Chapter 1

Introduction

"Human being is renewable creation of God,
Hence, they need renewable sources of energy" – **Prof. M. L. Mathur**

"Alternative energy is a future idea whose time is past,
Renewable energy is a future idea whose time has come." – **Bill Penden**

Abstract

This chapter deals with the future renewable energy source, namely – Hydrogen. The needs of hydrogen in the field of renewable and environmentally friendly energy sources are explained. A brief description of hydrogen technologies (Production, Delivery, Storage, Conversion, and End–Uses/Applications) – is explained. The obstacle to realize the hydrogen technology is neither production nor utilization, but rather effective and safe means of storing hydrogen. This implies the importance of hydrogen storage. The requirements of safe hydrogen storage are also presented. It is also shown that Magnesium based metal hydrides are promising for use as hydrogen storing materials. A motivation for the present work is also presented at the end of the chapter.

1.1 Introduction of New Era: Renewable Energy

Day by day, we hear more disturbing news about “Climate Change”, that is happening all over world. More and more peoples are getting seriously impacted by increasingly strong and more frequent hurricanes. We hear about unprecedented droughts in one area, while there is severe flooding in another. People are forced to leave entire regions due to desertification of the land. We heard also that many places are becoming “Seething City” due to rising temperature, where as other places are becoming “Frozen Out”. Every person living on this planet will ultimately have to face the consequences of dramatic environmental changes, which are induced by human intervention in the delicate ecological balance of the nature. Scientists have determined that the main causes of these changes are toxic emissions from industries and motor vehicles throughout the world. Increasing global pollution levels and urbanization together with rapid disforestation add to these problems [1].

For minimizing above problems, to need achieving a secure, efficient and clean energy sources. The main classifications of energy are commercial and non–commercial energy. The energy sources they are available in the market for a definite price are known as commercial energy sources like coal, oil, natural gas, etc. In opposite way, non-commercial energy sources include biomass such as fire wood, cattle dung, agricultural wastes, etc. Another ways, there are renewable and non–renewable energy. The non–renewable sources are those, which are likely to use up with time such as coal, oil, natural gas, etc.

The world at present relies on fossil fuels (coal, oil, natural gas, etc) to meet its energy requirements. The growth in global energy demand is projected to rise sharply over the coming years. Presently available energy systems, like fossil fuel and nuclear power may not be able to make up the future energy requirements. Moreover, the use of these energies causes environmental degradation and that endangers human health and affects ecological balance. Therefore, the rapidly increasing global energy needs to be met without damaging the environment. This requirement would be fulfilled by using renewable energy sources. These are those, which are essentially inexhaustible; like solar, wind, hydro, geothermal, biomass energies, tidal energies, etc [2, 3].

1.2 Hydrogen Energy Scenario

Increase in energy quality is one of the most significant transitions in global energy systems (Fig. 1.1). Each successive transition from one source to another has entailed a shift to fuels that had lower carbon content and higher hydrogen content. It is also evident that at each transition accompanied by greater energy density. Renewable energy sources that use indigenous resources have the potential to provide energy services with almost zero emission of toxic gases. Also, these are abundant, inexhaustible and widely available. But, they are very expensive and less energetic sources. Another high energy carrier source is hydrogen, which is also a renewable energy source [4].

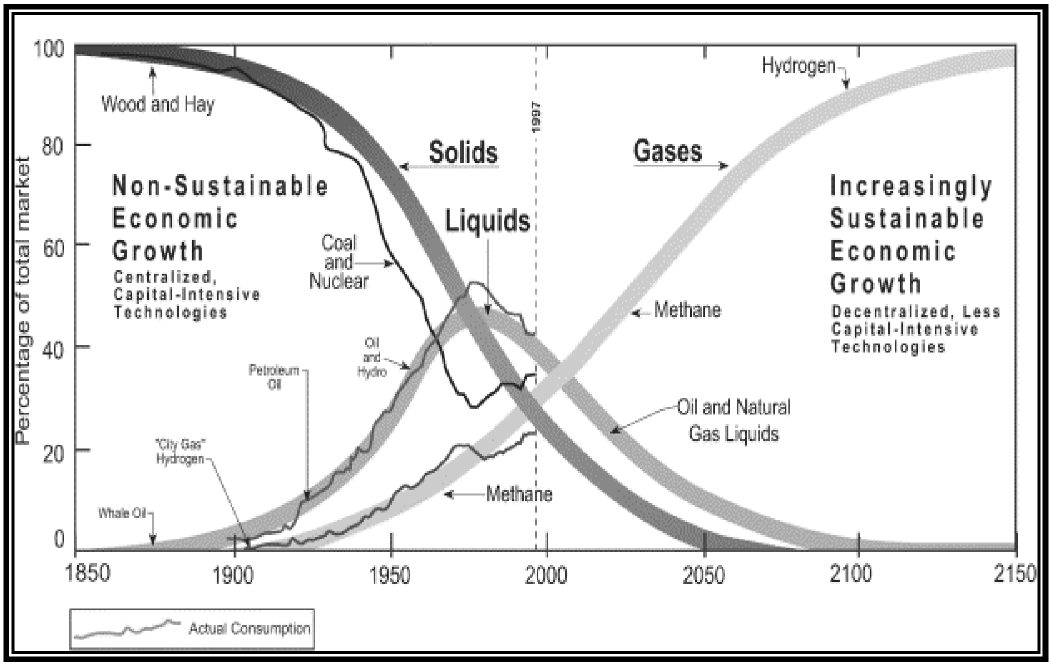


Fig. 1.1: Global energy systems transition, 1850–2150 [5, 6]

In India, interest in use of hydrogen as an alternate fuel started in 1976 by setting up a task force under Department of Science and Technology (DST), which received a fresh impetus in 1983 under Department of Non–conventional Energy Sources, when thrust areas were decided for a 15 year period 1985–2000, and small research projects were initiated to look into production (BARC, IIT–M, BHU, University of Madras), storage (ISRO, NPL, IIT–Kh, BHU) and utilization (IIT–M, BHU) [7]. However, momentum was lost due to stabilization of oil prices. Interest was renovated in 2003 by the planning commission, by forming a committee, to prepare plan for various aspects of development of hydrogen energy. Under this committee, four sub–committees have been formed to look into production – headed by secretary, DST; storage and distribution – headed by secretary, Ministry of Petroleum and Natural Gas (MoP and NG); applications – headed by secretary, Ministry of Non–conventional and Renewable Energy Sources (MNRES); and safety standards, security and policy issues – headed by director general, The Energy Resource Institute (TERI). The National Hydrogen Energy Board (NHEB) was set up in 2003 by MNRES, recently announced 'National Hydrogen Energy Road Map: Hydrogen Vision 2020' under Green Initiative for Future Transport (GIFT) and Green Initiative for Power Generation (GIP), which conceive of:

- ***1 million vehicles:*** ≈ 0.75 million 2 and 3 wheelers
  - ≈ 0.15 million cars–taxis
  - ≈ 0.1 million buses
- ***1000 MW power generation:*** ≈ 50 MW stand alone IC engine generators
  - ≈ 50 MW stand alone fuel cell generators
  - ≈ 900 MW centralized plants
- ***Hydrogen cost at delivery point:*** Rs 60–70 per kg
- ***Hydrogen storage capacity:*** 9 wt%
- ***Adequate support infrastructure including dispensing stations***
- ***Safety, regulations, codes and standards***

1.3 Why Hydrogen is Most Preferable ?

Hydrogen is not a natural fuel, but a synthetic energy carrier. It is made up of just one electron and one proton. It only carries energy generated by other processes. Hydrogen seems to be an attractive replacement for exiting fossil fuel system by the following reasons [8, 9]:

- Hydrogen can be totally non–polluting, when transformed into energy (only water is exhausted).
- Hydrogen can help prevent the reduction of fossil fuel reserves.

- Hydrogen can be produced in any country from a wide variety of energy sources.
- Hydrogen is an excellent energy carrier.
- Hydrogen can be economically competitive with gasoline or diesel.

Hydrogen holds more chemical energy than any other fuel. One kilogram of hydrogen provides as much energy as 4.5 litre of gasoline. Under the hood of today's automobiles, internal combustion engines capture only 15% – 20% of the energy stored in gasoline. Fuel cells running on pure hydrogen are more efficient. By applying the fuel's energy via an electrochemical rather than a thermo-chemical (combustion) reaction, a fuel cell can convert 40% – 65% of hydrogen energy into electricity to power a car. Table 1.1 shows the comparison of the fuel properties of hydrogen, CNG and gasoline and these are given as under [10, 11]:

Table–1.1: Properties of different fuels

Properties	**Hydrogen**	**CNG**	**Gasoline**
Lower heating value, MJ/kg	120	43.5	43.1
Density (gas) at STP (1 atm, 15 °C), kg/m^3	0.084	0.81	4.4
Octane rating	130	120	88
Auto ignition temperature, °C	585	540	390
Air/Fuel ratio (Stoichiometric) by mass	34.3	15.1	14.7
Energy of stoichiometric mixture, MJ/m^3	3.6	3.5	3.9
Flammability limits in air, V%	4–75	5.3–15	1–7.8
Minimum ignition energy in air, MJ	0.02	0.29	0.24
Maximum flame speed in air, cm/s	265	33.5	39.6
Diffusion co-efficient in air, cm/s	0.61	0.16	0.05
Toxicity	No	High	High

The cost of hydrogen produce by electrolysis is also feasible in future with respect to petrol. Let us, calculate the economics cost of H_2 production by applying equilibrium thermodynamics.

$H_2O_{(l)} \longleftrightarrow H_{2(g)} + \frac{1}{2} O_{2(g)}$ at P = 0.1 MPa and T = 25 °C ---------------- (1.1)

$$H_2 \longleftrightarrow 2H^+ + 2e^- \quad \text{--------------------- (1.2)}$$

Therefore, the electrical energy required to produce 1 kg hydrogen is,

$$E \quad = V \times F \times Z \quad \text{--------------------- (1.3)}$$

Where, V is the equilibrium cell voltage (≈ 1.229 V), F is the Faraday constant (96500 C/mol electron) and Z is the valency (2).

$$\therefore\ E = 1.229 \times 96500 \times 2$$
$$= 237.2 \text{ kJ/mole}$$
$$= 0.065 \text{ kWh/mole}$$
$$= 0.065 \text{ x } (1000/2)$$
$$= 32 \text{ kWh/kg of } H_2$$

But, in the real case, the efficiency of the electrolysis process will be a maximum of 50 %, then the required electrical energy to produce 1 kg of H_2 is,

$$\Rightarrow E = 1.5 \times 32 \cong 48 \text{ kWh/kg of } H_2$$

At Rs. 5 per unit, the electrolysis cost then becomes,

$$= 48 \times 5 = 240 \text{ / kg of } H_2$$

But, H_2 has three times the calorific value of petrol (1,18,000 kJ/kg against about 40,000 kJ/kg for petrol). Hence, the cost equivalent for H_2 = Rs. 80 per kg. Here, the electricity consumption cost in production of H_2 is considered. Hydrogen production costs are not cheaper than the currently prevailing cost of petrol (this indicates possibility of using renewable energy sources for hydrogen production). If transportation, storage and delivery cost are consider same as production, then the total cost of H_2 at delivery point becomes Rs. 160 per kg.

The current petrol cost in India is, Rs 67 per litre or, equal to Rs 67,000 per

m^3. But, the density of petrol is 865 kg/m^3. Therefore, the cost of petrol is really Rs 78 per kg at delivery point. Clearly, non renewable energy source based H_2 production does not compete economically with existing petrol production and distribution technologies.

Coming to safely aspects, hydrogen is safer than thought [12]. Gaseous hydrogen is 14 times lighter than air and four times lighter than Helium. In the event of an accidental release, it disperses rapidly upward into the atmosphere. Other fuels take longer to disperse or may spill onto the ground. Furthermore, gasoline requires specialized cleanup efforts and presents toxic hazards to the nearby environment. When fuels such as coal, oil, natural gas, propane or wood burn, they create pollutants like Carbon Monoxide, Carbon Dioxide, and a variety of hydrocarbon chemicals, Sulphur Dioxide and small solid smoke particles. Pure hydrogen produces only heat energy, water and trace amounts of oxides of nitrogen, when burned. Despite of all the above mentioned advantages, the world is slowly moving to a “Hydrogen Economy”. At the beginning, producing hydrogen may require many of the same energy sources (and so fuels) already in use today. Renewable energy sources may play bigger and bigger role with time in future hydrogen production.

1.4 Hydrogen Energy Systems

Widespread use of hydrogen will affect every aspect of the energy system, from production through end–use. The individual segments of a hydrogen energy system — production, delivery, storage, conversion, and end – uses/applications – are closely interrelated and interdependent (see Fig. 1.2) [13, 14]. Each technology is in different stages of development, and each offers unique opportunities, benefits and challenges. Local availability of feedstock, market applications and demand, policy issues, and the cost will influence the selection and timing of the various options for hydrogen energy systems. The brief introduction of each technology is given as under:

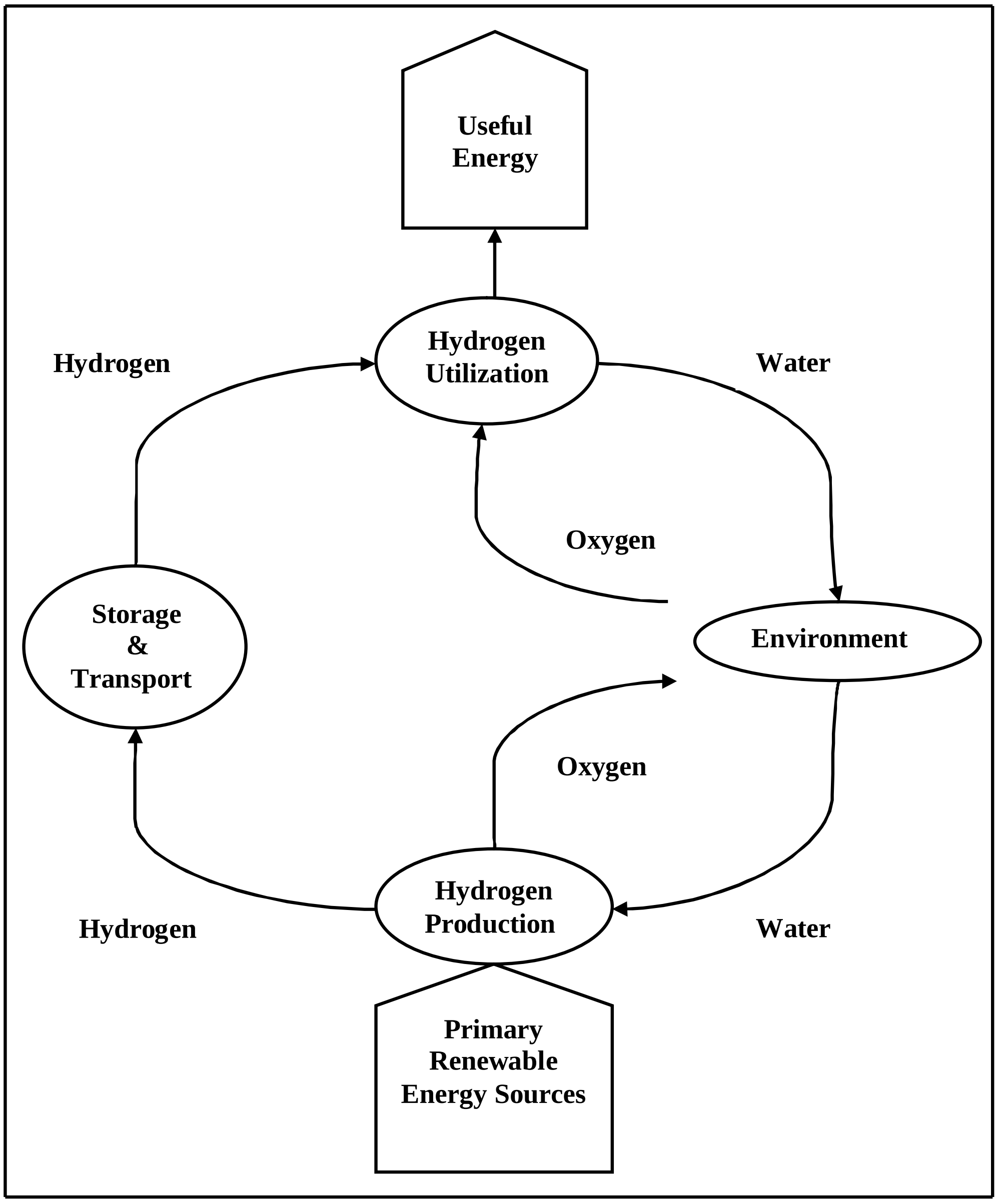


Fig. 1.2: Interrelation of hydrogen energy systems

1.4.1 Production

Hydrogen does not exist in a natural state on earth and must be manufactured using hydrogen – rich compound such as water as the raw material. Hydrogen can be produced from a variety of sources, including fossil fuels; renewable sources such as wind, solar, or biomass; nuclear or solar heat – powered thermo–chemical reactions; and solar photolysis and/or biological methods. The United States hydrogen industry currently produces nine million tons of hydrogen per year for use in chemicals production, petroleum refining, metals treating, and electrical applications. Hydrogen is primarily used as a feedstock, intermediate chemical. Only a small portion of the hydrogen produced today is used as an energy carrier. The various hydrogen production techniques are given as under:

1.4.1.1 From Fossil Fuels

There are many industrial methods currently available for the production of hydrogen. Hydrogen can currently be produced from natural gas by means of three different chemical processes [15]:

- Steam reforming
- Partial oxidation
- Auto-thermal reforming

Steam reforming involves the endothermic conversion of methane and water vapour into Hydrogen and Carbon Monoxide (Eq.1.4) [16, 17]. The heat is often supplied from the combustion of some of the Methane feed-gas. The process typically occurs at temperatures of 700 °C to 850 °C and pressures of 3 to 25 bar. The product gas contains approximately 12 % CO, which can be further converted to CO_2 and H_2 through the water–gas reaction (Eq.1.5).

$$CH_4 + H_2O + \text{Heat} \longrightarrow CO + 3H_2 \quad \text{---------------------} (1.4)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 + \text{Heat} \quad \text{---------------------} (1.5)$$

Partial oxidation of natural gas is the process, whereby hydrogen is produced through the partial combustion of methane with oxygen gas to yield carbon monoxide and hydrogen (Eq.1.6) [18]. In this process, heat is produced in an exothermic reaction, and hence a more compact design is possible as there is no need for any external heating of the reactor. The CO produced is further converted to H_2 as described in Eq.1.5.

$$CH_4 + {}^{1}/_{2}\,O_2 \longrightarrow CO + 2H_2 + \text{Heat} \quad \text{---------------------} (1.6)$$

Auto–thermal reforming is a combination of both steam reforming and partial oxidation. The total reaction is exothermic, and so it releases heat. The outlet temperature from the reactor is in the range of 950 °C to 1100 °C, and the gas pressure can be as high as 100 bar. Again, the CO produced is converted to H_2 through the water gas reaction (Eq.1.5). The need to purify the output gases adds significantly to plant costs and reduces the total efficiency. Its primary by – product is Carbon Dioxide.

1.4.1.2 Gasification Method

Hydrogen can be produced from coal through a variety of gasification processes. Gasification of coal is the traditional technique for making hydrogen. In practice, high temperature entrained flow processes are favoured to maximize carbon conversion to gas, thus avoiding the formation of significant amounts of char, tars and phenols. A typical reaction for the process is given in Eq.1.7, in which carbon is converted to carbon monoxide and hydrogen [19, 20].

$$C(s) + H_2O + \text{Heat} \longrightarrow CO + H_2 \quad \text{--------------------} \ (1.7)$$

Since this reaction is endothermic, additional heat is required. The CO is further converted to CO_2 and H_2 through the water-gas reaction, described in Eq.1.5. Hydrogen production from coal is commercially, but it is more complex than the production of hydrogen from natural gas. The cost of the resulting hydrogen is also higher.

1.4.1.3 Electrolysis

Hydrogen can be produced from the splitting of water through various processes. Here, water electrolysis, alkaline electrolysis, polymer electrolyte membrane (PEM), and high temperature electrolysis are briefly discussed.

i) Water Electrolysis

Water electrolysis is the process whereby water is split into hydrogen and oxygen through the application of electrical energy, as in Eq.1.8 [21, 22]. The total energy that is needed for water electrolysis is increasing slightly with temperature, while the required electrical energy decreases [23]. A high temperature electrolysis process might, therefore, be preferable, when high temperature heat is available as waste heat from other processes.

$$H_2O + \text{Electricity} \longrightarrow H_2 + {}^{1}/_{2}O_2 \quad \text{--------------------- (1.8)}$$

ii) Alkaline Electrolysis

Alkaline electrolysers are used an aqueous KOH solution as an electrolyte that usually circulates through the electrolytic cells [24]. Alkaline electrolyzers are suited for stationary applications and are available at operating pressures up to 25 bar. Alkaline electrolysis is a mature technology, a significant operating record in industrial applications that allows remote operation. The following reactions take place inside the alkaline electrolysis cell:

Electrolyte: $4H_2O \longrightarrow 4H^+ + 4OH^-$ ---------------------- (1.9)

Cathode: $4H^+ + 4e^- \longrightarrow 2H_2$ --------------------- (1.10)

Anode: $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$ --------------------- (1.11)

Sum: $2H_2O \longrightarrow O_2 + 2H_2$ --------------------- (1.12)

iii) Polymer Electrolyte Membrane (PEM) Electrolysis

The principle of PEM electrolysis is presented in Eqs.1.13 and 1.14 [25]. PEM electrolyzers require no liquid electrolyte, which simplifies the design significantly. The electrolyte is an acidic polymer membrane. PEM electrolyzer can potentially be designed for operating pressures up to several hundred bar, and are suited for both stationary and mobile applications. The main drawback of this technology is the limited lifetime of the membranes. The major advantages of PEM over alkaline electrolyzer are the higher turndown ratio, the increased safety due to the absence of KOH electrolytes, a more compact design due to higher densities, and higher operating pressures.

Anode: $H_2O \longrightarrow {}^{1}/_{2}O_2 + 2\,H^+ + 2e^-$ --------------------- (1.13)

Cathode: $2H^+ + 2e^- \xrightarrow{\qquad} H_2$ -------------------- (1.14)

iv) High Temperature Electrolysis

High temperature electrolysis is based on technology from high temperature fuel cells. The electrical energy needed to split water at 1000 °C is considerably less than electrolysis at 100 °C. This means that a high temperature electrolyser can operate at significantly higher efficiencies than regular low temperature electrolyzer. A typical technology is the solid oxide electrolyser cell. This electrolyzer is based on the solid oxide fuel cell, which normally operates at 700 °C to 1000 °C. Attempts are currently underway to develop systems, in which some of the electricity consumed by the electrolyser can be replaced with the heat available from geothermal, solar or natural gas sources, thus reducing the consumption of electricity significantly [26].

1.4.1.4 Thermal Decomposition

Direct decomposition of water into hydrogen and oxygen occurs only at temperature above 2000 °C. Only limited heat sources are available like nuclear reactor, which can provide the required range of temperature. The main problems with this method are materials required for extremely high temperature, recombination of the reaction products, and toxicity of some of the chemicals involved in separation of hydrogen.

1.4.1.5 Biochemical Method

The biological or biochemical method for the production of hydrogen by splitting water has also been under investigation. Micro organisms are capable of producing H_2 via either fermentation or photosynthesis. Photo biological production of hydrogen is based on two steps, first is photosynthesis and second one is hydrogen production catalyzed by hydrogeneses like green algae and cyanobacteria [27].

Photosynthesis: $2H_2O \xrightarrow{\qquad} 4H^+ + 4e^- + O$ ---------------- (1.15)

Hydrogen Production: $4H^+ + 4e^- \xrightarrow{\qquad} 2H_2$ -------------------- (1.16)

In biomass conversion processes, a hydrogen containing gas is normally produced in a manner similar to the gasification of coal [28]. However, no commercial plants exist to produce hydrogen from biomass. Currently, the pathways followed are steam gasification, and more advanced concepts such as gasification in supercritical water, application of thermo–chemical cycles, or the conversion of intermediates (Ethanol, Bio-oil, or Terrified wood).

Although, the technology for production of hydrogen from renewable sources is well understood, it is currently not used for producing hydrogen in large quantities, due to very expensive. Production of significant quantities of hydrogen using such methods would take considerable time and investment to develop, to allow capital costs to be reduced to a satisfactory level. However, in the long term, hydrogen offers a potential way of gaining energy independence from fossil fuels.

1.4.2 Delivery

Delivery is an essential component of hydrogen energy infrastructure. The hydrogen delivery infrastructure starts immediately after hydrogen is produced and ends at the point at which it is introduced into the end-use device. It includes delivery of hydrogen from large central production facilities as well as from small-scale distributed production facilities. Most distributed production facilities will need only the storage, compression, and distributing operations. There are three potential delivery paths: gaseous hydrogen delivery, liquid hydrogen delivery, and novel solid hydrogen carriers [29]. The liquid and gas paths transport pure hydrogen in its molecular form (H_2) via truck, pipeline, rail, or boat. The carrier path uses materials that transport hydrogen in a form other than free H_2 molecules, such as liquid hydrocarbons, absorbents, metal hydrides, or other hydrogen rich compounds.

1.4.3 Storage

The obstacle to realize the hydrogen economy is neither the production nor utilizing hydrogen, but rather effective and safe means of storing hydrogen. A range of storage technologies; like, compressed gas, liquefied hydrogen, slushiest form, and solid state storage systems are addressed many problems. Which choice is best, depends on several factors; like, the application, the amount to be stored and the storage time, the forms of energy available, maintenance requirements, and capital and operating costs. Hydrogen storage basically implies the reduction of the enormous volume of the hydrogen gas. In order to increase the hydrogen density in a storage system, work must either be applied to compress hydrogen or the temperature has to be decreased below the critical temperature.

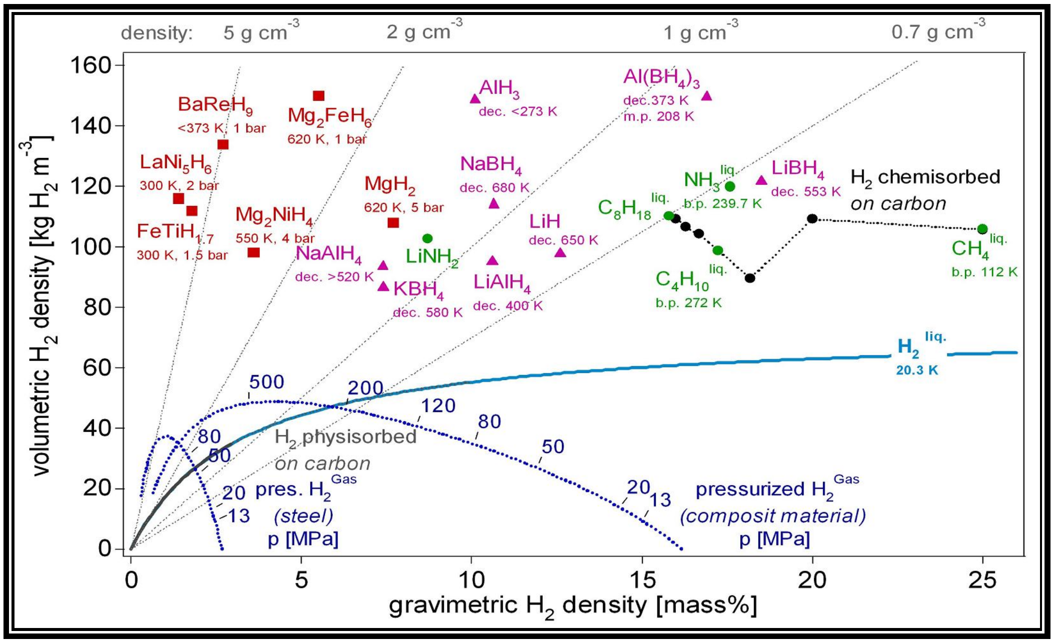


Fig. 1.3: Comparison of hydrogen storage densities of different hydrogen storage materials

Fig. 1.3 compares the volumetric and gravimetric hydrogen density of some of the most common storage options, and clearly, shows the theoretical potential of low volumetric densities for solid–state storage systems [30]. For stationary systems, the weight and volume of the system used for hydrogen storage is not a key factor. However, for mobile applications, such as fuel cell electric vehicles or hydrogen-fuelled (internal combustion) cars, hydrogen storage system has to be compact, lightweight, safe and low cost (See Fig. 1.4) [31 – 33]. The US Department of Energy (DOE), hydrogen plan has set a standard for this discussion by providing a commercially significant benchmark for the amount of reversible hydrogen storage, shown in Table–1.2 [34, 35].

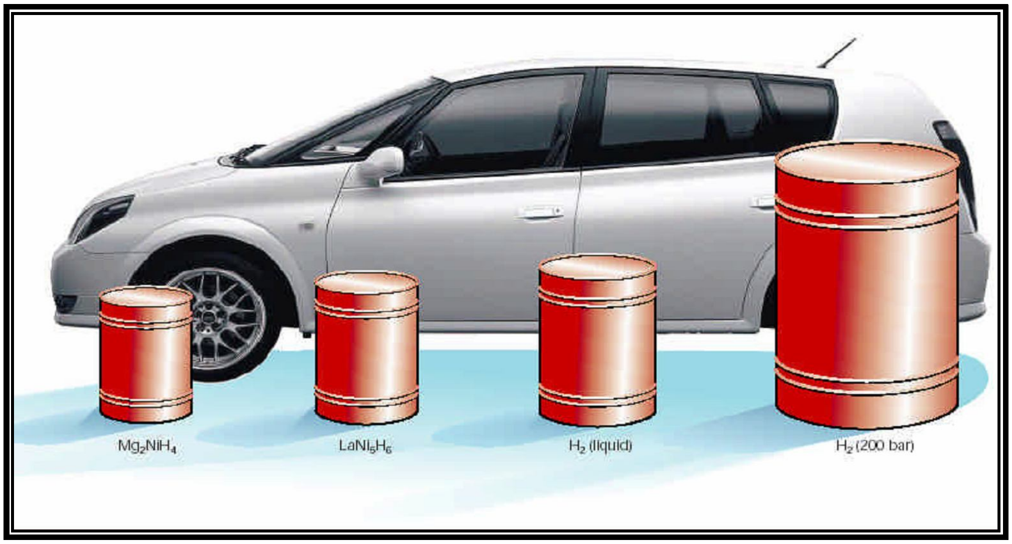


Fig. 1.4: The volume of 4 kg of hydrogen stored in different ways, relative to the size of a car

Table–1.2: DOE technical targets for on-board hydrogen storage

Sr. No.	Parameter	Unit	Target
1	Storage weight percent	wt %	7.5
2	Energy efficiency	%	97
3	Energy density	kWh/l	2.3
4	Specific energy	kWh/kg	2.5
5	Cost	$/kWh	5
6	Operating temperature	°C	–40 to 50
7	Hydrogen filling time (5 kg H_2)	min	2.5
8	Cycle life	cycles	1000
9	Recoverable usable amount	%	90

Table–1.3 shows the most probable (state–of–the–art) hydrogen storage methods today, which reveals the volume required for low temperature based metal hydride is quiet low with respect to other hydrogen storage media [36]. But, the hydrogen density is very low and also, weight is issue for system efficiency. To reach the high volumetric and gravimetric density suitable for mobile applications, reversible storage methods are known today.

Table–1.3: State–of–the–art of technology for hydrogen storage media of 3 kg H_2

Sr. No.	**Technology**	**Volume, litre**	**Weight, kg**	**Density, wt% of H_2**
1	35 MPa (350 bars) compressed H_2	145	45	6.7
2	70 MPa (700 bars) compressed H_2	100	50	6.0
3	Cryogenic liquid H_2	90	40	7.5
4	Low temperature metal hydride	55	215	1.4

1.4.3.1 Gaseous Form

The most common method to store hydrogen is as compressed gas. For storing compressed hydrogen are the simplest and presently the cheapest method, requiring a compressor and a pressure vessel only. The tanks can either be made from steel, aluminium and/or copper alloys, which may be encased in fiber-glass [37]. The steel tanks are most often used for stationary applications, where weight is not affected as it tends to be heavy. High pressure tanks also appear in some test cars. The main research task within the field of compressed gas storage is to develop a safe low weight composite cylinder suitable for high pressures. However, it is inevitable that a considerable amount of energy is used to compress the hydrogen. If the hydrogen is compressed to 100, 300 and 700 bar will approximately 12%, 18% and 24% respectively of the stored hydrogen energy be used to compress, if a compressor with 85% efficiency is used.

If 10 kg H_2 per 500 km at a typical highway moving speed, then a typical 400 liters (0.4 m^3) tank will have chamber pressure,

$$P = \frac{nRT}{V} \qquad \text{--------------------- (1.17)}$$

Where, n is the mole of hydrogen, R is the gas constant; T is the room temperature and V is the tank volume.

$$= \frac{5 \times 1000 \times 8.314 \times 303}{0.4}$$

$$\cong \ 32 \text{ MPa}$$

Assuming, a vessel having radius to thickness ratio, r/t is 10, then the principal stress is,

$$\sigma_{YY} = P \times r/t = 320 \text{ MPa} \qquad \text{---------------------} (1.18)$$

This is a very high value of principal stress in the vessel for hydrogen used on road applications.

A special case of gaseous hydrogen storage is the use of large underground cavities similar to those now used to store natural gas. Two methods of underground storage that are suitable for hydrogen is the use of cavities left after the mining of salt, and in empty geological formation. A salt dome under an urban area is used to store 1,000 tone of hydrogen for industrial use. In short, some of the major disadvantages of compressed hydrogen storage systems are high volume and weight of tank, high cost of compression and safety issues due to higher pressures [38].

1.4.3.2 Liquid Form

Hydrogen can be stored as a liquid (LH_2) at 20.28 K (– 252.87 °C) at ambient pressure in cryogenic tanks [39]. Liquid hydrogen has long been the fuel of choice for rocket applications. The cooling and compressing process requires energy, resulting in a net loss of about 30% of the energy stored in the liquid hydrogen. The storage containers lose energy due to boil–off of hydrogen, caused by diffusion of heat into the storage unit from the surroundings [40].

Another, possible storage option could be to store hydrogen in a hydrogen rich liquid. The hydrogen rich liquid should be in liquid form at ambient temperature, be cheap and easy to produce. It should not be toxic, and possible to reform on board in mobile applications. One possible liquid is Methanol. Methanol is a liquid at room temperature and has a boiling point at 65 °C. It is also possible to reform methanol from CO_2 and H_2. However, this is not an environmental friendly energy carrier due to the reforming by–product CO_2.

Moreover, the reversible catalytic dehydrogenation of methyl cyclohexane (C_7H_{14}) to toluene (C_7H_8) occurs according to the following reaction [41],

$$C_7H_{14(l)} \longleftrightarrow C_7H_{8\,(l)} + 3H_{2(g)} \quad (T_{des} = 300\ ^{\circ}C\text{–}400\ ^{\circ}C) \quad \text{-----------} \ (1.19)$$

Which, involves 6.1 wt % of hydrogen. The main disadvantages of organic liquids, when used for hydrogen storage are the rest product after dehydrogenation, which needs to be sent back to a recycle plant for rehydrogenation. Both, rehydrogenation and hydrogenation are catalyzed processes with selectivity and conversion well below 100%. This means that by–products have to be removed, which makes the process energy intensive, expensive, and dirty. The very limited cycle life is a restriction of this system. Furthermore, the methyl cyclohexane is a liquid, which can react strongly with oxidants resulting in explosion and fire. Therefore, the use of these types of storage systems for on-board storage is questionable.

1.4.3.3 Slush Form

Slush hydrogen is a combination of liquid hydrogen and solid hydrogen at the triple point with a lower temperature and a higher density than liquid hydrogen. It is formed by bringing liquid hydrogen down to nearly the melting point (–259.14 °C) that increases density by 16% – 20% as compared to liquid hydrogen [42]. It is proposed as a rocket fuel in place of liquid hydrogen in order to improve storage and thus reduce the dry weight of the vehicle. The continuous freeze technique used for slush hydrogen involves pulling a continuous vacuum over triple point liquid and using a solid hydrogen mechanical ice-breaker to cut off the surface of the freezing hydrogen [43].

1.4.3.4 Solid State Form

Storing the hydrogen in solid state is safe and the most advantageous. Hydrogen can be stored in solid state by combining the hydrogen with solid state material through chemisorptions, physisorption or by chemical reaction. There are number of ways, solid state hydrogen storage materials are classified. Mainly, there are three groups: i.e. carbon material, high surface area material and metal hydride (see Fig. 1.5).

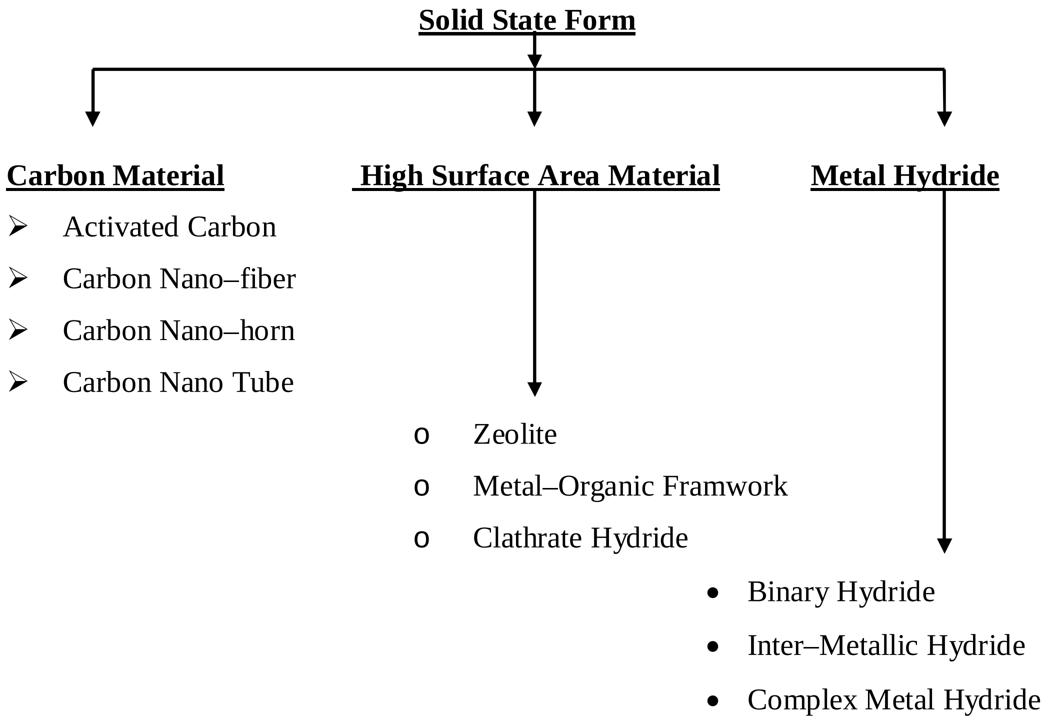


Fig. 1.5: Classification of the solid state hydrogen storage material

i) Carbon Material

A variety of carbon nanostructures like activated carbon, carbon nanofibers, carbon nanotubes, and carbon nanohorns are known in literature. Hydrogen can be stored into the carbon materials by chemisorption and/or physisorption [40]. The methods of trapping hydrogen are not known very accurately. Even though molecular hydrogen physisorption has been demonstrated, it is useful only at cryogenic temperature of nitrogen and extremely high surface area carbons are required. Pure atomic hydrogen chemisorption in carbon materials are reported, but the covalent bond hydrogen is liberated only at high temperatures (> 400 °C). Adsorption up to a few wt% of H_2 at room temperature is occasionally reported, but has not been reproducible. So far, the surface and bulk properties needed to achieve practical storage are not clearly understood. Moreover, the hydrogen storage capacity of carbon materials is limited to about 2 wt% of H_2 [44]. The basic concept and summary of various reported hydrogen storage capacity of carbon materials are given below:

- ***Activated Carbon***

Activated carbons are predominantly amorphous materials with large surface areas and pore volumes, often containing areas in excess of 2000 m^2g^{-1}. They are best described as “a twisted network of defective carbon layer planes cross–linked by aliphatic bridging groups”. The pore structure of an activated carbon is complex and ill-defined, making it challenging to study. An example of this complex, cross-linked structure is illustrated in Fig. 1.6 [45].

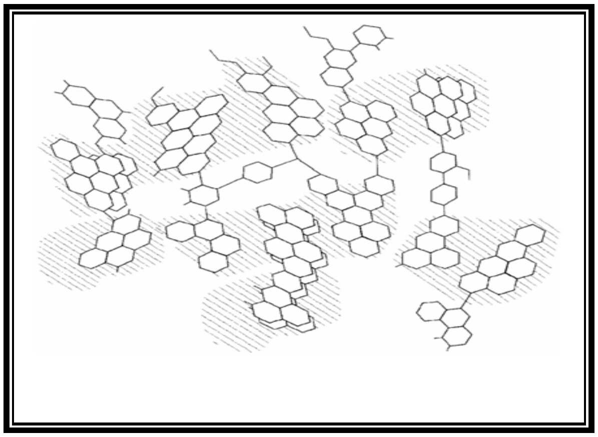


Fig. 1.6: Structure of activated carbon

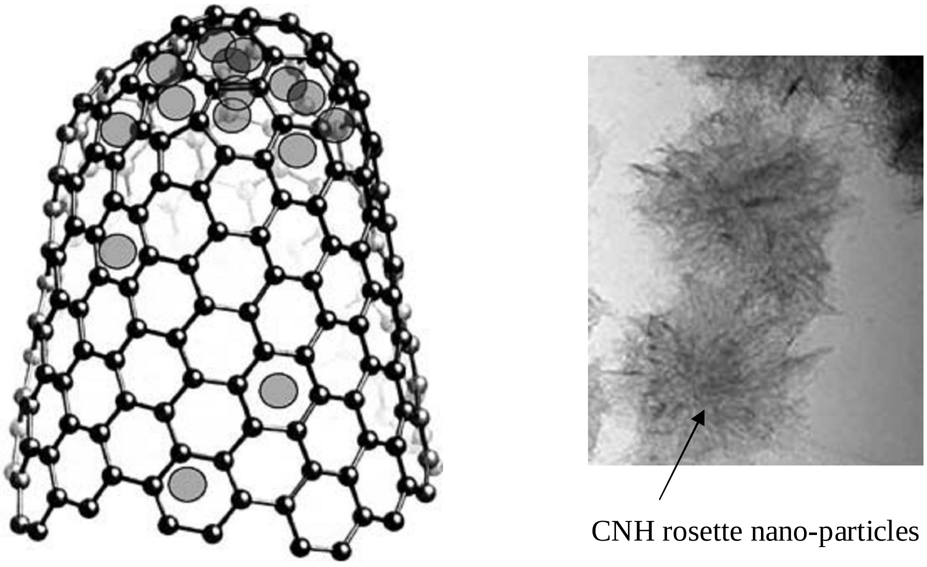
Physically activated carbon commonly is being used bituminous coal or coconut shells as a starting material. The two-stage activation process consists of carbonization, where oxygen and hydrogen are burned off, and gasification, where the char is heated in a steam or carbon dioxide atmosphere to create a highly porous structure from carbon burn-off. Carbon aerogels are a separate class of amorphous carbon, which can mimic the properties of activated carbon [46]. They are prepared by a sol–gel polymerization process and can be activated using the standard methods.

- ***Carbon Nano–Fiber***

Graphitic carbon nanofiber (GNF), or shortly carbon nanofiber (CNF), has been catalytically synthesized. They consist of graphene planes arranged in platelet stacks, either in parallel or in angled arrangements, which result in a conical fishbone structure. Very high hydrogen uptake values were claimed for these materials, up to H:C ratio equal to 24 (which gives 68 wt% of H_2) in GNF herringbone fibers and 55 wt% of H_2 in platelet stacks at 0 °C and about 12 MPa [47].

- ***Carbon Nano–Horn***

Single–walled carbon nano–horn (CNH) consists of single-walled graphitic structures formed out of a single graphene sheet rolled up to form conical (hornlike) shapes, which are rounded at the tip (Fig. 1.7a) [48]. Typically, their average size is of the order of 2 nm to 3 nm. These horn–like shapes aggregate to form spherical rosette structures with sizes of about 80 nm – 100 nm (Fig. 1.7b). CNH exhibits very large surface areas approaching 1,500 m^2g^{-1}. These phases are prepared by arc–discharge synthesis or laser cutting out. Low cost and high purity CNH material can be produced in scaled up process. Because of low cost, high purity and high surface area CNH become attractive candidates for gas and/or liquid hydrogen storage [49]. Indeed, recently it was reported isosteric heats of H_2 adsorption corresponding to 100 – 120 meV energy for binding of H_2 molecule to carbon. It is much more than for SWNT. This increase in the energy of hydrogen bonding and has been attributed to enhanced interaction of H_2 molecules at the conical tip of nano-horn, where gas–to–liquid transition and even solid–like H_2 was suggested to exist as a consequence of a quantum effect. Inelastic and quasi–elastic neutron scattering experiments showed unambiguous signature of strong interaction between H_2 molecule and CNH, and the character of this interaction is quantitatively different to that in CNT. In this context, recent ^{13}C NMR studies have identified two distinct processes with quite disparate relaxation times, one of them being attributed to slow motions of ^{13}C, which takes place inside conical tips, where hydrogen undergoes likely condensation process. However, the density of crack tips in highly disordered graphite should be lower than the density of conical tips in carbon nano–horn phase.



(a) ***(b)***

Fig. 1.7: Carbon nano–horn with hydrogen condensed at the end of conical tip: (a) Agglomerate to form nano-carbon particles that exhibit rosette shape and (b) TEM image

➢ ***Carbon Nano–Tube***

A clear potential has been demonstrated for room storage of H_2 molecules in carbon nano tubes, with reversible capacity 5 wt% – 10 wt%. Single and multi wall carbon nano tubes have the ability to quickly absorb high density of hydrogen at atmospheric pressure [50]. Exterior and interior absorption is possible, with different H/C coverage. Fig. 1.8 (a) and (b) show simple H/C coverage in case of exterior and interior absorption, respectively. In case of exterior absorption hydrogen is absorbed at the exterior of the tube wall by H–C bonds with H/C coverage 1.0, while at interior absorption H–H bonds are formed and the coverage can be raise up to 2.4. The absorption into the interior wall is also possible, but not stable. The hydrogen relaxes inside the tube, forming H–H bonds. The summary of various reported hydrogen storage capacity of carbon nano tubes are given in Table–1.4 [47, 51, 52].

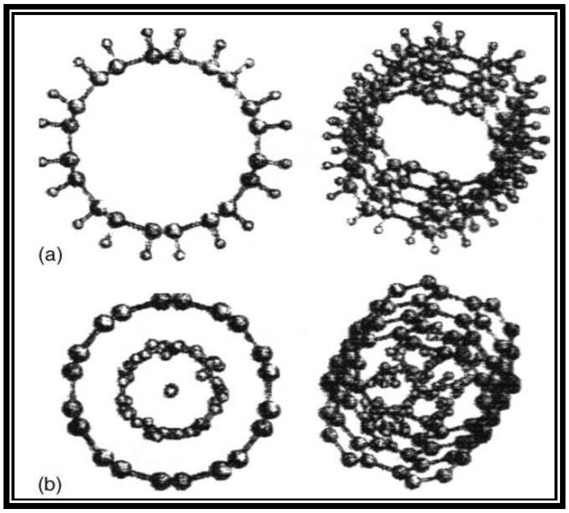


Fig. 1.8: Hydrogen absorption in a nano tube, with (a) Exterior and (b) Interior H_2 coverage

Table–1.4: Summary of the reported hydrogen storage properties in carbon nano-tube

Adsorbent	**Hydrogen storage wt %**	**Temperature °C**	**Pressure MPa**
Li doped MWNT	20	–73 to 127	0.1
K doped MWNT	14	27	0.1
SWNT (high purity)	8	–193	8.0
SWNT	6.5	27	16.0
SWNT(50% purity)	4	27	12.0
SWNT (low purity)	5 to 10	0	0.04
MWNT	5	27	10.0

ii) High Surface Area Material

The most predominant examples of high surface area materials are Zeolite, Metal–Organic Framework (MOF) and Clathrate Hydrate. In brief, the basic properties and literature survey of high surface materials are given below:

- ***Zeolite***

Zeolite is crystallite material composed of SiO_4 or AlO_4 building blocks. They contain an intra–crystalline system of channels and cages, which can trap guest H_2 molecules. The adsorption capacity of zeolite at – 196 °C is typically below 2 wt% [53]. A theoretical capacity of 2.86 wt% has been suggested as being an intrinsic geometric constraint of zeolite. Due to this low gravimetric density, zeolite is not typically considered feasible hydrogen storage materials. Isosteric heats on the order of 6 to 7 kJ mol^{-1} are typical for Hydrogen – Zeolite systems. Zeolite structures (see Fig. 1.9) can have intra–crystalline cavities on the order of the H_2 diameter itself [54]. They function as molecular sieves, blocking adsorption of larger gas molecules by steric barriers. When confined inside a molecular–sized cavity, the heavier D_2 molecule is adsorbed preferentially over the lighter H_2 molecule due to its smaller zero–point motion.

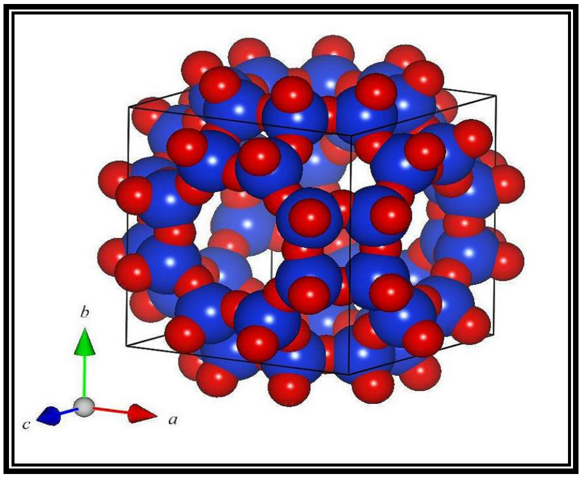


Fig. 1.9: Structure of a Zeolite

- ***Metal–Organic Framework***

Metal–Organic Framework (MOF) is synthetic crystallite material, which is somewhat analogous to Zeolite. Organic linker molecules form the building blocks of MOF and coordinative binding to inorganic clusters to form a porous framework structure. A good example of a MOF structure is provided by MOF–5, which consists of Zn_4O $(CO_2)_6$ units connected by benzene linkers in a simple cubic fashion (Fig. 1.10) [55]. It was not until fairly recently that MOF studied as a potential hydrogen storage material. By modifying the organic linkers, the pore size and effective surface area can be quite effectively. Hydrogen adsorption capacities of up to 1.25 wt% at –196 °C have been measured for MOF–177 [56]. A number of MOF contain coordinative unsaturated metal centers, which are known to enhance hydrogen binding interactions. In most cases this interaction is dominated by electrostatic contributions, but the possibility of stronger "Kubas" orbital interactions between the hydrogen and the open metal sites has generated considerable interest.

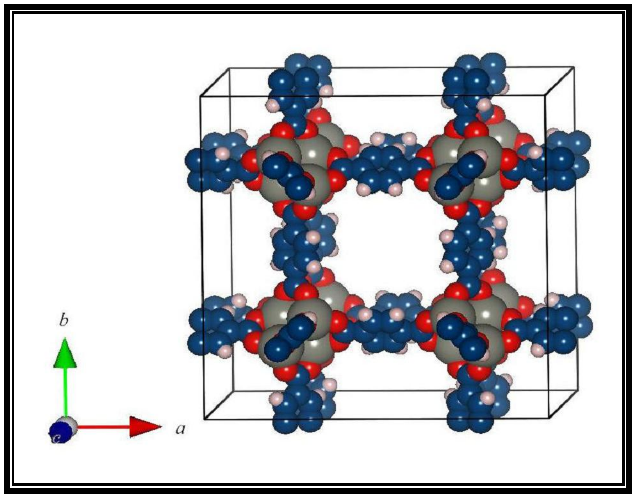


Fig. 1.10: Structure of MOF–5

- ***Clathrate Hydrate***

A clathrate is a molecule that traps a second kind of molecule inside. In this case, hydrogen is the guest molecule stored inside clathrate [57]. Large clathrate cages can accommodate multiple hydrogen molecules. Specific examples of the hydrogen storage clathrate family are the clathrate hydrate. They are formed by exerting huge pressures, approximately 2000 bar, to water. The water molecules then form a crystal with cages that can be filled with hydrogen molecules. The desorption mechanism of hydrogen from clathrate involves a structural break down of the clathrate crystal. Recent research focuses on clathrate that can be operated at lower pressures.

iii) Metal Hydride

The metal hydride is generally discussed under three types, namely binary hydride, inter–metallic hydride and complex hydride. The basic properties of each metal hydride groups are given below (see Fig. 1.11) [58]:

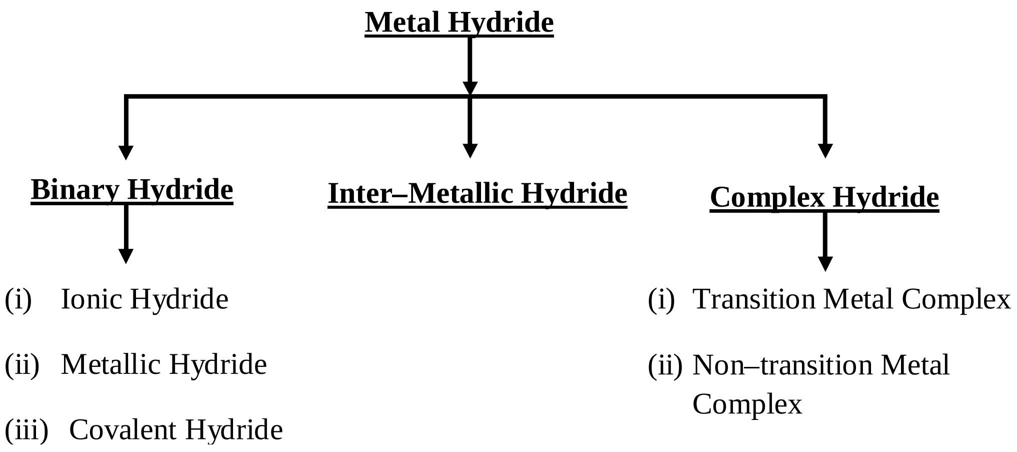


Fig. 1.11: Classifications of metal hydride

- ***Binary Hydride***

Binary hydride MH_x (M: metal and H: hydrogen) is the simplest hydride, which is principally divided into:

(i) ***Ionic Hydride:*** Bonding between M^+ cations from Group I–II (excluding Be and Mg) and H^- anions. The properties are similar to those of a salt (white colour, brittleness etc) [59, 60].

(ii) ***Metallic Hydride:*** Reaction between a transition metal (TM) in Group III–X and hydrogen. The 1s electron of the hydrogen atom is transferred to the conduction band of the TM, which creates new M–H bonding states. Although a TM from Group III–V easily forms a metallic hydride at moderate conditions, a TM from Group VI–X rarely forms the hydride under such conditions. The hydrides show metallic properties (metallic shininess and electrical conductivity) [61, 62].

(iii) ***Covalent Hydride:*** Reaction between an element in Group XI–XV and hydrogen. The bonding is relatively strong and involves shared electrons. Some of the hydrides exist in the gas state at room temperature. Be/Mg hydrides are exceptionally stable covalent hydrides, although MgH_2 has an ionic bonding component [63].

Magnesium is one the most attractive hydrogen storage materials in capacitive point of view; however, the desorption reaction is too slow for practical use and requires relatively high temperature [64–68]. It is most portable in mobile applications.

- ***Inter–Metallic Hydride***

In order to modify the hydrogen storage properties, alloys are used for making inter-metallic hydrides that can be used for hydrogen storage. These are the alloys of two or more metallic elements, usually with integer stoichiometry (A_aB_b) and crystal structures that are different from either of the parent elements (A and B), such as AB_2, A_2B, AB and AB_5 [69–75]. Thus all inter-metallic hydrides used for hydrogen storage forming "B" metal. The advantage of these systems is that the absorption and are combinations of a strongly hydride-forming "A" metal and a weakly hydride-desorption can be tuned by alloying the correct concentrations and types of elements. Although these classical hydrides have good volumetric hydrogen densities (~130 kg H_2/m^3 for $LaNi_5H_6$), due to their weight penalty (1–2 wt% H_2), they are mainly interesting for stationary applications.

- ***Complex Hydride***

Metal hydride based on metal–hydrogen complex, where hydrogen is more covalently bonded to the central metal atom, have been considered to be too stable. These hydrides fall in two main categories: containing transition metal and non-transition metal complex.

(i) Transition Metal Complex: When certain transition metals are combined with an alkali or alkaline earth metal in the presence of hydrogen at moderate pressure, a low-valence complex of the transition metal and several hydrogen atoms can be formed. Such complexes are stabilized by donation of electrons from the more electropositive alkali or alkaline earth metal. Hydrogen, contributes to smoothening out the electron density in metal hydrides. It can also support very high electron densities in formally low–valent metal complexes, such as in $Mg_2[NiH_4]$ [76]. This stabilization mechanism is, however, sensitive to lattice defects from doping and disorder. Modifying the $Mg_2[NiH_4]$ lattice has been reported to double the hydrogen release pressure at 180 °C.

(ii) Non–Transition Metal Complex: Several hydrides based on non-transition metal complexes can be described with the general formula $M(M'H_4)_n$, where M is a metal (typically an alkali or alkaline earth metal) with valence n, and M´ is a trivalent Group 13 (typically B, Al or Ga) (such as $LiBH_4$, $NaBH_4$, $LiAlH_4$, $NaAlH_4$ etc). The hydrides consist of M^+ cations and $M'H_4^-$ anions, where the hydrogen atoms are tetrahedrally coordinated around the M´ atom. These complex metal hydrides have very high hydrogen content by weight, $LiBH_4$ contains 18 wt % hydrogen, $NaAlH_4$ contains 7.4 wt% of H_2 [77–85].

1.4.4 Conversion

One of the fundamental principles of physics is the conservation of energy. Energy can take on many forms, and various processes convert one form into another. While total energy always remains the same, after most conversion processes the amount of useful energy remaining is reduced. The processes which convert energy into useful forms have limited thermodynamic efficiencies, typically only 10% to 40%. This means that typically 60% to 90% of the input energy becomes waste energy. Electricity is today the only energy carrier with no environmental impact at the point of utilization [86]. Hydrogen shows the same advantage. It is therefore very important to assess if the development of a new infrastructure based on hydrogen as an energy carrier is possible, feasible, or useful. From the primary energy production up to the final utilization of the energy, a great number of transformation and storage steps of the energy are required. There are mainly, associated with combustion of hydrogen in internal combustion engines and turbines [87], hydrogen/oxygen combustion for steam generation [88], electrochemical conversion in fuel cells [89, 90], catalytic combustion [91] and metal hydride technologies [92].

1.4.5 Application

Most of the hydrogen is used for industrial applications such as refining, treating metals, chemical process and food processing [93]. It is also used as a fuel to power generation. Coming years, hydrogen will be most suitable for cooking, pharmaceutical, electronics and aerospace applications [94, 95].

1.5 Importance of Hydrogen Storage

Public opinion on hydrogen is that it is a very dangerous fuel, because of several reasons like; there is a greater range of mixture of air, which would explode; when hydrogen rapidly exits from a tube, it heats instead of cool and thus combusts and, it diffuses more rapidly through leaks [96]. These three reasons, the hydrogen storage is very important for its use as an energy carrier. Another big issue of hydrogen storage is hydrogen embrittlement [97]. When a metal comes in contact with hydrogen, there is a significant amount of worsening in their mechanical properties. This phenomenon is known as hydrogen embrittlement. There are many variables on which this process depends like temperature, pressure, metals purity and its concentration and time of exposure to the gas. Some internal factors like physical and chemical properties, surface conditions, microstructure of the material, etc. also decide the type and extent of the embrittlement.

1.6 Requirement of Hydrogen Storage Media

The requirements for hydrogen storage materials are different for different applications. Low total weight is essential for mobile applications, but is not so important for the stationary ones (filling stations). The essential requirements, which should be satisfied by metal hydrides proposed for hydrogen storage application, are given below [98]:

- High hydrogen storage capacity.
- Reversibility of hydride formation and deformation reactions. The hydride should be decomposable at moderate temperature, which can be provided from locally available heat sources, like solar, automobile exhaust and waste heat resources.
- Absorption/desorption kinetics should be compatible with the charge/discharge requirements of the system.
- The equilibrium dissociation pressure of the hydride should be compatible with the safety requirements of the hydride containment system.

- The hydride should have a sufficient chemical and dimensional stability to permit its being unchanged over a large number of charge–discharge cycles.
- Minimal hysteresis in adsorption–desorption isotherms.
- The hydride should be reasonably resistant to deactivation by low concentrations such as O_2, H_2O, CO_2 and CO.
- Operating and maintenance costs and purchased energy requirements per storage cycle should be low. The total cost of hydride should be affordable for the specified application.

A careful combination of technical and economic considerations will determine the suitability of a hydride product for a given hydrogen storage or hydrogen containment application.

1.7 Why Magnesium Based Metal Hydride is Chosen ?

If metal hydrides are to become important energy carriers in mobile vehicles, the total mass of the storage system needs to be reduced, and this puts strong constraints on the applicable elements and alloy compositions. A very promising approach is to use magnesium based alloy compositions. Because of the hydride, MgH_2 can store up to 7.66% mass of hydrogen. Magnesium based alloy compositions are considered promising, because of following reasons [99–101]:

- ➢ Magnesium has high hydrogen storage capacity. These properties translate into theoretical energy storage density i.e. 2.33 kWh/kg.
- ➢ It has reversible hydrogen absorption/desorption characteristics.
- ➢ Light weight (1.74 g/cm^3 - lowest among structural metals).
- ➢ It is heat resistance, and vibration absorbing characteristics.
- ➢ It is low cost material.
- ➢ It is abundant available material.
- ➢ It is non–toxics.

1.8 Bench Marks on Pure Magnesium

The Magnesium based alloy compositions are used for hydrogen storage, due to a very high volumetric storage capacity. However, the rate at which hydrogen absorbs and desorbs in Magnesium is low, because of a number of reasons. There are mainly three bottlenecks, with the use of Magnesium in everyday industrial applications [102–104], which are as under:

i) The rate of absorption and desorption is too low, because diffusion of hydrogen atoms through the hydride is slow. And also, the H_2 molecules do not readily dissociate at the surface of Mg to generate the H atoms, which can diffuse into the metal.

ii) The hydrogen atoms bind strongly with Mg atoms, since the enthalpy of formation of hydride is large, and the hydride needs to be heated up to a very high temperature in order to release hydrogen gas at sufficiently above atmospheric pressure.

iii) The Mg easily capture oxygen and forms Magnesium Oxide on a Mg surface, when it is exposed to air, which are not diffuse to hydrogen molecules, and which resist the hydrogen storage capacity.

These characteristics result in poor diffusional kinetics and requirements of high temperatures for hydriding and dehydriding making Magnesium difficult to use for mobile power system applications such as in motor vehicles and power boats. However, for stationary power system applications such as in stand–alone generators, the only major bottleneck is diffusion kinetics. To improve the diffusion kinetics, approaches include incorporation of rapid diffusion channels in Mg by decreasing crystallite size and by blending in catalysts such as Ni, Fe, Sc, Mn, Al etc.

- ***Size Effect***

Materials reduced to the nano–scale can show very different properties compared to what they exhibit on a macro–scale. One main reason for these unique properties is the drastic change of the surface to volume ratio. This results in extremely enhanced chemical reaction ability. On the other hand the general physical properties of nano-scaled materials are becoming size dependent. There are the diffusion length, the electron free path and the dislocation distance scales with the size of the particle. The problem of absorption and desorption rate could be reduced by forming a compound of small Mg crystals. If the crystallite size is reduced, the desired diffusion length of hydrogen to reach the metal–hydride interface can be reduced. The best way to obtain the desired small crystallite size is to ball mill method [105, 106].

➢ *Catalyst*

Beside the size reduction, there are other possibilities to enhance the hydrogen absorption/desorption kinetics of Magnesium by blending with catalysts. The slow sorption kinetics at lower temperatures is mainly due to the low dissociation ability of hydrogen gas molecules on the metallic Mg surface. The probability of the absorption of a H_2–molecule on the Mg–surface is only 1 in 10^6. To overcome this problem, catalysts can be added to Magnesium. In the past, Pd, Ni and Fe are used to enhance H_2-dissociation at the surface [107]. For micro crystallite Magnesium the catalytic acceleration of V and Ti is also demonstrated. Lately, the transition metals as catalysts are in the focus of investigations. The catalytic effect of different metal oxides is also compared. Oxides of the transition metals Ti, V, Cr, Mn and Fe lead to significantly enhanced hydrogen sorption kinetics. CuO, Mn_2O_3, Cr_2O_3, Fe_3O_4 and V_2O_5 are compared to pure nano-sized MgH_2 [108, 109]. The highest desorption rates, according to literature survey, are achieved by the addition of Fe_3O_4 and V_2O_5. It can be seen, the addition of metal oxides leads to a notable enhancement of both absorption and desorption kinetics. The absorption takes place in 1 to 2 minutes, while desorption needs 3 to 5 min. In later studies, the outstanding effect of Nb_2O_5 is pointed out [110]. At 300 °C, absorption and desorption of 7 wt% of hydrogen are facilitated in 60s and 90s, respectively. To further understand, the catalytic reactions are investigated by nanocrystallite MgH_2 with additions of VN, VC and V [111]. The local electronic structure of the catalyst is important. Before dissociation of H-molecules, hydrogen has to be absorbed at the surface of the catalyst by electron exchange reactions.

To overcome the thermodynamic of Mg based alloys, the addition of a catalyst can play an important role. The main objectives of catalyst addition are “overcoming the dissociation barrier for hydrogen” and “destabilization of the hydride phase”. The addition of Ni and other transition metals (Ti, V, Mn, Zr, and Fe) also improves the hydrogenation behaviour of Mg and decreases the activation energy for hydrogen desorption [112].

1.9 Motivation of the Thesis

The main focus of this thesis is “hydrogen storage in Magnesium based alloy compositions”. Specifically, hydrogen storage properties of ternary Mg–V–Ni, Mg–Pd–Ni and quaternary Mg–Zr–Mn–Ni alloy compositions have been studied. The main motivation for studying Magnesium based hydrides, despite the fact that they probably fail to meet the DOE (Department of Energy, US) hydrogen storage criteria regarding capacity, kinetics and operating temperature. Hydrogen storage capacity of 7.66 mass% of pure Mg is very high. Also, Magnesium is both cheap and abundant. Thus, in terms of price, stored H_2 in Magnesium is superior to most traditional hydrides. However, Magnesium based metal hydrides have limited practical applications, so far, because both hydrogenation and dehydrogenation reactions are very slow and relatively high temperatures are required for both absorption/desorption processes. In this research work, investigations have been conducted for improvement of these bottlenecks of Mg based hydrogen storage materials. The central emphasis of the thesis is issues related to enhancing the performance of the Mg based system.

Magnesium based hydrides may find their way in hydrogen storage applications requiring less strict demands for hydrogen delivery temperature, such as in stationary power system applications. The main motivation for studying low temperature hydrides is obviously low desorption temperature of hydrogen (at near 100 °C).

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