

Hydrogen Storage Materials: A Review

Sanusi Kazeem Olajide^{a,c}, Sobowale Adeniyi Ademola^a, Oloyede Oloruntoba Oladapo^a, Ogundola Abayomi Cyril^a,
Fadipe Abimbola Omoyemi^a, Aiyeola Sikiru Yommy^b, Adedoyin Kayode James^{c,d}

a: Advanced Aerospace Engines Laboratory, Oka-Akoko, Ondo State Nigeria

b: Centre for Satellite Technology Development, Abuja, Nigeria

c: Federal University of Technology Akure, Ondo State, Nigeria

d: Nigerian Nuclear Regulatory Authority, Abuja, Nigeria

Abstract— Overdependence on fossil fuels for human energy needs coupled with its attendant adverse consequences on the environment in terms of greenhouse gas emission has shifted our attention towards renewable energy sources. The potential of Hydrogen as an energy source was first conceptualized in 1874 by Pencroft [1]. Hydrogen is an energy medium which can be stored, transported and converted. However, a key challenge to the full development of hydrogen based technologies is storing hydrogen safely, efficiently and economically. When stored in the solid state, it offers clear advantages over storage in liquefied form. It is safer and offers a better volumetric as well as gravimetric densities.

In solid-state storage, hydrogen is bonded by either physical or chemical forces, in which the strength of interaction between hydrogen and a host material ranges from weak van der Waals interactions typical of the physisorptive binding of molecular H_2 , to the strong chemisorptive binding of atomic hydrogen, Figure 1 below shows the physisorptive and chemisorptive representation of hydrogen in a material. It is possible to increase the density of hydrogen because in many hydride-type materials, hydrogen is packed with H–H distances up to 170 kg/m³, a factor of more than two greater than the density of liquid hydrogen [2].

Great efforts have been put into developing hydrogen storage materials with high gravimetric and volumetric densities, and studies have been expanded from conventional metal hydrides to complex hydrides, microporous materials, and clathrate hydrates. This review will look at each of this class of material in a view to give an educated opinion on the future of Hydrogen as an energy source.

Index Terms— Hydrogen Storage, Metal Hydrides, Complex Hydrides, Borohydrides, Clathrate Hydrides, Metal Aluminates, Microporous Materials, Activated Carbon.

1 INTRODUCTION

Developing safe, reliable, compact, and cost-effective hydrogen storage technologies is one of the most technically challenging obstacles to the widespread use of hydrogen as a form of energy medium.

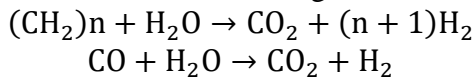
Hydrogen storage will be required onsite, in vehicles and at hydrogen production sites, hydrogen refueling stations, and stationary power sites. Possible methods to storing hydrogen include:

- Physical storage of compressed hydrogen gas in high pressure tanks (up to 700 bar)
- Physical storage of cryogenic hydrogen (cooled to -253°C, at pressures of 6-350 bar) in insulated tanks
- Storage in advanced materials — within the structure or on the surface of certain materials,

as well as in the form of chemical compounds that undergo a chemical reaction to release hydrogen.

Each of these technique suggests that there is a bright future for widespread acceptance of hydrogen as an energy source if well harnessed. Available technologies permit direct storage of hydrogen by converting it into gaseous or liquid form in pressurized or in cryogenic vessels. These forms of hydrogen storage are not so effective, because liquid hydrogen requires the addition of a refrigerant to maintain its cryogenic state thus adding extra weight and increasing the energy costs, this also results in energy loss of about 40% [3]. Storing hydrogen in pressurized tanks has a huge challenge in addition of extra dead weight of the storage cylinders to the system and

susceptibility to leakages. Consequently, storage of hydrogen in liquid or gaseous form poses important safety problems for on-board transport applications. Hydrogen is the most abundant element in the universe, however it does not exist in its elemental form. It is in this elemental state that it is required as an energy medium. Therefore, for a hydrogen based energy shift to be widespread, hydrogen must be readily available in its elemental form [4]. At present, hydrogen is mostly produced from fossil fuels via steam reformation and the water gas shift reactions:



Unfortunately, in collecting hydrogen from these reactions fossil fuels are used and CO_2 is released from these reactions and therefore the disadvantages clearly defeats the benefits. The ideal production of hydrogen would be such that is fossil fuel free, from an unlimited energy source and one that would not release CO_2 into the environment.

Electrolysis is one way of producing hydrogen cleanly, but this depends on the source of electricity. Electricity produced from renewable energy sources, such as photovoltaics, wind turbines and hydroelectricity provide the limitless 'green' energy required, but this approach deposits hydrogen in liquefied form. Hence, search for other sustainable methods of hydrogen production continues.

Nuclear power can also provide electricity without the release of CO_2 , however there are harmful by-products from the radioactive waste and is therefore not ideal as a long term replacement for fossil fuels. In the short to medium term however, it can help meet our growing energy demands.

Hydrogen is important as fossil fuels are fast being depleted and by burning them they release toxic CO_2 , that was locked away underground, into the atmosphere. CO_2 is a greenhouse gas and has been linked to global warming. The use of hydrogen as an energy medium is wound around the challenges associated with production, storage and use. Storage is arguably the biggest of these challenges and in the past 20 years or so concerted efforts have been made in dealing decisively with this problem with the Department of Energy (DOE) setting

guidelines for the minimum volumetric and gravimetric densities to be achieved for hydrogen to be considered a viable energy source. Hydrogen can be converted into gas and can also be liquefied, in these forms, they may easily be stored in tanks. Asides the possible dangers of leakages and explosion, as well as incorporation of extra dead weight resulting from the presence of steel tanks in systems as mentioned earlier, their volumetric and gravimetric densities are way below the minimum requirement for them to function as viable energy carriers. It has been found that hydrogen stored in solid state can as a matter of fact meet the set energy requirements by the DOE. The principle behind hydrogen being stored as an energy medium in solid state is based on the adsorption and desorption chemistry of hydrogen bearing materials. These materials store hydrogen within themselves and release same in a reverse process. While some materials have shown great potentials in storing hydrogen, they have failed in the area of releasing it, and this is what constitutes its efficacy as an energy medium. Materials such as Metal hydrides, Complex hydrides, microporous materials, and clathrate hydrates meet this reversible adsorption/desorption of hydrogen and have been in the eye of researchers in the past two decades, and these are reviewed in this work.

2 METAL HYDRIDES

Hydrogen, is the lightest of all the chemical elements, it forms compound (hydrides) with all elements except inert gases. Metal hydrides are a class of hydrogen compounds formed between hydrogen and metals, and the nature of the hydrogen-metal bond they possess gives them unique properties that places them at the focus of industrial technologies and advanced research. The host metal can be an element, an alloy, or metal complex. Metal hydrides make up the essential components in energy storage (hydrogen fuel tanks and secondary batteries), energy conversion (alkaline fuel cells), chemical processing (reducing agents, strong bases, strong reductants, catalysts), physical separation processing (desiccants, isotope separation, gas separation, and hydrogen purification), nuclear engineering (neutron moderators, reflectors, and shields), and thermal applications (heat pumps) [5]. Many of these applications have their roots in the field

of renewable energy, and as a result metal hydrides and their applications have formed an active area of research in recent years.

Metal hydrides offer a convenient and safe technology for hydrogen storage. The fact that the density of hydrogen per unit volume is highest in metal hydrides and the stored hydrogen can be released at the desired temperature makes it superior to liquid hydrogen or hydrogen cylinders. The ability of Pd metal to absorb a large amount of hydrogen was first discovered by Thomas Graham in 1866. However, the actual potential of metal hydrides for application purposes was realized after the discovery of reversible hydrogen absorption/desorption in intermetallic compounds [6]. The idea of ‘hydrogen economy’ is based on the assumption that hydrogen gas could be produced by decomposing water using inexpensive primary sources of energy such as solar energy, wind energy, tidal energy or biomass decomposition. In this way, hydrogen becomes an energy carrier, which transports the power from the generation site to another location.

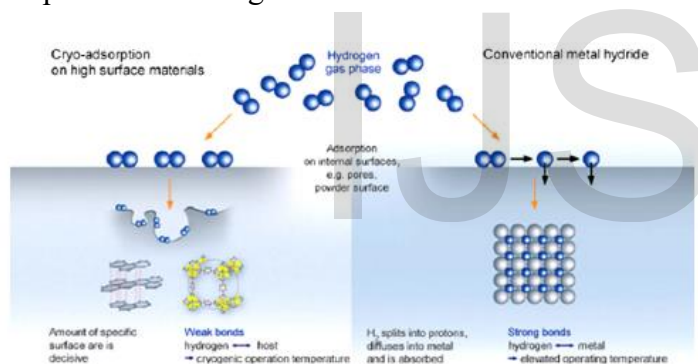


Fig.1 a representation of physiosorption and chemisorption of hydrogen in a material

2.1 Synthesis of Metal Hydrides

Metal hydrides can be prepared by reactions in the gaseous phase, in solution, or in solids formed from other hydrides. The proper synthesis method selected to produce metal hydrides depends on the metal hydride intended area of application [5].

Many metal hydrides can be synthesized by directly reacting hydrogen with a metal (element, Inter-metallic compounds, or other forms) in a process known as hydrogenation. While many metals and IMCs easily take up hydrogen, others form hydrides only under high hydrogen pressure, that is, equilibrium pressures from

103 to 109 Pa. High-pressure syntheses allow the stabilization of new metal hydride phases with high coordination numbers or high metallic oxidation states. In many cases, the hydrogen kinetics that govern the rate of hydrogenation is minimal at lower temperatures, but the hydrides are able to store more hydrogen than at higher temperatures. With these properties in mind, the typical hydrogenation process involves an initial heat-up step to an elevated temperature where the absorption of hydrogen is small but fast (1100 K, e.g., for Zr), followed by a slow cooling step in H₂ atmosphere. During cooling, the hydrogenation process reaches a hydride-formation temperature that balances kinetics and capacity, and the exothermic nature of the process maintains this temperature until the hydrogenation is complete. Sometimes, a spark is used to ‘ignite’ the hydrogenation process (overcome the activation barrier). Hydrogenation is also an effective way to produce metal powder, especially metals with extreme hardness or high ductility. Even partial hydrogenation is useful for producing metal powders, increasing brittleness and introducing microcracks to facilitate the crushing and grinding processes for powder formation. The products yielded from metal hydride synthesis are often fine powders that contain by-products. Many metal hydrides are sensitive to air and moisture and must be stored under an inert atmosphere. Metal hydrides containing heavy alkaline metals are extremely reactive and must be handled with utmost care. The combination of these properties can cause difficulties for metal hydride structure analysis and the study of its physical properties. Single crystal preparations are rarely successful because metal hydrides are in general insoluble in common solvents, and with their low thermodynamic stability, are unable to use high temperature methods. In some cases the addition of LiH as a flux agent has been helpful for single crystal growth.

2.2 Metal Hydrides for Hydrogen Storage

Metal hydrides are capable of absorbing and desorbing hydrogen depending on the hydriding conditions, and this unique feature places metal hydrides in a position where they can be used to store or release hydrogen on demand. Indeed, the most important property for a metal hydride is its reversible hydrogen storage capacity, which enables it for the use as a solid hydrogen storage material. The hydrogen–metal

interaction principles are invariably the same for all metal hydride systems.

In metal hydrides suited for hydrogen storage, atomic hydrogen is inserted into a matrix of host metal atoms; hence this type of metal hydride is also called an interstitial hydride. For crystalline host metals, the occupation sites can be either a tetrahedron as shown in Figure 2 (a) or an octahedron as shown in Figure 2(b). It should be noted that the tetrahedral and octahedral sites are part of the same FCC crystal structure, containing eight tetrahedral sites and four octahedral sites in a primitive unit cell composed of four host atoms. Not all sites can be occupied by hydrogen at the same time. In order for hydrogen (with an atomic radius of 0.53\AA) to occupy a site, requirements for the radius of the occupation site ($>0.4\text{\AA}$) and the distance between two H occupied sites ($>2.1\text{\AA}$) must both be met. Metal systems with large unit cell volumes usually form more stable hydrides, which are associated with more negative ΔH_h and lower equilibrium pressure of hydrogen. Metal systems with high degrees of disorder can have a range of local cell volumes and thus a corresponding range of ΔH_h , which can be advantageous for storage capacity and absorption/desorption kinetics [5]

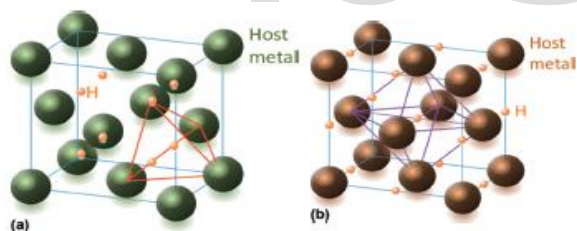


Fig. 2 Possible hydrogen occupation sites, tetrahedral and octahedral inside an FCC host metal

Table 2 Hydrogen Storage Properties of the Catalyst-Dope LiBH_4

Catalysts	Amount	Hydrogen Storage Properties		Operating Conditions	
		Desorption (wt%)	Absorption (wt%)	Desorption (K)	Absorption (K, [MPa])
SiO_2	10-25wt%	9-10	-	423-873	-
TiO_2	25-80wt%	4-9	3.5-8.3	373-873	873, [7-10]
ZrO_2	25wt%	8-9	-	448-873	-
V_2O_5	25wt%	8-9	8	448-873	873, [10]
SnO_2	25wt%	8-9	-	448-873	-
Nb_2O_5	50-80wt%	4-6	-	373-873	-
Fe_3O_4	50-66.7wt%	5.7-9	-	373-873	-
V_2O_5	50-66.7wt%	5.7-9	-	373-873	-
TiCl_3	10-88wt%	2.8-9.2	3.4	373-873	773, [7]
CoCl_2	5-100mol%	10.5-18.3	-	503-873	-
TiH_2	10-50mol%	6-15	2.5-4.5	573-873	773, [7]
TiF_3	10-50mol%	6.4-14	0.2-4.0	373-773	623-773, [7-10]
ZnF_2	10-50mol%	3.7-7	1-4	393-773	773, [7]
$\text{MgCl}_2\text{-TiCl}_3$	30mol%	5	4.5	333-873	873, [7]
Mg	10-20mol%	9	-	333-873	-
Al	20mol%	7.8	3.5	353-873	873, [10]
Sc	33mol%	2.9	-	673-773	-
Ti	33mol%	2.5	-	673-773	-
V	33mol%	4.4	-	673-773	-
Cr	33mol%	4.4	-	673-773	-

3 Complex Hydrides

In trying to develop high gravimetric capacities, more efforts has been devoted to the complex hydrides, many of which have very high hydrogen gravimetric densities that meet the Department of Energy (DOE) ultimate targets due to the light weight of constituent elements as shown in Table 1. Generally, the complex hydrides of interest for hydrogen storage applications can be roughly subdivided into two categories: group I and II—salts of $[\text{AlH}_4]^-$, $[\text{BH}_4]^-$, $[\text{NH}_2]^-$, i.e., alanates, borohydrides, imide and amides, and transition metal complex hydrides that have anionic complexes such as Mg_2FeH_6 with $[\text{FeH}_6]^{4-}$, attached to a cationic light metal, e.g., Mg^{2+} .

Table 1: Hydrogen storage properties of complex hydrides

Hydrides	Molar mass g/mol	Density g/cm	Gravimetric Hydrogen Density wt%	Volume Hydrogen Density (kg/m ³)	Td ec (K)	Reversibility
Mg_2FeH_6	110.52	2.74	5.5	150	593	+
LiAlH_4	37.95	0.917	10.6	72	398	-

NaAlH ₄	54.00	1.28	7.4	92	451	+
Mg(AlH ₄) ₂	86.33	1.046	9.3	72.3	413	-
Ca(AlH ₄) ₂	102.01	1.17	7.8	70.4	468	-
Na ₂ LiAlH ₆	85.95		6.3		528	+
LiMg(AlH ₄) ₃	124.28		9.7		438	-
LiBH ₄	21.78	0.66	18.5	122.5	653	+
NaBH ₄	37.83	1.07	10.7	113.1	673	-
KBH ₄	53.90	1.17	7.4	87.1	858	-
Mg(BH ₄) ₂	53.99	0.989	14.8	146.5	533	-
Ca(BH ₄) ₂	69.76	1.12	11.5	108	593	-
Zn(BH ₄) ₂	95.07		8.4		358	-
Al(BH ₄) ₃	71.51	0.7866	16.8	132	423	-

Mg(AlH₄)₂

3.1 Mg₂FeH₆

Among ternary transition metal complex hydrides, Mg₂FeH₆, possess a considerably higher hydrogen content (~5.5 wt%) than that of Mg₂NiH₄ (3.6 wt%), and a high volumetric density (150 kg/m³), exceeding, for instance, that of MgH₂ (55 kg/m³) by about 1.7 times [7]. Moreover, Mg₂FeH₆ is more cost effective for many applications compared with many other hydrides because its more readily available and each component metal (Mg and Fe) costs much lower. The synthesis of Mg₂FeH₆ is complicated by the non-existence of a Mg₂Fe intermetallic phase in the equilibrium Mg-Fe phase diagram. Synthesis of Mg₂FeH₆ has been widely carried out by means of mechanical milling, the reactive mechanical alloying under hydrogen



Fig.4 activated carbon sample

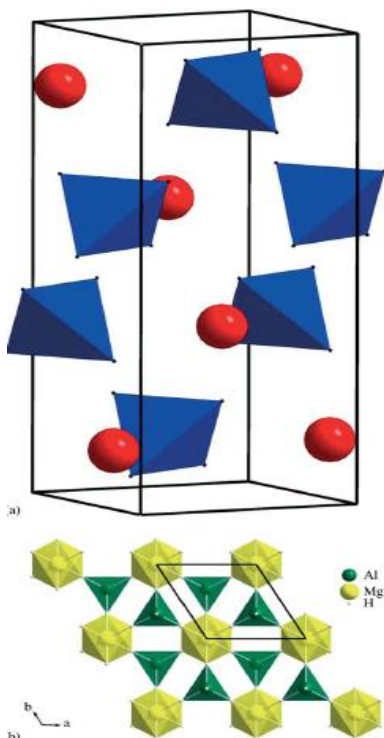
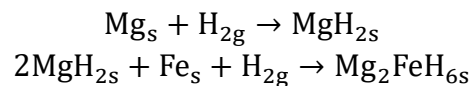


Fig.3 The structure of (a) NaAlH₄. And (b) crystal structure of

atmosphere, or sintering at elevated temperatures and high hydrogen pressures. In general, the following reactions are believed to occur in preparing Mg₂FeH₆ [2]



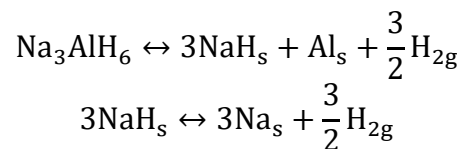
In a dehydrogenation process, the following reaction occurs:



Thermodynamic and kinetic analysis show an enthalpy change of ~77 kJ/mol of H₂ and apparent activation energy of ~166 kJ/mol for hydrogen desorption [8]. The TiO₂-doped Mg₂FeH₆ was found to desorb all of the stored hydrogen within 400 s at 853 K, almost three times improvement compared to the original sample. Considering higher stability of Mg₂FeH₆, Reiser et al. 2002 studied its potential application for thermochemical thermal energy storage, for example as the storage of solar or industrial exhaust heat [9]. Mg₂FeH₆ and a mixture MgH₂-Mg₂FeH₆ are highly suitable materials for thermochemical thermal energy storage in the temperature region around 773 K or higher, due to their excellent cyclic stability, a wide range of working temperature through controlling the applied hydrogen pressure, and no heat losses were reported during operation.

4 METAL ALANATES

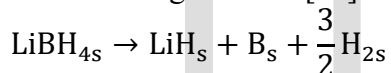
The tetra-alanates (hydridoaluminates) have general formula M_n(AlH₄)_n. M is typically an alkaline (n=1) or alkaline earth metal (n=2), but M can also belong to groups III and IV in the periodic table [10]. Alanates have been known for more than 50 years. Figure 3 shows (a) structure of a NaAlH₄ and (b) structure of Mg(AlH₄)₂. Alanates are composed of a “complex anion” [AlH₄]⁻ or [AlH₆]³⁻ and respective cation, which are salt-like, insulating materials. The bond between the hydrogen atoms and aluminum can be regarded as covalent with a strong ionic character, and the bond to the cation is ionic. Several alanates containing light cations have been rigorously studied for hydrogen storage purposes. The prototype compound is the sodium alanate (NaAlH₄) with a total hydrogen content of 7.4 wt% H₂. Hydrogen release from NaAlH₄ proceeds in a three-step reaction as described below



Although, they have high hydrogen contents, they haven't until recently been considered for hydrogen storage applications owing to their poor kinetic properties in hydrogenation/dehydrogenation. This situation has been drastically changed since Bogdanović and Schwickardi found that NaAlH₄ could be reversibly dehydrogenated/ rehydrogenated under much milder conditions by doping with a small amount of titanium-based catalysts [11]. This breakthrough opened up and helped in the development of catalyst doped alanates as a practical hydrogen storage medium. Following this, numerous transition and rare-earth metal-based catalysts, including metallic elements, alloys, halides, oxides, nitrides, and hydrides have been investigated as doping precursors for lowering the kinetic barriers of alanates [2]. Ti-based precursors, Sc-based precursors and, recently a Ce-based precursor all have exhibited excellent catalytic effects. Taking into account the catalytic activity and the loss of storage capacity due to the weight of the catalyst introduced, the optimum addition amount is believed to range from 2 to 5 mol% for chlorides of Ti, Sc, or Ce (TiCl₃, ScCl₃, or CeCl₃). Moreover, co-dopants have also been demonstrated to be more effective. The kinetics of the system doped with both Ti-containing dopants and another metal, such as Zr, HfCl₄, and KH, are superior to using Ti-based dopant alone [2]. In general, true active catalytic species are produced during the material preparation by ball milling. Regretably, these additives produce non-volatile by-products during ball milling that constitute dead weight and amount to a significant weight percentage in the system. In order to reduce the loss of cyclic capacity, a promising approach is to identify the active species and directly introduce them into the alanate system. A 4.77–4.92 wt% reversible hydrogen capacity (close to the expected capacity of 5.13 wt%) was accomplished in less than 20 min under moderate conditions by directly doping 2 mol% CeAl₄ into NaAlH₄ [2]

5 BOROHYDRIDES

Metal borohydrides, such as LiBH₄ with an 18.3 wt% theoretical hydrogen storage capacity, are also a very active area of hydrogen storage research for on-board applications at present due to their substantially higher hydrogen content. However, the onset temperature for LiBH₄ decomposition is 653 K and only half of the hydrogen is released below 873 K [12]. Decomposition of LiBH₄ releases only 13.5 wt% of hydrogen according to the following reaction [13]



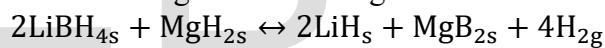
In response to their high thermal stability and unfavorable kinetics, current research efforts on the borohydrides have been geared towards reducing the decomposition enthalpy and decreasing the apparent activation energy by using the following measures [2]:

- i. the introduction of high-performance catalysts
- ii. the introduction of a chemical species that either destabilizes the hydrogenated state or stabilizes the dehydrogenated state
- iii. the formation of nanoscale powders, and the incorporation of the hydrides into nanoporous scaffolds, mesoporous gels or frameworks to inhibit agglomeration and sintering.

Mixing LiBH₄ with SiO₂ powder (3:1) substantially decreased its decomposition temperature so that 9 wt% of hydrogen could be liberated below 673 K (Yang, et al 2010). In this case SiO₂ acts as a catalyst instead of a destabilizer of the complex although SiO₂ generally would react with LiBH₄ at elevated temperatures. The rehydrating process proceeded to completion under 35 MPa at 873 K. Recently, various transition metals (Ti, V, Cr, Sc, Pd, Ni, etc.), metal halides (TiCl₃, TiF₃, TiF₄, ZnF₂, AlF₃, ZnCl₂, ScCl₃, etc.), metal oxides (TiO₂, V₂O₅, ZrO₂, SnO₂, etc.), and carbon-based materials

have been widely studied as catalysts for reducing the decomposition temperature of LiBH₄. Table 2 summarizes the hydrogen storage properties of the catalyst-doped LiBH₄. Apparently, the LiBH₄-0.2MgCl₂-0.1TiCl₃ composite exhibits the optimal hydrogen storage properties, in which approximately 5 wt% of hydrogen was released at 333–673 K, and 4.5 wt% of hydrogen was rehydrogenated at 873 K and 7 MPa. Unfortunately, no significantly effective catalyst for dehydrogenation/hydrogenation of LiBH₄, like the Ti-based catalysts for NaAlH₄, has been found yet.

Thermodynamic destabilization has been proposed as a very promising way to reduce the enthalpy of the dehydrogenation/hydrogenation process by using additives to form more stable metal borides (Vajo, et al 2005). Combining a 2:1 molar ratio of LiBH₄ and MgH₂ resulted in a 25 kJ/mol of H₂ reduction in the decomposition enthalpy relative to pure LiBH₄ due to the formation of MgB₂, instead of B, consequently decreasing the decomposition temperature by 250 K [14]. Approximately 8–10 wt% hydrogen is reversibly stored in the 2LiBH₄-MgH₂ system at temperatures of 588–673 K through the following reaction:



The operating temperature predicted thermodynamically is about 443 K at 0.1 MPa of hydrogen pressure on the basis of a reduced enthalpy change $\Delta H = 46$ kJ/mol of H₂. Since then, considerable efforts have been devoted to thermodynamic destabilization of metal borohydrides by means of forming CaB₆, AlB₂, ScB₂ instead of B, and investigations have been expanded from the LiBH₄-MgH₂ system to the systems of LiBH₄-CaH₂, LiBH₄-Mg(Al), LiBH₄-ScH₂, LiBH₄-LiAlH₄, LiBH₄-NaAlH₄, NaBH₄-LiAlH₄, etc. Also, catalysts, such as TiCl₃, TiF₃, NbF₅, CeCl₃, have been introduced into the destabilization systems for further reducing the dehydrogenation temperature and improving the hydrogen release/uptake kinetics. Specifically, ~8 wt% of hydrogen is released from the 2LiBH₄-MgH₂-0.01TiF₃ system within 30 min at 673 K, while only 2.5 wt% of hydrogen can be liberated for the net 2LiBH₄-MgH₂ system under the same conditions.

A synergetic thermodynamic and kinetic destabilization on the dehydrogenation/hydrogenation of LiBH₄ was achieved by the in situ formation of LaH₃ and MgH₂ originated by ball milling the mixture of LiBH₄ and La₂Mg₁₇ under 4 MPa of hydrogen pressure. The as-

prepared $\text{LiBH}_4\text{-}0.083\text{La}_2\text{Mg}_{17}$ composite could desorb/absorb reversibly ~ 6.8 wt% of hydrogen at 603 K with reasonable kinetics.

In addition, some efforts are being made for improving the reversibility and kinetics of LiBH_4 by reducing the particle size down to nanoscale range. LiBH_4 milled with carbon nanotubes and included in mesoporous carbon both lead to a decrease of dehydrogenation temperature. LiBH_4 loaded into carbon aerogel scaffolds with 13 and 25nm pores exhibits much faster dehydrating/rehydrating rates (up to 50 times faster) than the bulk material [2]. Moreover, the dehydrogenation temperature of LiBH_4 in the aerogels was reduced up to 373 K. LiBH_4 /carbon composites with a 33:67 weight ratio prepared by template method showed excellent desorption kinetics with a hydrogen release of 3.4 wt% in 90 min at 573 K, whereas the hydrogen decomposed from LiBH_4 alone is not detectable at the same temperature [15]. The enhancement of dehydrogenation kinetics of LiBH_4 confined in high surface area nanoporous carbon aerogels is kinetically related to the decrease in diffusion distances and reduction in activation energy, and thermodynamically related to the reduction in melting temperatures through lattice strain. In addition, a better retention of hydrogen capacity is achieved for the nanoscaffold-supported LiBH_4 upon cycling due to both sintering and agglomeration of samples are all stopped (Ngene, et al 2010).

More recently, considerable interest is coming up in research with alkaline earth metal borohydrides, transition metal borohydrides, and mixed metal borohydrides, such as $\text{Mg}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$, $\text{Al}(\text{BH}_4)_3$, $\text{Zn}(\text{BH}_4)_2$, $\text{LiK}(\text{BH}_4)_2$, $\text{LiZn}_2(\text{BH}_4)_5$, $\text{NaZn}(\text{BH}_4)_3$, and so on. Despite the promising hydrogen capacities of these materials, they exhibit poor reversibility of dehydrogenation/hydrogenation, and this is a major problem for using them as hydrogen storage media. Further efforts on making the decomposition of these borohydrides more reversible as well as on improving the reaction kinetics of dehydrogenation should be dwell upon in the future.

5 MICROPOROUS MATERIALS

Hydrogen adsorption on porous materials is one of the

alternative methods under consideration for onboard hydrogen storage for different onboard and onsite applications. Microporous materials are defined as materials with a regular organic or inorganic framework supporting a regular porous structure, with pore sizes between 0.2 and 2.0 nm ($2\text{-}20\text{\AA}$) [17], such materials include organic materials such as activated carbons and carbon nanotubes or inorganic materials such as zeolitic materials, and silicates. They could also exist in hybrid forms such as metal organic frameworks (MOFs).

5.1 Activated Carbon

Activated carbon, also called activated charcoal, is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions. Activated is sometimes substituted with active, that is, it is sometimes referred to as active carbon. Shown in Fig 4. Due to its high degree of microporosity, one gram of activated carbon has a surface area in excess of 3,000 meter square (32,000 sq ft) as determined by gas adsorption. An activation level sufficient for useful application may be obtained solely from high surface area. Further chemical treatment often enhances adsorption properties.

Activated carbon is usually derived from charcoal and is sometimes used as biochar. When derived from coal, it is referred to as activated coal. Activated coke is derived from coke. Activated carbon could be divided into activated carbon fibers (ACFs), activated carbons monoliths (ACMs) and powdered activated carbons (PACs), which are being widely used for gas storage and separation, and they could be made from various precursor materials. Mostly, ACFs are made from precursors such as polyacrylonitrile fiber, and PACs are gotten from different coals precursors anthracite or different kinds of ligneous materials such as coconut-shells, grains and bamboo, Whereas, ACMs are made by the PACs and ACFs under high pressure and temperature or using some binders [18].

Activated carbons' ability to store natural gas and hydrogen gas is being currently researched and tremendous progress is being recorded in this regard. The porous material acts like a sponge for different types of gases. The gas is attracted to the carbon material via Van der Waals forces. Some carbons have been able to achieve bonding energies of 5–10 kJ per mol. The gas may then be desorbed when subjected to

higher temperatures and either combusted to do work or in the case of hydrogen gas extracted for use in a hydrogen fuel cell. Gas storage in activated carbons is an appealing gas storage method because the gas can be stored in a low pressure, low mass, low volume environment that would be much more feasible than bulky on-board pressure tanks in vehicles.

6 CLATHRATE HYDRIDES

Clathrate hydrates, or gas clathrates, gas hydrates, clathrates, hydrates, etc., are crystalline water-based solids physically resembling ice, in which small non-polar molecules (typically gases) or polar molecules with large hydrophobic moieties are trapped inside "cages" of hydrogen bonded, frozen water molecules. In other words, clathrate hydrates are clathrate compounds in which the host molecule is water and the guest molecule is typically a gas or liquid. The lattice structure of hydrate clathrates would generally collapse into conventional ice crystals or liquid water. Most low molecular weight gases, including O₂, H₂, N₂, CO₂, CH₄, H₂S, Ar, Kr, and Xe, as well as some higher hydrocarbons and freons, will form hydrates at suitable temperatures and pressures. Clathrate hydrates are not officially chemical compounds, as the sequestered molecules are never bonded to the lattice. The formation and decomposition of clathrate hydrates are first order phase transitions, not chemical reactions. Their detailed formation and decomposition mechanisms on a molecular level are still not well understood [19]. Clathrate hydrates were first documented in 1810 by Sir Humphry Davy who found that water was a primary component of what was earlier thought to be solidified chlorine.

In addition to chemical reaction and physisorption, a third way of storing hydrogen is also currently receiving attention. It is encapsulation of the gas inside a guest (solid) structure to form a clathrate; from which hydrogen can be released by a pressure and temperature change. Historically, many natural gases (e.g. methane and carbon dioxide) are known to form water clathrates, also termed clathrate hydrates, but it was only in 1999 when the first reports on hydrogen clathrate hydrates appeared. It was a work by [20]. This

prompted research on this and other hydrogen clathrates as potential materials for hydrogen storage. As shown in figure 5, hydrogen-bonded H₂O molecules can generate polyhedral cages around guest molecules to form solid clathrate hydrates having three (common) structure types.

The structure-type sII (shown by hydrogen clathrate hydrates) consists of an ordered stacking of pentagonal dodecahedral and larger hexakaidecahedral cages. When empty, these cages are unstable (collapsing into the conventional ice crystal structure) but they can be stabilised by the inclusion of gas molecules.

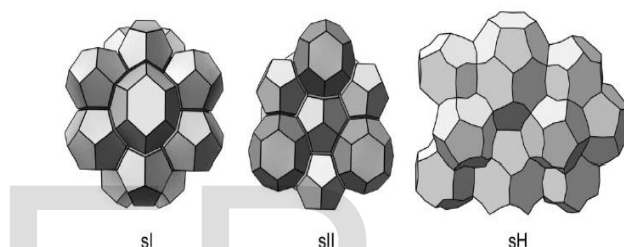


Fig.5: Schematic representation of the sI, sII and sH water clathrates, in which the shape of the cages and the connectivity between them are visible. The three- and four-connected vertices are the O-atoms of the water molecules and the H-atoms lie in the middle between two such vertices

7 CONCLUSION

This review on the state of knowledge in the field of hydrogen storage materials (including metal hydrides, complex hydrides, porous materials and clathrate hydrates) leads to two main conclusions. First, it should be recognized that, despite the enormous effort being put in research activities across the world, we are still far from reaching a widespread and safe use of hydrogen as our primary energy source.

Although, most of the materials that have been tested have shown great potentials and seem ready for less rigorous utilization in stationary on-site applications, however, the goal of the department of energy of the United States of America for more challenging on board applications (such as in automobiles) seem a couple of years away.

Secondly, the statement above notwithstanding, it should also be acknowledged that there seems to be ample room for improvement, building up on already

gained basic knowledge and practical experience. While this applies in general terms to each of the material type mentioned above, each class shows its own perspective for improving performance.

REFERENCES

- [1] A. W. C. Van Den Berg and C. O. Areán, "Materials for hydrogen storage: Current research trends and perspectives," *Chem. Commun.*, no. 6, pp. 668–681, 2008.
- [2] L. Yongfeng and P. Hongge, *Hydrogen Storage Materials Database*. Elsevier B.V., 2014.
- [3] B. Sakintuna, F. Lamari-darkrim, and M. Hirscher, "Metal hydride materials for solid hydrogen storage : A review," *Philos.*, vol. 32, pp. 1121–1140, 2007.
- [4] A. L. Kersting, "Light Metal Amides and Imides For Hydrogen Storage by," *A thesis Submitt. to Univ. Birmingham Degree Dr. Philos.*, no. September, 2011.
- [5] K. Young, "Metal Hydrides," *Ref. Modul. Chem. Mol. Sci. Chem. Eng.*, pp. 1–23, 2013.
- [6] K. Shashikala, *15 Hydrogen Storage Materials*. Elsevier Inc., 2012.
- [7] M. Felderhoff and B. Bogdanovi, "High Temperature Metal Hydrides as Heat Storage Materials for Solar and Related Applications," pp. 325–344, 2009.
- [8] X. Zhang, W. Tian, J. Yang, R. Yang, J. Zheng, and X. Li, "Synthesis and Hydrogen Storage Behaviour of Pure Mg₂FeH₆ at Nanoscale," vol. 52, no. 4, pp. 618–622, 2011.
- [9] A. Reiser, K. Schlichte, B. Spliethoff, B. Tesche, and B. Bogdanovic, "Thermodynamics and dynamics of the Mg–Fe–H system and its potential for thermochemical thermal energy storage," vol. 345, pp. 77–89, 2002.
- [10] B. C. Hauback, H. W. Brinks, C. M. Jensen, K. Murphy, and A. J. Maeland, "Neutron diffraction structure determination of NaAlH₄," vol. 358, pp. 142–145, 2003.
- [11] B. Bogdanovi and M. Schwickardi, "Ti-doped NaAlH₄ as a hydrogen-storage material – preparation by Ti-catalyzed hydrogenation of aluminum powder in conjunction with sodium hydride," vol. 223, pp. 221–223, 2001.
- [12] H. Yang, A. Ibikunle, and A. J. Goudy, "Effects of Ti-Based Additives on the Hydrogen Storage Properties of a LiBH₄ / CaH₂ Destabilized System," vol. 2010, pp. 2–9, 2010.
- [13] J. J. Vajo, S. L. Skeith, and F. Mertens, "Reversible Storage of Hydrogen in Destabilized LiBH₄," pp. 3719–3722, 2005.
- [14] F. E. Pinkerton, M. S. Meyer, G. P. Meisner, M. P. Balogh, and J. J. Vajo, "Phase Boundaries and Reversibility of LiBH₄ / MgH₂ Hydrogen Storage Material," pp. 12881–12885, 2007.
- [15] S. Cahen, J. B. Eymery, R. Janot, and J. M. Tarascon, "Improvement of the LiBH₄ hydrogen desorption by inclusion into mesoporous carbons," *J. Power Sources*, vol. 189, no. 2, pp. 902–908, 2009.
- [16] P. Ngene, M. (Rien) van Z. And, and Petra E. de Jongh, "Hydrogen web- based thematic issue," *Chem. Commun.*, 2010.
- [17] D. J. Collins and H.-C. Zhou, "Nano/Microporous Materials: Hydrogen-Storage Materials," *Encycl. Inorg. Bioinorg. Chem.*, pp. 1–7, 2011.
- [18] F. Chang *et al.*, "Microporous and mesoporous materials for gas storage and separation: a review," *ASIA-PACIFIC J. Chem. Eng.*, no. March, pp. 361–377, 2013.
- [19] S. Gao, W. House, and W. G. Chapman, "NMR/MRI study of clathrate hydrate mechanisms," *J. Phys. Chem. B*, vol. 109, no. 41, pp. 19090–19093, 2005.
- [20] Y. A. Dyadin *et al.*, "Clathrate hydrates of hydrogen and neon," vol. 9, no. 5, pp. 209–210, 1999.