

5. Consequences of catastrophic failure of high-pressure hydrogen storage (blast waves, fireballs, projectiles)

What happens if TRPD fails to activate in a fire? The studies carried out at the Southwest Research Institute, USA [10, 11] demonstrated that the catastrophic rupture of the tank will occur.

5.1 Potential hazards and safety issues associated with cGH_2: summary

The potential hazards associated with the on-board storage of compressed gaseous hydrogen include:

- Difficulty in identification of hydrogen release as the gas is odourless, colourless and tasteless. The odorants cannot be added to hydrogen.
- Hydrogen can cause *embrittlement* of metals. This may result in the decrease of material strength and consequently in container's fracture, leading to a hydrogen leak.
- Accumulation of hydrogen, over a long period of time, in enclosures such as a garage or mechanical workshop, vehicle passenger compartments. *Asphyxiation* might occur due to displacement of air with hydrogen.
- Formation of hydrogen-oxygen or hydrogen-air flammable mixtures. The intake of flammable mixture into a building ventilation system may lead to a deflagration or even to a detonation.

- High pressure hydrogen jets may cut bare skin [12].
- An overpressure and impulse can lead to: people's eardrum damage, tank rupture, flying debris, shattered glass, etc.
- *Pressure peaking phenomenon* may lead to a garage collapse in just one second (will be discussed in the following lectures).
- Hydrogen can be ignited easily as its MIE is 0.017 mJ (which is 10 times lower compared to other fuels). A static spark can ignite hydrogen released.
- When pure hydrogen is burning its flames are invisible in the daylight.
- Hydrogen burns rapidly and does not produce smoke.
- An external fire, heat or thermal radiation can cause a mechanical rupture of a tank due to the thermal decomposition of the polymeric and composite materials. The current value of fire resistance (publicly available) is up to 12 minutes before the catastrophic failure may occur.
- In case of a TPRD malfunction, a worst-case scenario is possible: a rupture (i.e. a catastrophic failure) of hydrogen storage tank, producing fireball, blast waves and burning projectiles.

6. Leak-no-burst safety technology

Composite vessels for onboard storage of high-pressure hydrogen have been produced and brought to the service for road, rail, marine and aviation applications in many countries around the globe. The weakest point of composite vessels is their reaction to fire. For example, in a localised fire, TPRD may not be initiated as, for instance, demonstrated, by accidents with compressed natural gas vehicles in the USA. Besides, TPRD could be blocked from a fire in an accident, etc. These potential hydrogen safety engineering flaws can turn highly critical for life and property protection due to devastating consequences of tank rupture, i.e. blast wave, fireball and projectiles.

6.1 New 2020 trend

Over the last 10 years, large Composite Overwrapped Pressure Tanks were practicable solution regarding the integration of the hydrogen storage system in the current vehicle architecture developed primarily for combustion engines. With the rapid expansion of BEV worldwide car manufacturers have the need to share the same vehicle architecture and look for new design of storage systems with conformable tanks. The integration of both energy systems in the same car body would enable economies of scale, simplify and reduce engineering and manufacturing processes and allow flexible production, which could buffer demand fluctuations without compromising customer expectations of space, performance, safety, or cost. As a result, the justification for the new geometries desired by car manufacturers comes down on the one hand to being able to use the same platform for BEV and FCEV vehicles (Figure 5). This involves "box" shape tanks. On the other hand, increase the range of vehicles by using the space lost.

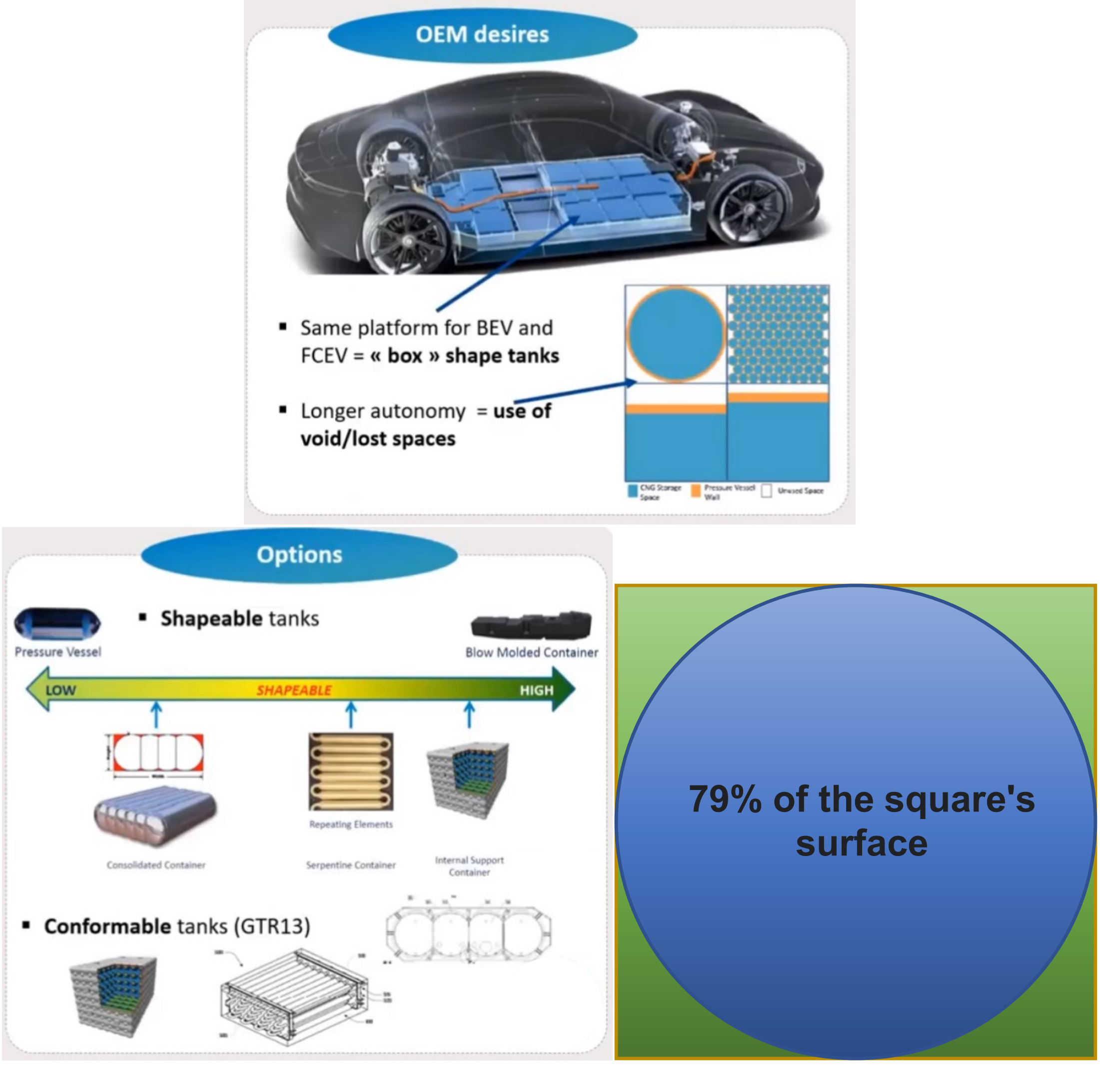


Figure 5 New trend for Compressed Storage System Integration and Geometries

7. Utilisation of the e-Laboratory

The e-Laboratory for hydrogen safety has been introduced in Lecture 1. A number of tools are particularly useful for storage applications. These include calculation of blow down dynamics from a storage tank, time to tank rupture and fireball correlations.

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