

# MATERIAL-BASED HYDROGEN STORAGE PROJECTION

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## Abstract

Massive consumption of fossil fuel leads to shortage problems as well as various global environmental issues. Due to the global climatic problem in the world, techniques to supply energy demand change from conventional methods that use fossil fuel as the energy source to clean and renewable sources such as solar and wind. However, these renewable energy sources are not permanent. Energy storage methods can ensure to supply the energy demand in need if the energy is stored when the renewable source is available. Hydrogen is considered a promising alternative feedstock owing to has unique properties such as clean energy, high energy density, absence of toxic materials, and carbon-free nature. Hydrogen is used main fuel source in fuel cells and hydrogen can be produced with various methods such as wind or electrolysis of water systems that supply electricity from renewable sources. However, the safe, effective, and economical storage of hydrogen is still a challenge that limits the spread of the usage of hydrogen energy. High pressed hydrogen gas and cryogenic hydrogen liquid are two applied storage pathways although they do not meet the above-mentioned requirement. To overcome these drawbacks, materials-based hydrogen storage materials have been mostly investigated research field, recently. The aim of the study is that exhibiting various material-based hydrogen storage systems and development of these techniques worldwide. Additionally, past and current status of the technology are explained and future perspective is discussed.

**Keywords:** Hydrogen; material- based; hydrogen storage; renewable energy

## 1. Introduction

All human activities are closely associated with energy so that it can be termed as has a crucial for our life. The increasing population of the World, consuming energy which is more than 80% are obtained from fossil sources create an energy crisis [1]. From the Industrial Revolution to now, most majority of energy has been taken by fossil fuels that are non-renewable and limited sources. No doubly that rapid utilization of fossil fuels arises from being less costly than other sources that involve renewable energy sources [2]. Consuming fossil fuels have resulted in a huge increase in CO<sub>2</sub> and other greenhouse gases and ultimately brings forth global warming. Hence, using alternative clean, sustainable end renewable energy for decarbonization of the energy activities is crucial for both sustainability of the future energy requirement and global security [3]. Considering the depletion of fossil fuels used to meet this need and the damage to the environment, the importance of renewable energy sources increases. Wind, solar, geothermal, and hydrogen can be given as renewable energy sources[4].

Among renewable energy sources, hydrogen is considered to be the most alternative energy due to has its unique properties such as clean fuel, not emitting toxic emissions, and easily applicable to fuel cells to generate electricity. Likewise electricity, hydrogen is a secondary energy form that is produced from different sources (both renewable and non-renewable) through different production methods [5,6]. Some of those; steam reforming, off-gas cleanup, electrolysis, photoprocessing, thermochemical process, radiolysis, solar hydrogen, partial oxidation of hydrocarbons [4].

Hydrogen is the most abundant element in the universe and has the highest heating value of 141.9 kJ/g that is approximately 2.6 times greater than that of natural gas (54 kJ/g), 4.8 times greater than ethanol (29.7 kJ/g), and 3 times greater than that of gasoline (47 kJ/g) [7]. Even if the chemical energy per mass of H<sub>2</sub> greater than the other hydrocarbons, the energy density of H<sub>2</sub> (on a volumetric basis) is very low than the other fuels. For instance, a liter of hydrogen compressed to 70 Mpa (4.7 MJ/L) has almost six times as lower energy as one liter of gasoline (31.7 MJ/L) [8]. Moreover, apart from low energy density, important safety issues regarding storage in the form of liquid or compressed hydrogen are a bottleneck on applications [9]. In order to broad usage of hydrogen energy and creating a hydrogen economy, hydrogen storage and transport are crucial issues.

The hydrogen economy is essential for humankind to reduce global warming-related problems and supply energy security. The hydrogen economy is termed as decreasing energy consumption and emissions while promoting economic growth and creating new jobs [13]. Within the hydrogen economy, the negative effects of utilizing hydrocarbon fuels in a variety of applications that resulted in carbon emit on the atmosphere can be solved. The present hydrocarbon economy is based on gasoline, diesel, and natural gas that are used for people's transportation and goods. Nevertheless, the processing of these kinds of hydrocarbon fuels leads to greenhouse gas emissions and other pollutants [14]. Not only transportation and goods but also industry and buildings can be decarbonized by utilizing hydrogen [15].

Therefore, hydrogen is considered as a potential solution for vehicles due to emerging only water when it is burned [10]. Thanks to possible applications for the stationary, portable, and transportation sectors, fuel cells are a renewable and clean energy sector [8]. The efficient storage of hydrogen is a drawback of not commercializing hydrogen fuel cell technologies. Even if it includes the highest energy per unit mass that the other hydrocarbon fuels, its energy density is very low that leading to storage efficiency in small volumes [11]. For example, liquefying hydrogen solves the storage volume problem but creates other technological hurdles. If the storage problem is solved, the hydrogen economy will improve [4].

Appropriate and sustainable materials within hydrogen storage are crucial for the hydrogen economy. For this reason, scientists have investigated methods of storing hydrogen more efficiently. In order to store hydrogen, certain properties must be possessed. These are high storage pressure, low storage temperature, or using a material that attracts large amounts of hydrogen molecules [12].

Physical-based and material-based storage are the main phenomenons of hydrogen storage technologies. Physical-based storage includes compressed gas, cold/Cyro-compressed, and liquid hydrogen storage while material-based hydrogen storage involves two main sub-groups that are chemisorption and physisorption [6,12]. Thus, material-based hydrogen storage has gained an attraction to store greater volumetric energy content.

In this study, material-based hydrogen storage technologies are evaluated. In order to exhibit the past and current situation of the technology, European Unite Project was examined. Moreover, patent research has been carried out to show the state of the technology closest to being commercialized and also state of the art. The study consists of the sub-titles of material hydrogen storage and the sub-groups and projects that constitute it, the patent study is included, and the result and future perspective.

## 2. Material-based hydrogen Storage

By the way of adsorption or absorption, various materials can be applied to store hydrogen in the solid-state. The first is a physical process in which hydrogen is stored on the surface of the material whereas chemical the second is a chemical process that includes storing hydrogen in the material and a chemical reaction occurs [13]. In view of high safety, high volume storage capacity, and low operating temperature and pressure, solid material-based hydrogen storage is considered a developed method [14]. To summarize, there are two main subgroups of material-based storage: chemical absorption and physical absorption. Surface adsorption, metal hydride, complex hydrides, chemical hydrides are subclasses that form material-based hydrogen storage [15]. In the next section, they are explained in detail.

### 2.1. Chemical/Chemisorption hydrogen storage

Chemical/Chemisorption storage is based on a chemical reaction that hydrogen is produced through this process. Ammonia ( $\text{NH}_3$ ), metal hydrides, formic acid, carbohydrates, synthetic hydrocarbons, and liquid organic hydrogen carriers are the materials that take place in chemical storage [16]. Compared to physisorbed, gaseous, and liquid hydrogen storage, chemisorption storage have more volumetric density of the systems. Nevertheless, this method requires to be developed in the aspect of high-cost, the low gravimetric density of hydrogen for alloys, and high operating temperatures for chemical hydrides [17].

#### 2.1.1. Metal Hydrides

Due to its high-density hydrogen storage and well safety option, metal hydride is one of the material that used in solid-state hydrogen storage. During the formation period of metal hydrides, hydrogen molecules are separated, and obtained hydrogen atoms are stored in suitable metal cages. Hydrogen reacts at high temperatures with many transition metals and alloys to form hydrides [13]. Hydrogen is stored in the metal hydrides in form of alloy or compound, and stored hydrogen is delivered in the form of hydrogen gas by diffusion [18].

Metals, intermetallic compounds, and alloys are materials that enable to absorption of hydrogen under average pressure at low temperatures to generate reversible metal hydrides. Among the conventional and the other methods, metal hydrides can store high volumetric hydrogen storage densities and they are safer than physical hydrogen storage methods such as compressed and liquified hydrogen storage systems [19]. Even if the first absorption of the large quantity of hydrogen within Pd metal was found by Thomas Graham in 1866, discovering reversible hydrogen absorption/desorption in intermetallic compounds that are namely ZrNi (1958),  $\text{Mg}_2\text{Ni}$  (1968),  $\text{LaNi}_5$  (1970), and FeTi (1974) became a milestone for metal hydrides [20].

Based on the type of chemical bond such as metallic, covalent, or ionic bond, hydrogen forms a bond with elements in solid-state interstitial and non-interstitial hydrides [21].

In interstitial hydrides, hydrogen creates a metallic bond with metal atoms while these types of bonds are switch to covalent and/or ionic bonds in non-interstitial hydrides. To give an illustration of interstitial hydrides and non-interstitial hydrides,  $\text{LaNi}_5\text{H}_6$ ,  $\text{TiCr}_2\text{H}_4$ ,  $\text{TiFeH}_2$ , Ti-V-Cr-H, and  $\text{NaAlH}_4$ ,  $\text{Mg}(\text{NH}_2)_2$ ,  $\text{LiBH}_4$ ,  $\alpha\text{-MgH}_2$ , respectively [21].

Among these interstitial hydrides,  $\text{LaNi}_5\text{H}_6$ ,  $\text{TiFeH}_2$ ,  $\text{ZrMn}_2$  were the focus of interest for the past decades in the view of hydrogen storage due to their reversibility and rapid kinetics under appropriate temperature and pressure [22]. On the other hand, these hydrides suffered from gravimetric density

(<2 wt% H<sub>2</sub>) and resulting in limited applications. Hence, the focus area switched from these hydrides to novel light-metal, for instance, Li, B, N, Na, Mg, and Al in hydride forms [23].

In the non-interstitial hydrides, either a covalent or ionic chemical bonding is carried out by hydrogen. Complex hydrides of metal alanates (M(AlH<sub>4</sub>)<sub>n</sub>), metal amides, (M(NH<sub>2</sub>)<sub>n</sub>), and metal borohydrides (M(BH<sub>4</sub>)<sub>n</sub>), Mg-based hydrides, Al hydride (AlH<sub>3</sub>), ammonia borane (NH<sub>3</sub>BH<sub>3</sub>), etc. take place on in this group [21]. Due to complex hydride is not be able to rehydrogenated under moderate conditions, it was not regarded as a hydrogen storage material. However, the first time, the reversible hydrogen storage of NaAlH<sub>4</sub> was founded via applying of Ti-based catalyst by Bogdanovic and Schwickardi in 1997 [24]. After then, research on the non-interstitial hydrides was centered.

The target of the gravimetric density of 6.5 wt.% and volumetric density of 62 kg/m<sup>3</sup> has been determined by The US Department of Energy for using hydrogen storage systems [20]. In view of the expected goal for vehicular applications, the hydrogen storage capacity of metals and intermetallic compounds is insufficient due to their lower gravimetric density, reaction kinetics, cycle life, reaction thermodynamics, and cost issues [13].

### 2.1.2. Complex hydrides

Complex hydrides are considered as potential hydrogen storage material due to being light-weight and including a large amount of hydrogen. Hydrogen and group 1, 2, 3 light metals such as Li, Na, B, and Al, originate complex hydrides and they are termed as a group of metals [25]. Alkali metal and alkaline earth metal alanates, borohydrides, amides, and ammonia are given as examples to those groups. Thanks to their low molecular weight, a larger amount of hydrogen storage is obtained. Some examples of complex hydrides and their theoretical hydrogen capacity as follows; NaAlH<sub>4</sub> (7.5 wt%), LiAlH<sub>4</sub> (10.6 wt%), Mg(AlH<sub>4</sub>)<sub>2</sub> (9.3 wt%), LiNH<sub>2</sub> (8.7 wt%), NH<sub>3</sub>.BH<sub>3</sub> (19.6 wt%) [20].

#### 2.1.2.1. Alanetes

M<sub>n</sub>(AlH<sub>4</sub>)<sub>n</sub> represents a general formula of the tetra-alanates. M is generally an alkaline or earth-alkaline metal and also M can be metal in which group III and IV in the Period Table [26]. Alanate is synonymous with alumino-hydride. They are hydrides to which 4 hydrogen atoms of an anion with Al element in the center are covalently bonded [27].

Alanates, lithium, and sodium salts are readily available commercially. Especially sodium alanate is the most suitable for necessity. However, problems such as capacity, thermodynamics, kinetics, and safety do not give precise information about its use in the future.

Although sodium alanate (NaAlH<sub>4</sub>) has a high gravimetric capacity, storing hydrogen is carried out in three-step reactions that the last one requires above 400 °C. Therefore, comparatively high desorption temperature and limited reversibility restrict its application. Recently, [28] have developed materials based on polymer nanocomposites for hydrogen storage with comparatively lower temperatures (120 °C). Although up to 1.2 wt% of H<sub>2</sub> was stored in the nanocomposite after 12 h at 32 bar, the polymer-based new nanocomposite is considered significant for technological development due to enhance hydrogen sorption capacity and protect fillers from moisture.

Lithium alanate (LiAlH<sub>4</sub>) has gained more attraction since 2001 due to its hydrogen storage capacity of 10.5 wt% and an enthalpy value of -113.42 kJ mol<sup>-1</sup> [29]. Despite its superior properties, it has high thermal stability and slow hydrogen absorption/desorption kinetics. Hence, studies turn to find efficient methods to enhance the hydrogen storage features of such complex hydrides. For LiAlH<sub>4</sub>, doping catalysts that containing the putting of nano-sized metal oxides, Ti-based catalysts, transition

metal halides, and so on, are applied to overcome the thermodynamic and kinetic problems [30]. Even if its theoretical hydrogen storage capacity is high, high dehydrogenation temperatures and comparatively slow kinetics are the bottlenecks of lithium alanate. Hence, Zang et al, [31] have studied the different ratios of LiAlH<sub>4</sub> doped with varied % mol of TiF<sub>3</sub> (1 mol%, 2 mol%, 4 mol%, and 6 mol%) to decrease dehydrogenation temperature. Results showed that prepared 3D flower-like nanocrystalline Ni/C catalyzed the dehydrogenation of LiAlH<sub>4</sub> and dehydrogenation of 48 °C as that is close to the ambient temperature was found out in the 10 wt% Ni/C+LiAlH<sub>4</sub> system.

#### 2.1.2.2. Borohydrides

Among hydrogen storage materials, tetrahydroborates are the highest hydrogen-containing compounds. Hydroborates are stable, thus dissolving in water creates non-danger. Hydroborates or the other name of complex metal borahydrates consist of a chemical structure of M(BH<sub>4</sub>)<sub>n</sub>. When all complex metal borohydrates were considered, LiBH<sub>4</sub> (18.5 wt% and 121 kg H<sub>2</sub>/m<sup>3</sup>), NaBH<sub>4</sub>, Mg(BH<sub>4</sub>)<sub>2</sub>, and Ca(BH<sub>4</sub>)<sub>2</sub> have been present a great possible hydrogen storage material because of their high gravimetric and volumetric hydrogen storage densities [19,32].

In contrast to their high gravimetric storage densities, they have incapable thermodynamics and slow kinetics for dehydrogenation and rehydrogenation. For instance, LiBH<sub>4</sub> needs to above 500 °C to release most of the hydrogen [32]. Recently, Zhang et al [33] achieved reversibility desorbs and absorbs approximately 9.2 wt% of hydrogen at comparatively low temperature (300 °C) via synthesized LiBH<sub>4</sub> nanoparticles decorated by Ni nanocrystals on graphene composite. Moreover, 100 cycles of stable cyclability were obtained.

#### 2.1.3. Chemical hydrides

Despite the disadvantages of physically adsorbed (i.e. porous nanomaterial) and chemically stored into hydrides of hydrogen, storing of H<sub>2</sub> in liquid compounds via binding atomic hydrogen to hydrogen-lean can be performed at ambient conditions. Based on hydrogen-lean molecules, indirect hydrogen storage can be divided into two pathways. In a first way, the atmosphere or exhaust gas mixtures are employed to produce the hydrogen-lean molecule (such as CO<sub>2</sub> and N<sub>2</sub>). Formic acid (HCOOH), alcohol, and ammonia are the modal hydrogenated forms of these hydrogen-lean molecules. The second way is that liquid organic hydrogen carriers (LOHCs) [34].

Any other option to store hydrogen is chemically storing. Chemical hydrogen is termed for storing hydrogen via synthesizing molecules that contain hydrogen. In this content, ammonia gives a promising alternative because of can be produced without carbon dioxide, having a high energy density of liquid ammonia is reaching 17.6 wt% [35]. Although solid oxide fuel cells are a possible way for the employ ammonia in the fuel cell, durability issues come across as the problem of these fuel cells.

##### 2.1.3.1. Ammonia borane

Due to its high gravimetric and volumetric hydrogen densities, B-H-N compounds have taken attraction themselves. One of epitomist is ammonia borane NH<sub>3</sub>BH<sub>3</sub> (AB). The first time was observed by Sch Schlesinger and co-workers, however, found out by Shore and Parry in 1955 [36]. Though as a hydrogen storage material, found of AB was occurred in the mid-2000s. AB has superior properties such as having a gravimetric H density of 19.5%, stability at ambient conditions, and under an inert atmosphere. Hydrogen generation is carried out in the water and the existence of a catalyst via hydrolyzation reaction [37].

At the ambient conditions, ammonia borane is a solid and it is a good candidate for chemical hydrogen storage owing to having high gravimetric H capacities, recovering of 13 wt% H<sub>2</sub> below 200 °C. However, recovering of 13 wt% of H<sub>2</sub> is expected to below 100 °C for application purposes [38]. Its high stability under environmental conditions, non-toxicity, and high solubility in solvents are its important advantages. Hydrogen can be released from ammonia borane by thermolysis or solvolysis in the presence of suitable catalysts. Hydrolysis of methanol are ways to produce hydrogen from ammonia borane for hydrogen fuel cell applications at ambient temperature [39].

#### 2.1.4. Formic acid

Even if H<sub>2</sub> density is low (4.4 wt%), formic acid is defined as a highly efficient hydrogen storage material. Due to H<sub>2</sub>/CO<sub>2</sub> is only produced as gaseous, formic acid is superior to other substrates that release by-products [40]. HCOOH (formic acid) is generated as a by-product through biomass processing like fermentation, pyrolysis, and supercritical reactions. Decomposition of formic acid (FA) to hydrogen and carbon dioxide is carried out the only existence of a catalyst. Electrochemically or catalytic hydrogenation is two methods for converting CO<sub>2</sub> to formic acid or formate hydrides. Due to the final product is liquid or solid at ambient conditions, it is enabled to be handled, stored, and transported readily [41]. It can be mentioned that catalyst has an enormous effect on temperature and pressure of decomposition of formic acid. In catalytic decomposition, pressure is the change from 1 to 200 bar while pressure can reach up to 750 bar in non-catalytic decomposition [40].

Even though the first homogeneous catalysts for FA-decomposition were informed in 1967, the practical potential of FA in hydrogen technology was informed in 2008 by the Beller group [42] and Laurency group who using water-soluble Ru based complexes to catalyze the dehydrogenation of FA [34].

In experiments, it has been observed that hydrogen produced from formic acid can be used directly in fuel cells without the need to remove carbon monoxide beforehand. This can form the basis for electricity generation by fuel cells. Such storage and distribution methods would greatly assist in improving the hydrogen economy [43].

#### 2.1.5. Carbohydrates

Thanks to its properties such as abundant, low cost, the high hydrogen storage density of > 8% H<sub>2</sub> mass%, and carbon neutrality, renewable carbohydrates are considered as promising hydrogen carriers [44]. Carbohydrates (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>) are a liquid that has high hydrogen storage density under lower pressurization and cryogenic restraint. Moreover, it also is stored as a solid powder. Carbohydrates are considered as a high energy density hydrogen carrier (14.8 wt %) thanks to full conversion and modest reaction conditions [16]. Although carbohydrates some advantages regarding low reactor cost, operation at 30-80 °C and under 1 bar, they have some disadvantages that limit the process such as enzyme cost and stability, cofactor cost and stability, reaction rate, etc. Therefore it is required to overcome these problems to use carbohydrates for hydrogen storage purpose[45].

#### 2.1.6. Liquid organic hydrogen carriers

Liquid Organic Hydrogen Carriers (LOHCs) store hydrogen through chemically bonding with hydrogen-lean molecules and by a catalytic dehydrogenation hydrogen is discharged. LOHCs are one of the promising choices among chemisorption [12].

The first research studies using LOHCs as hydrogen storage options go long way back to the 1980s. LOHC system toluene (TOL)/methylcyclohexane (MCH) is the early representative of focused studies. This system presents a hydrogen storage capacity of 6.1 wt % hydrogen (1.55 kWh/L) [46].

Cycloalkanes and heterocycles are unsaturated organic compounds that are employed as LOHCs to store hydrogen at room temperature. LOHCs are enabled to store/ transport hydrogen with large scale, long term, and long-distance at ambient temperature and pressure through currently used chemical tankers and infrastructures [21,47].

To summarize, currently, in order to enhance overall hydrogen storage capacity, modifications, form composites between various nanostructured metal hydrides, complex hydrides, chemical hydrides, and carbonaceous materials have been applied. Even though most hydrides have some unique properties such as being lightweight, low cost, easily accessible, and have high hydrogen density, their desorption temperature is a long way from the DOE target. Hence these materials are not suitable for practical applications even if they have high theoretical hydrogen storage capacity such as  $\text{LiBH}_4$  (18.4%),  $\text{Mg}(\text{BH}_4)_2$  (14.9%),  $\text{Fe}(\text{BH}_4)_3$  (12.1%) and  $\text{Ca}(\text{BH}_4)_2$  (11.6%) [48–50].

Due to their high hydrogen storage densities (gravimetrically and volumetrically), light-weight hydrides have taken attraction. However, the inability of metal/chemical hydrides is slow kinetics of hydrogen desorption/absorption, comparatively high thermal stability, irreversible hydrogen storage, and undesired side gases. Therefore, new strategies have been developed to improve the hydrogen storage qualification of metal hydrides. Development of reactive hydride composites, nonconfinement of hydride materials to enhance their thermodynamics and kinetics, new generation light-weight composite synthesis, hydride destabilization, catalyst additives to improve the kinetics of hydride, size reduction of metal hydride are examples of developed strategies [51,52].

## 2.2. Physical/Physisorption hydrogen storage

Physical storage occurs between molecular hydrogen and material that has a large specific surface area through physical van der Waals bonding via adsorption. Thanks to the weakness of the van der Waals bonding, important hydrogen storage densities can be obtained at low temperatures and elevated pressures [53]. The specific surface area and shape-size (void characteristic) have a strong effect on the efficiency of adsorbent material for physisorption. Hence, the carbonaceous material is one of the suitable candidates with having high specific surface area, high chemical and thermal stability, excellent kinetics, and lightweight [54].

Hydrogen molecules are adsorbed with little adsorption energy which is generally below  $10 \text{ kJ}\cdot\text{mol}^{-1}$   $\text{H}_2$  thus adsorption measurement is conducted at 77 K. Based on Chahine's empirical rule, every  $500 \text{ m}^2\cdot\text{g}^{-1}$  of the BET surface area can be adsorbed maximum of 1.0 wt% of excess hydrogen at 77 K and above 20 bar of pressure. This suggests that the larger hydrogen adsorption capacity can be obtained with the higher surface area [21].

Regarding the amount of adsorbed  $\text{H}_2$  porosity is essential. Therefore, many studies have a focus on to found suitable adsorbents, for instance, zeolites, metal-organic framework, activated carbons, and many others [55,56].

### 2.2.1. Metal-Organic Framework (MOFs)

Porous carbon with a large surface area that is termed as super-activated has been improved in the past while around 20 years ago some slowness emerged in the field. In the late 1990s, Metal-Organic Frameworks (MOFs) that have highly porous and crystalline materials were enhanced [57]. MOFs

have high porosity crystalline structures and large surface areas that can absorb a huge amount of gas molecules. Due to weak van der Waals force on the pores of the MOFs, adsorbed hydrogen can be easily desorbed under heat or pressure [58].

MOFs are composed of secondary building units and organic linkers. Thanks to modifications, they become more sufficient for storage. The BET surface area and porosity of MOFs represent comparatively higher than the other hydrogen storage material, for instance, CNT, hydrides, zeolites, and clathrates [58].

For physisorption materials, the enthalpy of adsorption is too low than chemisorption materials, hence it is thought that low hydrogen storage capacities are carried out at ambient temperature and pressure. In order to reach high storage capacities, the cryogenic temperature is necessary for sustaining a high density of hydrogen molecules on the material [51].

### 2.2.2. Zeolites

Zeolites have pores with regular intracrystalline networks and channels with sub-nanometre dimensions that lead to up to  $1000\text{m}^2/\text{g}$  of internal surface areas. The connection of tetrahedral building units,  $\text{TO}_4$  ( $\text{T}=\text{Si}$  or  $\text{Al}$ ), influences the structure of a zeolite framework [59].

This provides a high internal surface area, which is an important property for the physical absorption of hydrogen. Zeolites are a family of highly crystalline aluminosilicate materials. One of the advantages of using zeolites as hydrogen storage materials is their thermal and chemical stability, which are useful in catalytic applications. This is exemplified by the lack of flammability both in air and especially in the hydrogen atmosphere. Zeolites are more disadvantageous for mobile applications compared to carbon or metal-organic framework. This ensures that it is not preferred for storage[59].

### 2.2.3. Activated carbon

Carbonaceous materials have adsorption ability, high surface area, low mass density, and low price. Hence, they take attention to themselves for storing hydrogen. Among them, activated carbon presents high pore size and internal specific surface area (SSA) that permits these kinds of materials to apply as an effective adsorbent [60]. Significantly, hydrogen adsorption on these kinds of materials contingent extremely upon SSA and pore volume. Based on material, the experimentally measured hydrogen storage capacity change between 0.5 and 5.0 wt%. Depend on temperature and pressure conditions, activated carbon's hydrogen storage capacity shows a difference. To give an illustration of AC of hydrogen storage capacity; 0.67 w%  $\text{H}_2$  at 303K and 10 Mpa [61], 1.4 w% of  $\text{H}_2$  at 77 K and 0.1 MPa [62], 1.6 w% of  $\text{H}_2$ , at 296 K and 13 Mpa [63], 5.7 wt% of  $\text{H}_2$  at 77 K and 3 MPa [61], and 6.6 wt% of  $\text{H}_2$  at 77 K and 4 MPa for KOH-treated AC [64].

In order to enhance the specific surface area of porous carbon, physical or chemical activation is necessary [65]. Chen et al., [66] developed a porous carbon with a high specific surface area of almost  $4000\text{m}^2/\text{g}$  via carbonization of rice hull and activation with sodium hydroxide. The results showed that hydrogen storage capacity reached 7.7 wt% at 77 K and 1.2 MPa.

### 2.2.4. Carbon nanotubes

Carbon nanotubes (CNT) that consist of single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotube (MWCNT) store hydrogen through physisorption. Nano-type structure, high surface area, tunable characteristics, and lower mass density are accounted as superior features of CNT [67,68]. The first time, hydrogen of CNTs that store 1-10 wt% of hydrogen in single-walled carbon nanotubes was reported by Dillon et al in 1997 [69]. After two years later, high hydrogen uptake that



accounts for 14-20 wt% between 400 °C and the room temperature was achieved with alkali-doped carbon nanotubes by [70]. From that date to now, serious research has been performed to improve the hydrogen storage capacity of CNTs [71,72].

Owing to the low interaction energy between H<sub>2</sub> and the CNTs, hydrogen storage carried out only under cryogenic conditions, so this limited to using for mobile applications. In order to overcome low interaction energy, two main methods have been suggested; i)doping with heteroatoms, ii)incorporating light metal atoms [70]. Liu et al [73] have theoretically studied Ru decorated boron doped-SWCNT depend on the density-functional theory (DFT). Results showed that the binding energy of H<sub>2</sub> molecules increases 21.19 % compared to pure CNT. These findings implied that the boron-doped CNT system is capable of adsorbing hydrogen molecules much more.

### 2.2.5. Graphene

Graphene is 2-dimensional single sheets containing sp<sup>2</sup> –bonded hexagonal arranged carbon atoms hence it presents a wide surface area for gas adsorption. It is mentioned before, high surface area, surface porosity, good conductivity, and surface chemistry effect on adsorption behavior [67]. In the case of hydrogen storage in graphene, two pathways occur; i)physisorption and ii)chemisorption. Graphene and hydrogen present fast kinetics and small binding energies with graphene in physisorption whereas hydrogen strongly linked graphene layers in chemisorption [74]. In table 1, the hydrogen storage capacities of various carbonaceous materials are shown.

Table 1. Hydrogen storage capacities of different carbonaceous materials [75]

<b>Materials</b>	<b>Storage capacity; <math>P_m</math> (wt%)</b>	<b><math>P_{eq}</math>, T</b>
Activated carbon	5.5	80 bar, 298 K
Graphite	4.48	100 bar, 298 K
SWCNT	4.5	4 bar, 298 K
MWCNT	6.3	148 bar, 298 K
CNF	6.5	120 bar, 300 K

Carbonaceous materials and porous material have attracted attention due to their large surface area, facile reversibility, fast kinetics, low cost, and most abundant. On the other hand, reaching high hydrogen storage, a very low temperature is necessary. It has been reported in the most study, 1 wt% hydrogen storage is achieved under ambient conditions. Hence, they have required functionalization with a heteroatom, metal catalysts additives, etc to increase their sorption performance [76].

### 3. Projects

To enhance the competitiveness of the country, each nationality emphasizes the R&D projects to meeting scientific knowledge in academia with industrial stakeholders. Within the collaboration of academia, industry, and government, it can be supplied both improvements of knowledge level and also economic growth and competitiveness of the country are enhanced.

Under this view, each country prepares its road map and continues the necessary R&D activities. One of these countries is the EU. In specific to the issues identified under Horizon 2020, the government provides the necessary financial support. Under the subject of hydrogen storage, the projects that have been completed and completed, are still ongoing and will be newly started are shown in Table 2.

Table 2. EU project regarding material-based hydrogen storage

<b>Project Name</b>	<b>Date</b>	<b>Country</b>	<b>Description</b>	<b>Ref</b>
<b>Hydrogen storage in hydrides for safe energy systems (HYSTORY)</b>	2002 - 2005	Norway	HYSTORY aims to develop hydrides based on lightweight, low-cost elements with improved hydrogen storage properties. Cell applications that will integrate and test relevant hydrogen storage systems in stationary and marine fuel.	<a href="https://cordis.europa.eu/project/id/ENK6-CT-2002-00600">https://cordis.europa.eu/project/id/ENK6-CT-2002-00600</a>
<b>Hydrogen in mobile and stationary devices - safe and effective storage solution (HYMOSES)</b>	2002 - 2006	Germany	This project aims to improve and provide carbon and metal hydride materials. Thus, it will be a solution for the efficient and safe storage of hydrogen.	<a href="https://cordis.europa.eu/project/id/ENK6-CT-2002-00653">https://cordis.europa.eu/project/id/ENK6-CT-2002-00653</a>
<b>Development of novel inter-metallic materials with enhanced hydrogen storage properties</b>	2006 - 2008	France	This project is on magnesium-based materials. The aim is the synthesis of new magnesium-based alloys with high hydrogen capacity, including those prepared in nano, amorphous, or controlled micro gradient states.	<a href="https://cordis.europa.eu/project/id/INTAS2005-1000005-7671">https://cordis.europa.eu/project/id/INTAS2005-1000005-7671</a>
<b>Mechanically alloyed magnesium-based materials for hydrogen storage</b>	2006 - 2008	France	The aim is to develop research into the production of hydrogen storage materials. This material is a magnesium-based storage material. This material has absorption and desorption kinetics.	<a href="https://cordis.europa.eu/project/id/INTAS2005-1000005-7669">https://cordis.europa.eu/project/id/INTAS2005-1000005-7669</a>
<b>NEW ALANE: novel reversible hydrogen storage materials based on the alloys of Al</b>	2006 - 2008	Norway	The aim is to develop new types of absorption materials for hydrogen storage. The project includes the synthesis of materials aimed at achieving improved performance of aluminum-based alloys and composite materials as hydrogen storage materials.	<a href="https://cordis.europa.eu/project/id/INTAS2005-1000005-7665">https://cordis.europa.eu/project/id/INTAS2005-1000005-7665</a>
<b>Hydrogen generation and storage by highly porous Nanocomposites</b>	2006 - 2008	Germany	The proposed program is based on a new approach to hydrogen storage material synthesis. The aim here is to create the material for the production and storage of hydrogen from water with the composite material concept consisting of a porous matrix and hydride forming metal nanoparticles.	<a href="https://cordis.europa.eu/project/id/INTAS2005-1000005-7672">https://cordis.europa.eu/project/id/INTAS2005-1000005-7672</a>

<b>Metal-decorated single-walled carbon Nanotubes for hydrogen storage at ambient conditions</b>	2006 - 2008	Netherlands	The project aims to investigate and develop the applications of metal-decorated carbon single-wall nanotubes for in-vehicle hydrogen storage up to 5% by weight at ambient conditions. To get a basic understanding of the design and structures of carbon single-walled nanotubes is to examine hydrogen adsorption performance relationships.	<a href="https://cordis.europa.eu/project/id/INTAS2005-1000005-7726">https://cordis.europa.eu/project/id/INTAS2005-1000005-7726</a>
<b>Hydrogen storage in carbon cones (HYCONES)</b>	2006 - 2009	Greece	HYCONES is concerned with the use of carbon cones as a practical, inexpensive, lightweight, high-capacity hydrogen storage medium. It is very suitable for mobile applications.	<a href="https://cordis.europa.eu/project/id/32970">https://cordis.europa.eu/project/id/32970</a>
<b>Complex solid-state reactions for energy-efficient hydrogen storage</b>	2006 - 2010	Germany	The project aims to overcome the slow sorption kinetics of reactive hydride composites by investigating the basic structure in complex solid-state reactions.	<a href="https://cordis.europa.eu/project/id/35366">https://cordis.europa.eu/project/id/35366</a>
<b>Novel efficient solid storage for hydrogen (NESSHY)</b>	2006 - 2010	Greece	This project is about porous storage systems, regenerative hydrogen storage, and solid hydrides with reversible hydrogen storage and improved gravimetric storage performance.	<a href="https://cordis.europa.eu/project/id/518271">https://cordis.europa.eu/project/id/518271</a>
<b>Development of integrated advanced materials and processes for efficient hydrogen storage (DIAMENTE)</b>	2006 - 2010	UK	This project aims to develop and implement an integrated approach for optimum material and process design of hydrogen storage systems using advanced materials for economical, safe, and efficient storage.	<a href="https://cordis.europa.eu/project/id/29544">https://cordis.europa.eu/project/id/29544</a>
<b>Production and storage of hydrogen</b>	2006 - 2011	Netherlands	This project is about hydrogen production and hydrogen storage. The aim is to investigate the best reversible hydrogen storage material with a capacity above 5% by weight.	<a href="https://cordis.europa.eu/project/id/32474">https://cordis.europa.eu/project/id/32474</a>
<b>Boron-nitrogen based materials for hydrogen storage</b>	2007 - 2009	UK	In this study, computational methods of chemistry and solid-state physics were used for the basic chemical and physical properties of hydrogen release	<a href="https://cordis.europa.eu/project/id/46477">https://cordis.europa.eu/project/id/46477</a>

			and uptake of boron and nitrogen-based materials.	
<b>Novel Nanocomposites for Hydrogen Storage Applications (NANOHY)</b>	2008 - 2011	Germany	The project aims to combine the latest developments in the field of metal hydride and material properties with new concepts. It will work to achieve a basic understanding, along with significant progress in the development of new nanostructured materials for hydrogen storage.	<a href="https://cordis.europa.eu/project/id/210092">https://cordis.europa.eu/project/id/210092</a>
<b>Chip Integrated Hydrogen Generation-Storage-Power Micro System</b>	2009 - 2011	Germany	The project aims to develop a chip integrated hydrogen generator based on built-in hydrogen storage polymer electrolyte membrane water electrolysis and a bifunctional process option.	<a href="https://cordis.europa.eu/project/id/236667">https://cordis.europa.eu/project/id/236667</a>
<b>Computational study of hydrogen storage in metal-doped materials</b>	2009 - 2013	Greece	The study aims developing computational method using ab-initio DFT calculations, Monte Carlo simulations and macroscopic modelling to see effects of different materials such as metal-doped porous materials, including graphitic materials, carbon nanotubes, carbon foams, graphite-oxide materials, metal-organic and covalent-organic frameworks on hydrogen storage in metal doped materials.	<a href="https://cordis.europa.eu/project/id/249216">https://cordis.europa.eu/project/id/249216</a>
<b>Development and characterization of novel materials for hydrogen storage</b>	2010 - 2012	Norway	The scheme of the project is about hydrogen storage in boron-based light-weight complex hydrides.	<a href="https://cordis.europa.eu/project/id/253863">https://cordis.europa.eu/project/id/253863</a>
<b>Optimization of Hydrogen Storage via Spillover through a Combined Experimental and Modeling Approach</b>	2012 - 2013	Greece	The proposal aims to synthesize catalyzed nanoporous materials with superior hydrogen uptake and moderate pressures through the hydrogen propagation mechanism.	<a href="https://cordis.europa.eu/project/id/301076">https://cordis.europa.eu/project/id/301076</a>
<b>Fast, reliable, and cost-effective boron hydride based high</b>	2012 - 2015	Germany	This proposal relates to fuel cell applications. It includes an integrated approach to the development and testing of new, optimized, and cost-effective	<a href="https://cordis.europa.eu/project/id/303428">https://cordis.europa.eu/project/id/303428</a>

<b>capacity solid-state hydrogen storage materials (BOR4STORE)</b>			boron hydride-based hydrogen storage materials with superior performance.	
<b>High energy density Mg-based metal hydrides storage system</b>	2012 - 2016	Italy	This project aims to create scientific, technological, and industrial expertise in energy storage and recovery systems. It develops an efficient hydrogen storage system that combines magnesium-based materials with existing solutions on the market.	<a href="https://cordis.europa.eu/project/id/303472">https://cordis.europa.eu/project/id/303472</a>
<b>Novel Complex Metal Hydrides for Efficient and Compact Storage of Renewable Energy as Hydrogen and Electricity</b>	2013 - 2017	Germany	The project is about testing a prototype. The aim is to understand the material in hydrogen and electrochemical processes, and accordingly to enlarge the material production and to make a techno-economic evaluation.	<a href="https://cordis.europa.eu/project/id/607040">https://cordis.europa.eu/project/id/607040</a>
<b>Hydrogen fuelled utility vehicles and their support systems utilizing metal hydrides (HYDRIDE4 MOBILITY)</b>	2017 - 2022	Norway	The project objective is to focus essential problems towards a commercial integration of hydrogen-driven utility vehicles using metal hydride, hydrogen storage, and PEM fuel cells, jointly with the system for their refueling at industrial customer facilities.	<a href="https://cordis.europa.eu/project/id/778307">https://cordis.europa.eu/project/id/778307</a>
<b>Seeing hydrogen in matter</b>	2018 - 2023	Germany	The project will facilitate direct imaging and measurement of hydrogen atoms in candidate metal alloys and metal-organic frameworks for gaseous storage. It will also help discover new solid-state hydrides and improve fuel cell materials for power generation.	<a href="https://cordis.europa.eu/project/id/771602">https://cordis.europa.eu/project/id/771602</a>
<b>Advanced materials and Reactors for ENergy storage tHrough Ammonia (ARENHA)</b>	2020 - 2024	Spain	In this project, the potential of ammonia as a transporter material to produce pure hydrogen for hydrogen-driven, fuel cell integrated electric vehicles and potential fuel for internal combustion engines will be proved.	<a href="https://cordis.europa.eu/project/id/862482">https://cordis.europa.eu/project/id/862482</a>
<b>The sustainable</b>	2021 -	France	In this project will develop active and selective catalysts	<a href="https://cordis.europa.eu/project/id/101007223">https://cordis.europa.eu/project/id/101007223</a>

<b>and cost-efficient catalyst for hydrogen and energy storage applications based on liquid organic hydrogen carriers: economic viability for market uptake</b>	2023		with partial or total substitution of platinum group metal. To reduce energy intensity during the loading and unloading processes, project partners will develop a novel catalytic system architecture. To minimise the internal heat loss and increase space-time-yield, this architecture will range from the catalyst to the heat exchanger.	
<b>Computational Design for Lightweight Ca-Mg-based Laves Phases for Hydrogen Storage</b>	Terminated	Spain	The objective of the project is to examine lightweight Laves phase materials as possible candidates for hydrogen storage by using a combination of mathematical methods such as Density Functional Theory, kinetic Monte Carlo, and Calculation of phase diagrams.	<a href="https://cordis.europa.eu/project/id/300884">https://cordis.europa.eu/project/id/300884</a>

#### 4. The patent in regarding with H<sub>2</sub> storage

There are many studies on hydrogen storage. As a result of these studies, some new inventions are emerging. Patents are obtained in order to protect inventions and use them in sectors. Looking at the patent applications made in recent years, it is seen that hydrogen storage technologies are developing. Examining these patents is important for the future of hydrogen storage technologies and the hydrogen economy. After the patents received, the use and spread of the developed products can remove the obstacles in front of hydrogen. In this study, patent research was made using the patent database of worldwide-Espacenet. Patent research on some hydrogen storage systems since 2017 is discussed in this subsection.

The invention is a hydrogen storage system to a magnesium-based hydrogen storage material. According to the hydrogen storage method of the present invention, the waste heat of combustion can be used effectively and at the same time, hydrogen storage and controllable stability can be carried out. The invention solves the problem of a new controllable hydrogen supply system using solid hydrogen storage [77]. The other invention relates to a liquid hydrogen storage material. To provide a liquid hydrogen storage material consisting of a two- or three-component system as a eutectic mixture. This liquid hydrogen storage material is liquid at room temperature. It can be reversibly hydrogenated by adding a catalyst and a temperature. A small amount of heat is sufficient for this. The present invention contributes to the development of liquid hydrogen storage and a high-capacity energy storage technology [78]. The additional invention, metal amino borane composite hydrogen storage material, describes a metal amino borane composite hydrogen storage material. Metal ammonia borane can be used for high-density solid hydrogen welding due to its ability to release hydrogen rapidly at temperatures close to room temperature, its rapid hydrogen release kinetics, its simple preparation process, and its high efficiency [79]. There is a need to develop materials that are lighter than hydrogen storage alloys and have higher hydrogen storage capacity. The new innovative approach provides a carbon material having a carbon structure suitable for storing hydrogen and a method for

producing it. This hydrogen storage carbon material has a ratio of ultra-micropore volume to micropore volume of around 60% [80]. It is very important to develop systems based on solid hydrogen storage materials to solve the low volumetric storage density of high-pressure gaseous hydrogen storage systems. One of the inventions made for this is a composite material. Another innovative invention is directed to a hydrogen storage composite material having improved thermal conductivity and reduced thermal anisotropy and a method for its manufacture. This composite contains a solid hydrogen storage material, expanded graphite, and nanocarbon [81]. A new material-based invention relates to a porous ceramic hydrogen storage material and a method of preparation thereof. The porous ceramic hydrogen storage material disclosed by the invention consists of silicon dioxide, diatomite, aluminum powder, and activated carbon. The porous ceramic hydrogen storage material provided by the invention has very high porosity [82]. Therefore, it can be used as hydrogen storage material. It also has advantages such as high mechanical strength, large hydrogen storage capacity, simple hydrogen absorption, and desorption process, safe use. The invention provides a nanoscale-based hydrogen storage material and a method of preparation thereof. Nano magnesium-based hydrogen storage material is prepared from titanium dioxide and scandium trioxide catalyst loaded with magnesium and graphene. The prepared nano magnesium-based hydrogen storage material has high activity, high capacity, and excellent hydrogen absorption and desorption performance properties [83]. The new invention describes a liquid organic hydrogen storage material. Liquid organic hydrogen storage material contains benzyl toluene, phenylacetaldehyde, acetophenone, dibenzyl ketone, benzene, methylbenzene. Liquid organic hydrogen storage material has the characteristics of high hydrogen storage density, high environmental suitability, high hydrogen purity, simple production process, low cost, high hydrogenation, and dehydrogenation [84]. Considering the patent data given, material-based hydrogen storage technologies are promising.

## 5. Conclusion and future perspective

To create a hydrogen economy it is essential to develop its component; hydrogen production, hydrogen storage, and transportation/utilization. Hydrogen is the lightest and the most abundant element all over the World and its higher heating value is much more than the other fuel sources. However, the storage of hydrogen is a bottleneck of the hydrogen economy. Therefore, it has become the most studied topic on hydrogen storage technologies in recent years.

Hydrogen can be stored in three ways; high pressurized tank, cryogenic storage/liquified at very low temperature, and solid-state/material-based storage. Among them, material-based hydrogen storage is considered the long-term option due to its superior properties to the other two methods. Material-based storage is divided into chemisorption and physisorption material storage that each hydrogen storage methods have some challenges regarding slow kinetics, thermodynamics, hydrogen storage capacity, etc. To further enhance their hydrogen storage performance, the aforementioned strategies and new advanced materials are required to develop.

To create a hydrogen economy, it is required to emphasize R&D studies, develop strategies and standardization. It should be noted that without R&D research, the collaboration of academia, government, and industry is necessary for the accelerated transition from fossil resources to the decarbonized hydrogen economy. Therefore collaboration of each stakeholder is important for developing the hydrogen economy and reducing the adverse effect of conventional fuels.

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