Introduction

Both nationally and internationally, the need for alternative energy sources is getting urgent day by day, and hence the development of renewable energy is moving fast. Various individuals and research companies are looking for new energy systems, which can meet the requirements of a renewable and CO₂-free energy. The need for CO₂ – free clean energy arises primarily due to two main reasons [1].

Firstly, in future, even though there will be a surge in demand in energy, the world will be facing a decline in production of conventional fossil fuels. According to the BP Statistical Review of World Energy 2011, oil is the world’s largest primary energy source of global consumption till now. But as the demand of energy is expected to grow on an annual basis, an energy crisis is predicted in the near future. The report notes that the overall energy consumption growth is 5.6% annually. From various predictions, it is depicted that the global oil production would start declining sooner or later, and as global energy consumption rise rapidly, the oil prices will increase drastically. From Fig. 1.1 it is clear that, by the middle of the 21st Century, the demand of energy may significantly exceed the energy supplied by fossil fuel, hydrothermal and nuclear energy. The shortfall in energy becomes higher after the depletion of the fossil fuels, about 100 years in the future [2].
The second reason behind the search of a new form of energy is that, there are serious environmental problems accompanying the combustion of the fossil fuel. Fossil fuels are hydrocarbons, containing primarily carbon and hydrogen, thus when burned, they produce water and carbon dioxide. Fossil fuel use is responsible for the majority of carbon dioxide emissions and more carbon-intensive fossil fuels produce more carbon dioxide pollution. The increase in atmospheric CO₂ has driven a rapid rise in global temperature due to greenhouse effect [Fig. 1.2]. 72% of the totally emitted greenhouse gasses are CO₂. Recent investigations have shown that if the CO₂ concentration rises above 450 ppm, the global temperature will rise by 2°C, which will lead to inconceivable cataclysmic changes in the environment. Responses to these rising temperatures have already been documented in melting glaciers and ice sheets, shifting weather patterns, and changes in the timing of seasonal events.
As a consequence, investigations of alternative energy strategies have recently become important, particularly for the future world stability. The future energy systems must provide a secure, more sustainable, climate friendly and environmentally acceptable energy supply. In recent decades there has been intense international interest, discussion and agreements made, which have been directed at developing cleaner sources of energy to meet the ever-increasing energy demands without sacrificing the environment. In line with this characteristic, hydrogen economy represents such a means, with which these goals can be achieved.
1.1 Hydrogen as Energy Carrier

Hydrogen, the most common chemical element on the planet, does not exist in nature in the elemental form. The majority of it gets combined with oxygen and forms water [3]. As a result, to use hydrogen, we must first separate it from the other elements bonded to it. The hydrogen must be produced from some primary energy sources. That is why hydrogen is considered as an energy carrier, not an energy source, which transports the energy from the generation site to another location. The advantages of hydrogen as energy carrier are:

- When hydrogen is combusted or electrochemically oxidized to create heat or electricity, respectively, the only product is water. No pollutants or greenhouse gases are generated or emitted, allowing the potential of zero emission vehicles to become a reality.

- The chemical energy per mass of hydrogen (142 MJ Kg\(^{-1}\)) is almost three times higher than other liquid hydrocarbon fuels [Fig. 1.3].

- Hydrogen is highly abundant in nature.

- Hydrogen can be stored over relatively long periods of time.

- Hydrogen can be utilized in all parts of the economy (e.g., as an automobile fuel and to generate electricity via fuel cells).
Fig. 1.3 Comparison of specific energies of different hydrocarbon fuels with that of hydrogen [Adapted from green enocometrics research].

Much research, including experimental and theoretical studies, has recently been carried out to use hydrogen energy. However, it is necessary to understand the broader aspects of hydrogen energy to make it realizable [4]. For hydrogen-fueled transportation, the four most fundamental technological and economic challenges are:

- The costs of hydrogen production from renewable energy sources, is to be reduced sharply, over a time frame of decades.
- To capture and store (“sequester”) the carbon dioxide by-product of hydrogen production from coal.
- To develop and introduce cost-effective, durable, safe, and environmentally desirable fuel cell systems and hydrogen storage systems.
- To develop the infrastructure to provide hydrogen for the light-duty-vehicle user.
1.2 Hydrogen Production Methods

Many production processes for hydrogen exist. The hydrogen can be produced from the fossil fuels (e.g., steam reforming of natural gas or other light hydrocarbons, gasification of coal and other heavy hydrocarbons) or water (electrolysis of water, direct and indirect thermochemical decomposition, and processes driven directly by sunlight – photo catalytic route). Although having so many choices of resources sounds complicated, but indeed it is a great advantage, because no one region or country has to be dependant on one resource to produce hydrogen and which ever resources are suitable environmentally and economically can be used. In a developing country like India, by means of hydrogen economy, we can have decentralized energy, as many remote areas are not having access of direct electricity.

Presently, the commercialized hydrogen production processes are mostly fossil fuel based, like, steam methane reformation, partial oxidation of methane, auto-thermal reforming and coal gasification – the cheapest and largest being generated by steam-methane reformation. Though this processes generates CO₂, but the CO₂ generate from the reformation process is highly concentrated, therefore the recovery is much cheaper than the diluted exhaust gas of the fossil fuel. But the main advantages of hydrogen economy comes if hydrogen is extracted from water, using CO₂-free primary sources of energy such as solar energy, wind energy, or nuclear energy. The different production methods of hydrogen from water are described in the following section.
1.2.1 Hydrogen production from water

Hydrogen generation from water can be depicted by the following equation

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]

The reaction is highly endothermic (\( \Delta H = 243 \text{ KJ mole}^{-1} \) at 298 K), and for direct thermolysis of water, a very high temperature is required (>2500 °C). The energy required to split water can be provided by a primary energy source, like, solar, wind, nuclear heat or by a secondary energy source like electricity or a combination of these sources using a chemical process. So, a large collection of diverse processes have evolved for hydrogen generation from water and some of which are listed below in Table 1.1.

None of the above except electrolysis has been commercialized and although electrolysis is an established process, cost of hydrogen production is very high. So, efforts are being taken to improve efficiency and to minimize cost of these processes to make them commercially viable. Thus, R&D on various aspects like material development, catalyst development, reactor design etc. has to be carried out.

Table 1.1 Different hydrogen production methods, where hydrogen is produced from water

<table>
<thead>
<tr>
<th>Method</th>
<th>Process</th>
<th>Feed Stock</th>
<th>Energy</th>
<th>Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>Steam Reformation</td>
<td>Natural Gas</td>
<td>High temperature steam</td>
<td>Carbon sequestration can mitigate its small emission</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Coal Gasification</td>
<td>Coal, Biomass</td>
<td>Steam and oxygen at high temperature &amp; pressure</td>
<td>Small emission. Carbon sequestration can mitigate it</td>
</tr>
<tr>
<td>Method</td>
<td>Fuel</td>
<td>Source</td>
<td>Emission</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-----------------------</td>
<td>-----------------------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>Biomass</td>
<td>Moderately high temperature steam</td>
<td>Small emission. Carbon sequestration can mitigate it</td>
<td></td>
</tr>
<tr>
<td>Thermochemical Water Splitting</td>
<td>Water</td>
<td>Waste heat from high temperature nuclear reactor</td>
<td>No Emission</td>
<td></td>
</tr>
<tr>
<td>Electrochemical</td>
<td>Electrolysis</td>
<td>Water</td>
<td>Electricity from wind, solar, hydro, nuclear</td>
<td>No emission</td>
</tr>
<tr>
<td>Photo electrochemical</td>
<td>Water</td>
<td>Electricity from direct sunlight</td>
<td>No emission</td>
<td></td>
</tr>
<tr>
<td>Biological</td>
<td>Photobiological</td>
<td>Water &amp; Algae</td>
<td>Direct Sunlight</td>
<td>No emission</td>
</tr>
<tr>
<td>Anaerobic Micro organism</td>
<td>Biomass</td>
<td>High temperature heat</td>
<td>Small emission.</td>
<td></td>
</tr>
</tbody>
</table>

**1.3 Different Hydrogen Storage Methods**

Hydrogen is a potential fuel for various types of power sources, such as fuel cells, internal combustion engines, gas turbines, etc. However, a major problem is the difficulty encountered in its storage and bulk transport. Hydrogen offers tremendous gravimetric energy potential, but it has a low energy density by volume, meaning it requires a large storage container to make it practical for use in a motor vehicle. To run a standard sized car for 400 km, 24 kg of petrol or 8 kg of hydrogen is needed in a combustion engine, while 4 kg of hydrogen is needed for an electric car with a fuel cell. 4 kg of hydrogen occupies a volume of 45 m³ at ambient conditions. This volume is not practical for automobiles and requires the development of an efficient system for onboard hydrogen storage. Hydrogen in liquid form is very light with energy density of 77Kg/m³, just over one tenth that of petrol /gasoline (702
Kg/m$^3$) but its calorific energy density (39.4 kWh/Kg) is three times that of petrol (13 kWh/Kg).

A hydrogen storage system suitable for mobile applications must meet simultaneously the following six requirements, which has been set up based on economical and environmental considerations [5]

(i) High gravimetric (>4.5 wt. %) and volumetric (> 36g H$_2$/L) densities.
(ii) Operation temperature approximately in the range 60 – 120 °C.
(iii) Reversibility of the thermal absorption/desorption cycle.
(iv) Low cost.
(v) Low-toxicity.
(vi) Safety requirements.
(vii) Good cyclic stability.

Hydrogen can be stored in different ways, such as in gaseous and liquid forms and in solid state materials. Hydrogen stored as gaseous form in pressure vessels, pressurized to several hundred atmospheres. In liquid form hydrogen can be stored only at cryogenic temperature which is energy intensive. The main drawback in both these methods is low volume density of hydrogen [Fig. 1.4]. Solid state hydrogen storage has become an alternative method for storing hydrogen. For good hydrogen storage, the material should have greater storage capacity in terms of volume density and wt. %. The kinetics of hydrogen storage material should be very fast. In addition, the material should be lightweight, cheap and should release hydrogen under mild conditions. Refueling time of hydrogen storage materials is currently too long. There is a need to develop hydrogen storage system with refueling time less than three minutes.
Compressing a gas requires energy to power the compressor, and higher working pressures mean that more energy requirement for the compression step. Compression of hydrogen gas up to 35 MPa consumes nearly 20% of its total energy and the total volume of the tank comes out to be quite high. Because of this, even at a very high pressure, gaseous hydrogen is not an attractive storage medium on a volumetric basis. To store 4 kg of hydrogen in the gaseous form at 200 bar pressure, a traditional cylinder would have to have an internal volume of 220 litres, which may be suitable for buses and larger vehicles, but impractical for a modern compact car. This needs expensive containment vessels made from carbon fiber, capable of withstanding very high pressures, up to 70 MPa (about 10,000 psi). There are major designs challenges are to overcome to find suitable containers for storing hydrogen. Due to the small size of hydrogen molecule, leakage can be a potential danger at
refueling stations, as fuel tanks are refilled at very high pressures through mechanical dispensing couplings.

1.3.2 Storage in liquid form

For space travel, liquid hydrogen has been used as the fuel energy storage system since the 1960s [6]. Liquid hydrogen is light relative to other liquids, but it has a density over 800 times higher than the gaseous state and does not need the high pressure that is required for compressed gas storage, thus has less potential risks compared to gaseous storage. Cooling circuits and insulation are needed to keep it below its boiling point of 20.3°K (-252.9 °C). Considerable energy must also be expended to get and keep the temperature down. The disadvantage of this type of storage is that hydrogen has a liquefaction temperature of 20 K at 0.1 bar pressure and the energy required to liquefy hydrogen is very high, nearly 30 % of the energy content of hydrogen. This energy requirement is one of the major problems with storing hydrogen as a liquid but expenditure is compensated for as very high volumetric density of 25.9 wt. % achieved by liquid hydrogen [7]. Another problem with this method of storage is caused by the massive thermal gradient between the interior and exterior of the storage vessel requiring advanced insulation techniques in order to maintain the temperature of the liquid [3, 8]. Even so, the high thermal gradient results in hydrogen being lost due to boil-off which varies from 0.06 % per day from large static containers to 3 % per day from tanks sized for use in cars [9, 10]. For automotive applications, where space and weight limitations apply, these problems can be acute. Whether it is stored as a liquid or a gas, containment is also a problem since hydrogen molecules are very small and light; they are highly diffusive and tend to permeate through their container even at low pressures. Hydrogen boil-off, and the high cost of sophisticated insulating techniques required for maintaining the very low temperatures, coupled with the initial energy cost to create liquid
hydrogen, makes this method of hydrogen storage impractical for application in hydrogen fuel cell powered vehicles. Researchers is currently trying to find improved insulation and cooling methods. [11]

1.3.3 Solid state hydrogen storage materials

The storage of hydrogen in solid state material by absorption as chemical compounds or by adsorption on high surface area materials has definite advantages from a safety perspective [12]. In these cases some form of energy input is required to release the hydrogen for subsequent use. In solid state storage, hydrogen is bonded by either chemical forces, e.g., hydrides, imides and nitrides or by physical forces, e.g., MOF and carbon based materials. Physisorption has the advantages of higher energy efficiency and faster adsorption/desorption cycles, whereas chemisorption results in the adsorption of larger amounts of gas but in some cases it is not reversible and requires a higher temperature to release the adsorbed gas. The most well studied and practical solid state hydrogen storage material is metal hydride. In this case, hydrogen gets absorbed within the metal to form hydride, and upon heating the hydride, the hydrogen comes out. Extensive efforts have been made on solid state hydrogen storage systems, including metal hydrides, metal nitrides, metal imides, carbon based materials, metal organic frameworks (MOF), zeolites, hollow glass micro spheres and capillary arrays, doped polymers, and clathrate hydrates. Brief introductions of few of the above systems are given in the following sections.

1.3.3.1 Storage of hydrogen in the form of metallic hydride

The hydrogen storage in the metallic form is the safest method known today and it posses many advantages also. Intermetallic compounds are not only attractive as a hydrogen storage material, but also they are very well known for battery application. They can have rechargeable capacities upto 400 mAh/g. It can absorb relatively high amount of hydrogen
compared to liquid and gaseous storage (very high volumetric storage capacity) and also
many other form of the solid state hydrogen storage materials. Again many of the metal
hydrides show ideal thermodynamic criteria required for reversible hydrogen storage. In this
section the basic properties of the metal hydrides and different well studied metal hydrogen
systems has been discussed. The major challenges in the development of hydrogen storage
materials for batteries and fuel cell application are improved hydrogen storage density, lower
desorption temperature, good kinetics & cyclic stability, high stability against oxygen and
moisture. The traditional metal hydrides are useful for solid hydrogen storage applications.
They have excellent volume storage capacity, good and tunable kinetics and reversibility, but
the hydrogen storage capacity is poor by weight.

1.3.3.1.1 Bonding in the metal hydrogen systems

The bonding between metal and hydrogen can be divided into three broad types [13]:
(1) ionic (2) covalent and (3) metallic.

The first two groups of elements (S block) form ionic hydrides. The physical
properties of the ionic hydrides are same as metallic halide. These compounds act like a salt
(NaCl, KCl etc.). Thus, ionic hydrides are called saline hydrides [14]. The crystal structure of
alkali metal hydride is same as sodium chloride structure, whereas, the crystal structure of
alkaline earth metal hydride is similar to barium chloride structure.

Most of the metals of P block elements (Group IB through VB in periodic table) form
covalent hydrides, where the bonding is predominantly covalent. Because of the weak van
der Waals forces between covalent bonds, most of these hydrides have low boiling point and,
therefore, they are volatile under normal conditions. These hydrides are unstable at elevated
temperatures. As a matter of fact, many of them decompose below room temperature [14].
The transition metal and rare earth elements react with hydrogen forming metallic hydrides. Except some higher hydrides of rare earth metals, the metallic hydrides appear to have metallic conductivities.

Among the three types of hydrides, the metallic hydrides are found to be suitable for hydrogen storage applications. For a system to be useful for hydrogen storage, it must be capable of storing large quantity of hydrogen reversibly at room temperature. Alloys that form hydrides have generally been classified as AB, AB$_2$ or AB$_5$ systems, where A is a hydride forming element like a transition metal from group III to VI or a rare earth element and B is non hydride forming element like Fe, Co, Ni etc [13]. Most of the metal hydrides absorb and desorb below atmospheric pressure. By suitable substitution, the properties of metal hydrides can be tuned for proper application.

1.3.3.1.2 Mechanism of hydrogen absorption in the metal hydride system

Fig. 1.5 schematically shows the hydrogen absorption process on the metal surface. The hydrogen absorption process is exothermic and certain amount of heat is released during the hydrogen absorption depending upon the host material.

![Mechanism of metal hydride formation](image)
Initially the hydrogen molecule approaches to the metal surface [Fig. 1.5(a)] and interacts with the surface by van der Waals force. Here the hydrogen remains in the physisorbed state [Fig. 1.5(b)], with typical binding energy of ~10 KJ/mole. In the next step, the hydrogen molecule needs to overcome the activation barrier for dissociation of the H-H bond and after that the hydrogen molecule dissociates into hydrogen atoms [Fig. 1.5(c)]. The hydrogen atoms get chemisorbed on the surface with the binding energy in the order of 50 KJ/mol-H. After the dissociative chemisorption the hydrogen atoms, they penetrate into the interior of the metal crystal to form M-H solid solution, which is known as α-phase [Fig. 1.5(d)]. In most of the cases, the hydrogen atoms occupy interstitial positions (tetrahedral or octahedral) and the cell parameter of the crystal increases. The physical arrangement of the metal atoms may also change during hydride formation. The hydrogen absorption in α-phase is governed by Sievert’s law, which states that

\[ C_H = k p^{1/2} \]

Where \( C \) is the concentration of hydrogen in the α-phase, \( p \) is the hydrogen pressure and \( k \) is temperature dependent constant. After increase in the concentration of hydrogen in α-phase, the metal-hydrogen phase starts precipitating and the phase is called β-phase. This process can be explained by pressure composition isotherm.

### 1.3.3.1.3 Pressure-composition isotherm

A plot between hydrogen pressure and hydrogen to metal ratio at a constant temperature is called pressure-composition isotherm or PCT curve [14]. In the PCT curve [Fig. 1.6], initially the hydrogen pressure increases sharply that means hydrogen diffuse into the interstices of metal or alloy forming solid solution (α-phase).
Fig. 1.6 A typical pressure composition isotherm showing the hydrogen absorption-desorption profile

As the hydrogen concentration further increases in the lattice, the hydride phase precipitates. The hydride phase is known as the β-phase. The hydride formation is indicated by the plateau of the plot. In the plateau region, the solid solution and the hydride phase coexist (α & β-phases). The length of the plateau determines how much amount of hydrogen can be stored and recovered by means of a small change in pressure. The last portion represents the hydride phase only, the hydrogen pressure increases steeply with concentration in this region.

Many metal hydrides do not undergo absorption and desorption along the same path, i.e. the absorption curve & desorption curves of metal hydrides are not the same. The path difference between the absorption and desorption isotherms is known as hysteresis. In most of the cases, the desorption plateau is considered as the true plateau, as the equilibrium is reached faster during desorption. The hydride having higher desorption pressure is less stable than the lesser desorption pressure hydride.
1.3.3.1.4 Thermodynamics of hydride formation

The reaction of a metal with hydrogen to form metal hydride can be represented by the following equation:

\[ M + (x/2)H_2 \leftrightarrow MH_x, \]

When an intermetallic compound reacts with hydrogen the reaction can be written as follows:

\[ AB + (x/2)H_2 \leftrightarrow ABH_x, \]

Where, A & B are two elements forming the alloy.

We know from Gibbs free energy relation,

\[ \Delta G = \Delta H - T\Delta S, \text{ and } \Delta G = RT\ln P_{H_2} \]

The relation between hydrogen pressure and enthalpy of hydride formation can be written as follows.

\[ \ln P_{H_2} = \Delta H/RT - \Delta S/R \]

This relation is known as van’t Hoff relation. \( \Delta H \) and \( \Delta S \) are enthalpy and entropy per mole of \( H_2 \) gas respectively. Using van’t Hoff relation, the enthalpy and the entropy of the hydride can be found out by studying the pressure composition isotherm at different temperatures [Fig. 1.7]. The plateau pressure or equilibrium pressure of the PCT diagram depends on the working temperature. With increase in the temperature, the plateau pressure increases and the plateau region decreases. At a critical temperature \((T_c)\) no plateau exists. The plot of logarithm of hydrogen pressure verses reciprocal of temperature, i.e. the graph between \( \ln P_{H_2} \) and \( 1/T \) is known as van’t Hoff plot shown in Fig. 1.7. The slope of the Hoff calculates the enthalpy of formation of a metal hydride; where as the intercept of the curve gives the entropy. The value of \( \Delta H \) can be widely different for different metal atoms and alloys as it
varies from large negative to large positive value. Some of the typical hydride formation enthalpy values of different metals have been listed in Table 1.2.

![Diagram showing PCT diagram and van't Hoff plot](image)

**Fig. 1.7** Schematic PCT diagram at different temperature ($T_1<T_2<T_3<T_4<T_c$), and the van’t Hoff plot

**Table 1.2** Enthalpy of formation of transition metal hydrides in kJ/mol $H_2$[13]

<table>
<thead>
<tr>
<th></th>
<th>ScH$_2$</th>
<th>TiH$_2$</th>
<th>VH$_2$</th>
<th>CrH</th>
<th>MnH</th>
<th>FeH</th>
<th>CoH$_{0.5}$</th>
<th>NiH$_{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-200</td>
<td>-126</td>
<td>-54</td>
<td>-16</td>
<td>-9</td>
<td>+14</td>
<td>0</td>
<td>-6</td>
</tr>
<tr>
<td></td>
<td>YH$_2$</td>
<td>ZrH$_2$</td>
<td>NbH$_2$</td>
<td>MoH</td>
<td>TcH</td>
<td>RuH</td>
<td>RhH$_{0.5}$</td>
<td>PdH$_{0.5}$</td>
</tr>
<tr>
<td></td>
<td>-225</td>
<td>-165</td>
<td>-60</td>
<td>-12</td>
<td>+36</td>
<td>+42</td>
<td>+25</td>
<td>-40</td>
</tr>
<tr>
<td></td>
<td>LaH$_2$</td>
<td>HfH$_2$</td>
<td>TaH$_{0.5}$</td>
<td>WH</td>
<td>ReH</td>
<td>OsH</td>
<td>IrH</td>
<td>PtH</td>
</tr>
<tr>
<td></td>
<td>-210</td>
<td>-133</td>
<td>-78</td>
<td>+16</td>
<td>+52</td>
<td>+48</td>
<td>+42</td>
<td>+26</td>
</tr>
<tr>
<td></td>
<td>ThH$_2$</td>
<td>UH$_3$</td>
<td>PuH$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-146</td>
<td>-85</td>
<td>-155</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A stable hydride is the one for which the equilibrium pressure lies below 1 atmosphere at 300 K. These hydrides have enthalpy of formation more negative than −40kJ/mole of $H_2$. Several criteria have been established for the realization of a practical hydrogen storage bed [15].
The alloy should be readily prepared, easily activated to form hydride and inexpensive.

The enthalpy of hydride formation should be around ~40 KJ/mole.

The hydride should have high hydrogen content per unit mass.

The dissociation pressure of the hydride should lay in the range 0.2-2.0 MPa at near–ambient temperature.

The system should exhibit favorable and reproducible reaction kinetics.

The reactant bed should have high thermal conductivity.

The system should be capable of cycling thousands of times without degradation.

The alloy should not be poisoned by gaseous impurities.

The system should be safe on exposure to air and should not ignite.

Binary metal hydrides do not meet the above requirements. The first report of the intermetallic hydride came in 1958 and several other intermetallic compounds are reported. Till then many interesting alloys and intermetallic compounds has been identified as hydrogen storage materials, most of which consist of one hydride forming element and one non hydride forming element. Most typical examples are LaNi$_5$, FeTi, AB$_2$ type of Laves phase systems, TiV based solid solutions, and Mg based systems.

1.3.3.1.5 LaNi$_5$ based system

LaNi$_5$ based systems are the most well studied hydrogen storage materials. LaNi$_5$ forms hydride with the formula unit of LaNi$_5$H$_7$ (1.5 wt. %) and easy to activate. It shows very flat plateau region with low hysteresis. But the problem with this alloy is that after a few cycle the hydrogen storage capacity decreases due to the degradation of the alloy. The thermodynamic properties of the LaNi$_5$ compounds vary extensively with composition. Several multi components alloys in this series, La$_{1-x}$RE$_x$Ni$_{5-x}$M$_x$ (RE = mishmetal, Ce, Nd & M = Fe, Co, Ni, Mn, Cu Al, Sn etc.), has been studied comprehensively [16, 17].
1.3.3.1.6 FeTi intermetallic compounds

The hydrogen storage capacity of the FeTi based intermetallic compound is 1.9 wt. % (it forms FeTiH$_2$), and the major advantage of this system is that the constituent elements are inexpensive. But due to the formation of TiO$_2$ oxide layer the activation of FeTi system is troublesome process. Different substituent elements have been studies to improve its activation and kinetics, but the most effective one found to be Pd [18, 19].

1.3.3.1.7 Zr & Ti based Laves phase compounds

The Laves phase compounds are represented by general formula AB$_2$. They are having mainly three types of crystal structures: cubic C15 (MgZn$_2$ type), hexagonal C14 (MgCu$_2$ type), and double hexagonal C36 (MgNi$_2$ type). The advantages of these types of compounds are higher hydrogen storage capacities, faster kinetics, and relatively low cost compared to LaNi$_5$ systems. Their thermodynamics and the electrochemical properties of the Laves phase compounds Zr$_{1-x}$T$_x$M$_{2-y}$N$_y$ (T = Ti, Y, Hf, Sc, Nb & M/N = V, Cr, Mn, Fe, Co, Ni, Cu, Al, Sn, Ge) can be manipulated easily by substitution [20-25].

1.3.3.1.8 Ti-V based bcc phase alloy

The investigation of titanium-vanadium alloys for hydrogen storage dates back from 1970 with the work of Reilly and Wiswall [26]. Since then this system has been intensively studied. The series of alloys generally form two types of hydrides: a mono-hydride with a pseudo-cubic FCC structure and a di-hydride with a CaF$_2$ structure. Usually, the mono-hydride is too stable for practical applications; this makes the usable capacity smaller than the total capacity. If the mono-hydride could be destabilized without changing its hydrogen capacity then the bcc solid solution could be very attractive alloys for commercial applications. However, as vanadium is relatively expensive, the problem of cost should be taken into consideration. Nomura and Akiba, in their work on Ti-V-Fe alloy system, have
mentioned that ferrovanadium may be used as raw materials instead of pure vanadium [27]. Since then, use of ferrovanadium or mixture of vanadium and iron has been reported by numerous authors [27-34]. Recently, particular emphasis has been on Ti-V-Cr compositions [35]. Another system that was subject of many studies is Ti-V-Mn [36, 38].

Though transition metal hydrides provide high volumetric densities, good kinetic and thermodynamic properties and long term cyclic stability, but in most of the cases, the gravimetric storage capacities are lower for the vehicular application. It is likely however that the use of metal hydride in hydrogen storage will be confined to small applications, because of the low energy density and the cost. Due to the high volumetric densities the metallic hydrides can be used for advanced full cell driven submarines, prototype passenger ships, forklifts as well as auxiliary power unit in laptops.

1.3.3.1.9 Mg-based hydrogen storage materials

Light metal hydrides, including Li, Al and Mg, are considered to be potential in the vehicular application due to high gravimetric hydrogen storage capacities. Mg can form MgH$_2$ with a maximum hydrogen storage capacity of 7.6 wt. %. Furthermore, magnesium is cheap and its ore is abundantly available. It has a medium reactivity towards air and oxygen, which is an advantage over most other light-weight metal hydrides. But the major barrier towards its application as hydrogen storage material is that, it shows a quite sluggish kinetics of hydrogen absorption-desorption, which is mainly diffusion control. The high thermodynamic stability of MgH$_2$ results in a relatively high desorption enthalpy of 75 kJ.mol [H$_2$]$^{-1}$ at standard conditions, which corresponds to an equilibrium temperature of 561 K for H$_2$- desorption at 1 bar H$_2$. For practical use of MgH$_2$ as a reversible hydrogen storage material, both the hydrogen sorption rates and the desorption temperatures have to be improved.
In case of bulk Mg, the diffusion of hydrogen atom towards the bulk is very slow. Again after MgH$_2$ formation, the diffusion of hydrogen becomes much slower. It is documented that the diffusion of hydrogen through MgH$_2$ is 5000 times slower than pure Mg metal at 350 °C [39]. One of the approaches to increase the hydrogen absorption-desorption kinetics is ball milling the Mg powder or the MgH$_2$ powder. In many reports ball milling has been taken successfully as a mean to increase the kinetics [40-44]. By ball milling, the initial powders get heavily deformed and fractured, and slowly with time the particle size decreases. With ball milling, the diffusion path length decreases and the volume fraction inside crystallite becomes less, so the hydrogen diffusion rate increases. As a result, after ball milling both the hydrogen absorption-desorption rate increases. However, thermodynamics are not affected by such techniques, hence the desorption temperature of MgH$_2$ is not lowered.

Alloying or doping techniques are able to lower the desorption temperature of MgH$_2$ by 30-100 K, but this is accompanied by a lower hydrogen storage capacity due to the added weight [45-48]. Addition of catalytic elements like Pd, transition metal elements, Nb, can improve the kinetics of hydrogen absorption by easing the dissociation of hydrogen molecule on the Mg surface. By addition of suitable catalyst, Mg can absorb hydrogen at relatively faster rate at room temperature also. Recently, metal oxide catalysts (Nb$_2$O$_5$, V$_2$O$_5$, Mn$_2$O$_3$, Cr$_2$O$_3$, Al$_2$O$_3$, TiO$_2$ etc.) also have drawn much attention, as they also can improve the kinetics of hydrogen absorption in Mg based systems and the catalytic activity found to retain even up to 1000 cycles [49]. Lower desorption temperatures have also been reported for other bulk phases of magnesium hydride, such as, sputtered thin films of Mg [50-55], highly amorphous Mg [56-62], etc. Moreover, decrease in the particle size has been shown to have an effect on the hydrogen desorption temperature of metal doped magnesium hydrides [58, 59]. These results indicate that, after doping, due to the distortions of the MgH$_2$-lattice, there is a shift in the desorption temperature and enthalpy value [63-67].
1.3.3.2 Hydrogen storage in carbon based material

In recent decades, many advances have been made in the preparation of microporous and nano carbonaceous materials [68]. These materials have been found to have good adsorbing properties for hydrogen gas.

1.3.3.2.1 Activated carbon

Research to evaluate the potential of carbon for hydrogen storage at low temperatures began in the 1980s. Activated carbons are bulky carbon with very porous structures and a very large surface area, some in excess of 3000 m$^2$g$^{-1}$. It absorbs hydrogen in macroscopic pores. Hydrogen adsorption on AX21 activated carbon, formed from chemical treatment of coke, at -196 °C and room temperature has been reported [69]. The total hydrogen storage capacity is found to be 2 wt. %. The results illustrate the importance of micropore volume for the hydrogen capacity of a carbon material. Some other studies show that an activated carbon derived through a simple preparation method provides hydrogen storage values at 10 MPa close to 1 wt. %. Initially most of the hydrogen absorption studies on the activated carbon were based on the use of cryogenic systems, which are not useful from an economic point of view [70]. Recently, research has focused on the search for the ideal adsorbent that, used at room temperature, allows the storage of interesting amounts of H$_2$ [71]. The main problems with activated carbon are that, only some of the pores are ideal enough to catch the hydrogen atom and high pressure must be applied in order to get the hydrogen into the pore [72]. Further research is required to determine the merits and demerits of these materials.

1.3.3.2.2 Carbon nanomaterials

There are various types of carbon nanomaterials that are of interest as a candidate material for hydrogen storage. The most well studied materials are fullerene, carbon nanofibres (CNF), carbon nanotubes (CNT), carbon nano scroll, etc.
C60 fullerene itself is not very promising material for hydrogen adsorption, because C60 does not have real pores in its structure, which are accessible to hydrogen molecules. The tetrahedral void is too small (d = 2.24 Å) to accommodate hydrogen molecule (d = 2.4 Å), so the small hydrogen uptake of fullerene can be contributed to the octahedral void of fcc crystal (d = 4.12 Å) [73]. By modifying the fullerene molecule by means of doping and surface modification, the hydrogen storage capacities can be improved. There have been numerous research papers that associate the doping of fullerene with different metals, but they do not store hydrogen at the ambient temperature. Different metals have been reported, which can form complexes with fullerenes. Some of them are iron, titanium, niobium, rhodium, cobalt, sodium, potassium, lithium, barium, calcium, and strontium. [74-82] Hydrogen adsorption on the metal doped fullerene also has been studied by various researchers using both experimental and computational tools. Wang and Tu showed that [83], Pt-C60 compound show a hydrogen uptake of 1.6 wt. % at 473 K, which was probably contributed by the hydrogenation of the basic fullerene skeleton and its metal counterparts. Simulation shows very promising results on hydrogen storage on metal doped fullerene [84]. Another theoretical calculation shows that a fullerene-like compound Li_{12}Si_{60}H_{60} could adsorb 12.83 wt. % at 10 MPa and 77 K. Density functional theory based calculation reveals that calcium doped boron fullerene (B_{80}) is a promising hydrogen storage material [85]. Saha and Deng adopted a different approach to increase the hydrogen storage capacity of the fullerene. They have shown that the hydrogen uptake on C_{60} fullerenes can be increased by partially truncating and opening the cage of C_{60} [86]. It can be noted that most of the hydrogen storage studied on the metal doped fullerene was done at low temperature and high pressure, because of the very weak interaction energy between the fullerene and the material. Hydrogen sorption measurement on metal fullerides at ambient temperatures has never been reported.
CNF were first reported in the early 1970s. Due to the advancement of the microscopic technique allowed these materials to be observed [87]. In 2002, it was claimed by a team that CNF had been observed to adsorb hydrogen up to 6.5 wt. % at ambient temperatures and 120 bar [88]. They proposed that hydrogen chemisorption occurs at a rate controlled by dissociation of hydrogen at graphitic edge sites. Lueking et. al. has shown that pretreatment in certain environments results in the creation of catalytic sites that are favorable toward hydrogen storage. The best pretreatment resulted in a 3.8 wt. % hydrogen release after exposure at 69 bar pressure and room temperature [90]. The high hydrogen absorption value has been neither reproduced nor explained by theoretical calculations [91-92].

CNT were first prepared accidentally during the synthesis of fullerenes using the arc-discharge method in the early 1990s [93]. A nanotube is a graphene sheet rolled up in cylinder shape with diameter in the nanometer range. Carbon nanotubes can store hydrogen both by chemisorption and physisorption. Much research has been carried out to determine the potential of these systems as a hydrogen storage material. Grand Canonical Monte-Carlo simulations show that by varying tube diameter and the inter-tube spacing; the thermodynamic conditions of the tubes could be controlled and optimized for the adsorption of gases [94-95]. In 1997, Dillon et al has revealed experimentally that CNT might be capable of 5-10 wt. % hydrogen capacity [96]. The following year, a report claimed that more than 60 wt. % of hydrogen had been observed to adsorb on CNF at room temperature [89]. However, as yet, no group has been able to recreate these findings. In fact, against the results, a number of independent claims have done reporting the hydrogen storage capacities varying from 0-20 wt. %, for both CNF and CNT. Liu et. al. reported that single-walled nanotubes (SWNT) can show a reproducible hydrogen storage capacity of 4 wt. % at ambient temperature and 100 bar pressure [97]. Many theoretical studies claim that carbon nanotube can meet the United States Department of Energy target for gravimetric capacity for
hydrogen storage at cryogenic temperatures and high pressure where hydrogen gets absorbed by physisorption [98]. By chemisorption also SWNT can absorb a large amount of hydrogen and from a theoretical study using molecular simulation, a capacity of 14 wt. % was estimated for SWNT [99, 100]. The hydrogen storage properties of the pure carbon tube can be modified by doping and by creating defects. Many experiments and simulations have showed that the isolated transition metal (TM) [101] and alkali metal (AM) atoms or ions, [102] could bind a certain number of hydrogens in molecular form. After releasing hydrogen, however, the isolated transition metal atoms or ions would cluster together easily [103, 104], which is unfavorable for reversible hydrogen storage. Alkali metals doped CNT shows a great potential as hydrogen storage material and could adsorb up to 20 wt. % of hydrogen at 380 °C and 10 bar pressure [105]. However, it was later suggested that the presence of water might have influenced this result.

In pure carbon nanoscrolls the interlayer distance is too small to accumulate hydrogen. However, an opening of the spiral structure to approximately 7 Å followed by alkali doping can make them very promising materials for hydrogen storage application, reaching 3 wt. % at ambient temperature and pressure [106].

1.3.3.3 Other solid state hydrogen storage systems

1.3.3.3.1 Complex metal hydrides

There are few complex hydrides, which show quite high hydrogen storage capacities, but the reversibility is still not fully proven. Most of them are the ionic compound of Li, Al, B and are quite stable upto high temperature. In Al and B related chemical hydrides (alanates and borates respectively) the hydrogen atoms are located at the corner of the tetrahedron with the Al/B atom at the centre. The negative charge of [AlH₄]⁻ or [BH₄]⁻ tetrahedra gets compensated by the positively charged alkali or alkaline metal ion. Because of their structure,
they can hold large number of hydrogen atom, and the value goes up to 18 wt. % for LiBH₄.

The complex hydrides like sodium alanate (NaAlH₄), sodium boro-hydride (NaBH₄) undergo chemical reactions during absorption or desorption processes, thus restricting the kinetics and reversibility. Sodium alanate decomposes in two steps giving rise to 5.6 wt. % of hydrogen.

\[
\text{NaAlH}_4 \leftrightarrow \frac{1}{3}\text{Na}_3\text{AlH}_6 + \frac{2}{3}\text{Al} + \text{H}_2 (g) \quad 3.7 \text{ wt. %}
\]

\[
\text{Na}_3\text{AlH}_6 \leftrightarrow 3\text{NaH} + \text{Al} + \frac{3}{2}\text{H}_2 (g) \quad 5.6 \text{ wt. %}
\]

\[\text{NaH}\]

NaH can liberate the remaining amount of hydrogen only at the elevated temperature. Though both of the reactions are thermodynamically quite feasible, but they are kinetically limited due to the slower diffusion of the metal ions. Again, the reactions are reversible only at a temperature above the melting point of NaAlH₄ (183 °C) and at a hydrogen pressure of 10-40 MPa, which is nor practically feasible. Because of that, though the evolution of hydrogen by heating NaAlH₄ was known for many days, but it was not considered as a potential hydrogen storage material. The importance of the material revealed, only after Bogdanovic et. al., in 1996, [107] showed that the charging and discharging temperature of hydrogen can be lowered by doping the hydride with addition of Ti based catalyst. Titanium catalyzed NaAlH₄ has a thermodynamic properties comparable with low temperature metallic hydrides. The first decomposition step occurs at 50-100 °C, whereas, the second step occurs at 130-180 °C. After wards many other catalysts has been tried for fast and reversible desorption of hydrogen from NaAlH₄. The hydrogen storage capacity of NaAlH₄ can be increased by partial substitution of Na by Li.

Another very important complex hydride is sodium borohydride (NaBH₄). The alkali metal borohydrides are having higher hydrogen storage capacities than the corresponding alanates, but they decompose at higher temperatures. NaBH₄ and LiBH₄ show hydrogen storage capacities of 18.5 & 10.6 wt. % respectively, and starts decomposing above 350 °C &
300 °C respectively. Researches are going on to decrease the decomposition temperature by means of addition of catalyst, morphological changes, change in particle size, etc. Another way of using NaBH$_4$ as a hydrogen carrier is hydrolysis [108]. The hydrolysis reaction can be represented as,

$$\text{NaBH}_4 + \text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$$

The reaction is irreversible and gives rise to 10.9 wt. % hydrogen theoretically. A mini van designed by M/s Millenium cell, USA showed that using NaBH$_4$ system, the van can run up to 480 km. This technology is still in very initial stage and efforts are needed to decrease the cost of transport and also reprocessing operations are needed to regenerate the NaBH$_4$ back from NaBO$_2$.

Third type of complex chemical hydride is metal amide, which can generate hydrogen by thermal decomposition [109]. Metal amide can generate hydrogen in two steps. For example in the first step, lithium amide (LiNH$_2$) reacts with lithium hydride (LiH) at 300 °C, to generate lithium imide (Li$_2$NH), and liberates 6.5 wt. % of hydrogen. In the second step Li$_2$NH reacts with more LiH at 430 °C to produce lithium nitride (Li$_3$N), which releases 5 wt. % of hydrogen. There is a need to decrease the desorption temperature of both the steps. Investigations are going on to see the effect of ball milling and addition of additives like magnesium hydride [110].

1.3.3.3.2 Chemical storage of hydrogen

Some organic chemicals, which contain a significant proportion of recoverable hydrogen, can be considered as good hydrogen carrier [111]. One such example is cyclohexane, which can catalytically yield benzene and hydrogen at high temperature. The hydrogen content is 7.1 wt. %.

$$\text{C}_6\text{H}_{12} \leftrightarrow \text{C}_6\text{H}_6 + 3\text{H}_2$$
The benzene can be converted to cyclohexane by the hydrogenation reaction over nickel catalyst at 150-200°C. Similarly, methyl cyclohexane (C\textsubscript{7}H\textsubscript{14}) has also been proposed, which gives rise to 6.1 wt. % of hydrogen.

In addition to the above organic chemicals, some simple inorganic compounds also have been considered as hydrogen carrier. Ammonia Borane (NH\textsubscript{3}BH\textsubscript{3}) is one simple example which is solid at room temperature and releases about 12 wt. % of hydrogen around 100-200 °C. After hydrogen desorption the residual polymer (NHBH\textsubscript{n}) can be converted to NH\textsubscript{3}BH\textsubscript{3} in principle and research is going on to meet the practical challenges [112].

Liquid ammonia (NH\textsubscript{3}) and hydrazene (N\textsubscript{2}H\textsubscript{4}.H\textsubscript{2}O) are also being considered as hydrogen carrier. Ammonia is decomposed catalytically at the elevated temperature to yield hydrogen and nitrogen, reaching up to 17.7 wt. % of hydrogen storage capacity [113, 114]. The difficulties lies in the fact that NH\textsubscript{3} is highly toxic and can generate hydrogen only at elevated temperatures under catalytic condition. One of the ways to handle toxic ammonia is conveyance of ammonia as an inert solid rather than handling in the gaseous form. Metal ammine Mg(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2}, which is solid at room temperature and can desorb ammonia at 80-350 °C. It can hold 58 wt. % of ammonia and thus 9.1 wt. % H\textsubscript{2}. Hydrazene hydrate contains recoverable hydrogen of 8.0 wt. %.

1.3.3.3.3 Hydrogen storage within metal organic frameworks

A recent study has highlighted a new class of hydrogen storage compound, three dimensional metal organic frameworks (MOF), with extended porous structure. MOF are crystalline solids that are assembled by the connection of metal ions or cluster through molecular bridges. An outstanding porosity and very high surface area has promoted their study as hydrogen storage material. These types of structures can adsorb up to 2 wt. % of hydrogen at 10 bar pressure and 293 K temperature, and up to 4.5 wt. % at sub-ambient
temperatures [115]. As a potential hydrogen storage material, it is still in its infancy and the work is yet to be independently confirmed. However, the initial reported results are impressive with many favorable attributes like high porosity, reproducible & facile synthesis, and scope for chemical modifications for targeting desired properties [116]. The studies have highlighted that to increase the total hydrogen storage capacity, there is need to optimize the pore size and reduce the fraction of unutilized void space.

1.3.3.3.4 Hollow glass spheres

Glass spheres are small hollow glass micro-balloons whose diameter varies from 25 micrometer to 500 micro-meters and wall thickness is about one micrometer. The hydrogen storage in glass micro sphere occurs in three steps, charging, filling and discharging [117]. The spheres are filled with hydrogen at high pressure and temperature 200-400 °C. The high temperature makes the glass wall permeable and the hydrogen is able to fill in. Once the glass is cooled down the hydrogen is trapped inside the spheres. The hydrogen can be released by heating or crushing the spheres. The storage capacity of glass spheres is about 5-6 wt. % at 200-490 bars pressure. The glass spheres can also cause accident while breaking down, if not handled properly.

1.4 Objective and Scope of the Present Thesis

In the present thesis, the main focus is to modify the hydrogen storage properties by means of varying composition and alloying modification. The kinetics and desorption temperature also has been monitored for the practical application of the metal hydrides. In certain cases the cyclic stability has been demonstrated for a few cycles to find out any degradation of the material at the experimental conditions.
In chapter II of the thesis, the experimental methodologies have been discussed. Apart from the different instrumental techniques used for characterization, emphasis has been given to the measurement procedure of hydrogen storage capacity, pressure composition isotherm, kinetics of hydrogen absorption, thermodynamics of metal hydrogen system and the desorption profile.

In Chapter III, Chapter IV & Chapter V, we have discussed different transition metal based systems for their hydrogen storage properties. Ti-V-based BCC phase alloys have attractive prospects for use as hydrogen storage media and cathode materials for Ni-MH batteries, because they have higher room temperature hydrogen capacities than the materials currently used. Modifications have been done in the Ti-V based alloy and the effect of substitution on the structure and hydrogen storage properties have been reported. The effect of V on the hydrogen storage properties of ZrFe$_2$ type Laves phase alloy also has been studied in detail. Our work aims to enhance the hydrogen storage capacities of the alloys in a gas-solid reaction and improve their hydrogen storage properties mainly through partial substitution of elements and optimizing the composition. The objectives of the study are:

- Investigation of a variety of transition metal based alloys, known to store hydrogen, to determine the limit of performance and improvement upon them.
- Report the hydrogen storage behavior of certain material as a function of temperature and pressure.
- Understand the effect of doping on the structure, activation, hydrogen storage properties and kinetics of certain materials.

In Chapter VI, we have discussed the theoretical methodology adapted for the First Principle based calculation. In Chapter VII & VIII, magnesium and carbon systems have been studied
theoretically to see the effect of substitution, cluster size and geometry on the hydrogen storage properties. The objective of the study is to

- Fundamental understanding of the mechanism of hydrogen storage in Mg and C based materials
- Theoretical calculation to see the effect of doping elements and finite size on magnesium system to underscore their hydrogen absorption desorption behavior.
- Theoretical efforts are performed to design new carbon based materials that meets the requirements of a good hydrogen storage material.