1. Introduction

Towards Hydrogen Economy: the storage challenge

The recent awareness of the climate change and concern about the fossil fuel availability have underlined the necessity of developing new energy concepts to face the future energy supply challenges. A new economy can be developed based on hydrogen as a clean energy carrier but implies a complete change of consumption habits compared to an oil-based society. Oil, coal or gas are primary energy sources, because they are directly available without conversion in nature. Hydrogen, as electricity, is a secondary energy source also called energy carrier. This means that it cannot directly be extracted from earth. It is obtained by conversion of a primary energy source and can be used to transport and store more efficiently energy than the primary sources, e.g. solar or wind energy. Hydrogen is an abundant element and H_2 has the highest energy-to-weight ratio, its combustion releases only water and it can be produced at any place of the world. Hydrogen offers a good partnership with electricity; the latter being a well established energy carrier but difficult to store efficiently. Conversion to hydrogen is then a good alternative for energy storage and appears to be particularly interesting for transportation over long distances where batteries cannot be used.

1.1 Context

1.1.1 Hydrogen economy

The hydrogen cycle is given in **Figure 1.1** and shows the different steps necessary for the use of hydrogen as an energy carrier [1, 2]. Each step of this cycle, such as hydrogen production, transport and storage, and combustion, has to be newly developed and established worldwide to finally replace the oil-based economy.

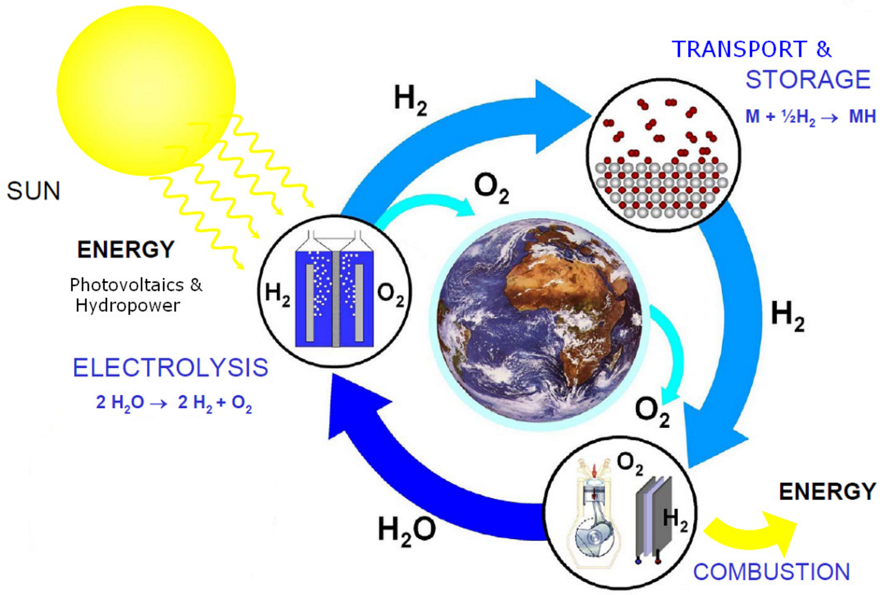

Figure 1.1: The hydrogen cycle (from [1]).

The production of hydrogen is the first challenge, because, despite its high abundance, because hydrogen is mainly present bonded to other elements (mostly oxygen), e.g. in water (H_2O). Hydrogen can be produced easily by reforming hydrocarbons but this process relies also on fossil fuels (oil). To ensure a clean process, hydrogen can be produced from the electrolysis of water using renewable energies sources (like wind or solar) for the supply of electricity. The electrolysis of water is a well known technology and consists of splitting water molecules to oxygen and hydrogen gas; it produces high purity hydrogen. However, the process requires a high quantity of energy (minimum of 39.4 kWh kg^{-1} H_2 [1]). There are then important concerns about the supply of electricity. Nowadays, the electrolysers have already a high efficiency (82%); this means that large technical challenges have to be overcome to reduce further the energy losses.

Energy can be liberated from hydrogen by direct combustion (heat). On the other hand, hydrogen can also be used to produce electricity using a fuel cell. This last solution is preferred for mobile applications. The fuel cell stacks are coupled to an electrical motor to power vehicles.

Some examples of fuel cell powered vehicles have been already developed and constructed by the automotive industry. The principle of a fuel cell is known since 1839 [3] and consists in the reverse reaction of water electrolysis. Oxygen and hydrogen react together to produce electricity and water. The most commonly used fuel cell is the proton exchange membrane fuel cell (PEMFC) (**Figure 1.2**) [4]. Nevertheless, there are still technical issues that limit the development of such technology. There is still space for improvement in fuel cell technology, for example by the use of non-noble catalysts [5]. With the present fuel cell technology, 4 kg of hydrogen are needed to power a car with an autonomy range of 400 km.

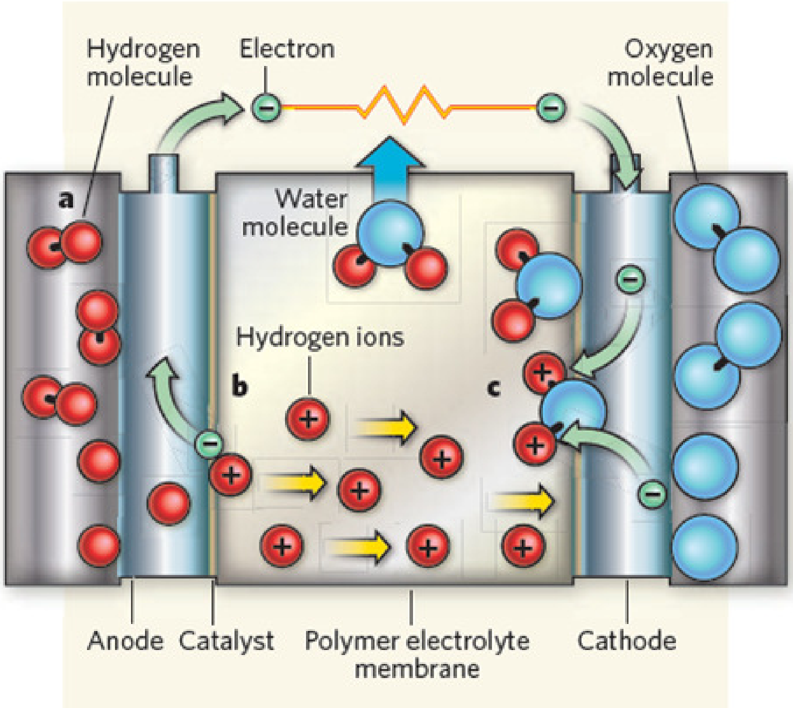

Figure 1.2: Principle of a PEM fuel cell (from [6]).
a: Hydrogen is channelled to the anode. b: a catalyst lining the anode causes the hydrogen atoms to split into hydrogen ions (H^+) and electrons. A polymer electrolyte membrane allows the hydrogen ions to pass between the anode and the cathode, but the electrons must pass through an external circuit to reach the cathode, creating a current. c: oxygen is channelled to the cathode, where it reacts with electrons and hydrogen ions to form water as the only side product.

Hydrogen production and combustion can be greatly improved but the bottleneck for the hydrogen cycle is transportation and storage [7]. As hydrogen is a gas at normal temperature and pressure, its storage and transportation is less convenient than liquid gasoline. Transportation can be done in pipelines but is usually limited to short distance. This means that efficient storage methods have to be found. Under standard conditions (room temperature and atmospheric pressure), 4 kg of hydrogen represent a volume of 45 m^3. Different methods have been proposed to reduce this volume. The largest challenge is for mobile applications since the space in a car is very limited. The different storage technologies, already available or in development, are described in the next section.

1.1.2 Hydrogen storage

After this short introduction to the hydrogen economy, it appears clearly that storage is a major issue. As already mentioned, hydrogen exists in the gas phase at standard conditions, which call for the development of efficient storage methods. There are different technologies available for the storage of hydrogen. They can be classified in physical and chemical storage [1, 7, 8] (**Table 1.1** and **Figure 1.3**).

Table 1.1: Classification and properties of different hydrogen storage technologies (adapted from [4] and [8])

Storage type	*Name*	*Examples*	*Maximum H_2 capacity (wt%)*	*Operating temperature (°C)*
Physical storage	Liquid hydrogen	-	100	-253
	Compressed gas	350 to 700 bar	100	25
	Cryo-adsorption	activated carbon MOF [a]	6.5 7.5 [b]	-200
Chemical storage	Chemical hydrides	$NaBH_4$	7.3	25
	Liquid hydrocarbons	Cyclohexane Decalin	7.1 7.2	300
	Interstitial hydride	$LaNiH_x$, $FeTiH_x$, Laves phases	2	0-30
	Salt-like metal hydride	MgH_2	7.6	330
	Complex hydrides	$NaAlH_4$ $LiBH_4$	5.5 18.4	70-170 400

[a] MOF: Metal Organic Framework
[b] for MOF177 with 5900 m^2 g^{-1} surface area

The US department of energy (DOE) has enumerated system requirements for the hydrogen storage media (**Table 1.2**) [9]. These targets are commonly used as guideline in the hydrogen storage research area, although very debated. The values have been set to resemble the use of a conventional gasoline vehicle (e.g. 5 min refuelling time), and to fit the technical requirement of a PEM fuel cell, which are thought to be used in cars (e.g. operating temperature). One important criterion is the gravimetric storage density: the target is 5.5 wt% H_2 for the tank system in 2015.

Table 1.2: DOE targets (revised) for on-board hydrogen storage systems of light-duty vehicles (Feb. 09) [9]

Storage parameters	*Units*	*2010*	*2015*	*Ultimate*
System gravimetric capacity: usable, specific-energy from H_2 *(net useful energy/max system mass)*	kWh kg^{-1} *(kg H_2 kg^{-1} system)*	1.5 *(0.045)*	1.8 *(0.055)*	2.5 *(0.075)*
System volumetric capacity: usable energy density from H_2 *(net useful energy/ max system volume)*	kWh L^{-1} *(kg H_2 L^{-1} system)*	0.9 *(0.028)*	1.3 *(0.040)*	2.3 *(0.070)*
Storage system cost & fuel cost	\$ kWh^{-1} net (\$ kg^{-1} H_2) \$ gge^{-1} at pump[a]	4 (133) 2-3	2 (67) 2-3	? - 2-3
Durability/operability				
• Operating ambient temperature	°C	-30/50	-40/60	-40/60
• Min/max delivery temperature	°C	-40/85	-40/85	-40/85
• Cycle life (1/4 tank to full)	Cycles	1000	1500	1500
• Minimum delivery pressure from storage system (FC)	atm	4	3	3
• Max delivery pressure from storage system	atm	100	100	100
Charging/discharging rate				
• System fill time (for 5 kg H_2)	min *(kg H_2 min^{-1})*	4.2 *(1.2)*	3.3 *(1.5)*	2.5 *(2)*
• Minimum full flow rate	(g s^{-1}) kW^{-1}	0.02	0.02	0.02
• Start time to full flow (20°C)	s	5	5	5
• Start time to full flow (-20°C)	s	15	15	15
• Transient response 10%-90% and 90%-0%	s	0.75	0.75	0.75
Fuel purity (H_2 from storage)	% H_2	99.99 (dry basis)		
Environmental health and safety				
• Permeation & leakage	Scc h^{-1} [b]	meets or exceeds applicable standards		
• Toxicity	-			
• Safety	-			
• Loss of usable H_2	(g h^{-1}) kg^{-1} H_2 stored	0.1	0.05	0.05

[a] gge: gallon gasoline equivalent (amount of alternative fuel to equal the energy content of 1 gallon gasoline)
[b] Scc h^{-1}: standard cubic centimetre per hour (gas flow unit in standard conditions of pressure, temperature and humidity)

The physical storage can be divided in three major technologies: the storage in compressed H_2 gas, the storage of liquid H_2 (cryotanks) and the adsorption of H_2 on materials with high surface area (cryo-adsorption). The chemical storage contains mainly the solid state storage in hydride compounds (metal or complex hydrides) or in hydrocarbons (reforming). The first two physical storage methods are the most established technologies, very similar to gasoline technology, including a tank that can be refilled on-board. The chemical storage methods include reversible and irreversible reactions. The irreversible reactions imply that the tank has to be refilled externally. The reversible reactions allow refuelling on-board as for gas or liquid hydrogen. A summary of the state-of-the-art performances of different storage methods is given in **Figure 1.3**. For compressed or liquid hydrogen, the maximum gravimetric or volumetric capacities have been reached, although technical improvements in the system might be possible. For the hydrides, it is expected that the H_2 capacity can be still greatly improved by the development of new compounds that are described in more detail below.

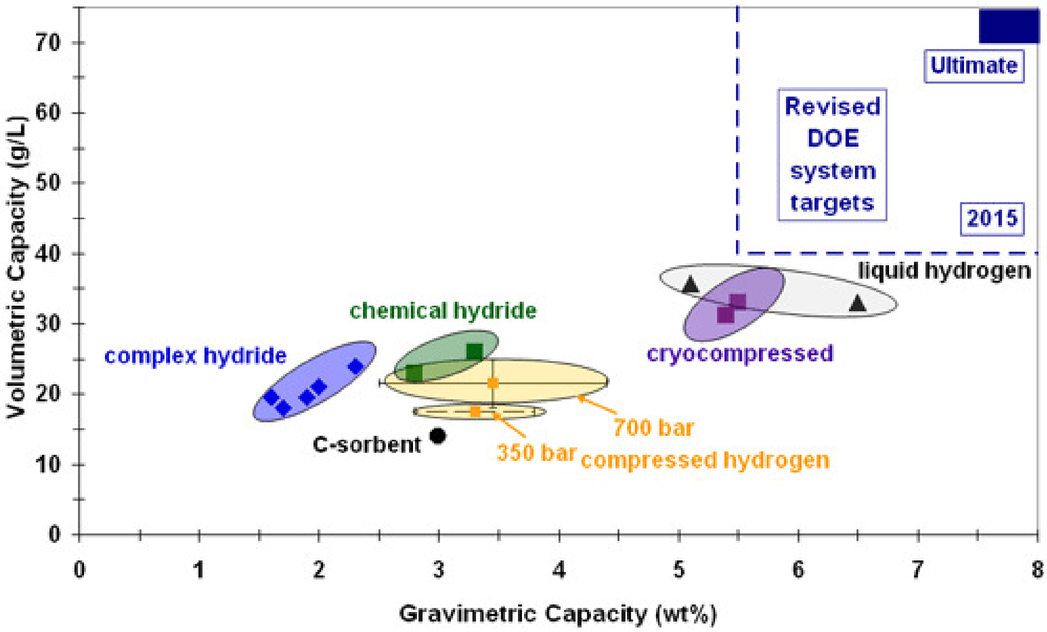

Figure 1.3: State-of-the-art of hydrogen storage technologies (values given for storage systems) [9]

1.1.2.1. Physical storage

To store 4 kg of hydrogen in the gaseous state in a sufficiently small volume, it is necessary to use high pressures (350-700 bar). The use of lower values would not be relevant because of too small amounts of hydrogen stored. The use of higher values would require too much energy compared to the additional quantity of hydrogen stored, because of the deviation from ideal gas behaviour. The compressed H_2 tank is the most established technology, which has been used with 300 bar tanks for a long time for the transportation and storage of H_2. Nevertheless, the development of new tank designs is necessary to resist the high pressures required for mobile applications (350-700 bar). This is achieved using high-strength materials like carbon composites. A 700 bar tank made of these materials weighs only 135 kg (for 4.2 kg H_2 stored) while an equivalent steel tank would weigh 700 kg [8]. This storage method has the best overall performance at present and also the highest maturity. However, it still requires a high amount of energy to compress the gas and technical issues are faced for the integration in cars. There are also questions about the public acceptance for using such high pressure tanks in cars and the cost of a reasonable safety system.

Liquid hydrogen has also been considered for storage because it has several advantages like easy refuelling and high mass density, in particular compared to compressed gas tanks. However, the liquid region of hydrogen in the phase diagram is small [10] and cryo-tanks have to keep a temperature of -253°C (21 K). Such cryo-tanks have been developed already. The main disadvantages of this technique are the significant gas losses and the high energy consumption for liquefying hydrogen. The losses are related to the boil-off effect and the evaporation of hydrogen gas from the tank. This has to be taken into consideration for long time storage with the necessity of venting hydrogen to prevent a pressure increase in the tank. In addition, a very efficient insulation is required to keep the very low temperature. All these drawbacks make liquid hydrogen not attractive for mobile applications.

The last method for physical storage is the adsorption of H_2 on the surface of large surface-area materials [8, 11]. This type of storage is classified with the physical method because it involves the storage of molecular hydrogen that has only weak interactions with the adsorbent. This method requires low temperature, -196°C (77 K), and/or high pressures. In general, the capacity of hydrogen adsorbed depends on the specific surface area and the pore structure and size of the adsorbents. Different classes of adsorbents have been developed: carbon materials (activated carbon, graphite), metal-organic frameworks (MOF), zeolites. MOF materials appear to have the highest gravimetric storage density with 7.5wt% H_2 reported for MOF177 (surface area 5900 $m^2\ g^{-1}$) at -196°C [8]. However, this performance cannot be obtained at room temperature and a high quantity of energy is necessary for the adsorption implying the necessity of a large quantity of liquid nitrogen. This causes severe engineering challenges and adds high costs that make this solution not attractive for mobile applications.

1.1.2.2. Chemical storage

In contrast to physical storage methods, the chemical methods involve the storage of atomic hydrogen and the breaking and formation of chemical bonds.

To ease handling, the use of liquid hydrogen carriers like hydrocarbons has been proposed [8, 12]. This includes for example methanol or cyclic hydrocarbons like benzene or cyclohexane. The cyclic hydrocarbons may be used directly in tanks but the release of hydrogen requires too high temperature to be used in mobile applications. Another route is the production of hydrogen on-board from the reforming of liquid hydrocarbons. Obviously, the addition of a reforming system in a car presents a technical issue. In addition, CO gas may be released, which is very poisonous for the fuel cell. Easier is then the use of methanol, of which reforming is less difficult than for other hydrocarbons. The use of methanol in a direct methanol fuel cell is also possible. This fuel cell has a lower power density than the hydrogen fuel cell but the technology is already available and can be an alternative for mobile applications.