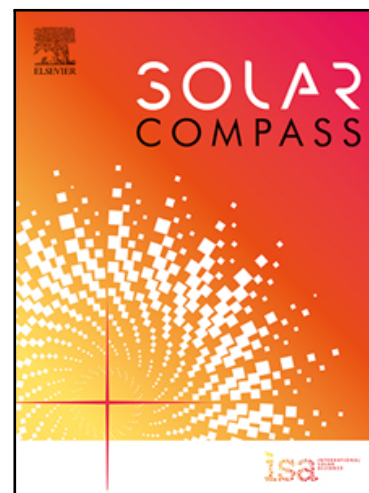


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Recent Developments in State-of-the-art Hydrogen Energy Technologies – Review of Hydrogen Storage Materials

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The salient highlights and novelty of our review manuscript are given in the following statement:

This review article is emerged out of the multi-national, multi-institutional collaborative research with hydrogen energy experts. The recent developments in artificial intelligence, machine, and deep learning, 3D/4D printing, combinatorial approaches are currently providing pathways for designing and developing novel hydrogen storage materials, for PEM fuel cell applications. The enrich knowledge gathered over 40 and odd years of research on hydrogen storage, that have seen wealthy of systems and materials based on metallic hydrides, functionalized magnesium hydrides, reactive hydride complexes, carbonaceous systems, and their hydrogen storage mechanisms, metal organic frameworks, perovskites structures and related systems. Hydrogen storage in an international stage is discussed on the countries' bold initiatives and targets to realize clean hydrogen technologies for the sustainability and infrastructure to address the ever alarming “Global Warming”. The applications of hydrogen for transportation and stationary power generation are discussed. Overall, this comprehensive review article will give the current trend research and future trajectories for developing novel materials and systems for hydrogen storage that is one of the

challenging tasks besides hydrogen production and hydrogen conversion, in realizing the “*Hydrogen Economy*”.

Abstract

Hydrogen energy has been assessed as a clean and renewable energy source for future energy demand. For harnessing hydrogen energy to its fullest potential, storage is a key parameter. It is well known that important hydrogen storage characteristics are operating pressure-temperature of hydrogen, hydrogen storage capacity, hydrogen absorption-desorption kinetics and heat transfer in the hydride bed. Each application needs specific properties. Every class of hydrogen storage materials has a different set of hydrogenation characteristics. Hence, it is required to understand the properties of all hydrogen storage materials. The present review is focused on the state-of-the-art hydrogen storage materials including metal hydrides, magnesium-based materials, complex hydride systems, carbonaceous materials, metal organic frameworks, perovskites and materials and processes based on artificial intelligence. In each category of materials’ discovery, hydrogen storage mechanism and reaction, crystal structure and recent progress have been discussed in detail. Together with the fundamental synthesis process, latest techniques of material tailoring like nanostructuring, nanoconfinement, catalyzing, alloying and functionalization have also been discussed. Hydrogen energy research has a promising potential to replace fossil fuels from energy uses, especially from automobile sector. In this context, efforts initiated worldwide for clean hydrogen production and its use via fuel cell in vehicles is much awaiting steps towards sustainable energy demand.

Keywords: Hydrogen Energy Technologies, Hydrogen Storage, Metal Hydrides, Carbonaceous, Nanoparticles, Metal Organic Frameworks, Perovskites, Fuel Cells

1. Introduction - Overview and Background of Hydrogen Energy Technologies

An unprecedented raise of global mean temperature over the several decades and associate *global warming* lead both developed and developing countries to device strategies for containing the global CO₂ emissions [1]. As it is known to everyone that conventional energy resources like fossil fuels such as petroleum products and coal have been used for a long time and created an impact on the environment especially *greenhouse effect* due to large production of CO₂ gases during the combustion of these fuels [2]. Due to this fact, researchers have focused on alternate source of energy which should be environmentally friendly and easily available [3]. One of the sources is solar energy though due to efficiency of solar cell and sturdiness inspire research fraternity to find another source which could be mobile and economical for the future prospectus [4]. In this review article, focus area is *hydrogen as a fuel*. The lightest and most available material on the earth is hydrogen which can be useful as energy source. The hydrogen is a fuel with less or almost zero emission of toxics as well non-polluting gas when it burns or used as renewable energy sources [5]. As hydrogen is an alternate source has extremely useful as a green

fuel for the current time. The hydrogen fuel is more than double efficiency than the other fuels like gasoline [6-7]

There are number of techniques available to produce hydrogen and utilize those with suitable aspects. Main source of hydrogen is the industrial steam reforming method [7], where 96% of hydrogen is produced. It is a well-established technology to extract hydrogen from fossil fuel stocks [8]. Almost 10 million tons of hydrogen requirements of U.S. is fulfilled using steam reforming every year [8]. While remaining 4% of hydrogen can be produced via electrolysis process [9]. Electrolysis process is the most important and emerging technology, in this method, water can be split into hydrogen/oxygen using the electrical energy. other methods like thermochemical, wind, biomass gasification and solar radiation are to be considered although those are under preliminary research level hence needs more experimental proof for the quantitative production of hydrogen [8]. One can consider hydrogen as a prospective fuel, but it requires a huge effort to make it commercially viable. Though, in recent era researchers have made significant contributions in the production of hydrogen gas, intermediate storage, and utilization in PEM fuel cells by state-of-art methodologies (Figure 1) [8]. The hydrogen storage is the bottleneck in implementing the hydrogen technologies to its fullest potential [10-12]. Looking into this, researchers are required to focus on storage of the hydrogen gas as a fuel. One of the solutions to this problem is the reversible storage of hydrogen in solid state materials. There are a number of solid materials available which have properties like microporous with high surface area, moisture sensitive complex hydrides and gas sorption can be utilized [13].

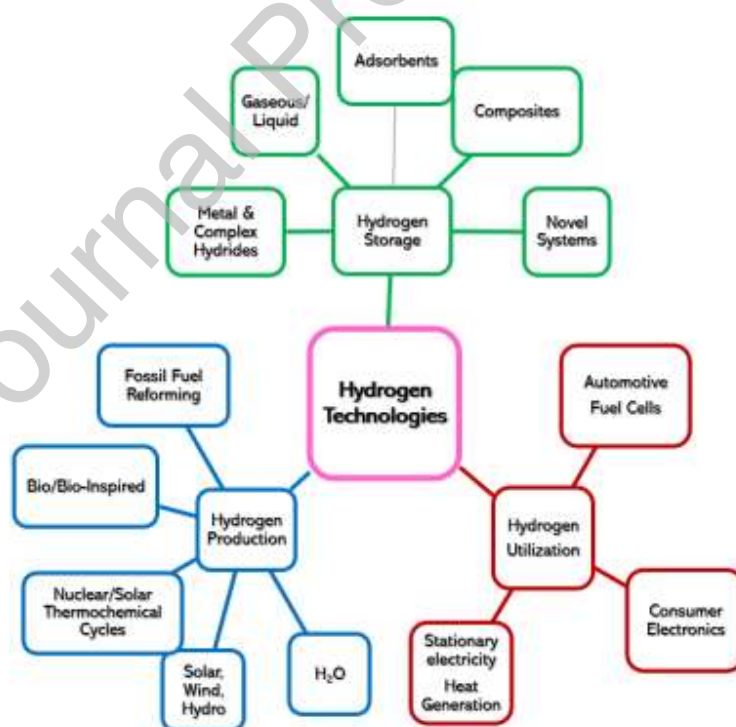


Figure 1. Hydrogen Energy Technologies

2. Hydrogen Energy Technologies – An International Perspectives

The US administration's bold "*Hydrogen Earthshot*" initiatives, "One-for-One-in-One", otherwise simply, "111" is driving and reviving the hydrogen-based research and development to realize for the generation of "clean hydrogen" at the cost of \$1.00 for one kilogram in one decade [14]. This initiative triggers not only to develop "US Hydrogen Hubs" but also catalyze the international hydrogen research. Another bold goal of this process on the international stage, a net zero or 100% renewable energy consumption (or 100% clean grid) must be achieved by 2050 with a short-term to realize the 50% of set-forth goals by 2030 [15]. Another bold initiative from the EU Commission to adopt renewable hydrogen to decarbonize at the cost-effective manner that is strategically developed by the REPowerEU; this leads to the "*hydrogen accelerator*" where a domestic hydrogen production of 10 MT (million tons) by 2030 [16]. Africa-EU Green Energy initiatives are on the horizon in developing 40 GW (Gigawatts) of electrolyzer capacity to generate renewable hydrogen and critical raw materials to support the green and digital technologies [17]. In 2021, the IPHE (International Partnership for Hydrogen and Fuel Cells in the Economy), the IEA (International Energy Agency), and the CEM (Clean Energy Ministerial)/MI (Mission Innovation) have collectively addressed the four issues and developed the strategies for scaleup, accelerate and deploy the hydrogen energy technologies that not only enhance the reduction of carbon footprints but also enable sustainable infrastructure [18].

On the Asia-Pacific initiatives towards implementing hydrogen energy technologies, very recently, China announced its first ever bold plan to reach its fullest potential of generating 100,000 tons to 200,000 tons of clean hydrogen and hence that lead to the reduction of CO₂ emissions of 1MT to 2MT per year by 2025. By 2035, China seeks the country's major energy consumptions that are catered by the green sources, especially hydrogen [19]. According to the 2019 IEA/IRENA's report, South Korea's bold plan and road map in volume production of at least 6.2 million fuel-cell electric vehicles, commissioning 1200 hydrogen-enabled refilling stations and at least 15 GW of fuel cell for power generation by 2040 [20]. The road map of Japan has been pushing the boundaries to cut down the cost of hydrogen by 2030 and by encouraging the deployment of ammonia in thermal power generation as a low-carbon transition fuel. Japan also strategically attempting to establish an integrated and international supply chain by 2030 for up-streaming (production), mid-streaming (storage and transportation) and down-streaming (utilization or consumption) the clean hydrogen [21]. India's bold hydrogen initiatives that propose to at least infuse four percent of hydrogen in the national energy mix by 2030 and at least 10 developmental projects on nation-wide deployment of hydrogen energy technologies [22]. Based on the statistics and overview, it is undoubtedly clear that the hydrogen energy technologies are the future vectorial strategies that can fully replace the much-depleted fossil fuels, especially gasoline for automotive transportation and stationary power generation.

3. Hydrogen: A green and sustainable energy resource

The steady decline and depletion of natural energy resources has placed considerable demands for the alternative energy sources. In addition, while an emerging climate crisis driven by global warming from greenhouse gas emissions [23-24] poses an imminent threat to modern-day society, the energy shortfall must be met by sustainability for a growing global population and

secure the imbalance to the environment with clean energy. The inherent fluctuations associated with wind or solar energy as renewable sources may have an impact on sustainability requiring a constant and steady supply from the source. Further, the lack of long-term energy storage capabilities with existing technologies underlines the growing importance for alternative strategies which can work alongside renewable forms. Hence, an alternative sustainable but continual energy source is necessary for power generation while renewable technology evolves. In this quest, hydrogen is the most promising candidate for the cleaner energy as a plentiful resource for zero-carbon emission [25-27]. Interestingly, hydrogen emits pure water vapor upon reaction with oxygen or upon combustion therefore, hydrogen-based technologies is likely to be one of the most significant determinants in reducing the carbon emission and thus playing an unprecedented role in driving fuel economy.

The Hype cycle methodology has been instrumental in understanding current and future impact of the most pivotal and exciting technological fields by estimating technological growth and maturation points. In view of the insight from the Garner Hype and Amara Hype cycle analysis for energy storage technology put forward by Khodayari et al and Fredrik Uddenfeldt [28-29] which suggests that chemical hydrogen storage technology is still at the innovation stage (Figures 2a and 2b), the projected low cost of hydrogen as a fuel source in comparison could be an attractive and real alternative (Figure 2c and 2d) [30]. Further, based on survey and interview with hydrogen council member experts, McKinsey & Company predictively proposes increasing efforts to apply the use hydrogen energy to various sectors of society with the expectation that by 2050, hydrogen will be accepted as the main energy source for mass transportation and will become the next generation green energy technology (Figure 2e) for power/electricity generation [29]. US Department of energy (DOE) in its Annual Energy Outlook (AEO) of 2020 projected threefold increases in the electricity generation based on renewable energy storage systems [31].

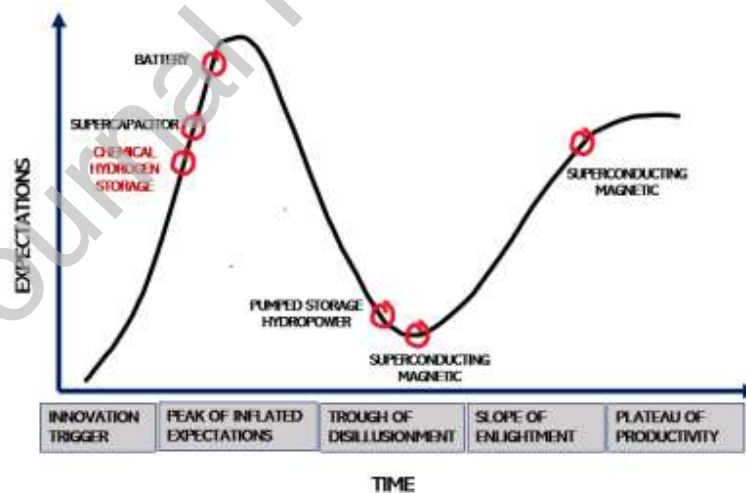


Figure 2. (a) Chemical Hydrogen Storage at the Innovation Stage of the industrial revolution

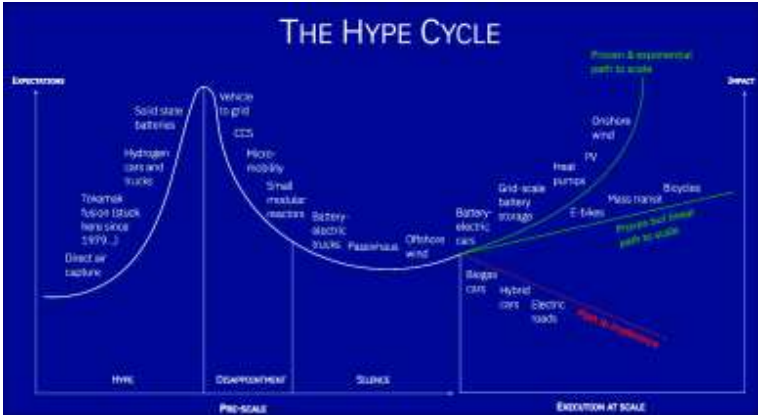


Figure 2. (b) The HYPE cycle.

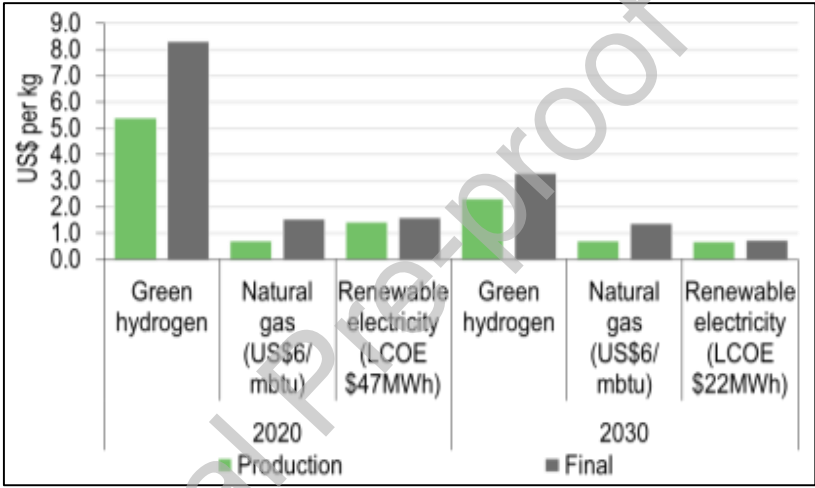


Figure 2. (c) Cost analysis of green hydrogen (US\$ per kg) with natural gas and renewable electricity.

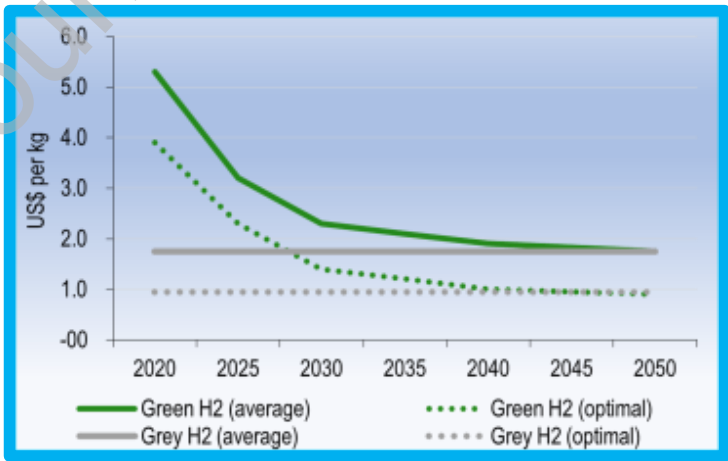


Figure 2. (d) Timeline chart of green and gray hydrogen cost of production (US\$ per kg).

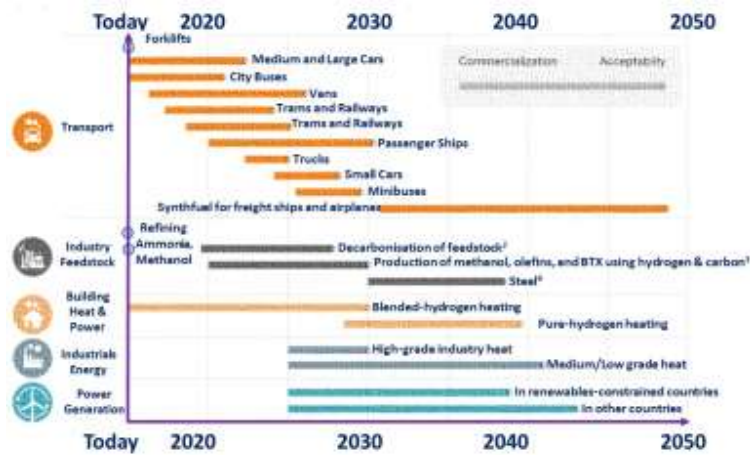


Figure 2. (e) Timeline chart of mass energy transportation and power generation

Energy economy heavily depends on energy storage systems which is a key player between supplies and utilization. As efficient energy storage system boosts the efficiency by reducing potential losses. As an excellent and cost-effective intermittent energy storage systems requires extensive research in a short space of time to achieve rapid solutions for climate change and exhausting resources. However, energy generation from electricity or gas energy sectors does not require storage. However, storing the excess supply would help in supplementing the shortfall. In their analysis spanning a period of years, M. Wieliczko et al highlighted the development of potential impact of technologies with low to high storage capacities on a timescale of ranging from seconds to months for the energy and climate problems [32]. Although such technologies namely supercapacitors, superconducting magnets, flywheels, pumped hydel storage, compressed air energy storage and batteries offer solutions for a variety of applications (depending upon the requirements), but the challenge here is that no single technology can be used for a given range of applications [33]. Interestingly, among these technologies, hydrogen is the only one energy technology which can fulfil the requirements of various sectors as shown in Figure 3a.

In addition, role of hydrogen becomes even more important because it can be produced not only by conventional SMR methods but also by harnessing other renewable sources such as solar, wind and geothermal among others. However, in spite of its advantage as a high specific energy material, safety, and elevated cost due to its low energy density (Figure 3b) are the biggest challenges for hydrogen technology [34]. Hydrogen storage systems are classified into two categories based on the type of stored hydrogen (Figure 3c). In physical storage system which are mainly liquid, or gaseous, free, or elemental hydrogen is stored. Another challenge is liquefaction of hydrogen which requires a high energy input (8-12kW/h) [35].

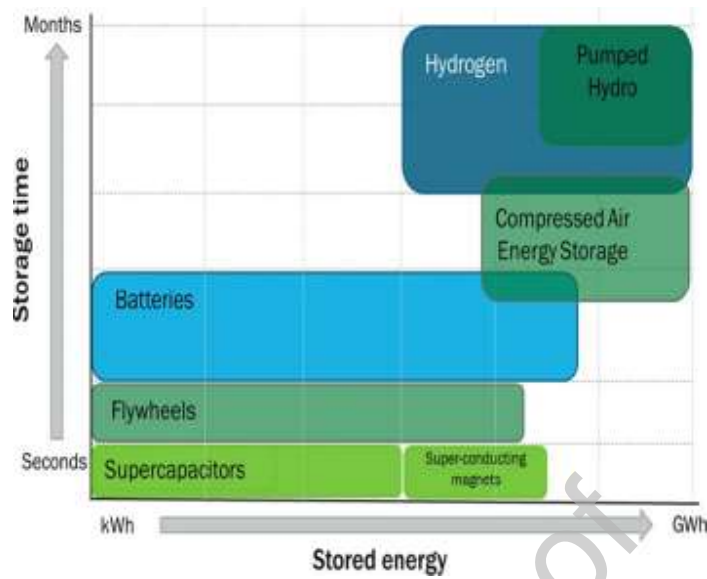


Figure 3. (a) Stored energy vs. storage time for various energy technologies.

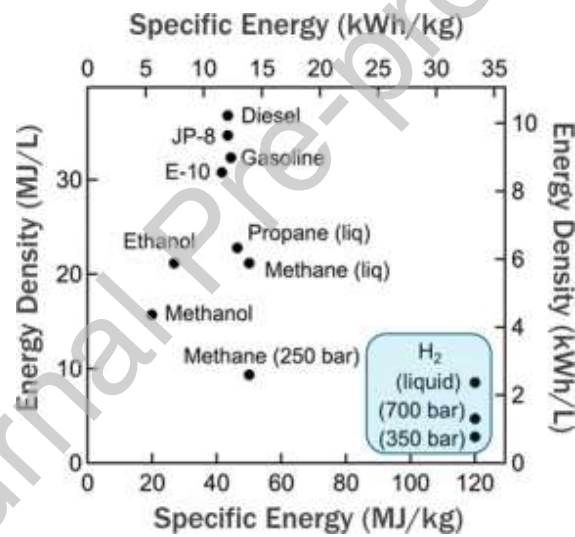


Figure 3. (b) Specific energy density vs volumetric density of number of fuel sources.

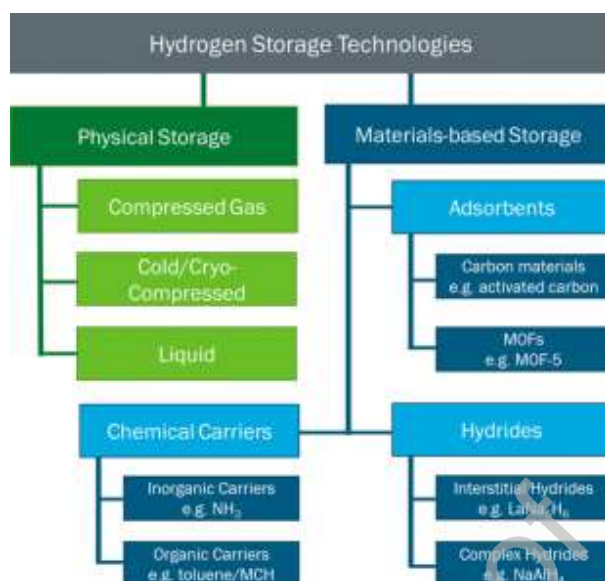


Figure 3. (c) Types of hydrogen storage technologies.

For gaseous hydrogen although the density is much lower than liquid hydrogen, the high cost of containment to store at high pressures pose major safety concerns [36-38]. On the other hand, in materials-based hydrogen storage system hydrogen atom bonded to materials are stored. Figure 3d and 3e shows a comparative study done by the Fuel Cell Technologies Office (FCTO) on the materials in terms of hydrogen gravimetric capacity as a function of hydrogen release temperature [39-40]. It took many years of investigations to develop these materials which are still facing challenges of cost, reproducibility, and recyclability along with high temperature desorption. Despite all these years of explorations material with desired thermodynamic, kinetic, and physical properties combination is missing. This suggest that in place of trial and error using periodic table a well-trained investigation based on AI (Artificial Intelligence) and ML (Machine Learning) are required. *AI/ML will help not only to identify the elemental, structural combinations but also will provide us the pathway for efficient synthesis.*

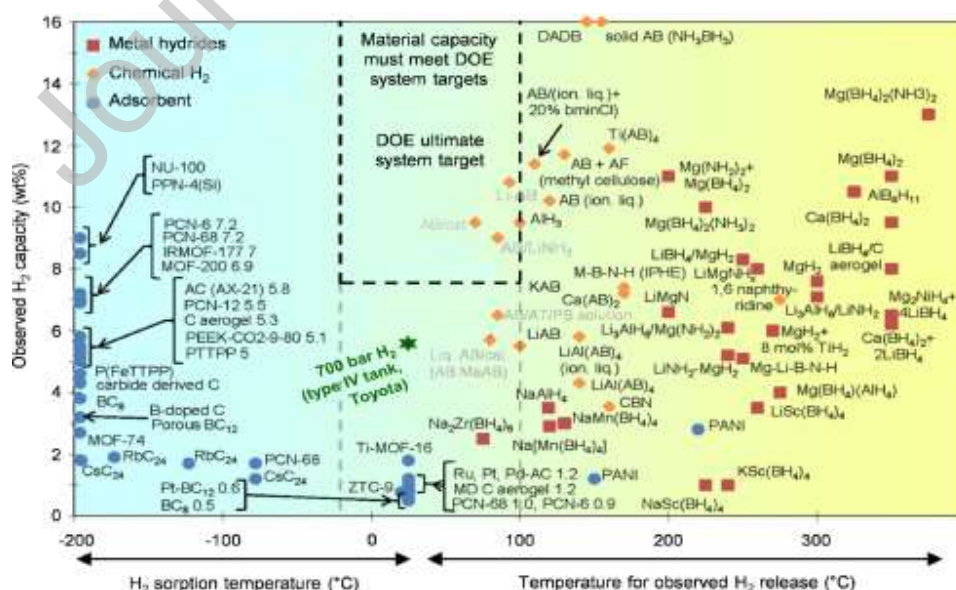


Figure 3. (d) metal hydrides, chemical hydrogen, and adsorbents temperature of operation with respect to the hydrogen storage capacity

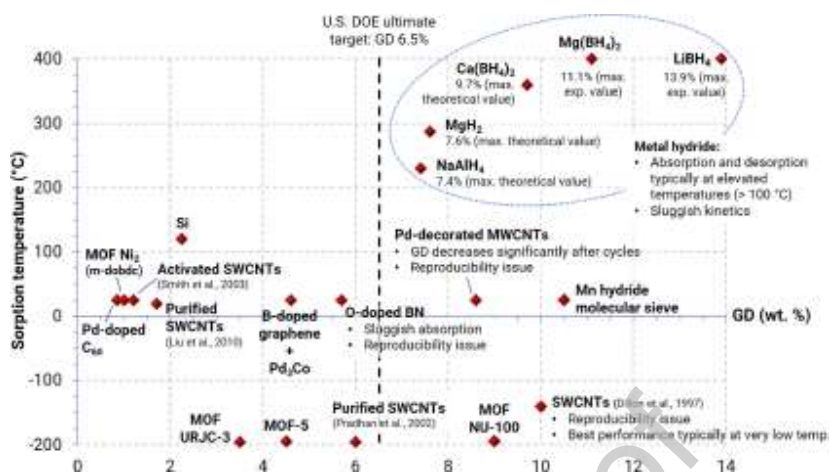


Figure 3. (e) Sorption temperatures of various soft materials and complex hydrides with respect to hydrogen storage capacities.

4. AI/ML Concepts in Hydrogen Storage Materials' Design

Increasing role of AI in changing our life is of paramount importance. AI is helping us to live in more comfortable and safer world. Figure 4a suggests that AI has three main stages: artificial narrow intelligence (ANI), artificial general intelligence (AGI) and artificial super intelligence (ASI). Out of these three stages first stage of AI is safe and useful for humankind. Recently research using ANI has become increasingly important in all sectors of research and development including hydrogen storage research (Figure 4b). Khare et al have outlined the importance of interconnectivity of disciplines and further utilizing this transdisciplinary approach in AI to enhance the utility of AI for materials discovery [41]. Web of science search with the keywords of hydrogen storage technology and AI suggests that research on AI for hydrogen storage technology triggered in all areas of importance. However, there are only 95 publications so far in past 10 years but frequency of publications in recent 3-4 years has increase manifold. There have been many algorithm techniques (Figure 4c) to predict materials and properties of the hydrogen storage system (Figure 4d).

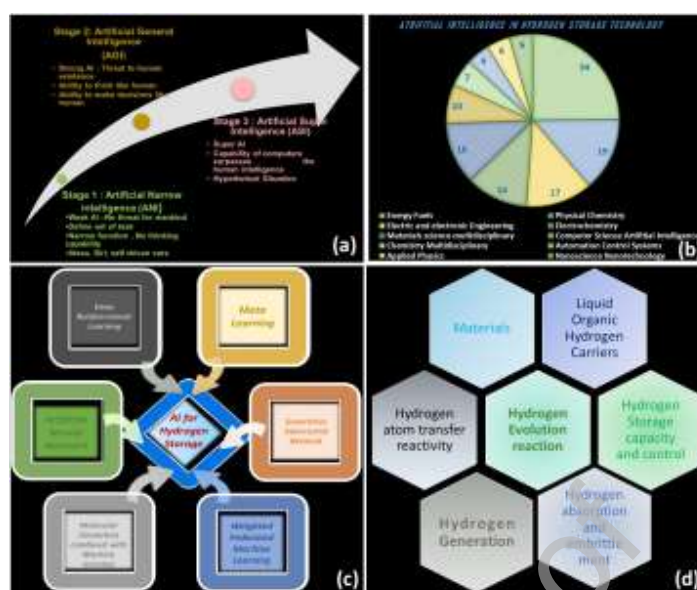


Figure 4. (a) Three main stages of AI, (b) AI in hydrogen storage technology, Different techniques of AI to predict (c) materials and (d) properties of the hydrogen storage systems.

Thornton et al utilized the findings of a very inspiring project called ‘The Materials Genome’ where millions of materials were predicted based on sequencing and modelling. In their work Thornton et al, targeted hydrogen storage system using a materials genome database to understand and identify the performance limits of hydrogen storage system [42]. In this work, the prediction of two hypothetical MOFs were shown to be associated with superior capability compared to the best performing MOFS synthesized to date. Interestingly, hypothetical MOFS predicted to enhance the net deliverable of energy by 30% when filled in a tank at cryo-compression condition (20k, 100 atm.) resulting in 30% increase in volumetric capacity. Further Jager et al have worked on a different scale i.e. on nanosized clusters for optimizing the prediction methods for assessing conditions for best property optimization. In their work using machine learning algorithms, Jager et al scanned a single and multiple nanoclusters applying atomic structural descriptors (SOAP, MBTR and ACSF) and this was predicted to be the best descriptor for the prediction of hydrogen adsorption (free) energy. This study concludes that the local symmetry is important for descriptor methods and therefore near-symmetric systems are ideal for the descriptor methods [43]. In an extensive work published in two volumes by Rahnama and co-workers have combined statistical analysis with supervised machine learning algorithms to obtain the best machine learning algorithms for quick identification for a desired class of materials with optimized properties such as hydrogen absorption wt.% [44-45]. More research efforts have been implemented for the prediction of components of hydrogen energy storage system which will be reviewed in detail in our future work with a focus on AI for the components of hydrogen energy storage systems.

5. Hydrogen Energy Storage – A Bird’s Eye View

The reversible hydrogen storage can be realized using metal hydrides and adsorbent materials. The hydrogen sorption capacity of materials is the most important factor to do hydrogen storage.

Looking into the storage part, the thermodynamic properties affect including the enthalpy of molecular hydrogen adsorption and the enthalpy of hydride formation or decomposition [13]. Hence, the kinetics of hydrogen adsorption, the activation energy, the hydrogen diffusion coefficient and the apparent rate of hydrogen absorption and desorption would be the key factors. There are quite a few good techniques available to measure gas sorption at laboratory scale which could be useful to determine the hydrogen storage capacity of the materials. Not only the storage capacity of the materials but also other physical and chemical properties are very important to optimize the hydrogen storage solid specimens which includes the microstructural properties using X-ray diffraction and electron microscopy. The spectroscopic studies can be used to analyze various chemical and molecular properties of the targeted storage materials. Though, the analysis data of the targeted specimens are not enough to give final sorption capacity of the potential storage materials for the hydrogen [13]. A very recent comprehensive review on the prospects of hydrogen storage and related issues have been discussed especially metal hydrides for sustainable energy applications [46].

6. Metal hydrides and Related Systems

Compounds formed between metals and hydrogen are termed metal hydrides. Here the metal can be in form of an element, an alloy, or a metal complex. The nature of bonding between metal and hydrogen depends on the electronegativity of the metal, which is responsible for the type of electrons shared among metal and hydrogen. For low electronegative metals alkali (Group 1a) or alkaline earth metals (Group 2a), the electron is transferred from the metal to the hydrogen and thus the ionic bond is formed. With the increase in the electronegativity of the metal, the metal-hydrogen bond is metallic. With the even higher value of electronegativity of metal, the bond becomes covalent in nature. Metallic metal hydrides are formed from transition metals, lanthanides, and actinides. In this case, the electron energy levels of metal and hydrogen overlap sharing delocalized electrons characterized by a metallic bonding. The hydrogen atom is occupied in either a tetrahedral or an octahedral void formed by metal atoms.

As mentioned above, in metal hydrides metal may be in form of an element, alloy or intermetallic compound (IMC). Metal hydrides formed by an element have limited properties. There is the large scope and greater flexibility for tailoring the hydrogenation characteristics through alloys and intermetallic compounds with a wider range of applications. Alloys and intermetallic compounds may be binary, ternary, quaternary, and more complicated systems. The class of alloys capable of storing hydrogen is also known as hydrogen storage alloys (HSA). The major binary IMC systems used as HSA are AB_5 ($LaNi_5$), AB_2 ($TiMn_2$), A_2B (Mg_2Ni) and AB ($TiFe$) (Table 1). The few other classes are A_3B (Nb_3Sn), AB_3 ($LaNi_3$), A_2B_7 (Nd_2Ni_7), A_2B_{17} (La_2Mg_{17}), A_6B_{23} (Ho_6Fe_{23}) etc. There may be more than one stable crystal structure for each system. The characteristics of the binary IMC may not be always available for a particular application. In such cases, partial substitution at A, B or both sites with elements containing the same or the similar number of outer shell electrons can be done. This substitution may specifically tailor the IMC for required hydrogenation properties (Table 2). One more popular

metal hydride corresponds to vanadium-based solid solution. In the following, each class of IMC and their progress (Figure 5) will be discussed one by one.

6.1. AB_5 system

It is the most easily operated intermetallic compound with the application at ambient conditions. In the AB_5 system, A usually comes from the rare earth (lanthanide) elements (at. no. 57-71) including Ca and B is a transition element basically Ni. It is synthesized through vacuum induction melting. This type of intermetallic compound is very brittle and easily reduced to the granular or powder form to fill hydride containers. The hydrogen storage capacity of $LaNi_5$ corresponds to 1.4 wt% with plateau pressure ~ 0.5 MPa. The heat of formation of $LaNi_5H_7$ is 7.3 kcal per mol H_2 [47].

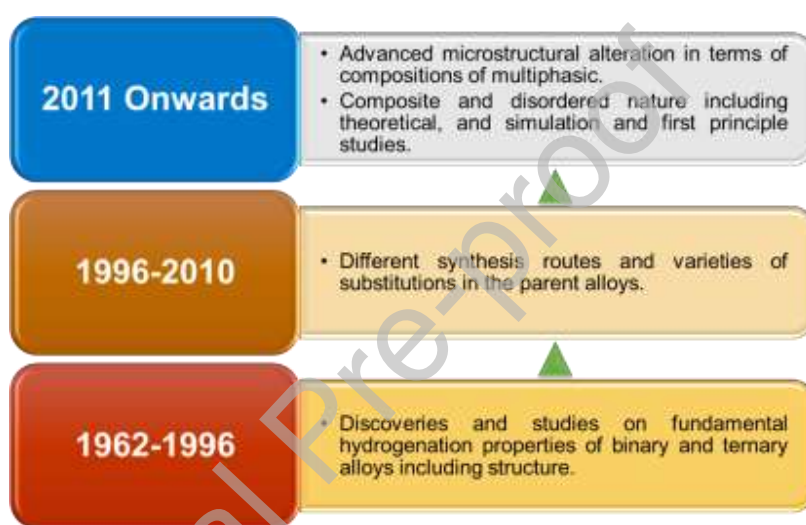


Figure 5. Progress in metal hydride-based research.

6.1.1. Crystal structure

AB_5 -type IMCs have $CaCu_5$ -type hexagonal structure with space group $P6/mmm$. Here the unit cell is hexagonal with one formula unit per cell. The calcium atoms occupy the positions (0,0,0) and copper atoms are found at positions (1/3, 2/3,0), (2/3, 1/3, 0), (1/2, 0, 1/2), (0, 1/2, 1/2) and (1/2, 1/2, 1/2) [48]. The representative compound of this family corresponds to $LaNi_5$. The $CaCu_5$ -type of structure is relatively common in AB_5 compounds when the atomic diameter of the B atom is smaller than that of the A atom. It happens within a range of radius ratio r_A/r_B from 1.3014 ($NbBe_5$) to 1.7656 ($RbAu_5$). In this hexagonal structure, the lanthanum atoms occupy the 1a crystallographic site in the basal plane, while the nickel atoms occupy the 2c site in the basal (N_I) and the 3g site in the $Z=1/2$ plane (N_{II}). Each lanthanum atom is surrounded by six lanthanum atoms in the basal plane at distances of 5.01 Å and by two lanthanum atoms in the c-direction located at about 3.98 Å. These La-La distances are to be compared with d_{La-La} : 3.75 Å in the pure fcc lanthanum lattice. The N_{II} atoms are surrounded by four N_{II} atoms at 2.46 Å, four N_I atoms ($d_{N_{II}-N_I} = 2.508$ Å) and four lanthanum atoms ($d_{N_{II}-La} = 3.202$ Å). It should be noted that these Ni-Ni distances are comparable with $d_{Ni-Ni} = 2.45$ Å in the fcc nickel lattice in which the coordination number is 12, thus much larger than in $LaNi_5$. There are in total 34 tetrahedral

holes in one AB_5 unit [49]. These are B_4 tetrahedral holes (4 in subgroup 4h), AB_3 tetrahedral holes Type I (12 in subgroup 12o), AB_3 tetrahedral holes Type II (12 in subgroup 12n), A_2B_2 tetrahedral holes (12 in subgroup 12n). In the hexagonal AB_5 structure, 9 sites are most probable for hydrogen occupancy.

- i. 3 clusters of 4 type-II AB_3 holes, centroids with subgroup 3f (H_I site)
- ii. 6 clusters of 1 A_2B_2 hole and 2 type-I AB_3 holes, centroids with subgroup 6m (H_{II} site)

Table 1. Types of metal hydrides.

S.N.	Class	Crystal structure	Representative compound					
			Composition	Hydrogen Storage capacity wt%	Plateau pressure (MPa)	Operating temperature °C	Heat of hydride formation kcal (mol H ₂) ⁻¹	
1	AB ₅	Hexagonal	CaCu ₅	LaNi ₅	1.5	0.5	Room temperature	7.3
2	AB ₂	C14 Hexagonal		TiMn ₂	2.0	1.4	Room temperature	7.2
3	A ₂ B	C16 Hexagonal		Mg ₂ Ni	3.8	0.1	300	15.3
4	AB	BCC		FeTi	1.9	0.5	40	6.7
5	Solid Solution (SS)	BCC	(V _{0.9} Ti _{0.1}) _{0.95} Fe _{0.05}		1.8	0.05	25	10.3

Table 2. Comparison of hydrogenation properties of metal hydrides.

Activation	AB ₅	>	AB ₂	>	SS	>	A ₂ B	>	AB
Kinetics	AB ₅	>	AB ₂	>	SS	>	A ₂ B	>	AB
Cyclic stability	AB ₂	>	SS	>	AB ₅	>	AB	>	A ₂ B
Cost	AB ₅	>	AB ₂	>	SS	>	A ₂ B	>	AB
Reversible hydrogen storage capacity	AB ₂	>	AB	>	SS	>	A ₂ B	>	AB ₅
Operating conditions	AB ₅	>	AB ₂	>	SS	>	AB	>	A ₂ B
Sensitivity to impurity	AB	>	A ₂ B	>	SS	>	AB ₅	>	AB ₂

6.1.2. Discovery

AB₅ IMC was accidentally discovered at the Philips Eindhoven Labs about 1969 during work on AB₅ permanent magnet materials SmCo₅ [50]. To study the positions of the H-atoms in SmCo₅ hydride by NMR, AB₅ compound LaNi₅ was selected. The reaction of LaNi₅ with H₂ was remarkable compared to SmCo₅ [51]. The reversible hydrogenation was confirmed with H/M>1 at ambient temperature at a pressure of less than 2.5 atm. Low hysteresis and fast kinetics were observed and LaNi₅ could also be easily activated at room temperature. Thus, a new and exciting hydrogen storage alloy LaNi₅ was discovered. Later on its cost-effective version, MmNi₅ evolved. Mm represents an unrefined rare earth mixture commonly known as mischmetal. Mm usually contains the four main rare earth elements Ce, La, Nd and Pr. The actual composition of mischmetal depends on the mineral and ore body from which it is derived. The typical composition (in weight %) corresponds to 48-50 % Ce, 32-34 % La, 13-14 % Nd, 4-5 % Pr and 1.5 % other rare earth. MmNi₅ had been synthesized in early 1973 at Brookhaven National Lab for H₂ separation trials and a high-pressure H₂ source tank [52]. The choice of Mm for La results in very high plateau pressures and hysteresis. This may be adjusted by substitution at Mm and Ni.

6.1.3. Development

For lowering the high hysteresis and high plateau pressure, initially, partial ternary substitutions were done to both the Mm and Ni sides of MmNi₅ [53-54]. At the B site other transition elements were tried as Al, Fe, Co, Si, Mn etc. [55-60]. Almost up to 2010 AB₅-type compounds were investigated for ternary substitutions at A, B and both sites for the study of their basic hydrogenation characteristics. The earlier study was focused on material development for NiMH cells and storage purposes. Within the last decade many more applications have been coming forward. To accommodate all these applications, the trends of multi-element substitutions have increased. The nano version of the compound and the mixing of alloys were also tried by researchers. A computer simulation study has thrown new insights at the understanding level.

The substitution at the B site is more common and has more options. Each substituted elements plays a specific role in hydrogenation properties according to the specific application. The substitution of Al at the Ni site lowers the plateau pressure of MmNi₅ from 1.4 MPa to around 0.2 MPa [61-62]. Mn and Si are substituted for improvement in cyclic performance [63-65]. Co stops the corrosion of metal hydride electrodes [66-67]. To improve the hydrogenation properties, melt-spun versions of IMC were also studied, which resulted in improved kinetics [68-70]. Melt-spun versions reflected higher storage capacity, fast kinetics, and fast activation in comparison to conventional induction melting. It has been noticed that more substitution at the Ni site reduces the hydrogen storage capacity of the parent alloy from 1.4 wt% to 1.0 wt% [68-70]. Fe substitution has a reverse effect on hydrogen storage capacity. It increases the storage capacity due to the presence of unfilled d-orbital [71]. The Ca substitution at A site is also known to enhance the storage capacity because of its lightweight [72]. However, the plateau pressure has been noticed to increase drastically. To lower this high plateau pressure simultaneous substitution was done at the Ni site also by Al and Fe. A series of IMCs were studied on Ca substitution [73-74]. High hydrogen storage capacity of 2.2 wt% was reported following the composite pellet formation route for the synthesis of the alloy. The multiphasic alloys have shown enhancements in all the hydrogenation characteristics of the LaNi₅ alloy with a major phase of LaNi₅ and minor phases of LaNi₃ and La₂Ni₇ [75-78].

Nowadays multi-element substitutions are preferred to achieve the required properties for specific applications [79-81]. Especially in Ni-MH electrode material, various substitutions are done at Ni sites, with the roles of each element. Such multi-element substitutions give stability to the electrode in alkaline electrolyte and lessen the pulverization, thus increasing cyclic stability with enhanced energy density [82-85].

In the recent decades, the nano-version of alloys has shown improvement in hydrogenation properties due to the larger surface area exposed to the hydrogen. This is achieved through mechanical alloying or ball-milling of the bulk synthesized alloy [86-89]. Ball-milling has resulted in improved hydrogen storage capacity with fast activation process and fast kinetics [90]. The use of a catalysts during ball milling has been found to improve the hydrogenation properties further [91-95]. Widely used catalyst in AB_5 compound corresponds to transition elements. Catalysts are known to favor hydrogen molecule dissociation and more entrance channel for hydrogen atom diffusion into the material at interstitial sites.

Several theoretical calculations and simulations works were also performed to expose the researchers to a better understanding of properties. Density functional theory has been proven to reveal information about energy levels and the positions occupied by hydrogen in the metal hydride [45; 80; 96-97]. Theoretical models have been developed to predict the heat of formation, structural properties, and electronic properties [44; 98-104]. Recently AB_5 -type IMCs have been applied in many new applications like actuators [105] and thermal management systems [106]. $LaNi_5$ has been reported in other forms as well for hydrogen storage purposes. Spray-dried composite microparticles of polyetherimide and $LaNi_5$ have been studied as versatile materials for hydrogen storage applications [107]. $LaNi_5$ has shown an excellent catalytic effect on the hydrogen storage properties of aluminum hydride at mild temperatures [108]. Hydrogen absorption by ~ 5 kg $LaNi_5$ has been studied in a metal hydride reactor through simulation studies to show that 290 and 375 s are required for 80% and 90% hydrogen storage saturation level in the reactor, respectively [109]. A monolayer model treated by statistical physics was applied employing the grand canonical ensemble to describe P-C-T isotherms for absorption of hydrogen by $LaNi_{3.6}Mn_{0.3}Al_{0.4}Co_{0.7}$ alloy to correlate with the experimental results [110].

6.2. AB_2 System

The A elements in the AB_2 system are from the IVA group (Ti, Zr, Hf) and/or rare earth series (at. no. 57-71) or Th. The B-elements can be a variety of transition or non-transition metals with a preference for atomic numbers 23-26 (V, Cr, Mn, Fe). In this system also, a wide variety of substitutions are possible for both A- and B-elements. Substitutions may help in developing materials with hydrogenation properties for specific requirements.

6.2.1. Crystal structure

The class of practical AB_2 intermetallic compounds for hydrogenation purposes belongs to the Laves phase. Laves phase structures have three varieties: C14, C15 and C36 [111]. The C14 and C15 are the most important structures. The C14 phase has hexagonal structure, with 4 AB_2 formula units per equivalent trigonal unit cell (4 A-atoms and 8 B-atoms). A representative hydriding C14 phase is $ZrMn_2$. The C15 phase has a cubic structure with eight AB_2 formula units per unit cell (8 A-atoms and 16 B-atoms). A representative C15 hydriding phase is ZrV_2 . In both cases, H-atoms tend to occupy $[A_2B_2]$ tetrahedral interstices [112]. The AB_2 intermetallics may have some homogeneity range (i.e., A: B need not be exactly 1:2), unlike the AB_5 line

compounds. ZrMn_2 and ZrV_2 have hydrogen storage capacities of 1.0 and 2.1 wt% respectively [113]. The heat of the formation of hydrides of ZrMn_2 and ZrV_2 have values close to 12.7 and 35.9 kcal per mole H_2 [114-115].

6.2.2. History

The first intentionally studied report on AB_2 intermetallic compounds is the formation of two AB_2 hydrides: $\text{ZrCr}_2\text{H}_{3.6}$ and $\text{ZrV}_2\text{H}_{4.14}$ [116]. This early study was focused mostly on high temperature ($>538^\circ\text{C}$) properties. Several years later the 1956 report of Trezeciak et al [116], a major pioneering hydriding survey of many binary intermetallic compounds was reported by Beck in 1962 [113]. However, AB_2 hydride activity was virtually dormant for the next decade and became quite active at several laboratories in the late 1970s.

6.2.3. Development

In the AB_2 system hydrogen storage capacities are not much if heavy A-atoms are incorporated (e.g., the rare earth elements or Zr). Using the lighter Ti as the A-element helps with a higher weight per cent of hydrogen storage capacity [117]. The practically popular alloy of the AB_2 class is TiMn_2 having a C14 structure. Plateau pressure, hydrogen storage capacity and other properties can be adjusted by substituting Zr for Ti and Cr for Mn. Zr substitution decreases the plateau pressure and storage capacity [118]. For this alloy, plateau pressure is 1.4 MPa with a hydrogen storage capacity of 2.0 wt%. Several studies have been reported on the substitution of Ti with Zr and the substitution of Mn with Co, Cu, V, Fe, Ni and Cr. The hydrogen storage capacity for these alloys corresponds to 1.5 to 2.0 wt%, while plateau pressure is below 1.0 MPa at ambient temperature. Sometimes a multi plateau is also seen in this system. $\text{TiMn}_{1.5}$ and $\text{Ti}_{0.98}\text{Zr}_{0.02}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ are popular compositions in the AB_2 system [119-122].

Melt-spun alloys have been prepared to improve the hydrogenation properties and electrochemical properties for application in Ni-MH cells [123-124]. High catalytic activity disorder in multi-component alloys has also been shown to improve the electrochemical capacity of 440 mAhg^{-1} [125]. It has been reported that the hydrogen absorption capacity of the TiMn_2 -based alloys is mainly governed by the atomic composition and atomic arrangement of the alloy within the TiMn_2 phase [124]. The degradation of the cyclic property of the alloy actively depends on the substituted elements in the hexagonal TiMn_2 Laves phase [126]. Centrifugal casting and gas atomization processes were applied to multiple-phase AB_2 alloys by Young et al. [127]. They reported that the centrifugal casting process provided the better cycle life. The gas atomization process has lower production cost but suffers from higher bulk oxygen content and thicker surface oxide, and thus inferior in all battery performance characteristics other than cycle life and charge retention. Various changes in the structure incorporated through phase abundance, defect and off stoichiometric have direct effects on the hydrogenation characteristics of the AB_2 alloy [128-130]. Phase abundance has shown higher gas phase and electrochemical storage capacities, lowering of the hydrogen equilibrium pressure, decrease in the half-cell high rate dischargeability, improvement of both charge retention and cycle life [105]. Defect in C15 $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{V}_2$ alloy improved the hydrogen absorption-desorption properties [106].

In a separate study carried out by Kazemipour et al. $\text{Ti}_{0.72}\text{Zr}_{0.28}\text{Mn}_{1.6}\text{V}_{0.4}$ alloy was synthesized using mechanical alloying and innovative vacuum copper boat induction melting. They showed that the samples consisted of two main phases, the C14 Lave phase and the V-base solid solution phase. The hydrogen capacity of the induction melted samples was higher than that of the

samples produced by the mechanical alloying method [131]. Studies through density functional theory on the total energy, electronic structure and bond of $\text{Zr}(\text{Cr}_{0.5}\text{Ni}_{0.5})_2$ alloy and its hydrides showed that A_2B_2 sites are preferentially occupied in the structure, followed by the AB_3 while B_4 remains empty. Among hydrogenations, the main contribution to the density of states is due to the d electrons of all components of the structure [132]. TiMn_2 has been reported to enhance the hydrogenation properties of MgH_2 nanocomposites synthesized through reactive ball-milling [133]. Several recent studies have pointed out the effective application of AB_2 alloys in electrochemical storage, compressor, and easy activation for storage purposes [134-135]. High entropy alloy has further enhanced the electrochemical capacity [136]. Qin et al. devoted their studies to demonstrating that ZrFe_2 -based alloys with a small Ga or Al substitution are suitable for high-pressure hydrogen storage applications [137]. Few researchers reported the hydrogenation characteristics of AB_2 alloys based on machine learning [138-139].

Normally freshly crushed AB_2 materials activate at room temperature. Sometimes heating at a few 100° C temperatures in a hydrogen atmosphere is needed for activation. The kinetics of hydrogen absorption-desorption is high. The intrinsic kinetics is faster than the heat transfer [97]. Less than 5% of capacity loss was seen in commercial alloy $\text{Ti}_{0.98}\text{Zr}_{0.02}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ during 2000 absorption-desorption cycles with high purity H_2 (0.1-5.0 MPa, 20-80°C) [97]. The AB_2 s are considerably less expensive than the AB_5 s.

6.3. A_2B system

In the A_2B system, PCT data does not fall in the 0-100°C temperature range and 0.1-1.0 MPa pressure range for most of the IMC of this class. Hence it is less useful for ambient condition applications. Mg_2Ni is the representative hydride phase with an H/M value of 1.33, a hydrogen storage capacity of 3.6wt%, 15.4 Kcal (mol H_2)⁻¹ heat of hydride formation 0.32 MPa plateau pressure at the temperature of 299°C [140].

6.3.1. Structure

Mg_2Ni has an Al_2Cu -type C16 hexagonal structure. It may be noted that Mg_2NiH_4 is not a metallic hydride in the sense of the other intermetallic compounds [141]. It is a more complicated hydride. Mg_2NiH_4 is not an interstitial hydride. Here Mg donates electrons to stabilize an $[\text{NiH}_4]^{-4}$ complex. 4 hydrogen atoms are bonded with a single Ni atom and the two electrons are donated by two Mg atoms each to stabilize the $[\text{NiH}_4]^{-4}$ transition metal complex. The structure of Mg_2NiH_4 is quite different from the starting Mg_2Ni structure. Mg_2FeH_6 and Mg_2CoH_5 A_2B stoichiometries are present only as hydride complexes. Mg_2Fe and Mg_2Co phases do not exist without hydrogen in the binary metal systems.

6.3.2. History

Historically Mg_2Ni was one of the earliest intermetallic compounds that were reported to be usable as a rechargeable hydride [118]. Mg_2Ni can absorb up to 3.8 wt% hydrogens [142]. This capacity is very large in comparison to AB_5 and AB_2 -type alloys [143]. Ni is known to improve the hydrogenation absorption-desorption capacity of Mg [144]. During reaction with Mg, Ni forms Mg_2Ni and MgNi_2 alloy. MgNi_2 alloy does not absorb hydrogen, but Mg_2Ni absorbs a good quantity of hydrogen.

6.3.3. Development

The A_2B system has desorption pressure usually less than 0.1 MPa. To increase the desorption pressure various substitutions have been done at the A and B sites. Partial substitution of Al for Mg and Zn for Ni does lower the desorption temperatures of Mg_2Ni a little, but it is difficult to reach the pressure of 0.1 MPa at 100°C [145]. The metallurgy and the basic chemistry of the hydrides of A_2B systems are fundamentally different compared to the AB_5 , AB_2 and AB families. Together with the principal plateaux at very low pressures, Zr_2Pd , Hf_2Pd and Hf_2Cu have additional plateaux at very high pressures (100 MPa) at room temperature [146]. These interesting intermetallics have the "non-close-packed" tetragonal Cl_{1b} $MoSi_2$ structure with various available interstitial sites [147]. The additional plateaux cover about 0.3-0.6 H/M, i.e., a relatively small part of the maximum capacity. Generally During the synthesis of Mg_2Ni final product is typically a three-phase mixture of Mg_2Ni , $MgNi_2$ and Mg. It may be noted that the $MgNi_2$ phase does not hydride. Hence the alloy is usually melted to slightly higher Mg levels than the stoichiometric Mg_2Ni . Single-phase Mg_2Ni can be made by mechanical alloying (high-energy ball milling) of elemental Mg and Ni powders [148] and by the reaction of Ni powder with Mg vapor [149].

Zaluski et al. reported on the synthesis of Mg_2Ni through mechanical alloying using a high energy ball mill to enhance the kinetic and activation properties [150]. In a similar work reported by Singh et al., the nano version of Mg_2Ni alloy prepared through ball milling has been found to show easy activation by annealing at 300 °C in a vacuum for 30 min [151]. Mechanical alloying has also revealed the enhancement in hydrogen diffusion and charge transfer reaction [152]. In a separate work on ternary $Mg_2Ni_{0.75}M_{0.25}$ ($M=Ti, Cr, Mn, Fe, Co, Cu$ and Zn) alloys synthesized by the ball milling; hydrogen desorption capacity reached the highest value after only two adsorption-desorption cycles after fluorination treatment [153]. In these alloys, 3.3 wt.% hydrogen desorption was measured at 250°C. Replacement of Ni by Cr, Mn and Co has lowered the decomposition plateau pressure; while Ti and Cu had the opposite effect and Fe and Zn had little effect. Mg_2Ni and Mg_2NiH_4 have been reported showing the catalytic effects on the hydrogen desorption characteristics of MgH_2 [154]. The catalytic efficiency of Mg_2NiH_4 was found considerably higher than pure Ni and Mg_2Ni phase. Cr doping to result in the alloy $Mg_2Ni_{0.9}Cr_{0.1}$ showed stable absorption capacity, and improvement in absorption/desorption rates after cycling [155]. The use of MWCNTs coupled with TiF_3 during the ball milling process has improved the hydrogen desorption property of Mg_2NiH_4 reasonably [156]. It was noticed that in the presence of above-mentioned catalysts, the dehydrogenation temperature, and the activation energy of Mg_2NiH_4 were reduced to 230°C from 244°C and 53.24 kJ/mol from 90.13 kJ/mol respectively. Hence the addition of proper catalysts has been proven to be an effective strategy to decrease the desorption temperature and activation energy of Mg_2NiH_4 hydrides.

Studies on the first-principle calculation have been performed to evaluate the hydrogen absorption energy on the Mg_2Ni surface and in the bulk alloy [157]. Reduction in hydrogen absorption enthalpy was observed through an ab initio study by substitution of Al, Ga, In, Si, Ge and Sn at the Ni site in Mg_2Ni alloy [158]. Mg_2NiH_4 powder was used for hydrogen generation via hydrolysis reaction in different types of solutions. The extremely intense hydrogen kinetics was observed using an acidic solution [159]. Moreover, Mg_2NiH_4 powder stored for two months disclosed almost identical hydrogen generation volume as as-received Mg_2NiH_4 powder. The hydrolysis reaction between Mg_2NiH_4 and the acidic solution was also applied for electricity production via the PEM fuel cell. Vanadium doping in Mg_2Ni during the ball milling process has

resulted in improved hydrogenation-dehydrogenation kinetics with extended plateau region as compared to pure-Mg₂Ni [160]. A few other A₂B-type alloys have also been reported for hydrogen absorption properties. Partial substitution of Mo for Ti increased the hydrogen storage capacity to 2.23 wt%. It was due to decreased dihydride stability after Mo substitution [161]. Density functional theory calculations have been employed to study the improvement in the adsorption, dissociation and diffusion of hydrogen on the Zr₂Fe(101) surface through Mn doping [162]. Zn substitution in Mg₂Ni alloy for Ni has shown a lowering in the activation energy as 17.01 kJ/mol in comparison to 46.07 kJ/mol for the Zn-free Mg₂Ni. The equilibrium hydrogen pressure in the PCT curve of alloys was increased with increasing Zn content [163].

6.4. AB system

Most of the practical AB compounds are based on TiFe and therefore represent low raw materials costs. They are historically important to the early development of ambient temperature hydrides and their application to the first H₂-fueled vehicles.

6.4.1. Crystal structure

The common AB structure corresponds to B1 CrB-type structure. Among AB compounds, practically applied alloys have simple B2 structure. It has a body-centred-cubic cell with one formula unit per unit cell. One A-atom is shared by the cell corners and one B-atom resides at the centre of the cubic cell. Each cell contains 12 tetrahedral and 6 octahedral interstices. H atoms occupy only the octahedral sites with the preference of [Ti₄Fe₂] co-ordination. [Ti₂Fe₄] octahedral sites may also be filled at high H/M value [164].

6.4.2. History

The first member of the AB hydride group was reported as ZrNi in 1958 as reversible hydride ZrNiH₃ desorption plateau pressure of 0.1MPa at 300°C [165]. This material was not studied for one more decade due to the high temperature of 300°C. The first practical room-temperature AB hydride was TiFe, discovered at Brookhaven National Lab in the U.S. around 1969 [166]. Two distinct hydrides (TiFeH and TiFeH_{1.95}) resulted in two separate plateaus. In this class, most of the members have multi-plateau PCT curves.

6.4.3. Development

TiFe has a hydrogen storage capacity of 1.9 wt%, the heat of hydride formation is 6.72 Kcal(mol H₂)⁻¹ and plateau pressure of 0.5 MPa at 40°C. In the AB system useful IMC are ZrNi, TiFe and TiCo, among which TiFe is the most popular one [167-168]. In TiFe IMC Zr can be partially substituted for Ti and Mn, Ni, V, Nb and Si can be substituted for Fe [169-171]. TiFe and TiFe_{0.85}Mn_{0.15} were the best-reported compounds during 1990 in the AB metal hydride system.

Chiang et al. studied the hydrogenation properties of TiFe, TiFe₂ and pure Ti during high-energy ball milling in a hydrogen atmosphere. Through ball milling, TiFe could absorb hydrogen without activation treatment [172]. To overcome the deterioration of the hydrogen absorption performances of TiFe-based hydrogen storage materials, surface modifications have been reported by the deposition of metals (including Palladium). This technique facilitated the hydrogenation of the material even after its exposure to air [173]. Benyelloul et al. found that the insertion of hydrogen into the FeTi crystal structure causes an increase in the bulk modulus. Using density functional theory they observed that the FeTi compound and its hydrides are

ductile and that this ductility changes with changing the concentration of hydrogen [174]. In separate research, plastic deformation created in intermetallics of TiFe using groove rolling and high-pressure torsion has resulted in 1.7-2 wt% of hydrogen absorption in the first few cycles thus improving the activation process significantly [175]. The samples were not deactivated by long-time exposure to the air. To further improve the activation process and hydrogen storage capacity Cu and Y were incorporated in Ti-Fe-Mn alloy as $\text{Ti}_{0.95}\text{Y}_{0.05}\text{Fe}_{0.86}\text{Mn}_{0.05}\text{Cu}_{0.05}$ [176]. The melted alloy had a TiFe matrix with a Cu_2Y secondary phase. The addition of element Y enhanced the hydrogen storage capacity as 1.85 wt% at 20°C. The activation and kinetic properties of the hydrogenated alloy were improved due to the presence of the secondary phase Cu_2Y . Due to its lightweight and low-cost TiFe was compared with LaNi_5 for their application in metal hydride beds [177]. Heat exchange was higher in the TiFe bed as compared to LaNi_5 filled in a similar tank. Silva et al. reported their work on Mg - 40 wt % TiFe nanocomposite prepared by high-energy ball milling. This process has improved hydrogen absorption at room temperature [178]. To produce active nanocrystalline TiFe compound TiH_2 and Fe powders were dry co-milled in a planetary ball mill for 5-40 h [179]. All samples absorbed hydrogen at 2 MPa without additional thermal activation cycles. Milling for shorter time of 10 h resulted in easy hydrogen absorption during the first cycle. However, the samples milled for longer times (25 and 40 h) have shown better results in terms of reversible and storage capacities (0.73 and 0.94 wt.%, respectively). In separate research carried out by Lv et al. hydrogen storage properties of air exposed $\text{TiFe} + x \text{ wt.}\% (\text{Zr}+2\text{V})$ ($x = 0, 4, 5$ and 6) alloys were studied [180]. Doped samples had bcc TiFe main phase and hcp secondary phase. The samples showed the fastest hydrogenation kinetics, highest hydrogen capacity and good cycling stability corresponding to $x=4$.

Another report focused on the effect of air exposure on the first hydrogenation kinetics of $\text{TiFe} + 4 \text{ wt}\% \text{ Zr} + 2 \text{ wt}\% \text{ Mn}$ alloy [181]. In this study researchers observed that the air-exposed alloy could be successfully hydrogenated after ball milling and after cold rolling with some loss in hydrogen storage capacity. To improve the hydrogen storage performances of TiFe-based alloys, $\text{TiFe}_{0.8-m}\text{Ni}_{0.2}\text{Co}_m$ ($m = 0, 0.03, 0.05$ and 0.1) alloys were synthesized. All the alloys were composed of the majority phase of TiFe and the non-hydrogenated phase of Ti_2Fe . The secondary phase favoured the lowering of activation temperature [182]. Zeaiter et al. have reported the effect of mechanical milling on the morphological, structural and hydrogen sorption properties of powdered $\text{TiFe}_{0.9}\text{Mn}_{0.1}$ alloy [183]. Ball milling has lowered the activation temperature and increased the hydride stability with a sloppy plateau in the PCT curve. Mn in TiFe alloy acted as a sacrificial element to prevent the bulk oxidation of alloys [184]. A very interesting study was reported by Patel et al. on the easy activation of TiFe alloy at room temperature [185]. They showed that the chunks of the alloy under hydrogen pressure can be activated without any additional grinding media. They termed their process as self-shearing reactive milling and observed the full hydrogenation of FeTi alloys. In another study, TiFeMn has been reported as a useful metal hydride for forklifts using numerical simulation [186]. The density functional theory studies made on hydrogen adsorption over TiFe surface and doped TiFe surface reflected that even a very small amount of dopant can influence the hydrogen adsorption properties of TiFe alloy [187].

Density functional theory calculations were applied to investigate the effect of Al, Be, Co, Cr, Cu, Mn and Ni in the TiFe system. Enthalpy of formation was approximated in terms of changes in lattice parameters without the need for Van't Hoff plot [188]. $\text{TiFe}_{0.85}\text{Mn}_{0.05}$ alloy has been

applied as a hydrogen carrier for an industrial hydrogen storage plant of about 50 kg of hydrogen [189]. In general, TiFe is very difficult to activate. It needs heating at a higher temperature of 300-400 °C for activation to break the oxygen layer present at the surface. The intrinsic kinetics of TiFe and related alloys are slower than the AB₅ compound, but heat transfer is rapid.

6.5. Solid Solution Alloy Hydrides

The term "solid solution alloy" designates a primary element used as a solvent into which one or more minor elements in form of solutes are dissolved. In the case of a solid solution, the solute need not be present at an integer or near-integer stoichiometric for the solvent. This feature is entirely different from the intermetallic compounds discussed here. The solute is present in a random (non-ordered) substitutional or interstitial distribution within the basic crystal structure. Various solid solution alloys have been reported as reversible hydrides, in particular, those based on the solvents Pd, Ti, Zr, Nb and V. Pd, Ti and Zr Solid Solutions represent the largest family of solid solution hydrides consisting of the face-centered-cubic (A1)Pd-based alloys. Many of the Pd solid solution alloys have PCT properties within the range of 0.1-1.0 MPa at 0-100°C with a low hydrogen storage capacity of 1.0 wt.%, but they are costly.

Hydrides of Ti- and Zr-base solid solution alloys are very stable. Nb and V solid solutions have simple body-centred cubic (A2) crystal structures and their dihydrides generally form a face-centered cubic structure. In vanadium-based solid solution various elements Ni, Cr, Fe, Mo, Ge, Si, Sn, Ti, Mn and Zr were used [190]. A representative alloy (V_{0.9}Ti_{0.1})_{0.95}Fe_{0.05} was reported with PCT properties as 0.05 MPa pressure at 25°C, the heat of hydride formation as 10.3 kcal(mol H₂)⁻¹ with a hydrogen storage capacity of 3.7 wt% and reversible capacity of 1.8 wt% [191].

Investigations were made on the interaction of hydrogen for the mechanochemically synthesised composition of Ti₄₅Zr₃₈Ni₁₇ solid solution alloy. The hydrogenation in this alloy started in the very first cycle even at a hydrogen pressure of less than 0.1 MPa [192]. Gao et al. studied the pulverization mechanism of the multiphase Ti-V-based hydrogen storage alloy consisting of a V-based solid solution phase of the BCC structure and a C14 Laves phase of the composition Ti_{0.8}Zr_{0.2}V_{2.7}Mn_{0.5}Cr_{0.6}Ni_{1.25}Fe_{0.2} alloy [193]. Fe substitution in hydrogen storage alloy Ti₁₂Cr₂₃V₆₅ leading to the composition Ti₁₂Cr₂₃V₆₄Fe₁ resulted in the increase of the lattice strain and the decrease of the crystallite size by hydrogen absorption and desorption thus improving the cyclic durability [194]. Ti₅₂V₁₂Cr₃₆ alloy was investigated by Kamble et al. for the first hydrogenation cycle [195]. They observed that doping of 4% Zr and reduced particle size had a direct effect on lowering the incubation time. In separate research, studies were performed on microstructural details of hydrogen diffusion and storage in Ti₂₅V₅₀Cr₂₅ and Ti₁₀V₇₅Cr₁₅ alloys activated through the surface and bulk severe plastic deformation [196]. Liu et al. have correlated the order of entropy of alloy with hydrogen absorption and reversible hydrogen desorption capacity on the alloys V₃₅Ti₃₀Cr₂₅Fe₁₀, V₃₅Ti₃₀Cr₂₅Mn₁₀, V₃₀Ti₃₀Cr₂₅Fe₁₀Nb₅ and V₃₅Ti₃₀Cr₂₅Fe₅Mn₅ [197]. The partial substitution with niobium and iron in Ti₂₅Cr₅₀V₂₅ hydrogen storage alloy increased the cyclic durability of the alloy [198]. In high entropy alloy TiVZrHfNb, it was observed that lower particle size had affected improving the kinetics of hydrogen absorption-desorption, while higher temperature decreased the incubation time for activation [199]. The hydrogen storage alloy specified by the composition Ti_{10+x}V_{80-x}Fe₆Zr₄ (x = 0, 5, 10, 15) resulted in the lowest incubation time of 12s and the highest storage capacity of 3.6 wt% [200]. High entropy equiatomic intermetallic alloy TiZrVCrNi has shown a stable reversible

hydrogen storage capacity of 1.52 wt% [201]. A hydrogen storage capacity of 3.5 and 6 wt % H_2 was noticed in nearly equimolar alloys TiVCrMo and TiZrNbH with Mg addition [202].

The disordered and amorphous materials have certain more specific advantages in context to hydrogenation characteristics. A disordered material lacks long-range order in both composition and structure. Such disordered and multiphasic materials lie in between crystal and amorphous materials. Due to the increasing degree of disorder in the metal hydride following

trends in hydrogenation characteristics may be observed:

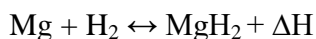
- The hydrogen storage capacity may increase.
- The plateau region in the pressure–concentration isotherm becomes short and slanted.
- Lattice expansion upon hydrogenation becomes less and results in less pulverization during hydride/dehydride cycling.
- In disordered material more surface-active sites are available to facilitate chemical/electrochemical reactions.

6.6. Metal Hydrides - Summary

Thus, metal hydrides offer varieties of materials for hydrogen storage and their applications accordingly. All the classes of metal hydrides may be summarized as given in Table 1. Different classes of metal hydrides have different hydrogenation characteristics. Some have high storage capacity, while others may have easy activation at ambient conditions. A comparison of important hydrogenation properties among metal hydrides is presented in Table 2. Hence, based on the requirement of specific properties, metal hydrides may be chosen for applications. The metal hydride-based research development has been completed for almost 60 years (1962-1995). These 60 years may be divided into three phases of progress (Figure 2). The first or early phase within the time range 1962-1995 includes the discovery and studies on fundamental hydrogenation properties like pressure-composition isotherm, hydrogen absorption-desorption kinetics, hydrogen storage capacity, the heat of formation, the structure of parent member and their ternary counterparts. In the middle phase (1996-2010) investigations were focused on the adoption of different synthesis routes mainly ball-milling, reactive ball-milling, melt-spinning etc. with emphasis on varieties of substitutions in the parent alloy. The present ongoing era (2011 onwards) is the witness to advanced microstructural alteration in terms of composition and structure. Nowadays multi-element compositions of multiphasic, composite, and disordered nature are preferred over simple parent alloys. Various theoretical, simulation and first principle calculations based on density functional theory have also come forward. The research on metal hydrides had some recession within the time frame of 2014-2020 due to their less hydrogen storage capacity in comparison to complex hydrides. But the ease of operation at normal temperature and pressure has proven metal hydrides as more feasible candidates for application point of view. Therefore, the research on metal hydrides has again gained a boom for the last few years.

7. Magnesium-Based and Related Systems

Magnesium (the 7th most abundant element in the crust of the Earth with an abundance of 2.3%) and hydrogen (the universe's most common element) reacts together and form the stable magnesium hydride (MgH₂).



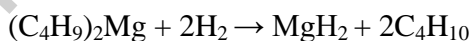
Where, ΔH is the enthalpy of reaction, describing the thermodynamic stability of hydride. The theoretical gravimetric and volumetric hydrogen content of MgH₂ is 7.6 wt.% and 110 kgm⁻³, respectively. This is at par with the required US-DOE target for onboard storage of hydrogen for vehicular applications [203]. Due to this high gravimetric and volumetric hydrogen density, MgH₂ is considered as a potential candidate for solid state hydrogen storage. However, the high thermodynamic stability of MgH₂ (enthalpy and entropy values are 74.7 kJ mol⁻¹ and 130 JK⁻¹mol⁻¹) hinders its hydrogen release/absorption (de-/hydrogenation) kinetics at low temperatures [204]. This is due to the fact that the bonding of hydrogen in MgH₂ is partially ionic and partially covalent in nature [205]. Moreover, the factors affecting the de-/hydrogenation behavior of MgH₂ are (i) surface oxide layer formation, (ii) slow hydrogen diffusion rate in the bulk Mg, (iii) poor hydrogen chemisorption on Mg, and (iv) low thermal conductivity [206]. Till date, researchers have adopted several strategies to improve MgH₂'s hydrogen storage properties and achieved significant improvement. Methods such as (i) nanostructuring; reduction of grain size providing shorter diffusion path for hydrogen [207-208] (ii) mechanical alloying; destabilize the hydride phase by alloy formation [209] (iii) nanoconfinement; preventing the grain growth by confining in porous scaffolds [210] (iv) additives; forming pathways that facilitate hydrogen diffusion through the diffusion barriers [211] have been employed for improving the MgH₂'s hydrogen storage behavior. So far, several techniques have been developed for the synthesis of MgH₂, such as mechanical milling, thin film deposition, melt spinning, electrochemical deposition etc. [212]. Herein, we describe some of the recent progress made on MgH₂ for improving its hydrogen storage behavior.

7.1. Nanostructuring

The properties of materials in the nano dimension may differ significantly when compared to their bulk form. Nanoparticles (NPs) exhibits (i) increased in surface to volume ratio, resulting in increased exposure of surface atoms (ii) reduced diffusion path (iv) closer proximity between different reacting solids, (iv) increased in the number of grain boundary atoms [213]. Due to the larger volume contribution of phase boundaries, nanocrystalline solids exhibit a higher level of disorder [214]. Hence, nanosizing of MgH₂ leads to reduced grains with high active interface/surface and short hydrogen diffusion path, which can accelerate the de-/hydrogenation kinetics of MgH₂/Mg. Nanosizing of MgH₂ not only increases the hydrogen diffusion rate but also increases the surface exposure of MgH₂ NPs [215]. Nanosizing affects the stability of Mg-H bond resulting in an improvement in the thermodynamic behavior of MgH₂. Theoretical studies predict that MgH₂ NPs may have reduced reaction enthalpy with improved kinetics when the size of the particle is below 50 nm. However, significant improvement in the thermodynamics of MgH₂ NPs was observed for < 5 nm size particles [176; 216]. In general, the methods employed for nanoscaling of MgH₂ are mechanical milling, hydrogenolysis, melt infiltration, physical and chemical vapor deposition, chemical reduction, electrochemical deposition and thermolysis of Grignard reagents [217-218]. Mechanical milling [219] is one of the most widely used methods for the particle size reduction and distribution of catalysts for MgH₂. Mechanical milling introduces a number of changes in the pulverized material, such as particle size reduction up to

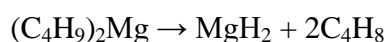
the order of few nanometers, an increase in specific surface area, a decrease in the crystallite size in the order of nanometers, increase in the crystal lattice defects and grain boundary volume fraction, and the formation of oxide-free surfaces that aid in hydrogen chemisorption [220].

Zaluska et al. [221-222] first reported the improved hydrogen storage behavior of ball milled MgH_2 . It was observed that the hydrogen sorption has dramatically improved due to the combined effect of surface modification and nanocrystalline structure of MgH_2 . Depending on the ball milling condition, the onset temperature (T_{ON}) for hydrogen desorption has been lowered by 100 °C. Varin et al. [223] have demonstrated the synthesis of nanostructured MgH_2 from elemental magnesium powder in a hydrogen environment using controlled reactive mechanical milling (CRMM). The nanocrystalline MgH_2 with an average particle size of 338 nm shows a significant change in enthalpy from 74 $\text{kJmol}^{-1} \text{H}_2$ (for commercial polycrystalline MgH_2 having an average particle size of 35.9 μm) to 57 $\text{kJmol}^{-1} \text{H}_2$ (for nanocrystalline MgH_2). Hence, the T_{ON} for hydrogen desorption has decreased from 409.4 °C (for commercial MgH_2) to ~325 °C (for nanocrystalline MgH_2). T_{ON} for hydrogen desorption was found to be decreased with decrease in the particle size of MgH_2 . It has been observed that the nanostructuring of MgH_2 , leads to the formation of metastable $\gamma\text{-MgH}_2$ phase. The presence of $\gamma\text{-MgH}_2$ improves the hydrogen kinetics and significantly modifies the thermodynamic parameters of MgH_2 . Shen C. et al.[224] have observed that the presence of $\gamma\text{-MgH}_2$ leads to a significant reduction in hydrogen reaction enthalpy with Mg from 74. 8 to 57.7 $\text{kJmol}^{-1} \text{H}_2$ with improved hydrogen sorption kinetics. Recently, Lototskyy et al. [225] synthesized MgH_2 NPs using high-energy reactive ball milling (HRBM) of Mg in the hydrogen atmosphere. The MgH_2 NPs synthesized by HRBM shows improved hydrogen reaction kinetics and the T_{ON} for dehydrogenation was lowered to 302 °C. However, with additives the T_{ON} for dehydrogenation of MgH_2 NPs synthesized using HHRBM was reduced significantly to 200 °C. More recently, Baran et al.[226] employed high temperature, high pressure reactive ball milling (HTPRBM) for the synthesis of MgH_2 NPs. A special milling jar with the capability of temperature control and pressure sensor was used for HPRBM. Huang et al. [227]described the synthesis of MgH_2 NPs on 40% graphene sheets by a one-step solvent-free hydrogenolysis method. The growth of MgH_2 NPs on graphene sheets is achieved by the hydrogenolysis of $(\text{C}_4\text{H}_9)_2\text{Mg}$ through the following reaction



Here, the size of MgH_2 NPs can be controlled by adjusting the MgH_2 to graphene sheets mass ratio. The T_{ON} for dehydrogenation of MgH_2 NPs dispersed uniformly on graphene sheets is lowered to 270 °C. Whereas, MgH_2 NPs synthesized by the same method without graphene addition exhibits T_{ON} for dehydrogenation at 300 °C.

Since the addition of 40% graphene acts as deadweight to the system, the hydrogen storage capacity is reported to be ~4.5 wt.%, which is significantly less than that of pure MgH_2 . Recently, Huang et al. [228] synthesized MgH_2 NPs with an average particle size of 8.9 nm by combining ball milling and thermal hydrogenolysis of di-*n*-butylmagnesium, $(\text{C}_4\text{H}_9)_2\text{Mg}$ through the following reaction.



With the effect of ball milling, the hydrogenolysis temperature was significantly reduced to 100° C. The nano-size effect significantly alters the thermodynamic properties of MgH_2 with enthalpy value of 69.78 $\text{kJmol}^{-1} \text{H}_2$ and the T_{ON} for dehydrogenation was observed at 225 °C.

Rambhujan et al. [218] have found that the MgH_2 NPs obtained by the thermolysis of di-tert-butylmagnesium exhibits two-staged hydrogen desorption attributed due to the presence of two MgH_2 phases; the thermodynamically stable $\beta\text{-MgH}_2$ and the metastable $\gamma\text{-MgH}_2$ phase, leading to a lower hydrogen desorption temperature with improved hydrogen sorption kinetics.

Even though several approaches have been proposed for the synthesis of Mg NPs, the high reactivity of Mg NPs in air leads the synthesis process to be a challenging task. Jeon et al. [229] synthesized an air-stable composite of Mg nanocrystals encapsulated in a polymer PMMA [poly(methyl methacrylate)] matrix, which permit only hydrogen and not O_2 or H_2O , thereby reactivity of Mg nanocrystals with air is prevented (Figure 6). The Mg nanocrystals were synthesized by using organometallic Mg precursor bis(cyclopentadienyl) magnesium (Cp_2Mg) and lithium naphthalide as a reducing agent. The PMMA encapsulation not only protects the reactivity of Mg nanocrystals with air but also effectively increases the hydrogen storage behaviour without the use of any heavy metal catalysts.

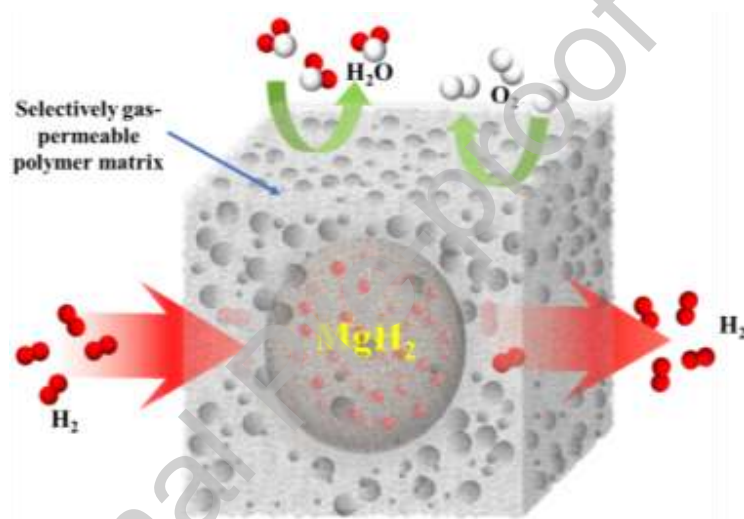


Figure 6. Schematic of Mg NPs encapsulated by a polymer matrix, which is selectively gas permeable [229].

The MgH_2 NPs undergo structural changes during hydrogen release and uptake cycles. The grain/particle size of MgH_2 is reported to increase during hydrogen release and uptake cycles, resulting in an agglomeration of particles leading to macroscopic phase segregation [230-231]. The macroscopic phase formation affects the hydrogen sorption kinetics. To prevent the macroscopic phase segregation, MgH_2 NPs can be scaffolded in porous materials.

7.2. Nanoconfinement

Nanoconfinement is the method of scaffolding nano dimensional particles inside the permanent nano dimensional pores of the host scaffolds. Nanoconfinement includes two aspects: nanosizing and confinement [232]. Recently, nanoconfinement or nano-scaffolding of hydrides has emerged as an interesting field of research for altering reaction pathways and tuning the thermodynamic and kinetic parameters of metal hydrides at the nanoscale [233]. This method of scaffolding hydride NPs inside the porous networks can effectively enhance the gas-solid interface, shorten

the hydrogen diffusion distance, and restricts particle sintering and macroscopic phase segregations, thus overcoming both the kinetic and thermodynamic barriers associated with MgH_2 NPs during de-/hydrogenation cycling. Here, the dimension of pores determines the dimension of particles confined in it. Experimental conditions such as the application of external temperature and pressures may cause structural deformation of scaffolding materials, affecting the pore structures. For nanoconfinement of hydrogen storage materials, porous materials which has high specific surface area, uniform distribution of pore sizes, chemical inertness and possess structural stability during the multiple de-/hydrogenation cycles are considered (Figure 7). Moreover, the scaffolds function as a deadweight to the hydrogen storage system and hence lightweight materials are preferred. The most commonly used scaffolds are carbon aerogels [234], activated porous carbons [235], metal-organic frameworks [236], porous polymer etc. [211]

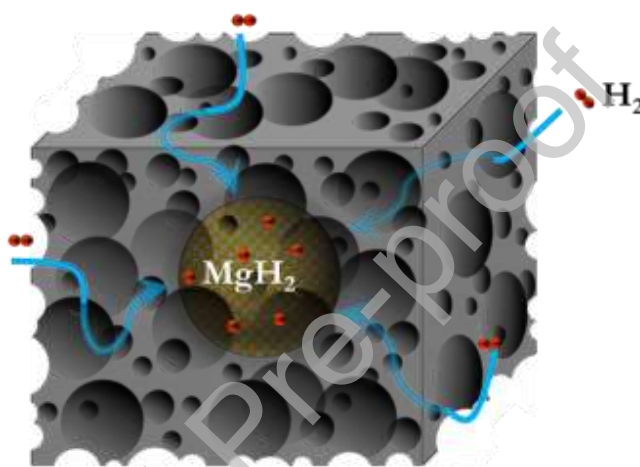


Figure. 7. Schematic representation of MgH_2 NPs confined inside the pores of scaffolding material. The scaffold restricts the movement of Mg/MgH_2 during de-/hydrogenation cycles and prevents the segregation of macroscopic phases.

Several methods have been adopted to infiltrate the MgH_2 NPs inside the pores of the scaffolding materials such as (i) melt impregnation (ii) solvent impregnation (iii) solution impregnation (iii) reactive gas evaporation (iv) sol-gel auto combustion and solution mixture [237] etc.

In the melt impregnation method, the molten state of MgH_2 is infiltrated into the pores of scaffolds by capillary condensation. With the benefit of physicochemical adaptability, carbon-based materials are often used as scaffolds. Generally, Carbon based porous scaffolds are considered for melt impregnation due to the wide range of porosity and chemical inertness during de-/hydrogenation cycles [238]. Gross et al.[239] employed melt infiltration method to confine MgH_2 NPs inside the micro and mesopores of carbon aerogels. The infiltration of molten Mg inside the pores of carbon aerogels (CA) followed by hydrogenation leads to the formation of confined MgH_2 NPs in CA scaffolds. The CA scaffolds have an average pore size of ~ 13 nm and since the confined MgH_2 particles are in the range of 13 nm, no significant change in enthalpy of MgH_2 is observed. However, significant improvement in the dehydrogenation kinetics of the confined MgH_2 is observed. Furthermore, nanoconfinement of MgH_2 in CA improves the efficacy of catalyst additive. Liu et al.[240] employed a solvent infiltration method for the confinement of MgH_2 NPs inside CA scaffold. The Mg NPs in the size range of 5 to 20

nm confined in CA were derived by hydrogenation of infiltrated dibutyl-magnesium. The ‘nanosize effect’ of Mg leads to a significant reduction in the thermodynamic stability of MgH_2 with improved kinetic behaviour. The hydrogen absorption/desorption enthalpies of Mg/MgH_2 in CA is estimated to be $-65.1 \pm 1.56 \text{ kJmol}^{-1} \text{ H}_2$ and $68.8 \pm 1.03 \text{ kJmol}^{-1} \text{ H}_2$, respectively.

Recently, nanoconfinement of MgH_2 with catalyst additives are becoming an interesting area of research for improving the kinetics and tuning the thermodynamics of MgH_2 . Ma et al. [241] have described the nanoconfinement effect of MgH_2 NPs in mesoporous CoS nano-boxes scaffold. The confined MgH_2 NPs were in the size range of 5 to 10 nm. The mesoporous CoS nano-boxes was first synthesized from ZIF-67 MOF then the MgH_2 NPs in CoS nano-boxes was derived by vacuum assisted impregnation of dibutyl magnesium solution followed by hydrogenation at 180°C under 48 atm. hydrogen pressure. The hydrogenation and dehydrogenation enthalpies of Mg/MgH_2 in CoS nano-boxes derived through solvent impregnated method is estimated to be $-65.6 \pm 1.1 \text{ kJmol}^{-1} \text{ H}_2$ and $68.1 \pm 1.4 \text{ kJmol}^{-1} \text{ H}_2$, respectively. The enthalpy values are similar to that observed for the nanoconfined 5 to 20 nm MgH_2 NPs in CA [201]. Apart from lowering the thermodynamic parameters of MgH_2 , the CoS nano-boxes scaffold plays an important role on providing active catalyst for enhancing the hydrogen sorption kinetics of Mg/MgH_2 . Ren et al. [242] synthesized nanoconfined MgH_2 in the slit pores of 2D graphene like TiO_2 nanosheets. The $\text{MgH}_2/\text{TiO}_2$ nanosheets heterostructure was synthesized by hydrogenation of Mg NPs derived by impregnating dibutyl magnesium solution in the slit pores of TiO_2 nanosheets. The confined MgH_2 in TiO_2 nanosheets has T_{ON} for dehydrogenation at 180°C . Additionally, the confined MgH_2 exhibits superior hydrogen sorption kinetics and good cyclic stability with negligible degradation even after 100 cycles of de-/hydrogenation. Zhu et al. [243] investigated MgH_2 NPs confined in 3D architecture of $\text{Ti}_3\text{C}_2\text{X}$ MXene nanosheets. The synergistic nanosize effect and catalytic effect by MXene leads to a significant reduction in the MgH_2 T_{ON} for dehydrogenation to 140°C with good cyclic stability without loss in kinetics. Ren et al. [244] demonstrated the confinement effect of MgH_2/Ni NPs in MOF derived from N-doped hierarchically porous carbon nanofiber. The T_{ON} for desorption of MgH_2/Ni NPs in MOF is lowered to 200°C and hydrogen absorption occurs at 100°C . Thus the ‘nanosize effect’ of the confined Mg/MgH_2 plays a vital role for improving the reaction kinetics and modifying the thermodynamic parameters of MgH_2 , which is favorable for hydrogen storage.

7.3. Catalyzing

Catalyst doping is one of the most effective ways to enhance the hydrogen storage characteristics of MgH_2 . Catalyst provides an alternative reaction path with lower reaction energy barrier. Research efforts on catalyst-assisted de-/hydrogenation behavior of MgH_2 have made significant progress on improving the thermodynamics, kinetics, and reversibility of MgH_2 . Till date several catalysts such as transition metals [245-246], metal oxides [247-249], metal halides [250-253] metal carbide [254], metal sulfide [255-256] metal and oxide nanoparticles [208; 257-263] quantum dots [264], additives supported by carbon structures [230; 265-272]s et al. have been investigated by researchers. Among the various catalyst additives, Nb_2O_5 is one of the most effective and widely investigated catalyst precursors for MgH_2 . With Nb_2O_5 additive, the dehydrogenation temperature of MgH_2 was significantly reduced to a peak temperature at 230°C and the hydrogen absorption in Mg catalyzed by Nb_2O_5 takes place even at 40°C . This is attributed to the reduction of Nb_2O_5 during hydrogenation of dehydrogenated MgH_2 which leads to the formation of a catalytically active state. As Nb_2O_5 reduces further its catalytic activity in MgH_2 increases. Therefore, during de-/hydrogenation cycles more reduction of Nb_2O_5 occurs,

resulting in further reduction in hydrogen absorption temperature. It has been found that the chemical state of Nb and the initial structural stability of Nb_2O_5 is vital for realizing superior catalytic activity in MgH_2 [273]. Shinzato et al. [274] observed that the meta stable phase of Nb_2O_5 exhibiting pillar crystallite morphology and pyrochlore structure show superior catalytic effect in improving the de-/hydrogenation kinetics of MgH_2 . Zhang et al. [275] found that the hydrogen desorption/absorption kinetics of MgH_2/Mg are greatly improved by the superior catalytic effect of NbN NPs (~20 nm size). The NbN catalyzed MgH_2 released nearly 6.0 wt.% hydrogen in 12 min at 275 °C and the sample absorbs 6.0 wt.% hydrogen within 24 min at 100 °C. The Nb^{3+} -N and Nb^{5+} -N valence state of Nb_4N_3 may be the key factor for increasing MgH_2 's hydrogen storage capabilities. The catalytic effect of in-situ NbN and Nb_2O_5 from N-doped Nb_2C supported Nb_2O_5 ($\text{N-Nb}_2\text{O}_5@/\text{Nb}_2\text{C}$) on MgH_2 was investigated by Lan et al. [276] They observed that the catalyzed MgH_2 sample exhibit T_{ON} for hydrogen desorption at 178 °C and the hydrogen absorption temperature has been reduced to 90 °C. The catalyst additive also helps to maintain a good de/redoxygenation cyclic stability.

Recently, catalytically active hydrogen spillover receptors have gained significant research interest for enhancing the hydrogen sorption kinetics of MgH_2 (Figure 8). Here, during hydrogen spillover process, the molecular hydrogen will get initially adsorbed on the surface of the spillover receptor and get dissociated into atoms and the atomic hydrogen can easily diffuse into Mg, which is generally poor for hydrogen chemisorption [277].

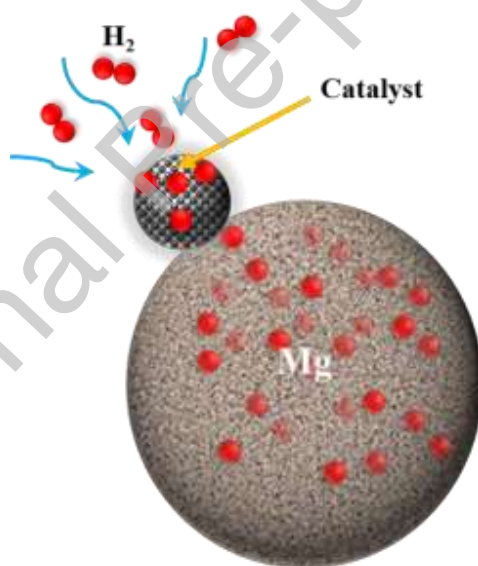


Figure. 8. Schematic representation of hydrogen spillover process during the hydrogen absorption process of Mg.

Hou et al. [278] have employed Ni/C as a catalyst for improving the hydrogen storage properties of MgH_2 . They observed that the addition of 9 wt.% Ni/C with MgH_2 leads to a significant reduction in the hydrogen release temperature to 195 °C and with improved hydrogen sorption kinetics and good cyclic stability. The in-situ formation of $\text{Mg}_2\text{Ni}/\text{Mg}_2\text{NiH}_4$ serves as a ‘hydrogen pump’ in MgH_2 for enhancing the hydrogen diffusion during de-/hydrogenation cycles. Shao et al. [279] explored the catalytic activity of TiO_2 NPs (5 – 10 nm) supported on 3D ordered macropores (3DOM) as a catalyst for enhancing the hydrogen storage behavior of MgH_2 .

It has been observed that 5 wt.% 3DOM-TiO₂ as an additive improves the de-/hydrogenation behavior of MgH₂. The in-situ formed multiple valence state Ti helps to destabilize MgH₂ and the dehydrogenated sample shows hydrogen uptake at 100 °C with reasonably good kinetics. Recently, catalyst nanoparticles derived metal organic framework (MOF) and 2D Metal Carbides and Nitrides (MXenes) have gained enthusiastic research interest due to its unique structure, rich element composition and functional surface. [280] Gao et al. [281] reported the catalytic activity of Ni derived from MOF.

Yang et al. [282] used Ni@C derived from trimesic acid-Ni based metal organic framework (TMA-Ni MOF) as a catalyst for enhancing the hydrogen storage characteristics of MgH₂. The formation of the Mg₂NiH₄ phase serves as a ‘hydrogen pump’ for improving the thermodynamic and kinetic parameters of MgH₂. Lakhnik et al. [283] synthesized MgH₂/Ti₃AlC₂ MAX-phase composite by reactive ball milling followed by hydrogenation of Mg. The dehydrogenation temperature of MgH₂/7wt.% Ti₃AlC₂ MAX-phase composite is observed at 236 °C. Zhang et al. [284] have investigated the MOF-derived bimetallic Co@NiO as catalyst for enhancing MgH₂’s hydrogen storage behaviour. The formation of Mg₂NiH₄/Mg₂CoH₃ interfaces lowers the energy barrier of H diffusion channels, promoting the hydrogen desorption and absorption kinetics of MgH₂/Mg. Gao et al. [285] have employed self-assembled TiO₂ NPs (15 - 20 nm in size) intercalated between layers of Ti₃C₂T_x MXene as a catalyst for improving MgH₂’s hydrogen storage characteristics. The interfaces not only serve as lower energy barrier for hydrogen diffusion channels but also serve as a conduction path for the electrons released from the multiple valence transition state of Ti. In another study, Geo et al. [280] have described the facet dependent catalytic effect of Ti₃C₂T_x MXene. The active edge facets have a stronger affinity towards hydrogen than basal facets of Ti₃C₂T_x MXene, resulting in the formation of more catalytically active metallic Ti from edge facets of Ti₃C₂T_x. The T_{ON} for dehydrogenation of 5 wt.% edge facet exposed Ti₃C₂T_x MXene catalyzed MgH₂ was observed at 199 °C, which is 101 °C lower than that of ball milled MgH₂ without any additives. Haung et al. [286] described the catalytic effect of carbon-wrapped Ni and Co NPs (8 - 16 nm) as catalysts in the MgH₂. Among the two catalysts, carbon-wrapped Ni (Ni/C) exhibits superior effect in improving the de-/hydrogenation kinetics of MgH₂. The 6 wt.% Ni/C catalysed MgH₂ sample has peak desorption temperature at 275.7 °C, which is 142.7 and 54.2 °C lower than that of pristine MgH₂ and ball milled MgH₂. Furthermore, the Ni/C catalysed dehydrogenated MgH₂ sample reabsorbs 5.0 wt.% H₂ within 20 s at 100 °C. It has been observed that higher concentration of Ni/C in MgH₂ further improves MgH₂’s de-/hydrogenation behaviour. Ma et al. [287] showed the superior catalytic effect of carbon supported Ni NPs (Ni@C) towards improving the de-/hydrogenation properties of MgH₂. The T_{ON} for hydrogen desorption of 5 wt.% Ni@C catalyzed MgH₂ has been reduced to 187 °C, which is 113 °C lower than that of ball milled MgH₂ without any additives.

Chen et al. [288] described the catalytic effect of carbon-encapsulated ZrO₂ (C/ZrO₂) NPs (5 – 10 nm) in MgH₂. It has been observed that with carbon encapsulation ZrO₂ exhibits superior catalytic effect for improving the hydrogen release kinetics of MgH₂. The T_{ON} for hydrogen desorption of C/ZrO₂ catalyzed MgH₂ is observed at 208 °C, which is 40 and 101 °C lower than that of ZrO₂ and additive-free MgH₂. Wang et al. [289] reported the superior catalytic effect of uniformly dispersed Ni NPs on porous hollow carbon nanospheres (Ni@PHCNSs) towards the de-/hydrogenation of MgH₂. The T_{ON} for dehydrogenation of 5 wt.% Ni@PHCNSs catalyzed MgH₂ was lowered to 190 °C. Moreover, the dehydrogenated sample absorbed hydrogen at 150 °C with improved kinetics. Wang et al. [259] demonstrated the catalytic effect of vanadium oxide

NPs on cubic carbon nanoboxes (nano- $V_2O_3@C$) towards the de-/hydrogenation of MgH_2 . The 9 wt.% nano- $V_2O_3@C$ catalyzed MgH_2 exhibits T_{ON} for hydrogen desorption at 215 °C, which is 60 °C lower than that of MgH_2 without any additives. The dehydrogenated sample reabsorbed hydrogen even at room temperature under 50 atm hydrogen. Lan et al. [290] studied the catalytic effect of nanoporous carbon encapsulated Ni and V_2O_3 NPs ($(Ni-V_2O_3)@C$) for enhancing the de-/hydrogenation kinetics of MgH_2 . The 10 wt.% $(Ni-V_2O_3)@C$ catalyzed Mg/MgH_2 sample absorbs hydrogen even at room temperature. Zhao et al. [291] have employed core-shell $CoNi@C$ as a catalyst for improving the hydrogen sorption properties of MgH_2 . The 8 wt.% core-shell $CoNi@C$ catalyzed MgH_2 exhibits T_{ON} for dehydrogenation at 173 °C and the dehydrogenated sample absorbs 6 wt.% of hydrogen at 150 °C within 200 sec. Ren et al. [292] studied the catalytic activity of core-shell structure of Ni/Fe_3O_4 in porous metal carboxylate salts, MIL ($Ni/Fe_3O_4@MIL$) as a catalyst for improving the hydrogen storage properties of MgH_2 . The T_{ON} for dehydrogenation of MgH_2 with $Ni/Fe_3O_4@MIL$ additive was observed at 244 °C. The formation of Mg_2Ni/Mg_2NiH_4 in Ni catalyzed MgH_2 serve as a 'hydrogen pump' to improve MgH_2 's hydrogen storage behavior [244; 281; 284; 290; 292-293].

7.4. Alloying

Another strategy to destabilize MgH_2 and modify the reaction pathway and thermodynamics is through the addition of reactive additives. The reactive additive reversibly reacts with Mg and forms a new phase, whose reaction enthalpy with hydrogen will be lower than that of the formation reaction of MgH_2 . Thus, the alloying additive destabilizes the Mg-H bond and reduces the enthalpy of MgH_2 through formation of new phase, thereby decreasing the dehydrogenation temperature of MgH_2 .

Zhong et al. [294] have described the use of Al as a reactive additive to destabilize MgH_2 . Supersaturated $Mg(Al)$ solid solution alloy was prepared by ball milling and it was found that during hydrogenation and dehydrogenation, $Mg(Al)$ solid solution and $Mg_{17}Al_{12}$ intermetallic compound were formed reversibly. This transition of $Mg(Al)$ solid solution and $Mg_{17}Al_{12}$ leads to the thermodynamic destabilization of MgH_2 . Thus, the dehydrogenation enthalpy of 5 and 10 at.% Al in $Mg(Al)$ solid solution was estimated to be 72.1 and 70.8 kJ mol⁻¹. The addition of Al forms numerous hetero interfaces with high interfacial energy, which could improve hydrogen diffusion and speed up the formation of Mg/MgH_2 , thereby lowering the hydrogenation/dehydrogenation enthalpy. Furthermore, the addition of Al increases the thermal conductivity of Mg/MgH_2 and improves the hydrogen sorption kinetics. Cermak et al. [295] studied the hydrogen storage properties of Mg-In-amorphous carbon (Mg-In-CA) alloy synthesized by ball milling and observed that the dehydrogenation enthalpy of MgH_2 was decreased down to 51.5 kJmol⁻¹ attributed to the formation of MgIn phase. The enthalpy value was found to decrease with increase in concentration owing to the phase changes from Mg_2In to Mg_3In . Ershova et al. [296] observed that T_{ON} for desorption of hydrogenated Mg-Al-Fe alloy was observed at 250 °C, which is 65 °C lower than that of Mg without any additives. More recently, Lu et al. [297] have investigated the hydrogen storage behavior of carbon covered nanocrystalline Mg_2Ni . The hydrogenation of sample was achieved at room temperature and the T_{ON} for hydrogen desorption was lowered to 180 °C. The hydrogenation and dehydrogenation activation energy of carbon covered nanocrystalline Mg_2Ni were estimated to be significantly lower than that of pristine MgH_2 . The hydrogen desorption enthalpy of carbon covered nanocrystalline Mg_2NiH_4 was determined to be 67.0 ± 0.5 kJ mol⁻¹. Thus, the combined effect of nanocrystalline strategy, carbon encapsulation/support and alloying help to improve the MgH_2 's

hydrogen storage properties. Thus, alloying of Mg with reactive additives helps to lower the hydrogen reaction enthalpy and enhances the hydrogen sorption kinetics of MgH_2 .

8. Complex Hydrides and Related Systems

In section 6 of the present paper discussion started with the metal hydrides of AB_5 , AB , A_2B , AB_2 types for hydrogen storage. Ideally, the metal hydrides shows either interstitial or substitutional hydrogen intercalation where that enhances at least 25% volumetric expansion that leads to reversible hydrogen sorption behavior. Therefore, the volumetric hydrogen storage capacity in metal hydrides is much greater when compared the gravimetric densities. The drawback with such metal hydrides is in addition to the low gravimetric hydrogen storage capacities, they are prepared by the combination of two, three or multi elements from the periodic table, that are heavy, for examples, elements from lanthanide group (La, Ce, Mm, etc.) and from transition metals (Ni, Co, Fe, Ti, V etc.) [298]. For transportation and other automotive applications, the candidate materials supposed to have light weight with high gravimetric energy storage. Hence, in search of light weight metal hydrides, the section 5 of this article demonstrated the magnesium hydrides and related systems which are not only possess the highest hydrogen storage capacity of 7.6 wt% but also, shows less weight penalty. However, these lightweight magnesium hydrides and systems offer the high reversibility at an expense of high temperatures, $\sim 325^\circ\text{C}$ and pressures close to sever tenths of atmosphere of hydrogen [299].

The alloying, complex formation, catalytic doping, and nanoparticle formation of these magnesium greatly demonstrated the sorption behavior at affordable temperatures and pressures, but these modified versions of hydrides still involved the usage of heavy metals such as transition metals [300] and in some cases lanthanide group metals [301]. For example, magnesium-iron based complex hydrides and related systems (for example, Mg catalyzed with neodymium oxides) showed of at least 5-6 wt% reversible hydrogen storage capacities at temperatures close to 200°C and exhibited longer life cycles and are deployed in hydrogen energy applications, in heat pumps, and automotives [301]. Though the so called, the birth of complex hydrides evolved with the emergence of Mg-based complex hydrides, that are known to the scientific community, the real breakthrough research in developing lightweight, high-capacity complex hydrides based on alkali, alkaline, metalloids and other non-metals combinations [302]. In 1990s, Bogdanovic and coworkers discovered lightweight sodium aluminum tera- and hexa- hydrides with few moles of catalytic transition metals/compounds doping [301; 303] that triggers the hydrogen storage community for researching and exploring new sodium aluminum hydrides [304], lithium aluminum hydrides [305], and magnesium based complex hydrides [300] and related systems that are not only push the boundaries of both thermodynamics and kinetics but also addressed the requirement of lightweight materials for PEM fuel cells driven vehicles.

In a very recent comprehensive review published from the international group of hydrogen experts of the Task 40, of the Hydrogen Energy Technologies Program of the IEA, the advantages of the complex hydrides and tunable systems are detailed with respect to their materials' design, synthesis, characterization and scale-up for hydrogen enabled applications

[306]. In general, the complex hydrides, are categorized according to their bonding characteristics. such as (i) alanes and alanates [307], (ii) borohydrides [308] and borates [309], (iii) amides and imides [310-311], (iv) ammines, and (v) reactive hydride complexes (RHCs) and (vi) other novel complex hydride systems. The reactive hydride complexes are in general composed of multinary complex hydride systems with the presence of core-shell catalytic nanoparticles, one such system is reported based on the synthesis process, and DFT calculations where the Ti (core) and Mg(shell) with hydrogen bonding are shown in Figure 9 [312]. The pristine and modified RHCs are currently under investigation by the author of this review article. These RHCs are proposed to enhance the hydrogen storage characteristics based on the nanocatalytic effects of $\text{TiH}_2/\text{MgH}_2$ core-shell effects in the candidate complex multinary hydrides. The chemical reactions below demonstrate the pristine and modified RHCs and with enhancement of hydrogen uptake and release from 6 to 9 moles of hydrogen (Table 3). Table 4 represents different types of complex hydrides and their hydrogen storage capacities at specific operating temperatures.

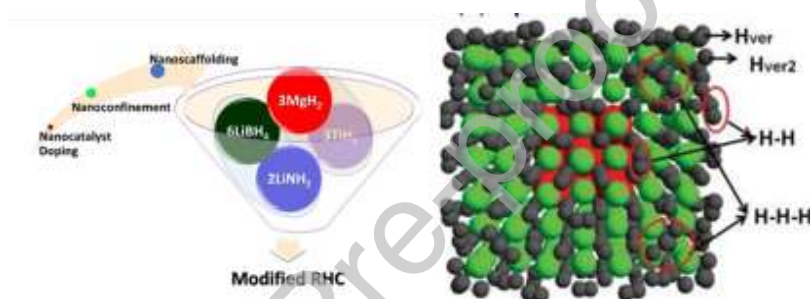
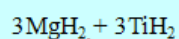


Figure 9. (a) Synthesis process and (b) DFT calculations of the structure of modified RHCs. Reprinted with permission from Tao, S. X., Notten, P. H. L., van Santen, R. A., Jansen, A. P. J., First-principles predictions of potential hydrogen storage materials: Nanosized Ti(core)/Mg(shell) hydrides, Physical Review B 83 (2011) 195403. 10.1103/PhysRevB.83.195403.by the American Physical Society.[312]

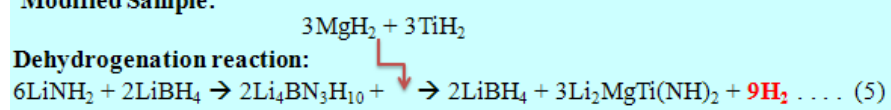
Table 3. Dehydrogenation and rehydrogenation reactions of RHCs

Pristine reactive hydride complex - $2[n(\text{LiBH}_4) + 3n(\text{LiNH}_2)] + 3n(\text{MgH}_2)$ (1)	
Modified reactive hydride complex - $2[n(\text{LiBH}_4) + 3n(\text{LiNH}_2)] + 3n[(\text{MgH}_2) + (n\text{TiH}_2)]$.(2)	
Pristine Sample:	
Dehydrogenation reaction:	3MgH_2
$6\text{LiNH}_2 + 2\text{LiBH}_4 \rightarrow 2\text{Li}_4\text{BN}_3\text{H}_{10} +$	$\rightarrow 2\text{LiBH}_4 + 3\text{Li}_2\text{Mg}(\text{NH})_2 + 6\text{H}_2$ (3)
Rehydrogenation reaction:	
$3\text{Li}_2\text{Mg}(\text{NH})_2 + 2\text{LiBH}_4 + 6\text{H}_2 \rightarrow 2\text{Li}_4\text{BN}_3\text{H}_{10} + 3\text{MgH}_2$ (4)

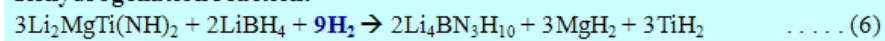
Modified Sample:



Dehydrogenation reaction:



Rehydrogenation reaction:



"n" signifies nano-form of host hydride.

Table 4. Types of complex hydrides, their hydrogen storage capacities, and operating temperatures

Amides, Imides and Multinary Complex Hydrides		Capacity (wt.%)	Temperature [C]	References
$\text{LiNH}_2 + 2\text{LiH} = \text{Li}_2\text{NH} + \text{LiH} + \text{H}_2 = \text{Li}_3\text{N} + 2\text{H}_2$	$\text{LiNH}_2 + 2\text{LiH}$	10.5	300	T. Ichikawa et al. [313]
$\text{CaNH} + \text{CaH}_2 = \text{Ca}_2\text{NH} + \text{H}_2$	$\text{CaNH} + \text{CaH}_2$	2.1	500	Roshan et. al. [314]
$\text{Mg}(\text{NH}_2)_2 + 2\text{LiH} = \text{Li}_2\text{Mg}(\text{NH})_2 + 2\text{H}_2$	$\text{Mg}(\text{NH}_2)_2 + 2\text{LiH}$	5.6	175	Chen et. al. [315-316]
$3\text{Mg}(\text{NH}_2)_2 + 8\text{LiH} = 4\text{Li}_2\text{NH} + \text{Mg}_3\text{N}_2 + 8\text{H}_2$	$3\text{Mg}(\text{NH}_2)_2 + 8\text{LiH}$	6.9	225	Aoki et. al. [317]
$\text{Mg}(\text{NH}_2)_2 + 4\text{LiH} = \text{Li}_3\text{N} + \text{LiMgN} + 4\text{H}_2$	$\text{Mg}(\text{NH}_2)_2 + 4\text{LiH}$	9.1	225	Leng et. al. [318]
$2\text{LiNH}_2 + \text{LiBH}_4 = \text{"Li}_3\text{BN}_2\text{H}_8\text{"} = \text{Li}_3\text{BN}_2 + 4\text{H}_2$	$2\text{LiNH}_2 + \text{LiBH}_4$	11.9	250	Pinkerton et. al. [319]
$\text{Mg}(\text{NH}_2)_2 + 2\text{MgH}_2 = \text{Mg}_3\text{N}_2 + 4\text{H}_2$	$\text{Mg}(\text{NH}_2)_2 + 2\text{MgH}_2$	7.4	20	Hu et. al. [320]
$2\text{LiNH}_2 + \text{LiAlH}_4 = \text{LiNH}_2 + 2\text{LiH} + \text{AlN} + 2\text{H}_2 = \text{Li}_3\text{Al} + \text{N}_2 + 4\text{H}_2$	$2\text{LiNH}_2 + \text{LiAlH}_4$	5	500	Xiong et. al. [321]
$3\text{Mg}(\text{NH}_2)_2 + 3\text{LiAlH}_4 = \text{Mg}_3\text{N}_2 + \text{Li}_3\text{AlN}_2 + 2\text{AlN} + 12\text{H}_2$	$3\text{Mg}(\text{NH}_2)_2 + 3\text{LiAlH}_4$	8.5	350	Xiong et. al. [322]
$\text{Mg}(\text{NH}_2)_2 + \text{CaH}_2 = \text{MgCa}(\text{NH})_2 + 2\text{H}_2$	$\text{Mg}(\text{NH}_2)_2 + \text{CaH}_2$	4.1	500	Yongfeng et. al. [323]
$\text{NaNH}_2 + \text{LiAlH}_4 = \text{NaH} + \text{LiAl}_{0.33}\text{NH} + 0.67\text{Al} + 2\text{H}_2$	$\text{NaNH}_2 + \text{LiAlH}_4$	5.2	200	Chua et. al. [324]

$2\text{LiNH}_2 + \text{CaH}_2 = \text{Li}_2\text{Ca}(\text{NH})_2 + 2\text{H}_2$	$2\text{LiNH}_2 + \text{CaH}_2$	4.5	215	Wu et. al. [325]
$4\text{LiNH}_2 + 2\text{Li}_3\text{AlH}_6 = \text{Li}_3\text{AlN}_2 + \text{Al} + 2\text{Li}_2\text{NH} + 3\text{LiH} + 15/2\text{H}_2$	$4\text{LiNH}_2 + 2\text{Li}_3\text{AlH}_6$	7.5	300	Kojima et. al. [326]
$2\text{Li}_4\text{BN}_3\text{H}_{10} + 3\text{MgH}_2 = 2\text{Li}_3\text{BN}_2 + \text{Mg}_3\text{N}_2 + 2\text{LiH} + 12\text{H}_2$	$2\text{Li}_4\text{BN}_3\text{H}_{10} + 3\text{MgH}_2$	9.2	250	Niemann et. al. [327]
Borohydrides				
$2\text{LiBH}_4 = 2\text{LiH} + 2\text{B} + 3\text{H}_2$	$2\text{LiBH}_4 + 2\text{LiH}$	13.6	375	Zuttel et. al [328]
$2\text{LiBH}_4 + \text{MgH}_2 = 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2$	$2\text{LiBH}_4 + \text{MgH}_2$	11.5	355	Soulie et. al. [329]
$3\text{Mg}(\text{BH}_4)_2\text{-NH}_3 = \text{Mg}_3\text{B}_2\text{N}_4 + 2\text{BN} + 2\text{B} + 21\text{H}_2$	$3\text{Mg}(\text{BH}_4)_2$	15.9	250	Nakamori et. al. [330-331], Soloveichik et. al. [332]
$\text{Ca}(\text{BH}_4)_2 = \text{CaH}_2 + 2\text{B} + 3\text{H}_2$	$\text{Ca}(\text{BH}_4)_2$	8.6	400	Kim et. al. [333]
$\text{Zn}(\text{BH}_4)_2 = \text{Zn} + \text{B}_2\text{H}_6 + \text{H}_2$	$\text{Zn}(\text{BH}_4)_2$	2.1	115	Jeon et. al. [334], Srinivasan et. al. [335-336]
Ammonia borane and Amido boranes				
$n\text{NH}_3\text{BH}_3 = (\text{NH}_2\text{BH}_2)_n + n\text{H}_2 = (\text{NHBH})_n + 2n\text{H}_2$	NH_3BH_3	12.9	135	Stephens et. al. [337], Todd et. al. [338]

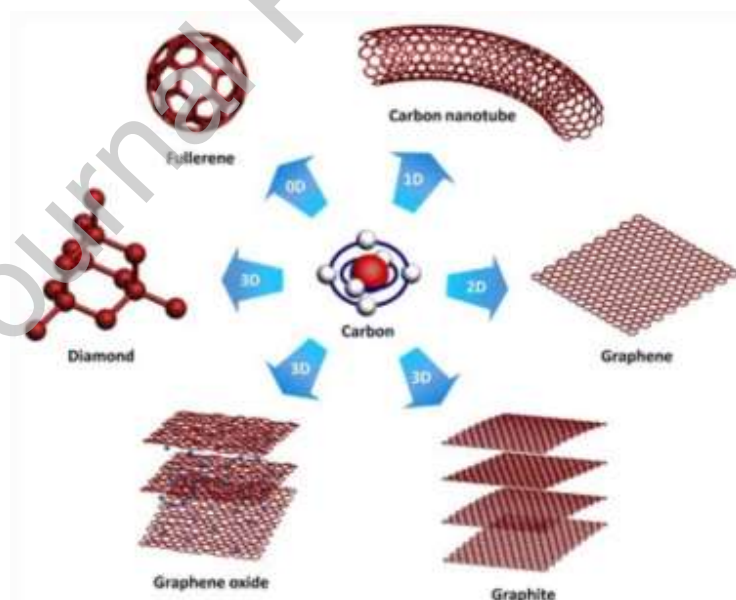
$\text{LiNH}_2\text{BH}_3 = \text{LiNBH} + 2\text{H}_2$	LiNH_2BH_3	10.9	85	Xiong et. al. [339]
$\text{NaNH}_2\text{BH}_3 = \text{NaNBH} + 2\text{H}_2$	NaNH_2BH_3	7.5	85	Xiong et. al. [339]
$\text{Ca}(\text{NH}_2\text{BH}_3)_2 = \text{Ca}(\text{NBH})_2 + 4\text{H}_2$	$\text{Ca}(\text{NH}_2\text{BH}_3)_2$	8	167.5	Kim et. al. [340]

9. Carbonaceous and Related Systems:

This section discusses the uniqueness of carbon as an element and then specific applications in the field of hydrogen storage.

9.1. Carbon: The extraordinary canvas

Carbon is one of the special and unique elements in the Periodic Table. It has atomic number 6 with electronic configuration of $1s^2 2s^2 2p^2$ which gives it enormous options of formation of covalent bonds with itself or other elements of the Periodic Table. It forms bonds through hybridization that can involve sp^3 , sp^2 and/or sp^1 combinations. Its chemically inert nature, good physical strength, mechanical flexibility, light weightness, and different allotropes gives researchers a canvas that can be engineered in various ways. For instance, it can be transformed into many forms namely, zero-dimensional fullerenes, one-dimensional carbon nanotubes, two-dimensional graphene, three-dimensional graphite, hybrid structures thereof, activated carbon, etc., can be chemically modified by attaching functional groups, decorated by nanoparticles of metals/metal oxides or non-metal nanoparticles, and doped by elements like N, B, etc. [341-344] Thus, a vast number of possibilities exist for researchers to explore 'carbon' as a material. Further, the high surface to volume ratio of the carbon nanomaterials gives them the edge of possessing very high specific surface areas. The porosity along with high specific surface areas lead to the presence of many adsorption sites. With these desirable properties, carbon nanomaterials present themselves as prospective materials in the field of solid-state hydrogen storage. Figure 10 depicts the common allotropes of carbon that differ in their dimensionality



[345].

Figure 10. Different allotropes of carbon that differ in dimensionality. Reprinted from D. Veeman, M.V. Shree, P. Sureshkumar, T. Jagadeesha, L. Natrayan, M. Ravichandran, P. Paramasivam, Sustainable Development of Carbon Nanocomposites: Synthesis and

Classification for Environmental Remediation, Journal of Nanomaterials 2021 (2021) 5840645,
Copyright © 2021, content available under Creative Commons Attribution License [345].

9.2. The carbon connection

For solid state hydrogen storage, one requires a good volumetric or gravimetric storage of hydrogen in near-ambient conditions, on-demand desorption at ambient temperatures, quick and reversible storage, and surety of a safe and economical means [300; 346-347]. The storage can be in the form of molecular or atomic hydrogen. The molecular or atomic form of hydrogen storage depends upon the underlying mechanism of storage. And it is here where the carbon nanomaterials make a difference. Pure carbon nanomaterials are unsuitable for hydrogen storage. However, functionalization of carbon support or decoration of carbon support with nanoparticles can significantly improve the hydrogen storage properties. In case of carbon nanomaterials, the two mechanisms have been reported in literature namely, (a) Kubas interaction and (b) spillover mechanism. The spillover mechanism is a much-debated mechanism in literature where empirical evidence exists both in favor and against it [277; 348-352]. The two mechanisms are discussed in sections 5.6 and 5.7 later. It has been discussed above that carbon can form bonds in multiple ways. Thus, when a hydrogen molecule approaches a pure or functionalized carbon network at close atomic distances, the hydrogen molecule's bonding configuration gets affected resulting in physisorption/chemisorption of molecular H_2 or atomic H_2 , respectively. In all these approaches, the activation energy is reduced to facilitate either formation of atomic hydrogen from molecular hydrogen or formation of covalent bonds with the carbon support. Because this interaction is tunable by either using different carbon nanoforms, functionalization or nanoparticle dispersion over the carbon support, supports the interaction energies, carbon-based hydrogen storage is a promising field.

9.3. Hydrogen uptake capacity of various carbon materials

A recent review of hydrogen storage by different carbon forms by Mohan *et al.* reports the highest values reported [352]. At room temperature, the highest reported uptake capacities for activated carbon (5.5 wt.% H_2), graphite (4.48 wt.% H_2), carbon nanotubes (4.5 wt.% single tubes and 6.3 wt.% H_2 multiwalled tubes), and nanofibers (6.5 wt.% H_2) were reported. However, these are the best reported values and many research groups have reported lower hydrogen uptake capacities than these values. Hence, a pure carbon network (combination of sp^3 , sp^2 , sp^1) cannot serve as a hydrogen storage material. The carbon materials can be functionalized using various schemes as shown in Figure 11 [353]. Functionalized or doped carbon materials are promising materials in this regard [346-347; 354-358].

Nitrogen-doped activated carbon has been evaluated for H_2 uptake capacity. The activated carbon after treatment in the presence of ammonia gas was successfully doped with nitrogen and then subsequently decorated by metal nanoparticles. The average size of the nanoparticles used for decorating the nitrogen doped carbon network ranged from 35 nm for Ru to 64 nm Ni nanoparticles. The hydrogen uptake profiles were different at cryogenic temperatures as compared to room temperature uptake profiles. While at cryogenic temperatures a sequential filling of pores (micro- followed by meso- and macro-pores) takes place, and an overlap of Type I and Type IV Langmuir adsorption isotherm is seen suggesting a gradual transition from mono- to-multilayer adsorption. During the filling of micropores alone, the hydrogen molecules present

at the surface cause an excess Gibbs energy which is seen to increase the uptake capacity as pressure is increased. Whereas at room temperature, the adsorption in all levels of pores was seen to occur. For nitrogen doped activated carbon, 57% increase was recorded for nitrogen doped activated carbon at 100 MPa pressure and 298 K. For other systems, the maximum uptake capacity was observed to increase by 42% for Pt-decorated nitrogen-doped activated carbon. For Ni and Ru, the improvement in uptake capacity was relatively low at 10 % and 8%, respectively [350]. Doping of nitrogen within the carbon network to form g-C₃N₄ and then using Pd nanoparticles over g-C₃N₄ support resulted in a hydrogen uptake capacity of 1.8 wt.% and 2.5 wt.%, respectively at room temperature and 3 MPa hydrogen pressure. The uptake capacity could be improved to 2.6 wt.% and 3.8 wt.%, respectively at lower temperatures of 0 °C [359]. In another study, Ni nanoparticles dispersed over graphite network demonstrated 4.48 wt.% hydrogen uptake at 298 K and hydrogen pressure up to 10 MPa [360]. A dipole induced hydrogen uptake mechanism was proposed for achieving this relatively higher gravimetric storage. However, high pressure conditions like 10 MPa make the material commercially less attractive.

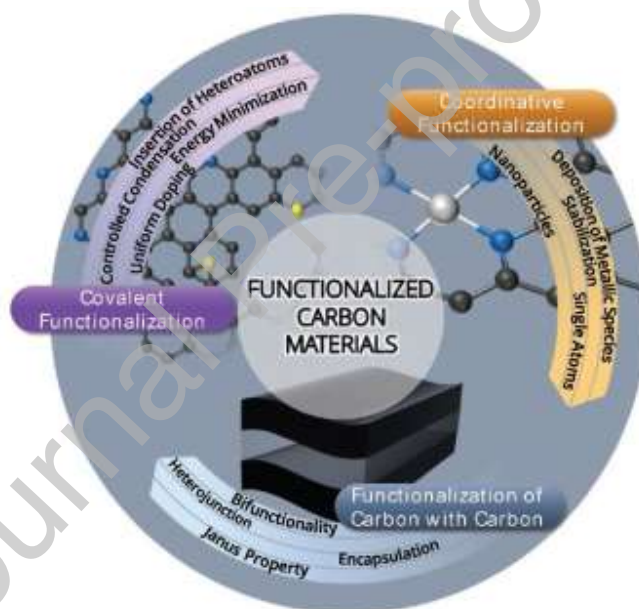


Figure 11. Some of the ways to functionalize carbon nanomaterials. This figure is reproduced from M. Perovic, Q. Qin, M. Oschatz, From Molecular Precursors to Nanoparticles—Tailoring the Adsorption Properties of Porous Carbon Materials by Controlled Chemical Functionalization, 30 (2020) 1908371 available under the Creative Commons CC-BY-NC license [353].

9.4. Ordered mesoporous carbons:

Ordered mesoporous carbons have also been studied for hydrogen storage properties after treating them in ammonia atmosphere. Hard template method was used by Giraudet *et al.* to synthesize nitrogen-doped mesoporous carbon. One of the important conclusions of the study

was that nitrogen doping was more influential for electrochemical H_2 storage indicating that nitrogen doping participated in redox reactions directly and that the effect on van der Waal's types of forces was not significant. However, the porosity of the mesoporous carbons played a role at lower temperatures [361]. Other means to store hydrogen have also been reported. For instance, metal hydrides are known to suffer from great thermodynamic stabilities thereby resulting in slow desorption kinetics and high temperatures of adsorption. However, improved thermodynamic properties, better desorption kinetics and the better reversibility by $LiBH_4$ - MgH_2 nanocomposites was demonstrated by making use of a porous carbon aerogel scaffold by Nielsen and coworkers [362]. The carbon aerogel scaffold with pores of maximum size of ~ 21 nm served as a nano-sized confined system where the reversible reaction could take place. Composites of Ni, Co and Ni-Co were dispersed over nitrogen doped graphene and tested for hydrogen storage. The authors reported a 1 wt% release of hydrogen at $226^\circ C$ and with Ni nanoparticles, 6.5 wt% H_2 release was recorded at $325^\circ C$. Thus, the above studies show that hydrides alone may not be useful for hydrogen storage while their composites with carbon support materials can be useful.

Other systems containing carbon have also been proposed in the recent past. Here, the subset of Liquid Organic Hydrogen Carriers (LOHCs) is promising as it is very easy to transport liquid fuel through the infrastructure supporting the storage and distribution of petroleum-based fuels. LOHCs store hydrogen in liquid state. These are organic in nature and can attach to hydrogen atoms in liquid state and de-hydrogenate. Such systems that include cyclohexane, decalin, etc. are seen as easy substitutes for the present diesel/ petrol liquid fuels. Hydrogenation processes are well understood and can be carried out at large scale. However, efficient, fast, and safe dehydrogenation needs to be achieved. In this regard, some catalysts (Pt, Pd, Rh, etc.) have been used for improving the kinetics of dehydrogenation. However, the goal is to use non-noble metal catalysts (Figure 12).

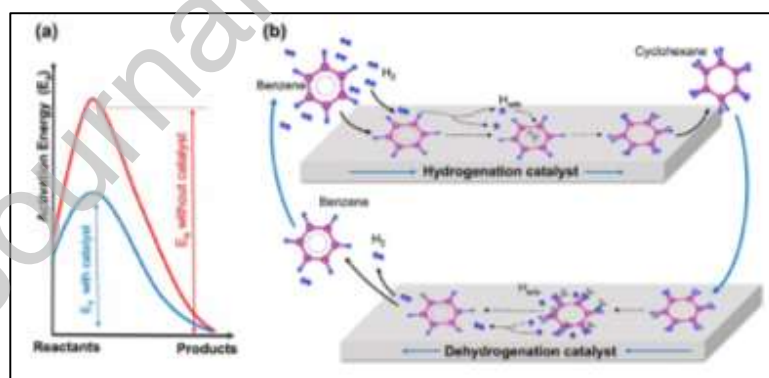


Figure 12. General principles for adjusting the kinetics of hydrogenation and dehydrogenation reactions with catalysis. (b) Illustration showing the catalytic hydrogenation/dehydrogenation mechanism for the capital CBH cycle. Reprinted with permission from M.S. Salman, N.

Rambhujun, C. Prathana, K. Srivastava, K.-F. Aguey-Zinsou, *Catalysis in Liquid Organic Hydrogen Storage: Recent Advances, Challenges, and Perspectives*, Industrial & Engineering Chemistry Research 61 (2022) 6067-6105 [363]. Copyright 2022 American Chemical Society [363].

Some theoretical studies too are pertinent for discussion. First principles study on fullerenes have shown a theoretical capacity of 7.5 wt.%, which can be increased to 10.5 wt.% for Ti-doped fullerene in the temperature range from 100-300 K. The study showed that 56 H₂ molecules could be stored on the fullerene balls. The desorption of H₂ molecules was shown to occur in the temperature range of 245-256 K [364]. Multiwalled carbon nanotubes of varying diameters were also investigated for hydrogen storage properties. A meagre uptake of 0.01-0.6 wt.% of hydrogen could be successfully stored reaching 0.6-0.87 wt.% [365]. Doping the carbon nanotubes improved the uptake capacity marginally for Pd-MWNTs and the maximum reported value was 0.87 wt.% [366-367].

The next-generation graphene materials have been explored theoretically [368-369]. Graphdiyne (GDY) is a two-dimensional carbon allotrope which has two stable di-acetylenic groups [370]. Theoretically, the GDY can store hydrogen storage via the van der Waals forces and the interaction strength of about 60-70 meV per molecule. To enhance the interaction strength, GDY was doped with boron and later decorated with Ni to improve the hydrogen bonding. The theoretical study shows that a significant enhancement of about 1.2 eV/H₂ molecule is predicted by exploring Ni-GDY in comparison to undoped or B-GDY. However, Ni-GDY is unsuitable for room temperature adsorption/desorption of H₂ due to high binding energy. Boron doping proved beneficial as it facilitates charge transfer from Ni to GDY resulting in better synergy between the Ni atoms and the supporting GDY network. An improvement in the binding energy values was predicted when B-GDY was used, and Ni atoms added suitably. The desorption temperature was also predicted to be in the 300 K to 500 K range (Figure 13). Thus, co-doping of GDY network with B and Ni gives better options for hydrogen storage. Few other theoretical reports also discuss the utility of next-gen graphene derivatives in hydrogen storage. A lithium-doped graphene system was studied theoretically by Hussain *et al.* which was doped by replacing two hydrogen atoms by Li atoms [371]. The positive charges on Li atoms influenced the polarization of approaching hydrogen molecules and resulted in van der Waals bond formation between incoming hydrogen and the substrate. A value of 9.37 wt.% and 12.12 wt.% were reported for zero and non-zero lattice strain, respectively. The binding energy was calculated as falling in the range 0.15 to 0.20 eV [372-373].

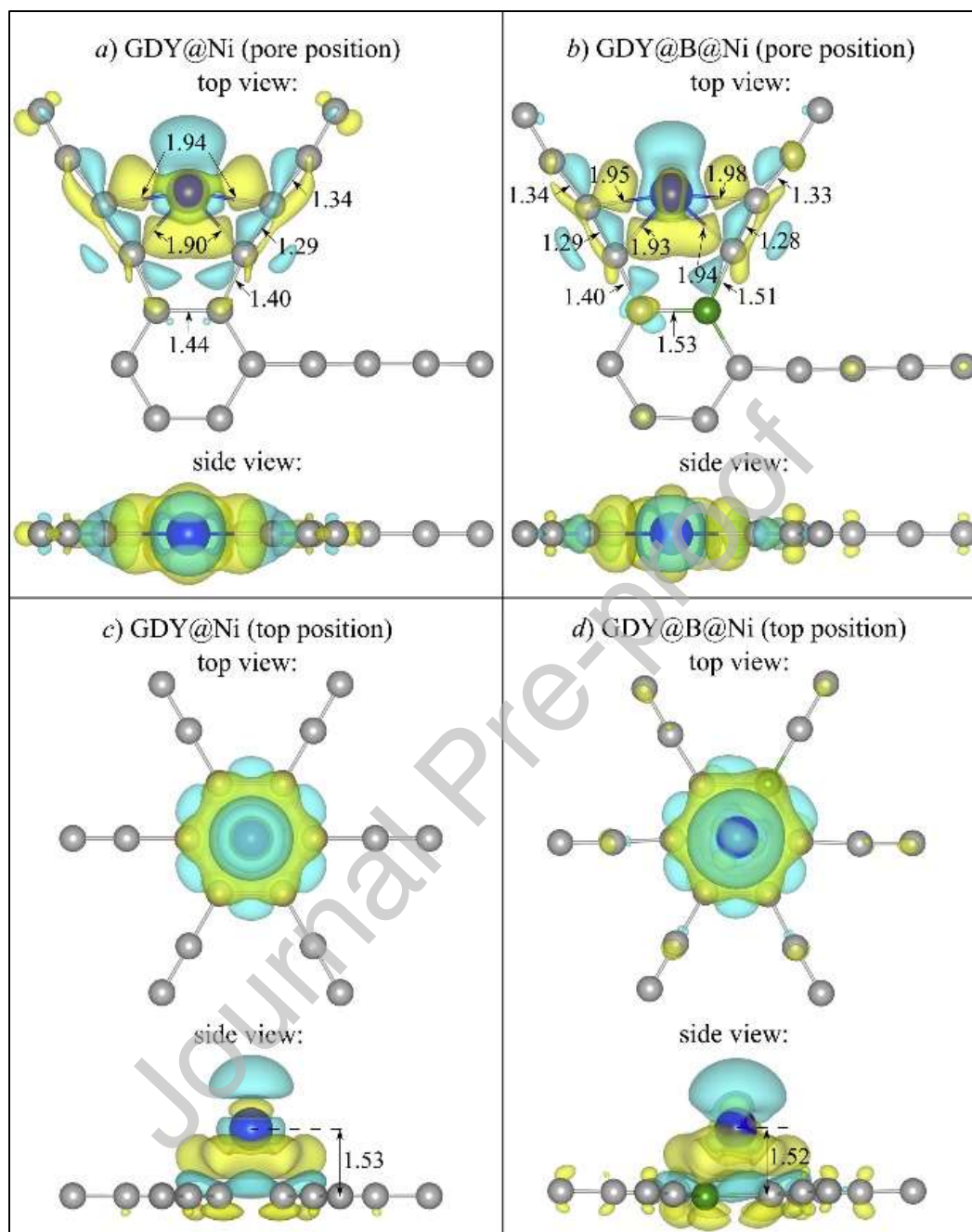


Figure 13. “Relaxed structures of pristine and B-doped GDY with Ni a) and b) inside the big pore; c) and d) on top of the small pore. Ni, C, and B atoms are blue, gray, and green, respectively. All bond lengths and distances are in Å. Cyan and yellow isosurfaces (0.0025 e) show charge depletion and accumulation, respectively.” Reprinted from Materials Today Energy, 16, E.V. Anikina, A. Banerjee, V. P. Beskachko, R. Ahuja, Influence of Kubas-type interaction

of B–Ni codoped Graphdiyne with hydrogen molecules on desorption temperature and storage efficiency, 100421, Copyright (2020), with permission from Elsevier [370]

9.5. The mechanisms of hydrogen storage with carbonaceous materials

A carbon network (combination of sp^3 , sp^2 , sp^1) purely cannot serve as a hydrogen storage material. Upon hydrogenation, a carbon network will get passivated soon and then not offer adequate and favorable adsorption sites. Thus, there are no means to increase adsorption on these materials. The interaction strength of adsorbed H_2 molecule is feeble and may lead to undesirable desorption at ambient conditions. For room temperature storage, a range of 20–40 kJ/mol binding enthalpies has been suggested. Cases where physisorption is the primary interaction between H_2 molecules and the adsorbate, the binding enthalpies fall below the suggested range. Examples include pure carbon-based nanomaterials, zeolites, or some metal organic frameworks. Cases where chemisorption is the primary interaction between hydrogen atoms and adsorbate, the binding enthalpies are quite high resulting in stronger covalent bonds. Therefore, even if the adsorption events are favorable, their rates, high heat of adsorption and desorption processes pose a problem for room temperature storage. Therefore, routes that favor binding energies from 20 to 40 kJ/mol need to be explored. Studies indicate that either functionalized carbon supports, or nanoparticle dispersed carbon supports are promising candidates. Depending upon the type of functionalization and nanoparticles, primarily two mechanisms are reported which are discussed now.

9.6. Kubas interaction

Kubas interaction deals with the interaction of hydrogen molecules in the presence of transition-metal (TM) nanoparticles. Studies show that the H–H bond loosens from the 0.74 Å bond length of free hydrogen molecule to more than 0.84 Å for Kubas-type interaction. This loosening of H–H bond occurs due to the interaction of hydrogen bonding electrons that are donated to empty 3d orbitals of TM nanoparticles and then back donated to the anti-bonding of hydrogen. In the whole process, the H–H molecules get oriented towards the metal bonds as shown in Figure 14. This coordinated molecule can bind hydrogen to the metal and hence improve the hydrogen storage.

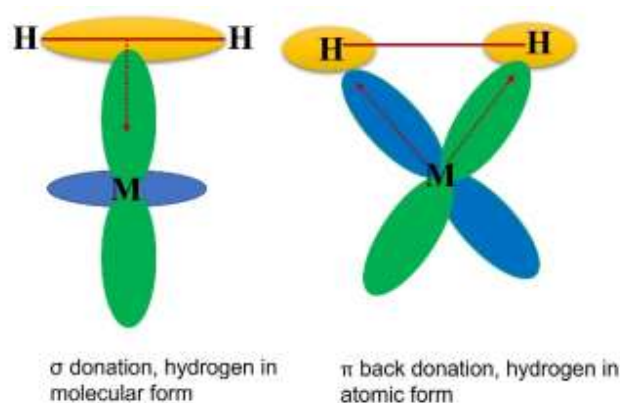


Figure 14. Kubas interaction depicting sigma donation and pi-back-donation.

9.7. Spillover mechanism

Spillover mechanism addresses the bonding of hydrogen over the carbon support. In this type of mechanism, the support influences the H-H bond strength, which loosens and two dissociated hydrogen atoms form. The energy required for this dissociation is lowered by using nanoparticles as catalysts over the carbon support. Dissociation of H_2 molecules into H atoms is now discussed. In the presence of nanoparticles, the polarizability of the H_2 molecule is affected and hydrogen atoms get chemisorbed on the nanoparticles, which are usually metallic in nature. As the H-atoms chemisorb on metal nanoparticles, their H-H bond loses strength and ultimately breaks. If surface diffusion is favorable on the support material (graphene, functionalized graphene, nanoparticle-decorated graphene, etc. two-dimensional material), then the H-atoms first saturate the nanoparticles, and then diffuse on the underlying support. As H-atoms migrate from the catalyst nanoparticles and *spill* onto the support, the catalyst can dissociate subsequent incoming H_2 molecules and further dissociate them. Thus, a good synergy between the catalyst nanoparticles and carbon support can result in higher storage of hydrogen. Figure 15 depicts the role of functionalized graphene that favors spilling of the hydrogen atom over the graphene support [351]. Further, if the carbon support is functionalized, then it can bond with the metal nanoparticles and the spilled-over hydrogen atoms resulting in higher uptake capacities [356; 359; 373]. In both the above mechanisms, nanoparticles act as catalysts. Smaller the size of the nanoparticles, better are their catalytic properties. However, smaller nanoparticles have high cohesive energies. Thus, they tend to agglomerate resulting in reduction of the loss of improved catalytic activity due to smaller-sized nanoparticles. Functionalized carbon support has shown tremendous improvement in this regard [351].

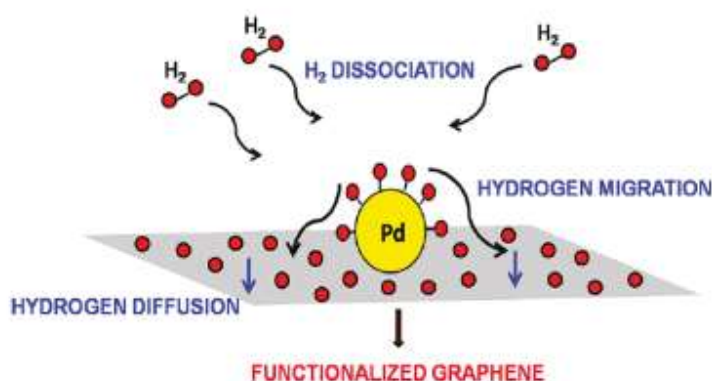


Figure 15. Schematic of hydrogen spillover on functionalized graphene [351].

9.8. The future of carbon nanomaterials in hydrogen storage

The benefits of carbon nanomaterials have been discussed in detail in the earlier sections. Functionalized carbon nanomaterials also provide the right binding energy via the physico-chemical bonding options. As it is very easy to handle carbon nanomaterials and functionalize them, their popularity as potential storage materials will always exist. Hence, their use as hydrogen storage materials is promising. With predictions of newer two-dimensional graphene derivatives, it is likely that the new generation of carbon nanomaterials picks up research efforts in the field of hydrogen storage and meets the DOE targets.

10. Metal Organic Frameworks (MOFs) and Related Systems

Hydrogen storage is an emerging field of study for future transportation. After low-cost MOF-5 discovery, it was selected to be evaluated in hydrogen storage. MOFs are organometallic materials or coordination polymers that contain a metallic center and organic ligands interconnected with each other. They have been studied mainly in catalysis, adsorption, and gas separation. Recent reviews are available in the literature [374-377]. Some important conclusions emerge: i) Gaining a deeper understanding of the interaction between gas and MOFs materials will be possible through the computational and machine learning techniques, it will promote the design and development of ideal MOFs [377]. ii) Total hydrogen storage lies on 6–15 wt% at 77 K and high pressure, which is good since the US DOE target is 5.5 wt%; but storing at room temperature, typically in 0.5-1wt%, is still a challenge. Important factors are shown in Figure 16 [374]. iii) There are still challenges to obtain MOFs modified with nanoparticles [375], and iv) MOF modifications such as doping with metal ions, nanoparticles or formation of composites could favor hydrogen storage [378].

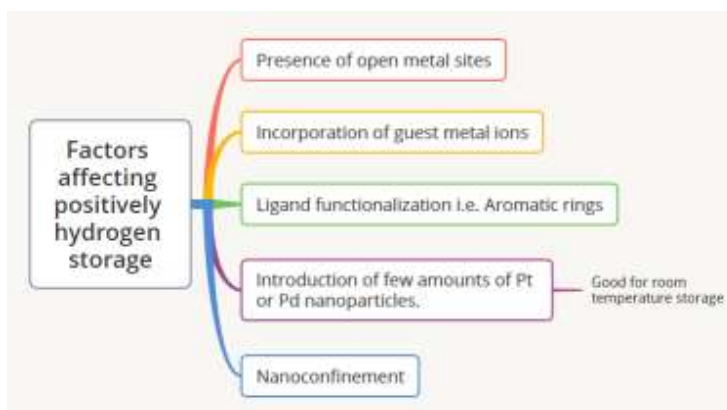


Figure 16. Factors affecting hydrogen storage.

MOFs were discovered in 1999 [378]; they have been researched as hydrogen storage material with a capacity of 5.2 wt% at 77 K and 50 atm. [379]. Table 5 summarize the hydrogen storage capacity of recent literature with a better potential than the former reference. Among materials, MgH_2 occupies high hydrogen capacity of 7.6% w/w together with good reversibility and low cost, but high operating temperature ($>300^\circ\text{C}$) and slow dehydrogenation kinetics seriously hinder its practical application [284], however modification with Niobium oxide decreased the temperature (Table 5, entry 2). A MOF-derived bimetallic Co@NiO catalyst was synthesized and doped with MgH_2 to enhance the capacity hydrogen desorption, and resorption kinetics. Doped Co@NiO catalyst decreased dehydrogenation temperature since the beginning by 160°C , compared with un-doped MgH_2 (Table 5, entry 2).

In the other hand, through computational evaluation of near 7444 MOF database H_2 storage capacities were among 8.044 and 12.191 wt% at 77 K and 100 atm., this is the highest value of that was reported by the authors (Table 4, entry 5). Jia et al. have recently reviewed the use of MOF for hydrogen storage showing important facts prior to commercial scale of MOF [377]; the most representative for hydrogen storage are illustrated in Table 5, entries 6 to 8. Also, by computational calculations Heterofullerene $\text{C}_{48}\text{B}_{12}$ -impregnated MOF-5 and IRMOF-10 have been evaluated in hydrogen storage showing adsorption up to 7.1 wt% (Table 5, entry 3). Several MOFs modified with copper were evaluated by computational calculations with the best results in Table 5, entry 4. Bian et al. reported also by computational calculations boron-phosphorus cube based covalent organic frameworks (BP-COFs), being the best storage 8.57 wt% (Table 5, entry 9) [380]. Shet et al. have reviewed MOF for hydrogen storage [376], the most representative materials are in Table 5, entries 10 and 11. NU-1501-Al exhibits a high BET surface area equal to $7310\text{ m}^2\text{ g}^{-1}$ that contributes to hydrogen storage capacity (Table 5, entry 12). Through computational calculations MOF-19 conformed by octahedral Al and modified with ligands (octametallic inorganic secondary building units exhibited a high hydrogen storage capacity (Table 5, entry 13). It is shown in Table 5, entries 15 and 16, typical values of storage at low pressure, furthermore, increasing temperature strongly reduce the adsorption capacity (Table 5, entry 14).

Table 5. Storage capacity of MOFs

Entry	MOF	Storage capacity (wt%)	Ref.
1	MgH ₂ + 9% (mass) Co@NiO composite	5.4 at 165 °C and 30 atm.	Zhang et. al [284]
2	7 wt% Nb ₂ O ₅ @MOF doped MgH ₂	6.5 at 175 °C and 32 atm.	Zhang et. al [381]
3	Heterofullerene C ₄₈ B ₁₂ - impregnated IRMOF-10	7.1 at 77 K and 12 atm. (verified with computational calculation)	Yu et. al [382]
4	Cu-MOF-399	8.3 at 77 K and 50 atm. 0.46 t 298 K and 140 atm. (Computational calculations)	Srivastava et. al [383]
5	BOQQAD	12.191 at 77 K and 100 atm. (Computational calculation)	Lu et. al [384]
6	MOF-210	17.6 at 77 K and 80 atm.	Furukawa et. al. [385]
7	NPF-200	13.1 at 77 K and 100 atm.	Zhang et. al [386]
8	NU-100	16.4 at 77 K and 70 atm.	Sen Wang et. al [387]
9	BP-COF-5	8.57 at 77 K and 100 atm. (Computational calculation)	Bian et. al. [380]
10	she-MOF-1	12.6 at 77 K and 100 atm.	Gomez- Gualdron et. al. [388]
11	DUT-32	14.21 at 77 K and 80 atm.	Gruner et. al. [389]
12	NU 1501-Al	14.5 at 77 K and 100 atm.	Chen et. al. [390]
13	MOF-519	16 at 77 K and 100 atm. (Computational calculation)	Rahali et. al [391]
14	Li- MOF-C30	6.6 at 300 K and 100 atm. (Computational calculation)	Volkova et. al. [392]
15	Zn BTC Rb ⁺	0.15 at 77 K and 1 atm	Almasi et. al. [393]
16	C ₄ H ₁₈ B ₂ Na ₂ O ₁₄	0.108 at 77 K and 1 atm.	Ozer et. al. [394]

The literature review indicates that computational could accelerate the finding of the best MOFs for hydrogen storage, but it is still an open field in the production of selected structures based on MOFs. It is preferred materials with high surface areas, but factors such as composition, adding ligands, or confinement effects are important to promote hydrogen storage capacity. The most reported methods of synthesis are based on precipitation (either hydrothermal treatment or not).

11. Perovskites and Related Systems

Another type of materials researched for hydrogen applications are perovskites [395-398]. The first perovskite was discovered in 1839 by the Prussian mineralogist Gustav Rose in mineral deposits in the Ural Mountains with formula CaTiO_3 [399]. Subsequently, synthetic perovskites were obtained by different preparation routes. The crystal structure of this compound, initially thought to be cubic, was later shown to be orthorhombic. The general formula is derived from the composition ABX_3 . To some extent the multiplicity of phases that belong to the perovskite family can be rationalized by assuming that perovskites are simple ionic compounds, where A and B are metal cations, and X is non-metal anion [399]. Depending on the composition, perovskite can have quite different structures, such as oxides, oxyhydrides and hydrides; with several applications as shown in Figure 17, where oxyhydrides and hydrides have also been investigated to measure hydrogen storage capacity. Gencer et al. approached their study on XNiH_3 perovskite type hydrides (being X atoms of Li, Na or K) perovskite type hydrides and reported that LiNiH_3 had better results related to hydrogen storage capacity and desorption temperature (4.40 wt%, 446.3 K) while KNiH_3 had the lowest ones (3.30 wt%, 367.5 K). Among the conclusions mentioned by the authors is the influence of X atom type from Li to K, due to the hydrogen storage capacity decreases with the increasing of the mass of the element in the perovskite; and they also found in this study, that these compounds are energetically, mechanically and dynamically stable and synthesizable [395]. Another study, NaXH_3 perovskite (being X atoms of Mn, Fe, Co) have also been investigated and the results of the structural optimizations showed that all these compounds have negative formation energy implying the thermodynamic stability and synthesizability. Regarding the investigation on hydrogen storage characteristics of NaXH_3 compounds resulted in hydrogen storage capacities of 3.74, 3.70 and 3.57 wt% for X equal to Mn, Fe and Co, respectively. The authors indicated that their study is the first investigation of NaXH_3 perovskite type hydrides as known up to date and may provide remarkable contributions to the future research in hydrogen storage applications [397]. Garara et al. [398] focused their research on hydrogen storage properties using the MgCoH_3 perovskite were found a structure mechanically stable, formation energy equal to $-71.30 \text{ kJ.mol}^{-1} \cdot \text{H}_2$, comparable value with the theoretical value $-73.32 \text{ kJ.mol}^{-1} \cdot \text{H}_2$, desorption temperature equal to 545.52 K, and storage capacity equal to 3.505 wt%. Hayat et al. published in their work perovskites type hydrides with composition XCuH_3 , (being X atoms of Co, Ni, or Zn); and their effect in the properties of each material.

The results showed that NiCuH_3 is more appropriate for hydrogen storage. The gravimetric ratio of hydrogen storage capacities was determined as 2.8 wt.%, 3.0 wt.%, and 2.7 wt.% for CoCuH_3 , NiCuH_3 and ZnCuH_3 , respectively. Anti-ferromagnetism was reported for NiCuH_3 and ZnCuH_3 while magnetism has been observed for CoCuH_3 . According to the authors, the current study is the first computational attempt of XCuH_3 , which may contribute outstanding amelioration for future investigations in hydrogen storage applications [400]. Besides, they indicate that regarding hydrogen storage capacity is consistent with the values reported in the literature for different materials and concluded that hydride perovskites XCuH_3 are suitable materials for hydrogen storage devices due to occurrence of sufficient value of hydrogen storage capacity, and large

values of negative formation energy produce energetically stable and synthesizable materials [400].

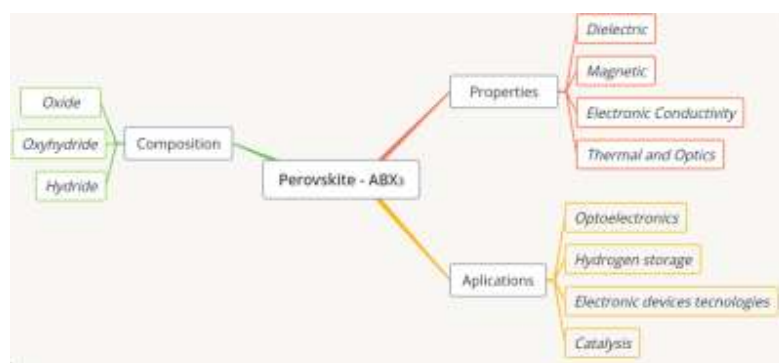


Figure 17. Important issues about perovskites

Regarding perovskite type oxyhydride, Gencer et al [396] reported the gravimetric hydrogen storage capacity of CaTiO_3H_6 equal to 4.27 wt.% and the hydrogen desorption temperature is equal to 827.1 K. They compared with other materials as MgTiO_3H_x and CaTiO_3H_x perovskite compounds and their hydrogen storage application that provides some insights for the future theoretical and experimental studies. And they conclude that this type of research is crucial to promote usage of hydrogen technology especially for on-board applications. In this sense, MgTiO_3 and CaTiO_3 perovskite compounds are investigated for hydrogen storage in terms of structural, mechanical, electronic and hydrogen storage properties systematically by using first-principle calculations. Another material, BaYO_3H_3 was reported with a gravimetric hydrogen storage capacity equal to 1.09 wt%. And they found that the composition based in BaYO_3H_9 , the structure is unstable, and it is not suitable for hydrogen storage purposes [401]. The authors conclude in this study that the perovskites for solid state hydrogen storage method could be useful in the future theoretical.

12. Hydrogen Storage for mobility and energy applications:

The rising demand for energy production with lesser resource depletion and environmental damage leads to the development of high-performance, inexpensive, and environmentally friendly energy production and storage technologies. The main factor in lowering greenhouse gas emissions is the dependence on fossil fuels. In this regard, we are compelled to investigate new environmentally friendly energy sources for the expanding population and rising demand for electricity. In a future energy economy built on sources and carriers that are ecologically friendly, hydrogen is anticipated to play a significant role. Its advantages as a preferred fuel are lightweight, high-energy density, and the absence of dangerous chemicals by-products from combustion. In addition, hydrogen is regarded as green energy because it can be produced using renewable resources and is non-polluting. However, the lack of a secure and convenient means of storage continues to be a significant obstacle to the widespread use of hydrogen as the

preferred fuel in mobile transportation [402]. To improve the performance of energy storage devices like supercapacitors, Li-ion batteries, fuel cells and hydrogen storage systems, researchers focus on using hydrogen as an energy carrier for the anticipated hydrogen economy.

Fuel cell electric vehicles (FCEVs) would become more widely available and more quickly commercialized with a low-cost, lightweight, and small hydrogen storage system, which could help cut net carbon emissions if hydrogen fuel is developed using low-carbon techniques. An in-depth understanding of the hydrogen storage technologies pertinent to transportation applications is needed. The desirable characteristics of an ideal storage medium are high volumetric and gravimetric energy densities, quick fuel uptake and release, operation at standard room temperature, and atmospheric pressure [403]. These characteristics should be optimized to produce a safe and balanced, cost-effective product. There are numerous problems with the present hydrogen storage solutions, including complicated heat management systems, boil-off, low efficiency, costly catalysts, stability problems, sluggish response times, high working pressures, low energy densities, and dangers of violent and uncontrolled spontaneous reactions. Even though it is far from ideal, the leading industry standard for compressed hydrogen now on the market offers a workable solution and shows that, in contrast to other technologies, it can provide a storage alternative for mobility.

In this regard, we must assess the hydrogen storage possibilities for transportation-related applications. Refueling for transportation needs to be quick, safety must come first, and the storage system's size and weight should be as small as feasible. It is essential to take the system into account to develop a viable solution that the industry can accept. Given present battery technology, it is critical to discuss whether hydrogen storage is required for mobility applications.

Evaluation of hydrogen storage system-related parts, including the tank, valves, piping, insulation, and reactants, while material-based value solely considers reactants or materials that contain hydrogen is needed [404]. In addition to gravimetric and volumetric requirements, the US Department of Energy has also addressed the difficulties in achieving other important system performance objectives, including cost, charge and discharge kinetics, and durability. Each method has benefits and drawbacks, and no technology is now available that can satisfy every need. Although there is still room for many advancements and fresh discoveries, hydrogen production, storage, and conversion have reached a technological level. The hydrogen storage is frequently viewed as the bottleneck of the hydrogen-based renewable energy industry. Numerous hydrogen storage techniques and materials have already been discussed; further research is required.

13. Conclusions

Research efforts are underway globally to address the energy and environment challenges that the world faces. With growing awareness and government initiatives all over the world, attempts and intentions are being converted into actions. While alternatives like nuclear, solar, wind, geothermal, electrochemical, etc. energies are also being looked into, no one energy technology would be sufficient to meet the demands. In this regard, hydrogen energy presents a very good and competitive alternative for vehicular energy demands. Hydrogen production, storage and distribution are the three main concerns, of which safe and reversible storage of hydrogen is seen

as the biggest bottleneck. This article presents an overview of potential materials, the solid-state storage journey of hydrogen in different materials, existing challenges, their processing, and design strategies. While alloying, nanostructuring, scaffolding, hierarchical designs, 2-D materials, newer derivatives of existing materials have shown a positive and upward trend in the storage capacity of solid materials, the world still awaits its alternate commercial prototype that meets the DOE targets. Combination of chemi-physisorption mechanism may be the answer to the long-standing storage challenge that provides the pathway for tackling both the thermodynamic and kinetic constraints.

Abbreviations Used:

IPHE - International Partnership for Hydrogen and Fuel Cells in the Economy

IEA -International Energy Agency

CEM - Clean Energy Ministerial

MI - Mission Innovation

MT – Million Tons

IRENA – International Renewable Energy Agency

AEO – Annual Energy Outlook

US-DOE – United States Department of Energy

LCOE – Levelized Cost of Electricity

SMR – Steam Methane Reforming

KWh – Kilo Watt-hour

MOF – Metal Organic Frameworks

FCTO – Fuel Cell Technologies Office

AI – Artificial Intelligence

ML – Machine Learning

SWCNT – Single Wall Carbon Nanotube

MWCNT – Multiwall Carbon Nanotube

ANI – Artificial Narrow Intelligence

AGI – Artificial General Intelligence

HSA – Hydrogen Storage Alloys

IMC – Intermetallic Compounds

Pa - Pascal

MPa – Mega Pascals

Atm. – Atmosphere

BCC – Body Centered Cubic

SS – Solid Solution

Ni-MH – Nickel-Metal Hydride

P-C-T (or PCT) – Pressure Composition Temperature

Wt% (or wt%) – weight percentage

kJ – Kilo Joules

PEM – Proton Exchange Membrane

H/M – Hydrogen to metal ratio

CRMM – Controlled Reactive Mechanical Milling

HRBM – High-Energy Ball Milling

NPs – Nanoparticles
 PMMA - Poly(methyl methacrylate)
 CA – Carbon Aerogels
 2D and 3D – Two and Three Dimension
 DFT – Density Functional Theory
 RHC – Reactive Hydride Composite
 K – Kelvin (Temperature scale)
 C (or °C) – Degree Celsius (Temperature scale)
 CC – Creative Commons
 LOHC - Liquid Organic Hydrogen Carriers
 MWNT – Multiwall Nanotubes
 GDY – Graphdiyne
 TM – Transition Metal
 H-H – Hydrogen-Hydrogen
 FCEV – Fuel Cell Electric Vehicle

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Conflicts of Interest

There is no conflict of interest found.