

## A Review on metal hydride based hydrogen energy storage

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### ABSTRACT

*Hydrogen, the most abundant chemical element on earth, is of enormous importance as a feed stock in chemical industry with a worldwide annual production of over 25 million tons currently and assumed potential for accelerated growth. Hydrogen has a great merit as an energy vector is its high gravimetric energy density (about three times more than gasoline), however, its low ambient temperature density results in a low energy per unit volume. This makes hydrogen a challenge to store therefore requiring the development of advanced storage methods that have potential for higher energy density. Particularly within the size and weight constraints. Developing safe, reliable, compact, and cost-effective hydrogen storage technologies is one of the most technically challenging barriers to the widespread use of hydrogen as a form of energy. Scientists are investigating several different kinds of materials, including metal hydrides, adsorbent materials, and chemical hydrides, in addition to identifying new materials with potential for favorable hydrogen storage attributes. Most research into hydrogen storage is focused on storing hydrogen as a lightweight, compact energy carrier for mobile applications.*

**Keywords:** Compressed hydrogen, storage, Pressure, Temperature, material choices, Surface adsorption, Intermetallic, Complex and Chemical Hydrides.

### INTRODUCTION:

According to present researches, possible approaches to storing hydrogen include:

Storage of hydrogen as a gas typically requires high-pressure tanks (350–700 bar [5,000–10,000 psi] tank pressure).

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.

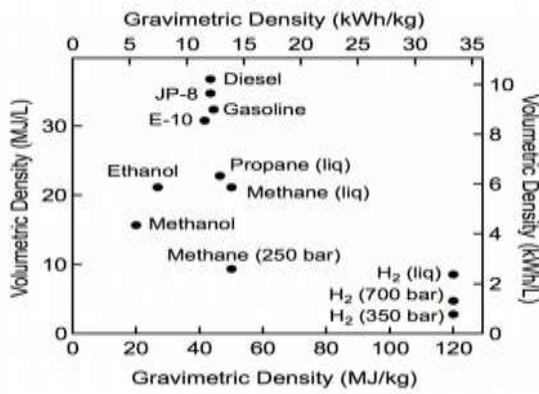
### CHALLENGES:

Hydrogen storage in materials offers great promise, but additional research is required to better understand the mechanism of hydrogen storage in

materials under practical operating conditions and to overcome critical challenges related to capacity, the uptake and release of hydrogen (i.e., kinetics), cost, and life cycle impacts.

High density hydrogen storage is a challenge for stationary and portable applications and remains a significant challenge for transportation applications. Presently available storage options typically require large volume systems that store hydrogen in gaseous form. This is less of an issue for stationary applications, where the footprint of compressed gas tanks may be less critical. On a mass basis,

hydrogen has nearly three times the energy content of gasoline—120 MJ/kg for



hydrogen versus 44 MJ/kg for gasoline. On a volume basis, however, the situation is reversed; liquid hydrogen has a density of 8 MJ/L whereas gasoline has a density of 32 MJ/L, as shown in the figure 1. comparing energy densities of fuels based on lower heating values.

**STORAGE:**

Hydrogen can be stored in different forms some such widely used methods includes,

**Compressed hydrogen:** Compressed hydrogen is a storage form where hydrogen gas is kept under pressures to increase the storage density. Compressed hydrogen in hydrogen tanks at 350 bar (5,000 psi) and 700 bar (10,000 psi) is used as hydrogen tank systems.

**As cryogenic hydrogen:** cryogenic hydrogen (cooled to -253°C, at pressures of 6-350 bar) in insulated tanks.

**Chemical storage:** Chemical storage could offer high storage performance due to the strong binding of hydrogen and the high storage densities. However, the regeneration of storage material is still an issue. A large number of chemical storage systems are under investigation, which involve hydrolysis Reactions,

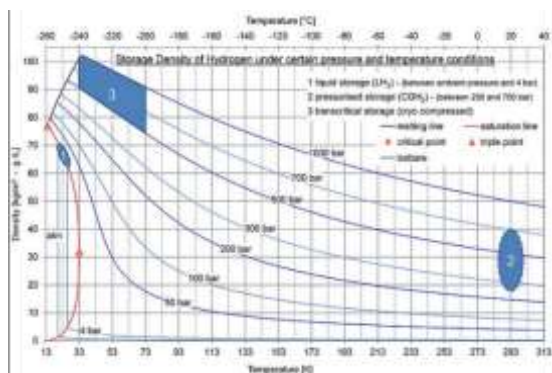


Fig. 2 Storage density of hydrogen at certain temperature and pressure

hydrogenation/dehydrogenation reactions, ammonia borane and other boron hydrides, ammonia, etc. Storage in hydrocarbons may also be successful in overcoming the issue with low density. These liquids would use much smaller, cheaper, safer storage tanks.

**METAL HYDRIDES**

Metal hydrides, such as MgH<sub>2</sub>, NaAlH<sub>4</sub>, LiAlH<sub>4</sub>, LiH, LaNi<sub>5</sub>H<sub>6</sub>, TiFeH<sub>2</sub> and palladium hydride, with varying degrees of efficiency, can be used as a storage medium for hydrogen, often reversibly. Some are easy-to-fuel liquids at ambient temperature and pressure, others are solids which could be turned into pellets. These materials have good energy density by volume, although their energy density by weight is often worse than the leading hydrocarbon fuels. Most metal hydrides bind with hydrogen very strongly. As a result, high temperatures around 120 °C (248 °F) – 200 °C (392 °F) are required to release their hydrogen content. This energy cost can be reduced by using alloys which consists of a strong hydride former and a weak one such as in LiNH<sub>2</sub>, LiBH<sub>4</sub> and NaBH<sub>4</sub>.<sup>[12]</sup> These are able to form weaker bonds, thereby requiring less input to release stored hydrogen. However, if the

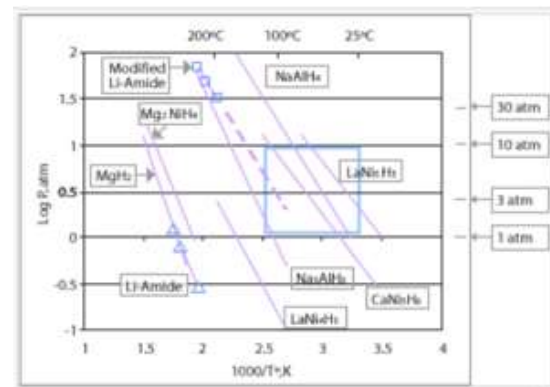


Fig. 3 Metal hydride hydrogen storage

interaction is too weak, the pressure needed for rehydrating is high, thereby eliminating any energy savings. The target for on-board hydrogen fuel systems is roughly <100 °C for release and <700 bar for recharge (20–60 kJ/mol H<sub>2</sub>). Currently the only hydrides which are capable of achieving the 9 wt. % gravimetric goal for 2015 (see chart above) are limited to lithium, boron and aluminium based

compounds; at least one of the first-row elements or Al must be added. Research is being done to determine new compounds which can be used to meet these requirements. Hydrides chosen for storage applications provide low reactivity (high safety) and high hydrogen storage densities. Most acceptable materials are lithium hydride, sodium borohydride, lithium aluminium hydride and ammonia borane.

**Carbohydrates:** Carbohydrate provides high hydrogen storage densities as a liquid with mild pressurization and cryogenic constraints; it can also be stored as a solid powder. Carbohydrate is the most abundant renewable bio resource in the world. Possible demonstration has been made to produce nearly 12 moles of hydrogen per glucose unit from cellulosic materials and water. Proposal is made that use of carbohydrate as a high energy density hydrogen carrier with a density of 14.8 wt%.

**Synthesized hydrocarbons:** An alternative to hydrides is to use regular hydrocarbon fuels as the hydrogen carrier. Then a small hydrogen reformer would extract the hydrogen as needed. However, these reformers are slow to react to changes in demand.

**Lots of material choices:**

- Crystalline Nano porous Materials
- Polymer Microspheres
- Self-assembled Nanocomposites
- Advanced Hydrides
- Inorganic-Organic Compounds
- BN Nanotubes
- Hydrogenated Amorphous Carbon
- Mesoporous Materials
- Bulk Amorphous (BAMs)
- Iron Hydrolysis
- Nano size Powers
- Metallic Hydrogen
- Hydride Alcoholises

**Different forms in chemical storage:**

**Surface Adsorption:**

It is a process during which hydrogen molecules are bound with weak van der Waals interactions to the surface of the adsorption material. The hydrogen stays in its molecular form and no

chemical reaction like dissociation occurs. In this view physisorption

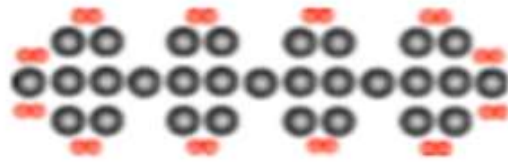
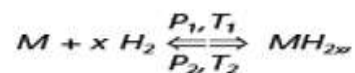


Fig. 4 Surface Adsorption

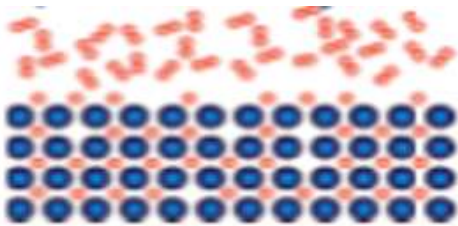
can be an extremely fast process and fully reversible. Hydrogen gas can be adsorbed and desorbed during several cycles without any losses. With this characteristics part of the imposed requirements for onboard application can be already fulfilled. Since the strength of adsorption interaction is very weak low, cryogenic temperatures must be applied to obtain reasonable hydrogen storage capacity. Even at low temperature, usually ~77 K, only a monolayer of hydrogen can be adsorbed. For this reason, materials with very big specific surface area are specifically desirable.

**Intermetallic Hydride:** An initial report on the ability of alloys and intermetallics to form compounds with hydrogen dates back to 1958, when Libowitz showed that ZrNi easily and reversibly reacts with hydrogen forming ZrNiH<sub>3</sub>. However, the birth of a new field, chemistry of intermetallic hydrides, is usually considered to be coincident with the discovery a decade later of hydride forming compounds such as SmCo<sub>5</sub> and other rare earth AB<sub>5</sub> and AB<sub>2</sub> intermetallics.

Practical applications of intermetallic hydrides are based on their chemical interaction with hydrogen. In general, this reaction may be described by the following equation



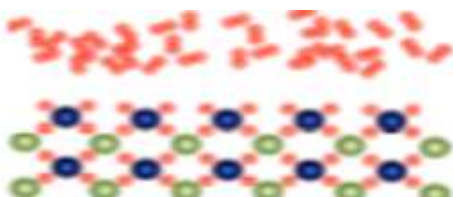
where M is a metal or an intermetallic compound. The rates of reaction for intermetallic compounds differ dramatically from those for individual metals.



**Fig.5 Intermetallic Hydride**

This peculiarity immediately brought attention to intermetallic hydrides as prospective materials for hydrogen storage and distribution. A majority of conventional materials absorb hydrogen at high rates at room temperature and low pressure. However, practical interest in these intermetallic hydrides is rather limited due to their relatively low reversible gravimetric hydrogen absorption capacity (1.4–1.9 mass.%). At the same time, in light of the greater safety of intermetallic hydrides compared to the hydrides of light metals, and the breadth of experience in applications, the development of new materials with a wide range of operating hydrogen pressures is of great practical interest. Moreover, current availability of novel high-pressure vessels (up to 250–350atm), and development of 800atm vessels, facilitate the investigation of high-pressure metal hydrogen systems. Indeed, storing hydrogen in a high-pressure vessel filled with a metal hydride combines the advantages of both compressed gas and solid state hydrogen storage techniques, thus increasing total capacity of the storage container by at least 10%. The metal hydrides based systems with high hydride dissociation/hydrogen desorption pressures are also extremely attractive for applications in high-pressure compressors and internal combustion engines as a part of cold-start ignition systems.

**Complex Hydride:** Complex metal hydrides are salts wherein the anions contain hydrides. In the older chemical literature as well as contemporary



**Fig. 6 Complex Hydride**

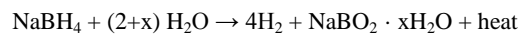
materials science textbooks, a "metal hydride" is assumed to be non-molecular, i.e. three dimensional lattices of atomic ions. In such systems, hydrides are often interstitial and nonstoichiometric, and the bonding between the metal and hydrogen atoms is significantly ionic. In contrast, complex metal hydrides typically contain more than one type of metal or metalloid and may be soluble but invariably react with water. They exhibit ionic bonding between a positive metal ion with molecular anions containing the hydride. In such materials the hydrogen is bonded with significant covalent character to the second metal or metalloid atoms.

**Chemical Hydride:** This is an investigation of a gas/solid chemical reaction between steam and chemical hydrides that liberates pure hydrogen gas. The aim is to obtain fundamental kinetic, chemical, catalytic, and thermodynamic data on the reaction so



**Fig. 7 Chemical Hydride**

that sufficient information is known to evaluate this technology rigorously for its potential as a means of delivering hydrogen for fuel cells and internal combustion engines. It is known that simple chemical hydrides (e.g. LiH, CaH<sub>2</sub>) as well as complex hydrides (NaBH<sub>4</sub>, LiBH<sub>4</sub>, and others) react with liquid water to produce H<sub>2</sub>. For example, NaBH<sub>4</sub> has been extensively studied:



In the above equation, x is the "excess hydration factor", representing the fact that the solid byproduct can exist in varying degrees of hydration. This liquid reaction has some disadvantages. For example, in the case of NaBH<sub>4</sub>, an acid catalyst is required to liberate 100% of the hydrogen, because dissolved NaBH<sub>4</sub> is stable in basic solution, and the byproducts (sodium borate and similar compounds) are basic in solution. In this reaction, the ideal case is where x = 0, in which case the mass yield is 10.3 kg H<sub>2</sub> per 100 kg of reactants. In practice, excess water is required (x=2 is more realistic) so that the NaBH<sub>4</sub> and byproducts remain completely

dissolved. Excess water rapidly reduces the mass efficiency of the system. A recent discovery shows that by vaporizing water prior to contact with the hydride, hydrogen yields in excess of 90% may be obtained without the need for a catalyst. Thermodynamic considerations show that, in principle, the heat liberated by the reaction is more than sufficient to vaporize the stoichiometric water required for the steam. Thus, there is the possibility of developing a hydrogen reactor/delivery system that is auto thermal at steady state, that produces pure hydrogen in 100% yield, that requires no catalyst, that does not involve strongly caustic solutions, and that uses a minimum of water. Furthermore, the solid reaction products should be nearly free of water, which in the long term will facilitate recycling and regeneration to the hydride.

All the above new types of materials and processes are only for two reasons,

To increase the maximum amount of hydrogen storage in a safer and economical way,

To decrease the absorption and Desorption time and constant maintenance of external temperature for such operation to be a desirable and economical one.

Main two factors which are important over these aspects are absorption and desorption of hydrogen.

#### **Absorption:**

In chemistry, absorption is a physical or chemical phenomenon or a process in which atoms, molecules or ions enter some bulk phase – gas, liquid or solid material. This is a different process from adsorption, since molecules undergoing absorption are taken up by the volume, not by the surface (as in the case for adsorption). A more general term is sorption, which covers absorption, adsorption, and ion exchange. Absorption is a condition in which something takes in another substance.

In many processes important in technology, the chemical absorption is used in place of the physical process, e.g., absorption of carbon dioxide by sodium hydroxide – such acid-base processes do not follow the Nernst partition law.

For some examples of this effect, see liquid-liquid extraction. It is possible to extract from one liquid phase to another a solute without a chemical

reaction. Examples of such solutes are noble gases and osmium tetroxide.

The process of absorption means that a substance captures and transforms energy. The absorbent distributes the material it captures throughout whole and adsorbent only distributes it through the surface.

However, it should be remarked that the distinction between adsorption and absorption vanishes as we go from perfectly crystalline macroscopic materials to structured materials, aggregates and composites made out of increasingly smaller grains, viz., micron-sized particles to nanoparticles, sub-Nano particles and finally molecules (or atoms). In such Nano-composites, the internal surface area of particulate matter is very large. Then the adsorption on internal surfaces simply becomes absorption. Then the distinction between adsorption and absorption vanishes. On the other hand, the distinction is clearest between bulk solids without internal structure, but having only surfaces where only adsorption can occur on the outer surfaces and nanocomposites or aggregates with internal structure where absorption by the host material is simply adsorption on internal surfaces of the host material. As an example, we may consider a crystalline piece of silicon dioxide (quartz) which can adsorb water molecules on its surface. However, if the quartz is ground into very fine sand, the pile of sand (an aggregate) has a very large internal surface area. A very large amount of water can be adsorbed by the "internal" surfaces of the grains in the pile of sand, and this absorption is simply "internal adsorption. If water is made to flow through such a pile of sand, ions and toxins may be preferentially adsorbed by the surfaces of the grains of sand, providing a simple, well-known water purification application.

#### **DESORPTION:**

Desorption is a phenomenon whereby a substance is released from or through a surface. The process is the opposite of sorption (that is, either adsorption or absorption). This occurs in a system being in the state of sorption equilibrium between bulk phase (fluid, i.e. gas or liquid solution) and an adsorbing surface (solid or boundary separating two fluids).

When the concentration (or pressure) of substance in the bulk phase is lowered, some of the sorbed substance changes to the bulk state.

In chemistry, especially chromatography, desorption is the ability for a chemical to move with the mobile phase. The more a chemical desorbs, the less likely it will adsorb, thus instead of sticking to the stationary phase, the chemical moves up with the solvent front.

In chemical separation processes, stripping is also referred to as desorption as one component of a liquid stream moves by mass transfer into a vapour phase through the liquid-vapour interface.

### **CONCLUSION:**

It is clear that until now none of the available metal hydrides or complex metal hydrides with high gravimetric storage capacity meets the required conditions for onboard application. Thus it is a reasonable idea to choose one compound which is able to absorb relatively large amount of hydrogen and try to improve its kinetics and thermodynamics. Techniques such as ball milling and adding proper catalyst are implemented successfully to improve the sorption kinetics. By reducing particle and grain sizes more surface area is accessible for the hydrogen and the diffusion path becomes shorter; therefore, the speed of the absorption process can increase. Additives that contain usually transition metal elements are believed to have the role of hydrogen molecule splitter. Thanks to adding the appropriate catalyst to the certain metal hydride systems the kinetics and reversibility can be improved. The conditions of pressure and temperature at which loading and unloading processes occur can be more desirable for applications. An additional function of the catalyst is to act as additive that leads to Nano scale grain refinement.

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